Fertilizer Manual

This manual is a successor to and in part a revision of the IFDC/UNIDO *Fertilizer Manual* Published in December 1979

Editors:
United Nations Industrial Development Organization (UNIDO) and
International Fertilizer Development Center (IFDC).

Kluwer Academic Publishers in cooperation with:

United Nations Industrial Development Organization (UNIDO)
Vienna, Austria

International Fertilizer Development Center (IFDC)
Muscle Shoals, Alabama (U.S.A.)

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-7923-5032-4(HB)
ISBN 0-7923-5011-1(PB)

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Hardbound Edition:
Sold and distributed in the U.S.A. and Canada
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Softbound Edition:
Sold and distributed
by IFDC,
P.O. Box 2040, Muscle Shoals, AL 35661, U.S.A.

Printed on acid-free paper

This manual has been prepared by the United Nations Industrial Development Organization (UNIDO) and International Fertilizer Development Center (IFDC) within UNIDO project XP/GLO/93/094.

The views expressed in this publication are those of the authors and do not necessarily reflect the views of the Secretariat of UNIDO or of IFDC.

Mention of firm names and commercial products does not imply the endorsement of UNIDO or IFDC.

Printed in the Netherlands

Preface

According to the United Nations, world population will reach 8.5 x 10^9 in 2025. Over 93% of the growth will occur in the developing countries. Such unprecedented growth in population will create equally unprecedented pressures on the natural resource base–land, water, and air–to produce adequate food, fiber, and raw materials to meet the growing demand.

The United Nations projects that the number of people living in absolute poverty will increase from 1.2 x 10^9 today to 1.5 x 10^9 by 2025. Today more than 700 million people in the developing countries do not have access to sufficient food to lead healthy, productive lives. If current trends in population growth and food production continue, by the year 2025, the World Bank estimates that Africa alone will have an annual food shortage of 250 million tonnes.

To solve these seemingly insurmountable problems, the United Nations forecasts that agricultural output must be tripled and people must have the income to buy it. With increasingly limited land under cultivation, sustainable food security cannot be achieved without the benefits of intensified agriculture–the key to alleviating poverty. The adoption of improved technology and the application of modern inputs of agriculture, including inorganic and organic fertilizers, can significantly boost food supply and help to protect the environment. In fact, Dr. Norman Borlaug, 1970 Nobel Peace Prize recipient, has said that "the use of chemical fertilizers must be expanded two- to threefold to maintain soil fertility and productivity in the developing countries over the next 25 years if the world is to feed itself."

The publication of this edition of the *Fertilizer Manual* is timely in that the World Food Summit was held in Rome in November 1996. At this Summit, policymakers from around the world discussed the global challenges created by a burgeoning population, shrinking land area available for food production, and mounting food insecurity.

The last revision of the *Fertilizer Manual* was published in 1979. Since that time major advances in fertilizer technology have occurred whereby more energy-efficient processes and reductions in the cost of production have resulted. This edition of the *Fertilizer Manual* provides planners with information on these new advances.

Editorial Note

In the 3rd edition of the *Fertilizer Manual*, basic information from the 2nd edition has been retained. The contents of the chapters were reviewed by consultants; professionals in the given fields of agronomics, technology, and economics. The names of contributors are as follows: Chapter 1 – D. W. Rutland (IFDC); Chapter 2 – B. H. Byrnes (IFDC); Chapter 3 – W. C. Brummit (IFDC); Chapter 4 – B. L. Bumb (IFDC); Chapter 5 – S. J. Van Kauwenbergh, T.A.B. Lawendy, and J. W. Foster (IFDC); D. E. Garrett, P. Rozwadowski, and B. Groover (UNIDO); Chapters 6 and 7 – B. Groover (UNIDO); Chapter 8 – D. P. Aleinov (UNIDO); Chapter 9 – J. R. Lazo de la Vega and G. R. Coleman (IFDC); Chapter 10 – F. P. Achorn (UNIDO); Chapter 11 – P. Rozwadowski (UNIDO); Chapters 12, 13, and 14 – A. Davister (UNIDO); Chapter 15 – D. E. Garrett (UNIDO); Chapter 16 – J. J. Schultz (IFDC); Chapter 17 – J. Mortvedt and R. G. Lee (IFDC); Chapter 18 – D. W. Rutland (IFDC); Chapters 19, 20, and 22 – J. A. Kopytowski (UNIDO) (S. A. Ahmed from East West Center, Honolulu, Hawaii, contributed with the EWC methodology on projection of fertilizers consumption); Chapter 21 – D. E. Nichols, J. R. Polo, and D. I. Gregory (IFDC). The technical editors of the *Fertilizer Manual* were R. G. Lee (IFDC) and J. A. Kopytowski (UNIDO). Internationally acknowledged fertilizer manufacturers, licensors, and engineering companies were asked to contribute nonconfidential information related to their processes. The following companies responded and their special contribution is appreciated and acknowledged in the *Fertilizer Manual* where needed: Babcock-King-Wilkinson, Chiyoda Corp., Lurgi GmbH, Snamprogetti SpA, M. W. Kellogg, H. Topsoe, Kemira Engineering Oy, Uhde GmbH, Stamicarbon SA, and Raytheon Engineers. Other companies' processes are described on the basis of publicly available information. Also information published by IFDC in workshop proceedings from 1990 to 1995 was used in some chapters, and references to this information are given. The information from these workshops has been especially useful in preparation of Chapters 2, 16, 19, and 21.

IFDC and UNIDO have used their best efforts in development of the information contained in the *Fertilizer Manual*. The use of the information contained herein shall be at the sole discretion of the user. It is unavoidable in a work of this magnitude that some of the information will require frequent updating. Readers should keep in mind that when authors refer to "current" or "present" situations, they usually mean 1996 unless otherwise specified.

Special thanks are extended to the following collaborators in the preparation of this manual.

- R. Rejewski (UNIDO) – preparation of the flow diagrams.
- Marie R. Stribling, Elizabeth N. Roth, and Marie K. Thompson (IFDC) – proofing and editing.
- Lynda F. Young (IFDC) – computer graphics.
- Jane L. Goss, Alicia K. Hall, Janice C. Gautney, and Donna W. Venable (IFDC) – word processing and layout.
- The contribution by Donna W. Venable is especially recognized.

Acronyms of Organizations

AAPFCO	Association of American Plant Food Control Officials
APC	Arab Potash Company
APPER	African Priority Program of Economic Recovery
BASF	Badische Anilin-und Soda-Fabrik
BFL	Beladune Fertilizers Limited
BP	British Petroleum
CERPHOS	Centre d'Etudes et de Recherches des Phosphates Mineraux
CFCA	Co-Operative Farm Chemical Association
CFL	Coromandel Fertilizers Limited
CIL	Chemetics International Ltd.
CNTIC	China National Technical Import Corporation
COFAZ	Compagnie Française de l'Azote
DSM	Dutch State Mines
EFMA	European Fertilizer Manufacturers' Association
EPA	U.S. Environmental Protection Agency
EWC	East-West Center
FAO	Food and Agriculture Organization of the United Nations
FERTIMEX	Fertilizantes Mexicanos
FW	Foster Wheeler
GIAP	State Institute of Nitrogen Industry
GNFC	Gujarat Narmada Valley Fertilizers Company Limited
GSFC	Gujarat State Fertilizers Company, Limited
HAIL	Hydro Agri International Licensing
IAALD	International Association of Agricultural Libraries and Documentalists
ICI	Imperial Chemical Industries
IDDA	Industrial Development Decade for Africa
IFA	International Fertilizer Industry Association
IFDC	International Fertilizer Development Center
IMI	Israel Mining Industry
IMO	International Maritime Organisation
IMPHOS	Institut Mondial du Phosphate
IPC	International Potash Company
ISO	International Organization for Standardization
KT	Koppers-Totzek
MAPCO	Mid-America Pipeline Company
OPEC	
ORNL	Oak Ridge National Laboratory
PCA	Potash Company of America
PCS	Potash Corporation of Saskatchewan
PEQUIVEN	Petroquímica de Venezuela
ROFOMEX	Roca Fosfórica Mexicana
SAI	Scottish Agricultural Industries
SQM	Sociedad Quimica y Minera de Chile
TEC	Toyo Engineering Company
TFI	The Fertilizer Institute
TVA	Tennessee Valley Authority
UNCED	United Nations Conference on Environment and Development
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organization
UNPAAERD	United Nations Program for Action for African Recovery and Development
USBM	U.S. Bureau of Mines
USGS	U.S. Geological Survey
WHO	World Health Organization of the United Nations

Mathematical Symbols, Abbreviations and Conversion Factors Used in This Manual[a]

Monetary Value

$	U.S. dollar (unless otherwise indicated)
DM	Deutsche mark

Linear Measurement

m	meter = 3.28 feet (ft) = 39.37 inches (in)
cm	centimeter = 0.01 meter = 0.3937 inch (in)
mm	millimeter = 0.001 meter
μm	micrometer or "micron"
km	kilometer = 0.62 mile (mi)

Area Measure

m^2	square meter = 10.76 square feet (ft^2)
cm^2	square centimeter = 0.155 square inch (in^2)
km^2	square kilometer = 0.386 square mile (mi^2)
ha	hectare = 10,000 square meters (m^2) = 2.471 acres (A)

Weight

g	gram = 0.032 troy ounce (oz) = 0.035 avoirdupois ounce (oz)
mg	milligram = 0.001 gram (g)
μg	microgram = 0.000001 gram (g)
kg	kilogram = 1,000 grams (g) = 2.205 pounds (lb)
t	tonne (metric) = 1,000 kg = 2,205 lb = 1.102 short tons (st)
g-mole	gram mole = the molecular weight of a compound multiplied by 1 gram

Volume

gal	U.S. gallons = 3.785 liters
m^3	cubic meter = 35.34 cubic feet (ft^3) = 1,000 liters (l)
cm^3 or cc	cubic centimeter = 0.061 cubic inch (in^3)
l	liter = 0.264 U.S. gallons (gal) = 1.057 quart (qt)
bbl	barrel (of petroleum) = 42 gallons (gal) = 159 liters (l)
ml	milliliter = 1 cubic centimeter (cm^3) approximately
Nm^3	cubic meter (of gas) measured at "normal" temperature
ft^3	cubic foot = 0.0283 m^3

Yields or Application Rates

kg ha^{-1} or kg/ha	kilograms per hectare = 0.892 pounds per acre (lb/A)
g/ha	grams per hectare

Weight Per Unit of Volume (Density)

sp gr	specific gravity = the ratio of the weight of a substance to the weight of an equal volume of water at 4°C; no dimensions; numerically equal to density in g/cm^3
g/cm^3	grams per cubic centimeter = 62.43 pounds per cubic foot (lb/ft^3)
kg/m^3	kilograms per cubic meter = 0.0624 lb/ft^3
t/m^3	tonnes per cubic meter = g/cm^3
°Bé	degrees Baumé

Note: For definitions of true, apparent, and bulk densities or specific gravities, see Chapter 18.

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[a] Factors for converting metric units to English or SI units (Système International d'Unités) or vice versa.

Concentrations

g/l	grams per liter
mg/m^3	milligrams per cubic meter
μg/m^3	micrograms per cubic meter
ppmw	parts per million by weight
dm^3	cubic decimeter = 1 liter

Work-Energy-Heat

MMBtu	million Btu
cal	calorie = 4.184 joules (J)
kcal	kilocalorie = 1,000 cal = 3.968 British thermal units (Btu)
MMcal	million calories
kJ	kilojoule = 0.239 kcal
GJ	gigajoule = 10^9 joules = 0.948 million Btu = 0.239 million kcal
Gcal	gigacalorie = 10^9 calories = 3.97 million Btu
kWh	kilowatt-hour = 3,413 Btu = 36,000 joules
mWh	megawatt hours = 1,000 kWh

Power

W	watt = 1 joule per second (J/s)
kW	kilowatt = 1,000 watts (W) = 1.34 horsepower (hp)
MW	megawatt = 1,000,000 watts

Heating Value Per Unit of Volume or Weight

cal/g	calories per gram = kilocalories per kilogram (kcal/kg) = 1.8 Btu/lb = 4.187 J/g
kcal/m^3	kilocalories per cubic meter = 0.1123 Btu/ft^3

(Used to denote heating value of fuel gas; the temperature and pressure should be stated; usually 0°C and 1 atm in scientific work. The U.S. natural gas industry uses "standard conditions" of 60°F and 14.7 lb/in^2).

Pressure

kg/cm^2	kilograms per square centimeter = 14.2 pounds per square inch (lb/in^2)
atm	atmosphere = 14.7 lb/in^2
atm	101.325 kilonewtons per square meter (kN/m^2) = 101.325 kilopascals (kPa)
mm Hg	millimeters of mercury = 133.3 Pa = 0.0013 atm
psia	pounds per square inch absolute
psig	pounds per square inch gauge
MPa	megapascal = 1,000 kPa
bar	0.987 atm = 100 kPa

Temperature

°C	degrees Celsius or centigrade; (°C x 1.8) + 32 = °F
°F	degrees Fahrenheit (°F - 32) 5/9 = °C
°K	absolute temperature = °C + 273

Plant Capacity or Production Rate

tpd	tonnes per day
tph	tonnes per hour
tpy	tonnes per year

Note: All tonnes are metric unless otherwise specified.

Other Abbreviations

kN/cm	kilonewtons per centimeter
BL or B/L	battery limits
pCi/g	picocuries per gram (a measure of the concentration of a radioactive material)
f.o.b.	free on board = cost at plant or port including loading on a ship or other conveyance
pH	logarithm of the reciprocal of the hydrogen ion concentration in grams per liter (pH = log $1/H^+$ g/l). A solution of pH 7 is neutral; lower pHs are acidic and higher pHs are alkaline.
gpm	U.S. gallons per minute
dia	diameter
CRH	critical relative humidity
LPG	liquefied petroleum gas
LNG	liquefied natural gas
SNG	substitute (or synthetic) natural gas
HTS	high temperature shift (catalyst)
LTS	low temperature shift (catalyst)
LHV	lower heating value (gas)
CEC	cation exchange capacity
BPL	bone phosphate of lime, 1% P_2O_5 = 2.185% BPL
BFW	boiler feed water

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Chapter 1. General Concepts, Classification, Terminology, and Definitions

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Chapter 1. General Concepts, Classification, Terminology, and Definitions

1.1 Introduction

A fertilizer is a material that furnishes one or more of the chemical elements necessary for the proper development and growth of plants. The most important fertilizers are fertilizer products (also called chemical or mineral fertilizers), manures, and plant residues. A fertilizer product is a material produced by industrial processes with the specific purpose of being used as a fertilizer. Fertilizers are essential in today's agricultural system to replace the elements extracted from the soil in the form of food and other agricultural products.

1.2 Plant Nutrients

Chemical elements that are essential for the proper development and growth of plants are typically referred to as plant nutrients. The list of plant nutrients recognized as being necessary for plant growth has increased over the years and now totals sixteen, as shown in Table 1.1.

Table 1.1. Classification of Elements Essential for Plant Growth

Major elements (macronutrients)	(Available from air or water)	Carbon Hydrogen Oxygen
	Primary nutrients	Nitrogen Phosphorus Potassium
	Secondary nutrients	Calcium Magnesium Sulfur
Minor elements (micronutrients)		Boron Chlorine Copper Iron Manganese Molybdenum Zinc

1.2.1 Classification

Nine plant nutrients are required in relatively large amounts and are referred to as major elements or macronutrients. Of these, carbon, hydrogen, and oxygen are obtained from the carbon dioxide in the atmosphere and water and therefore are not dealt with as nutrients by the fertilizer industry. These three plant nutrients make up 90%-95% of the dry matter of all plants. The other major elements are subdivided into primary nutrients (nitrogen, phosphorus, and potassium) and secondary nutrients (calcium, magnesium, and sulfur). The remaining seven plant nutrients are required in much smaller amounts and are known as micronutrients or minor elements.

In addition to the 16 essential elements listed in Table 1.1, some other elements have been shown, in certain circumstances, to be helpful in increasing crop yields or in improving the value of crops for animal or human nutrition. Examples are sodium, silicon, cobalt, and vanadium.

1.2.2 Expression

Many countries express quantities or percentages of the primary nutrients in terms of elemental nitrogen (N), phosphorus pentoxide (P_2O_5), and potassium oxide (K_2O). Secondary nutrients and micronutrients usually are expressed on an elemental basis although calcium and magnesium sometimes are expressed in the oxide form. However, several countries express all plant nutrients on an elemental basis. Plants actually use neither the pure element nor the pure oxide form, so the difference is largely academic. Conversion factors for those plant nutrients that may be expressed in the elemental or oxide form, depending on the country, are shown in Table 1.2.

1.3 Fertilizer Grade

It is customary to refer to a given fertilizer product by a series of numbers separated by dashes. This set of numbers is called the "grade" of the fertilizer product. Each of the numbers indicates the amount of a nutrient that the manufacturer guarantees is contained in the fertilizer product. This number includes only the amount of nutrient found by prescribed analytical procedures, thereby excluding any nutrient present in a form that is deemed to be unavailable for plant nutrition. The content of each nutrient is always expressed as a percentage by

Table 1.2. Conversion Factors of Plant Nutrients (From Oxide to Elemental and From Elemental to Oxide Form)

P_2O_5	x	0.44	=	P
P	x	2.29	=	P_2O_5
K_2O	x	0.83	=	K
K	x	1.20	=	K_2O
CaO	x	0.71	=	Ca
Ca	x	1.40	=	CaO
MgO	x	0.60	=	Mg
Mg	x	1.66	=	MgO
SO_3	x	0.40	=	S
S	x	2.50	=	SO_3

weight, or in other words as kilograms of nutrient per 100 kg of the fertilizer product. These percentages are guaranteed minimum rather than actual content, which is usually slightly higher.

Usually, three numbers are used when giving the grade of a fertilizer product, and these three numbers always refer, in order, to the content of the primary nutrients: nitrogen, phosphorus, and potassium. If other nutrients are present, their content can also be indicated in the grade of the fertilizer product; each extra number is followed by the chemical symbol of the nutrient it represents. Many countries indicate the content of phosphorus and potassium not in the elemental form but in the oxide form, P_2O_5 and K_2O. When references are made to the phosphorus content of a fertilizer product, it is common to call it phosphate, which is the form in which it is mostly present within the fertilizer products, although all calculations and expressions of content are made using either the oxide form (P_2O_5) or the elemental form (P).

Some examples of fertilizer grades follow:

- A fertilizer product with a grade of 18-46-0 is guaranteed by the manufacturer to have the following content:

  18% N, or 18 kg of N in every 100 kg

  46% P_2O_5, or 46 kg of P_2O_5 in every 100 kg

  0% K_2O, or no K_2O

- A fertilizer product with a grade of 12-6-22-2MgO is guaranteed by the manufacturer to contain:

  12% N, or 12 kg of N in every 100 kg

  6% P_2O_5, or 6 kg of P_2O_5 in every 100 kg

  22% K_2O, or 22 kg of K_2O in every 100 kg

  2% MgO, or 2 kg of MgO in every 100 kg

Expressed on an elemental basis, the fertilizer grade of this product would be 12-2.6-18.3-1.2Mg (Table 1.2).

In this manual, the oxide form will be used unless otherwise specified.

The value of using fertilizer grades in identifying a fertilizer product cannot be overemphasized. This is a constant reminder to the consumer that he is purchasing plant nutrients, not a named fertilizer product. For example, the fertilizer product single superphosphate (SSP) is known worldwide by that name or acronym. However, the P_2O_5 content in commercially available SSP products around the world ranges from 14% to 20%.

1.4 Nutrient Availability

A commercial fertilizer is a material containing at least one of the plant nutrients in a form assimilable or "available" to plants in known amounts. Generally, a plant nutrient is taken up by plant roots or foliage in the form of a solution in water. Plant nutrients form many different chemical compounds having varying degrees of solubility in water. Thus, it would seem that water solubility should provide a simple conclusive measure of the availability to plants. Unfortunately, the situation is far too complex for water solubility alone to serve as a measure of availability. All materials are soluble in water to some extent, even the most "insoluble."

Many sparingly soluble materials have been found to be available to plants and, in some cases, even more effective than readily water-soluble materials. However, some materials are so insoluble as to be virtually worthless as fertilizers. Therefore, most countries specify some degree of solubility of the nutrient content in water or other reagents or alternatively require identification and approval of the source of the material.

For example, natural organic materials may be acceptable on the basis of total N, P_2O_5, and K_2O content, provided the source of the material is identified and approved. Synthetic organic materials, if sparingly soluble, may require special methods of analysis, particularly if intended for controlled-release fertilizers. Likewise, special tests may be required for coated controlled-release fertilizers.

Because most common nitrogen and potassium fertilizers are readily water-soluble, water solubility usually is accepted as evidence of plant availability, and special methods are applied to less soluble materials only when there is some evidence to indicate that the low (or controlled) solubility may be advantageous.

In the case of phosphate fertilizers, there is a wide variety of both readily water-soluble materials and sparingly water-soluble materials, and several methods are in use for evaluating their agronomic availability. The most common methods other than water solubility are based on solubility of P_2O_5 in neutral or alkaline ammonium citrate solutions or in solutions of citric or formic acid. In addition, the total P_2O_5 may be acceptable for some materials. Examples of the solubility criteria used for quality control of phosphate fertilizers follow.

Germany – Phosphate is expressed as the sum of P_2O_5 soluble in water and (alkaline) ammonium citrate. For superphosphate, at least 90% of the sum must be soluble in water. For compound fertilizers, at least 30% of the sum must be soluble in water.

Belgium – For TSP, 38% P_2O_5 soluble in neutral ammonium citrate must be guaranteed; 93% of the indicated content must be water soluble.

Soft rock phosphate must contain not less than 25% P_2O_5 soluble in mineral acids, of which not less than 55% must be soluble in 2% formic acid. It must be ground to a fineness so that at least 90% passes through a 63-micron sieve; 99% must pass through a 125-micron sieve.

For compound fertilizers, the P_2O_5 content may be expressed as that which is soluble in neutral ammonium citrate, soluble in water, or soluble in water and neutral ammonium citrate. If the compound fertilizer contains Thomas (basic) slag as the only source of phosphate, the P_2O_5 claimed is that which is soluble in 2% citric acid.

United States – The guaranteed P_2O_5 content of all fertilizers is based on the "available phosphate" content, which is the P_2O_5 content soluble in neutral ammonium citrate including that soluble in water. There is no provision for determining or stating the water-soluble P_2O_5 content separately. The total P_2O_5 may be stated but is not included in the guaranteed available phosphate content.

European Union (EU) – Directives specify the following permissible solvents as a basis for evaluating phosphate fertilizers:

1. Water for those materials "where applicable."
2. Formic acid (2%) for soft natural phosphates.
3. Citric acid (2%) for basic slag.
4. Petermann's solution at 65°C for precipitated dicalcium phosphate dihydrate.
5. Petermann's solution at ambient temperature for "disintegrated phosphates."
6. Joulie's solution for all straight and compound fertilizers in which phosphate occurs in alumino-calcic form.
7. Neutral ammonium citrate solution for all fertilizer.

Joulie's and Petermann's solutions are alkaline ammonium citrates containing free ammonia. Solvent compositions, extraction methods, ratios of sample to solvent, and methods for analysis are specified for each solvent.

It is beyond the scope of this manual to describe in detail the analytical methods that are used for fertilizers. The development of suitable methods for analyzing fertilizers for availability has claimed the attention of agricultural chemists since the beginning of the industry. The methods are constantly being revised and improved as new knowledge and new tools become available to the chemist.

1.5 Fertilizer Regulations

Given the wide variety of natural and synthetic materials that are beneficial to the growth of plants, a virtually unlimited number of products could truthfully be labeled "fertilizer" and marketed as such. The main drawback to uncontrolled marketing of fertilizer materials is the problem of the relative effectiveness of the product, and this depends on its composition. Unless the farmer can be sure that each lot of fertilizer he buys will have the same effectiveness as the preceding lot, he cannot be sure that he is fertilizing his crops in a rational manner, regardless of his stock of personal experience or advice from experts.

Another drawback to uncontrolled marketing of fertilizer is the lack of a rational basis for pricing. A tonne of low-analysis fertilizer is less valuable to the farmer than a tonne of higher analysis fertilizer; therefore, the farmer should have a simple method for determining the best buy from the existing market.

Because of the foregoing factors, regulations (some of them in the form of laws) have been established in many parts of the world to govern the labeling and marketing of commercial fertilizers at the retail level. These regulations are intended for local conditions and thus may vary from place to place; however, their primary purposes are to ensure uniformity and to provide a simple method whereby the farmer can select the most economical product available to him.

Regulations add to the cost of fertilizer. In order to guarantee a given nutrient percentage, the manufacturer must provide some surplus, and the amount of the surplus depends on the degree of technical control during manufacture. Enforcement of regulations adds further to the cost of fertilizers. These costs, inherent in controlling fertilizer composition at the retail level, are compensated by the inherent benefits. Without basic regulations, the fertilizer trade would become chaotic.

As with other regulations, care should be taken to limit them to the essentials.

1.6 Fertilizer Specifications

Specifications are the requirements with which a fertilizer should conform, as agreed upon between buyer and seller. Fertilizer specifications meet differing requirements depending on the use or intent of the specification information.

Specifications are normally used in the contract between the buyer and seller of a fertilizer to ensure agreement on product characteristics or more often to define the product in sufficient detail to effect the satisfaction of both buyer and seller.

Normally a farmer (consumer) gets a specification on the fertilizer bag or, for a bulk delivery, on the invoice. This type of specification typically consists of the fertilizer grade, a guaranteed analysis, the net weight, and sometimes additional information about the product. This information is typically that which is required by government regulations, not necessarily by the customer.

More commonly, when one refers to specifications, it is to specifications that have legal implications for buyers and sellers of large quantities of materials. A well-written fertilizer specification should include the following elements in detail:

1. Nutrient contents and concentrations.
2. Nutrient chemical composition.
3. Moisture content.
4. Particle size distribution.
5. Physical condition.
6. Solubility and/or availability.
7. Conditioner.
8. Special limitations pertaining to phytotoxic production byproducts or additives.
9. Packaging details (if any).
10. Methodology used in quantifying or qualifying items 1 through 9.
11. Penalties or discounts for deviation from the stated values and conditions.

Fertilizer specifications that include all of the above items may or may not meet the buyers' standards when bids are received. Usually when the buyer issues invitations to bid accompanied by the product's desired specifications, the seller tries to meet all items in order to have a chance for his bid to be accepted. If the seller cannot meet all the terms and conditions of the specification, he would expect that his bid would be rejected by the buyer. However, there are instances where the seller will include exceptions with his bid. This is the seller's way of telling the buyer that he knows the product is not to the specification, but that he (the seller) is bidding a different (usually slightly different) material. Once the buyer accepts a bid with exceptions, the exceptions supplant the original specification and become part of a new contractual agreement between buyer and seller.

From a buyer's standpoint, one might consider that the more detailed a specification, the more certain the buyer becomes of the product quality. Usually, the more detailed a specification, the more difficult it is for the manufacturer to meet all the requirements, resulting in a more expensive material or severely limiting the number of sellers who are qualified to bid.

It is, therefore, to the purchaser's advantage to use standard products with the "normally accepted" specifications whenever possible. This approach allows more suppliers the opportunity to bid, resulting in a competitive market for the buyer.

Even when the material purchased meets all of the buyer's bid specifications, the material or product may not be well suited for its intended use. This is especially true of phosphate rock. Phosphate rock is quite variable in phosphate content from deposit to deposit and in quantities of impurities that drastically affect the rock's performance in production of nitrophosphates, phosphoric acid, superphosphates, and ammonium phosphates. Thus, the material purchased may not be what was initially wanted. Even though this material may meet all the stated specifications, it is possible for unspecified contaminants or impurities to affect the performance of the materials in subsequent processing or the crop response in finished fertilizers.

It is important then to state in the specifications not only what is wanted in the product but also what is not wanted in the product.

1.7 Terminology and Definitions

The following terminology and definitions commonly used in the fertilizer industry are limited to those whose meaning might not be obvious from usual dictionary definitions.

Fertilizer – In the simplest terminology, a material, the main function of which is to provide plant nutrients.

In Japan, fertilizer is defined as being any substance that is applied to the soil for the purpose of supplying nutrients to plants or producing a chemical change in the soil that will contribute to the cultivation of plants or that is applied to the plant to supply plant nutrients.

In the Republic of the Philippines, the term fertilizer includes substances (either solid or liquid), nutrient elements (either organic or inorganic, single or in combination), and any materials applied directly to the soil for the purpose of promoting plant growth, increasing crop yields, or promoting their quality.

In Thailand, fertilizer means an organic or inorganic substance, whether of natural formation or produced through any method whatsoever, that is used as a nutrient element for plants or for causing a chemical change in the soil for the growth of plants.

In some countries, terms such as chemical fertilizer, mineral fertilizer, or inorganic fertilizer are used to distinguish the manufactured product from natural organic materials of plant or animal origin. The latter materials are called organic fertilizers.

Chemical Fertilizer – In Thailand, a fertilizer derived from inorganic substances or synthetic organic substances, including single fertilizer, mixed fertilizer, and compound fertilizer as well as organic fertilizer mixed with chemical fertilizer but excluding white lime, marl, plaster, or gypsum.

In Mauritius, chemical fertilizer means any substances containing one or more of the basic elements (nitrogen, phosphorus, potassium, calcium, magnesium, and silicon) used as a fertilizer.

Inorganic (Mineral) Fertilizer – A term used by the International Organization for Standardization (ISO) for fertilizer in which the declared nutrients are in the form of inorganic salts obtained by extraction and/or by physical and/or chemical industrial processes.

The Association of American Plant Food Control Officials (AAPFCO) defines "synthetic" as any substance generated from another material or materials by means of a chemical reaction.

Organic Fertilizer – Carbonaceous materials mainly of vegetable and/or animal origin added to the soil specifically for the nutrition of plants (ISO).

In Australia, organic fertilizers are defined as those manufactured from animal and vegetable byproducts. In Thailand, organic fertilizer means a fertilizer derived from organic material; it is produced through the process of drying, chopping, grinding, fermenting, sifting, or other methods but is not a chemical fertilizer. In Malaysia, organic fertilizers are fertilizers that are derived mainly from biological products (plant or animal) where most of the nutrient elements are present as organic compounds. In Japan and the Philippines, the term "special fertilizer" is used to define organic-type fertilizer products.

AAPFCO, in the United States, uses the term "natural organic fertilizers" and gives the following definition:

> Materials derived from either plant or animal products containing one or more elements (other than carbon, hydrogen, and oxygen) which are essential for plant growth. These materials may be subjected to biological degradation processes under normal conditions of aging, rainfall, sun-curing, air drying, composting, rotting, enzymatic, or anaerobic/aerobic bacterial action, or any combination of these. These materials shall not be mixed with synthetic materials or changed in any physical or chemical manner from their initial state except by manipulations such as drying, cooking, chopping, grinding, shredding, ashing, hydrolysis, or pelleting.

AAPFCO also defines organic fertilizer as a material containing carbon and one or more elements, other than hydrogen and oxygen, essential for plant growth.

The ISO and AAPFCO have defined several other terms relating to organic-type products. Some of the ISO terms are semi-organic fertilizer, organic nitrogenous fertilizer, synthetic organic nitrogenous fertilizer, manure, organic soil conditioner, and semi-organic soil conditioner. Some of the AAPFCO terms are compost, natural inorganic fertilizer, natural fertilizer, natural base fertilizer, organic base fertilizer, and animal manures.

Soil Conditioner – Material added to soils, the main function of which is to improve their physical and/or chemical properties and/or their biological activity (ISO).

In Malaysia, soil conditioner is defined as any substance that is added to the soil for the purpose of improving its physical or chemical character, enhancing soil productivity, or promoting the growth of crops – exclusive, however, of commercial fertilizers and farmyard manure. In Malaysia, "soil amendment" has the same definition as soil conditioner, except it includes the statement that a soil amendment supplies some nutrients.

AAPFCO defines soil amendment as any substance that is intended to improve the physical characteristics of the soil, except commercial fertilizers, agricultural liming materials, unmanipulated animal manures, unmanipulated vegetable manures, and pesticides.

Liming Material – An inorganic soil conditioner containing one or both of the elements calcium and magnesium, generally in the form of an oxide, hydroxide, or carbonate, principally intended to maintain or raise the pH of soil (ISO).

In Malaysia, a liming material is defined simply as a material used to neutralize soil acidity. AAPFCO in the United States defines "agricultural liming materials" as products whose calcium and magnesium compounds are capable of neutralizing soil acidity.

Fertilizer Material – A fertilizer that meets any of the following conditions (AAPFCO):

1. Contains important quantities of no more than one of the primary plant nutrients (nitrogen, phosphorus, or potassium).
2. Has 85% or more of its plant nutrient content present in the form of a single chemical compound.
3. Is derived from a plant or animal residue or byproduct or natural material deposit which has been processed in such a way that its content of plant nutrients has not been materially changed except by purification and concentration.

Straight Fertilizer – A qualification generally given to a nitrogenous, phosphatic, or potassic fertilizer having a declarable content of only one of the primary plant nutrients, i.e., nitrogen, phosphorus, or potassium (ISO).

In Malaysia, straight fertilizer is a generally loose term used in the fertilizer trade to signify a fertilizer that usually contains one nutrient element. In Australia, straight fertilizer is the term used to describe fertilizer containing only one of the elements nitrogen, phosphorus, or potassium. In Thailand, the term "single fertilizer" is equivalent to straight fertilizer.

Compound Fertilizer – A fertilizer that has a declarable content of at least two of the plant nutrients nitrogen, phosphorus, and potassium, obtained chemically or by blending, or both (ISO).

This term is defined and used around the world with several different meanings. Additionally, terms such as complex fertilizer, composite fertilizer, mixed fertilizer, mixture of fertilizers, fertilizer mixture, granulated mixture, physical mixture, and NPK fertilizer are also used in a similar vein and often have conflicting and/or overlapping definitions. A few examples follow:

1. **Compound Fertilizer (Malaysia)** – Any homogeneous product containing two or more of the following plant nutrient elements for fertilizing crops: nitrogen, phosphorus, potassium, and magnesium. It may also contain trace elements. The material is also known as composite fertilizer, complex fertilizer, and multinutrient fertilizer. The material shall be in the form of granules, pellets, prills, or crystals and shall be free-flowing.
2. **Compound Fertilizer (Thailand)** – A chemical fertilizer produced by chemical process and having at least two primary nutrient elements.
3. **Compounds (Australia)** – The term applied to fertilizer manufactured by a chemical reaction and containing two or more of the three main elements – nitrogen, phosphorus, and potassium.
4. **Compound or Complex Fertilizer (India)** – A fertilizer containing two or more essential plant nutrients that have undergone chemical reaction during the production process.
5. **Complex Fertilizer (Malaysia)** – A term used in the fertilizer trade to denote a compound fertilizer, all the nutrient contents of which have undergone chemical interaction during the manufacturing process.
6. **Mixed Fertilizer (AAPFCO)** – A fertilizer containing any combination or mixture of fertilizer materials (see AAPFCO definition for fertilizer materials).
7. **Mixed Fertilizer (Australia)** – The term applied to a fertilizer that is a physical mixture of two or more of the straight fertilizers. Mixed fertilizer may be powdered or granulated.
8. **Mixed Fertilizer (Philippines)** – A fertilizer containing any combination or mixture of commercial fertilizers.
9. **Mixed Fertilizer (Thailand)** – A chemical fertilizer derived from a mixture of various kinds or types of chemical fertilizers to obtain required nutrient elements.
10. **Fertilizer Mixture (Malaysia)** – A product obtained by mixing different fertilizer stock materials and containing more than one of the major plant nutrients, namely, nitrogen, phosphorus, potassium, and magnesium.
11. **Granulated Mixture (India)** – A mixture of fertilizers containing any two or more essential plant nutrients made by intimately mixing two or more fertilizer materials with or without inert material, and granulating them together, without involving any chemical reaction.
12. **Physical Mixture (India)** – A mixture of fertilizers containing any two or more essential plant nutrients made by physically mixing fertilizers with or without inert material necessary to make a required grade, without involving any chemical reaction.
13. **NPK/NP/PK Fertilizers** – Terms similar to and often used in conjunction with mixtures and compounds. They signify that the fertilizer contains nitrogen (N), phosphorus (P), and/or potassium (K).

Blended Fertilizer – A fertilizer, obtained by dry mixing, that has a declarable content of at least two of the plant nutrients nitrogen, phosphorus, and potassium (ISO).

In the United States, bulk-blended fertilizer is generally defined as a compound fertilizer produced by mixing two or more fertilizers whose granules are similar in size. These fertilizers are also called blended fertilizers or bulk blends.

In Australia, bulk blends are considered to be mixtures of two or more compounds or compounds and straight fertilizers, preferably in a pelletized (granular) form.

Granular Fertilizer – Solid material that is formed into particles of a predetermined mean size (ISO).

In the United States, AAPFCO defines granular fertilizer as a product, 95% or more of which can be retained on a series of sieves within the range of U.S. No. 4 (4.75-mm opening) to and including U.S. No. 20 (850-mm opening) and whose largest particle can pass through a sieve having an opening not larger than four times that of the sieve which retains 95% or more of the product.

In the AAPFCO definition, granular fertilizer denotes a particular size range for products. The definition for "pelletized fertilizer" in the United States (AAPFCO) is similar to that of the ISO definition for granular fertilizer, although more specific. The AAPFCO defines a pelletized fertilizer as a product, uniform in size and usually of globular shape, containing one or more nutrients and produced by one of several methods including (a) solidification of a melt as it falls through a countercurrent stream of air, (b) application of dried layers of slurry to recycling particles, (c) compaction, (d) extrusion, and (e) granulation.

In Australia, the comparable term is "granulated or pelleted fertilizers" and refers to fertilizers that have been treated in such a way that the granules are uniform in size.

In Malaysia, the comparable term is "granulated fertilizer" and is defined as a fertilizer that has been made into particles of approximately uniform size, with 90% of the material falling in the range of 1 mm to 4 mm diameter.

Coated Fertilizer – Granular fertilizer that is covered with a thin layer of a different material in order to improve the behavior and/or modify the characteristics of the fertilizer (ISO).

Other similar definitions or variations are as follows:

1. **Coated Fertilizer** – Granular fertilizer that has been coated with a thin layer of some substance to prevent caking or dust formation, or to control dissolution rate.
2. **Conditioned Fertilizer** – Fertilizer treated with an additive to improve physical condition or prevent caking. The conditioning agent may be applied as a coating or incorporated in the product.
3. **Filler (AAPFCO)** – A substance added to fertilizer materials to provide bulk, prevent caking, or serve some purpose other than providing essential plant nutrients.
4. **Filler (ISO)** – Substance incorporated in a fertilizer solely to reduce the nutrient content and without any declarable fertilizer nutrients.

Slow-Release Fertilizer – A fertilizer whose nutrients are present as a chemical compound or whose physical state is such that the nutrient availability to plants is spread over time (ISO).

In Malaysia, a slow-release fertilizer is defined as a fertilizer whose rate of release is regulated by the use of coatings of such materials as sulfur and polymeric compounds.

The AAPFCO defines a slow- or controlled-release fertilizer as a fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference "rapidly available nutrient fertilizer" such as ammonium nitrate or urea, ammonium phosphate, or potassium chloride. Such delay of initial availability or extended time of continued availability may be achieved by a variety of mechanisms. These include controlled water solubility of the material (due to semipermeable coatings, occlusion, or the inherent water insolubility of polymers, natural nitrogenous organics, protein materials, or other chemical forms), slow hydrolysis of water-soluble, low-molecular-weight compounds, or other unknown means.

Other related terms are:

1. **Coated Slow-Release Fertilizer (AAPFCO)** – A product containing sources of water-soluble nutrients, release of which in the soil is controlled by a coating applied to the fertilizer.
2. **Polymer-Coated Fertilizer (AAPFCO)** – A coated slow-release fertilizer consisting of fertilizer particles coated with a polymer (plastic) resin. It is a source of slowly available plant nutrients.
3. **Controlled-Release Fertilizers** – Fertilizers in which one or more of the nutrients have limited solubility in the soil solution, so that they become available to the growing plant over a controlled period.

The ideal in such a fertilizer would be the release of nutrients at a rate exactly equal to the needs of the plant. The limited solubility may be an inherent characteristic of the fertilizer, or it may be imparted to a soluble fertilizer by coating the particles.

4. **Nitrogen Stabilizer (AAPFCO)** – A substance added to a fertilizer to extend the time that the nitrogen component of the fertilizer remains in the soil in the ammoniacal form.
5. **Nitrification Inhibitor (Australia)** – Complex chemical substance that has the effect of killing or temporarily reducing the activity of the soil bacterium Nitrosomonas, which is responsible for the conversion of ammonium-nitrogen in the process of nitrification. The effect is similar to that of slow-release fertilizers. Nitrification inhibitors are added to nitrogen products before application.
6. **Urease Inhibitor (Australia)** – Complex chemical substance that has the effect of temporarily preventing the activity of the soil enzyme urease.

Liquid Fertilizer – A term used for fertilizers in suspension or solution and for liquefied ammonia (ISO).

In Malaysia, this term includes anhydrous ammonia, ammoniating solutions, liquid mixed fertilizer solutions, suspensions, and slurries. The principal materials used in making liquid fertilizer are ammonia, ammonium nitrate, urea, phosphoric acid, and potassium chloride.

In the United States, the term liquid or fluid fertilizer is a general term usually including fertilizers wholly or partially in solution that can be handled as a liquid. This includes clear liquids, liquids containing solids in suspension, and usually anhydrous ammonia; however, anhydrous ammonia sometimes is referred to as a gaseous fertilizer even though it is applied as a liquid. AAPFCO defines liquid fertilizer as a fluid in which the plant nutrients are in true solution.

Other related terms are:

1. **Solution Fertilizers (ISO)** – Liquid fertilizer free of solid particles.
2. **Suspension Fertilizer (ISO)** – A two-phase fertilizer in which solid particles are maintained in suspension in the aqueous phase.
3. **Suspension Fertilizer (AAPFCO)** – A fluid containing dissolved and undissolved plant nutrients. The suspension of the undissolved plant nutrients may be inherent with the materials or produced with the aid of a suspending agent of nonfertilizer properties. Mechanical agitation may be necessary in some cases to facilitate uniform suspension of undissolved plant nutrients.
4. **Suspension Fertilizer** – A liquid (fluid) fertilizer containing solids held in suspension, for example, by the addition of a small amount of clay. The solids may be water-soluble in a saturated solution, or they may be insoluble, or both.
5. **Slurry Fertilizer (AAPFCO)** – A fluid mixture that contains dissolved and undissolved plant nutrient materials and requires continuous mechanical agitation to assure homogeneity.

Specialty Fertilizer – A fertilizer recommended or used principally for golf courses, lawns, home gardens, house plants, or for any purpose other than growing farm crops. The AAPFCO defines specialty fertilizer as a fertilizer distributed for nonfarm use.

Powder – A solid substance in the form of very fine particles (ISO).

Powder is also referred to as "nongranular fertilizer" and is sometimes defined as a fertilizer containing fine particles, usually with some upper limit such as 3 mm but no lower limit.

Very few fertilizer materials are sold now in the powder form. This was the standard form of fertilizer materials many years ago, before granulation processes were developed. Powders present problems in handling and application because of their tendency to cake (becoming cemented in large blocks), their usual inability to flow freely, and their dustiness during application. Powders are not amenable to machine broadcasting because the fine particles cannot be spread evenly by the machine. Some fertilizer materials of low solubility are made into very fine powders to enhance their availability to the crops by increasing their surface area. Amendments such as agricultural limestone are applied as finely divided powders to speed reaction with the soil.

Run-of-Pile (ROP) – Products that are taken from the production piles without undergoing careful control of the particle size. This form of material consists of particles of many different sizes, from very fine powders to coarse, pebble-like particles. Usually the coarse particles are very friable and can be crushed under finger pressure. Typical examples of fertilizers sold as run-of-pile materials are some forms of single superphosphate and monoammonium phosphate.

Granulation – A general term for processes such as agglomeration, accretion, or crushing used to make a granular fertilizer (ISO).

Granulation has a number of advantages, particularly in reducing the quantity of dust in a fertilizer, improving uniformity of flow when it is being applied, and minimizing segregation when these fertilizers are blended.

Prill – A granule obtained by solidification of droplets of fertilizer or by crystallization under special conditions (ISO).

Prills are smooth, spherical particles. In the fertilizer industry, by far the most common method of producing prills is by the solidification of molten drops of the fertilizer product. The molten fertilizer is sprayed from a height inside a closed tower while a stream of air is moved upward inside the tower. As the drops fall, they cool and solidify. Prills are usually smaller than particles produced by other processes. This process is mostly used in producing urea, ammonium nitrate, and some NPK grades.

Granules – Relatively spherical particles produced by enlarging small particles through successive deposition of a liquid or slurry material, which solidifies on the surface through crystallization and/or drying. Different processes are used depending on the material being granulated. The surface of granules is not as smooth as that of prills, although some granulation processes will produce surfaces that are much smoother than others. These particles are usually stronger (have greater resistance against crushing) than prills. Granular diammonium phosphate (DAP) is a typical example of slurry granulation.

Crystals – Particles that have flat sides and sharp edges and corners, resembling the particle shape of sugar and table salt. These particles are made by letting the fertilizer crystallize from a strong solution by removal of water through heat and, in some cases, vacuum. The final processing steps for some crystalline materials sometimes include tumbling to break off some of the edges and corners, which tends to give a more spherical particle. Some forms of ammonium sulfate and muriate of potash are produced by crystallization. The large crystals are often separated from the smaller particles by screening. The large crystals are often called granules.

Compacted Particles – Particles that have totally irregular shapes. They resemble the shapes of crushed rocks. These particles are made by crushing down to size from thick and wide continuous sheets made by pressing solid particles of the component materials between cylindrical rolls under high pressure. Some muriate of potash products are typical compacted materials.

Recycle – In a fertilizer process, a portion of the finished or partially finished product that is returned to an early stage of the process for an additional pass through the subsequent processing steps. In fertilizer granulation processes, it is common practice to return undersize product and crushed oversize product as recycle to the granulator. Such recycling not only reclaims these off-size materials but also serves the important functions of reducing moisture content and lowering temperature in the granulator. The latter functions are of such importance that frequently it is beneficial to also crush and recycle some product-size material.

Formula – A term used in some countries to express, by numbers, in the order N-P-K (nitrogen-phosphorus-potassium), the respective content of these nutrients in a compound fertilizer.

The AAPFCO defines "fertilizer formula" as the quantity and grade of the crude stock material used in making a fertilizer mixture. Malaysia uses the same definition. Another common definition is a list of the kind, nutrient content, and amount of stock materials required to produce a given weight of mixed fertilizer of a given nutrient content.

Bulk – Qualification given to a fertilizer or soil conditioner not packed in a container (ISO).

The AAPFCO defines a "bulk fertilizer" as a fertilizer delivered to a purchaser either in solid or liquid state in a nonpackage form to which a label cannot be attached. Malaysia uses the same definition.

Guarantee (of Composition) – Quantitative and/or qualitative characteristics with which a market product must comply for contractual or legal requirements (ISO).

Other similar or related terms are:

1. **Declarable Content (ISO)** – That content of an element (or an oxide) which, according to national legislation, may be given on a label or document associated with a fertilizer or soil conditioner.
2. **Guaranteed Analysis (Japan)** – The minimum amount of each of the main components, expressed as percentages, which are guaranteed by the producer, importer, or dealer to be contained in any fertilizer he produces, imports, or sells.
3. **Guaranteed Analysis (Philippines)** – A statement guaranteeing the contents in terms of the minimum percentage of plant food claimed on the manufacturer's label.
4. **Guaranteed Analysis (AAPFCO)** – The minimum percentage of plant nutrients claimed in the following order and form:

   A. Total nitrogen (N) _____ %

   Available phosphate (P_2O_5) _____ %

   Soluble potash (K_2O) _____ %

   B. For unacidulated mineral phosphatic material and basic slag, bone, tankage, and other organic phosphatic materials, the total phosphate and/or degree of fineness may also be guaranteed.

C. Guarantees for plant nutrients other than nitrogen, phosphorus, and potassium may be permitted or required by regulation. The guarantees for such other nutrients shall be expressed in the form of the element. The source (oxides, salts, chelates, etc.) of such other nutrients may be required to be stated on the application for registration and may be included on the label. Other beneficial substances or compounds, determinable by laboratory methods, also may be guaranteed with permission from the regulatory authority and with the advice of the Director of the Agricultural Experiment Station. When any plant nutrients or other substances or compounds are guaranteed, they shall be subject to inspection and analysis in accord with the methods and regulations prescribed by the regulatory authority.

Fertilizer Unit – The unit mass of a fertilizer nutrient (in the form of the element or an oxide), generally 1 kg (ISO).

In the United States, fertilizer unit is defined as 10 kg of plant nutrients or 1% of a 1,000-kg tonne of fertilizer.

Plant Food Ratio – The ratio of the numbers of fertilizer units in a given mass of fertilizer expressed in the order N-P-K (ISO). In other words, it is the ratio of two or more nutrient percentages to another. A 5-10-15 grade has a 1-2-3 ratio; 10-20-20 a 1-2-2 ratio; 0-10-20 a 0-1-2 ratio.

Label – Piece of paper or plastic, or a printed area of a package or container, marked with the necessary information to identify the product and make known its essential characteristics (ISO).

The AAPFCO defines label as the display of all written, printed, or graphic matter, upon the immediate container, or a statement accompanying a fertilizer.

The Philippines defines label as a display or written, printed, or graphic matter designed in any manner or by any means upon the immediate container of commercial fertilizer.

Brand – Term, design, or trademark used in connection with one or several grades of fertilizer (AAPFCO). The Philippines uses the same definition.

Custom Mixture – A fertilizer formulated according to specifications that are furnished by/for a consumer prior to mixing, usually based on the results of soil tests.

Chloride-Free Fertilizers – Fertilizers containing less than some specified amount of chlorine. Because the usual source of chlorine in fertilizer is potassium chloride, the term usually means a fertilizer containing potassium from some other source such as potassium sulfate or potassium nitrate. Low-chlorine fertilizers may be preferred for agronomic reasons or, in the case of some compound fertilizers containing ammonium nitrate, to avoid hazardous thermal instability. The maximum chloride content of chloride-free fertilizers may be in the range of 1.0%-2.5% depending on the type of fertilizer and country regulations.

Standard Chemical Fertilizer – A chemical fertilizer for which the Minister has announced the formula and minimum or maximum quantity of nutrient element or poisonous substance and other necessary characteristics for each kind of soil chemical fertilizer (Thailand).

Sampling Unit – A defined quantity of material having a boundary which may be physical – for example, a container – or hypothetical – for example, a particular time or time interval in the case of a flow of material (ISO).

A similar term, "lot," is defined by the AAPFCO as any identifiable quantity of fertilizer that can be sampled officially.

Investigational Allowance – An allowance for variations inherent in the taking, preparation, and analysis of an official sample of fertilizer (AAPFCO).

In the Philippines, a similar term, "tolerance," means the variation from the guaranteed analysis authorized by laws or rules and regulations.

Solubility of a Fertilizer Nutrient – The quantity of a given nutrient that will be extracted by a specific medium under specified conditions, expressed as a percentage by mass of the fertilizer (ISO).

The AAPFCO defines available phosphate as the sum of the water-soluble and the citrate-soluble phosphate. Malaysia defines phosphate available as the sum of the water-soluble and the citrate-soluble phosphoric acid (as P_2O_5).

The term "available," as applied to each of the three primary fertilizer constituents, nitrogen, phosphorus, and potassium, has somewhat different meanings. For each nutrient, all the content that is soluble in water is available. In addition, however, some of the content that is not soluble in water is available to plants.

It is preferable to use the terms "active" and "inactive" as applied to insoluble nitrogen, unless the results of actual field or growing tests can be used. Animal and vegetable materials may decompose in damp, warm soils, and part or all of the nitrogen thus becomes available to growing plants. Some of the nitrogen may, however, remain unavailable. In order to anticipate the relative value of the nitrogen contained in organic (animal and vegetable) materials, empirical laboratory methods have been developed which give results in reasonable agreement with field tests.

Available phosphate in ammonium phosphates, superphosphates, or mixed fertilizers is the water-soluble plus the ammonium citrate-soluble phosphate. For basic slag, fused phosphates, and phosphate rocks, the available phosphate is determined as the part soluble in a 2% citric acid solution.

Available potash is considered to be that which is soluble in water, aqueous ammonium oxalate, or aqueous ammonium citrate.

"Available plant nutrient" is intended to mean that which is in a form capable of being assimilated by growing plants or of being converted into such a form in the soil during the growing season.

Moisture – Free water held by solids as distinguished from water of crystallization and water of constitution which are in chemical combination and no longer have the properties of water.

Heavy Metals – Metallic elements that are located in the transitional series of the periodic chart of elements. These metals are not required in plant nutrition and usually are found in relatively small amounts in nature. Toxicity to plants could result with high concentrations of some heavy metals in soil, and problems in animal and human health may result if heavy metal concentrations in the diet are above certain critical levels. Examples are cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and vanadium (V). Levels of heavy metals may be a problem in some phosphate rock deposits, sewage sludge, animal manures, and some industrial byproducts used as a source of fertilizer.

Fines – Fertilizer particles that are smaller than the size of particles intended to be manufactured for sale.

Deficiency – The amount of nutrient found by analysis to be less than that guaranteed, which may result from a lack of nutrient ingredients or from lack of uniformity (AAPFCO).

In the Philippines, deficiency is defined as the amount found by analysis to be less than that guaranteed.

Deteriorated Chemical Fertilizer – A chemical fertilizer which has expired or, as a result of any factor, has deteriorated in quality so that the quantity of nutrient element is reduced or its condition changed (Thailand).

Misbranding – A fertilizer shall be deemed to be misbranded:

A. If its labeling is false or misleading in any particular.

B. If it is distributed under the name of another fertilizer product.

C. If it is not labeled as required by regulation.

D. If it purports to be or is represented as a fertilizer, or is represented as containing a plant nutrient or fertilizer unless such plant nutrient or fertilizer conforms to the definition of identity, if any, prescribed by regulation (AAPFCO).

Adulteration – A fertilizer shall be deemed to be adulterated:

A. If it contains any deleterious or harmful ingredient in sufficient amount to render it injurious to beneficial plant life when applied in accordance with directions for use on the label, or if the label does not contain adequate warning statements or directions for use that may be necessary to protect plant life.

B. If its composition falls below or differs from that which it is purported to possess by its labeling.

C. If it contains unwanted crop seed or weed seed.

Application – General term for all processes of administering fertilizer and soil conditioners to a crop or soil or both (ISO).

This term embraces broadcasting, spreading/spraying, or dusting, as well as more specific placement methods including injection into the soil and the drilling of seed and fertilizer combined. It may be broadened to cover nutrient film techniques and the addition of fertilizers to irrigation water (fertigation).

Dose Rate; Dose – The mass or volume of a fertilizer or soil conditioner or nutrient applied to unit area of cultivated land or unit mass of growth medium (ISO).

Plant Food – Marketing term used to express plant nutrients in a fertilizer.

Fertilizer Distribution – General term for transportation, intermediate storage, and marketing of fertilizer, including all operations after the fertilizer leaves the factory and before it reaches the farm.

Abbreviations – Many of the more common fertilizers are often identified or referred to by abbreviations. The following list indicates those abbreviations most commonly encountered:

Abbreviation	Name of Product	Typical Grade
AN	Ammonium nitrate	33%-34% N
APS	Ammonium phosphate sulfate	16-20-0
APP	Ammonium polyphosphate solution	10-34-0
AS	Ammonium sulfate	21% N
CAN	Calcium ammonium nitrate	21%-26% N
CN	Calcium nitrate	15% N
DAP	Diammonium phosphate	18-46-0
KCl	Potassium chloride	60%-62% K_2O
MAP	Monoammonium phosphate	10-50-0 to 11-55-0
MOP	Muriate of potash (fertilizer-grade potassium chloride)	60%-62% K_2O
SOP	Sulfate of potash (fertilizer-grade potassium sulfate)	50% K_2O
Sul-Po-Mag®	Sulfate of potash-magnesia	22% K_2O; 18% S; 10%-18% MgO
SSP	Single superphosphate	16%-22% P_2O_5
TSP	Triple superphosphate	44%-48% P_2O_5
–	Urea	45%-46% N
UAN	Urea-ammonium nitrate solution	23%-32% N

Note: Sul-Po-Mag® is a registered trade name of IMC Global USA.

1.8 Fertilizer-Related Information Sources

The directories, handbooks, magazines, and books in the following list provide sources of information on various subjects relating to fertilizer.

Publication	Subject Coverage
World Fertilizer Market Information Sources Reference Manual R-9, June 1991 International Fertilizer Development Center P.O. Box 2040 Muscle Shoals, Alabama 35662, U.S.A. Telephone: 205-381-6600 Telefax: 205-381-7408	Information sources, publications, fertilizer manufacturers, international fertilizer trading companies, fertilizer-related associations and organizations
Agricultural Information Resource Centers – A World Directory, 1990 International Association of Agricultural Librarians and Documentalists (IAALD) IAALD World Directory Working Group 716 West Indiana Avenue Urbana, Illinois 61801-4836, U.S.A. Telephone: 217-333-7687 Telefax: 217-244-0398 (Attention 3-7687)	Information resource centers that have agriculture-related collection and/or information services
Directory of Sources of Fertilizer-Related Information With Special Reference to Asia the Pacific-United Nations 1991 FADINAP/ARSAP ESCAP Agriculture and Rural Development Division United Nations Building Rajadamnern Avenue Bangkok 10200, Thailand Telephone: (66+2) 282 9161 to 282 9200 Telefax: (66+2) 281 2403	Technology suppliers, fertilizer and producers and traders, surveyors, suppliers of bags and of packaging and handling equipment, government ministries and agencies, international and national organizations and associations, academic and research institutes, and information services

Publication	Subject Coverage
Farm Chemicals Handbook 1995 Meister Publishing Company 37733 Euclid Avenue Willoughby, Ohio 44094, U.S.A. Telephone: 216-942-2000 Telefax: 216-942-0662	Pesticide directory, fertilizer directory, regulatory file, environmental and safety section, buyers' guide, company addresses
Agricultural Research Centres: A World Directory of Organizations and Programmes, 1993 Longman Group UK Limited Longman Information and Reference Division Westgate House The High, Harlow Essex CM20 1YR, United Kingdom Telephone: (0279) 442601 Telefax: (0279) 444501	Directory of laboratories and industrial companies in all aspects of agricultural research including agronomy, crop protection, environmental science, horticulture, and natural resources
Green Markets 1994 World Directory of the Fertilizer Industry Green Markets (Pike & Fischer, Incorporated) 4600 East-West Highway, Suite 200 Bethesda, Maryland 20814, U.S.A. Telephone: 301-654-6262 Telefax: 301-654-6297	World directory of fertilizer companies listed by country
Yearbook of International Organizations, 1993/1994 Union of International Associations 40 rue Washington B-1050 Brussels, Belgium Telephone: (32 2) 640 18 08 Telefax: (32 2) 646 05 25	Directory of international organizations
Directory: Fertilizer Plants in the United States...1992 (Including Canada) Association of American Plant Food Control Officials, Inc. c/o Joel Padmore North Carolina Department of Agriculture 4000 Reedy Creek Road Raleigh, North Carolina 27607, U.S.A. Telephone: 919-733-7366 Telefax: 919-733-6801	Listing of fertilizer manufacturers, blenders, and retail outlets in the United States and Canada
North American Sulphur Fertilizer Producers, 1992 The Sulphur Institute 1140 Connecticut Avenue, NW, Suite 612 Washington, D.C. 20036-4002, U.S.A. Telephone: 202-331-9660 Telefax: 202-293-2940	Directory of North American sulfur fertilizer producers

Publication	Subject Coverage
European Sulphur Fertilizer Producers, 1991 The Sulphur Institute 1140 Connecticut Avenue, NW, Suite 612 Washington, D.C. 20036-4002, U.S.A. Telephone: 202-331-9660 Telefax: 202-293-2940	Directory of European sulfur fertilizer producers
World Sulphur and Sulphuric Acid Plant List & Atlas, 1993 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	Directory of world sulfur and sulfuric acid plants and their locations
World Fertilizer Plant List & Atlas, 1994 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	Directory of world fertilizer plants and their locations
World Directory of Fertilizer Products, 1992 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	World directory of fertilizer products and who produces them
World Directory of Fertilizer Manufacturers, 1993 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	World directory of fertilizer manufacturers
N-P-K-S Process & Plant Suppliers World Directory, 1994 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	Process design, engineering, construction, equipment supply
Maritime Fertilizer Terminals, 1983 British Sulphur Publishing 31 Mount Pleasant London WC1X OAD, England Telephone: (+44 71) 837 5600 Telefax: (+44 71) 837 0292	Directory of global maritime fertilizer terminals

Publication	Subject Coverage
Directory of Fertilizer References, 1992 The Fertilizer Institute 501 Second Street, N.E. Washington, D.C. 20002, U.S.A. Telephone: 202-675-8250 Telefax: 202-544-8123	Producers, suppliers, trading firms, equipment manufacturers, engineering and construction services, export associations, industry services
The Blue Book of World Fertilizer, 1994 FMB Consultants Limited, FMB House 6 Windmill Road, Hampton Hill Middlesex TW12 1RH, England Telephone: (+44 81) 979 7866 Telefax: (+44 81) 979 4573	Worldwide capacities, production, trade, quarterly sales review, price trends
Who's Who in Fertilizer and Ag-Chemical Supply, 1993 Stalsby/Wilson 15995 North Barkers Landing, Suite 320 Houston, Texas 77079, U.S.A. Telephone: 713-496-1734 Telefax: 713-531-7229	Directory of U.S. fertilizer producers, suppliers, distributors, and marketers
Directory of American Agriculture, 1993/1994 Agricultural Resources & Communications, Inc. 4210 Wam-Teau Drive Wamego, Kansas 66547-9377, U.S.A. Telephone: 913-456-9705 Telefax: 913-456-9705	Directory of organizations, agencies, and others serving American agriculture
Green Markets: Mergers, Acquisitions, & Joint Ventures in Fertilizer, 1994 Green Markets (Pike & Fischer, Incorporated) 4600 East-West Highway, Suite 200 Bethesda, Maryland 20814, U.S.A. Telephone: 301-654-6262 Telefax: 301-654-6297	Mergers, acquisitions, and joint ventures
National Directory of Organic Wholesalers, 1993 California Action Network P.O. Box 464 Davis, California 95617, U.S.A. Telephone: 916-756-8518 Telefax: 916-756-7857	Organic information and resources
Scientific and Technical Organizations and Agencies Directory, 1994 Gale Research, Inc. 835 Penobscot Building Detroit, Michigan 48226-4094, U.S.A. Telephone: 313-961-2242 Telefax: 313-961-6815	A guide to over 25,000 organizations and agencies concerned with the physical science, engineering, and technology

Publication	Subject Coverage
Mineral Industry Surveys United States Bureau of Mines 810 7th Street, NW Washington, D.C. 20241, U.S.A. Telephone: 202-501-9409 Telefax: 202-501-3751	Directories for producers of limestone, phosphate, nitrogen, sulfur, and potash
Research Centers Directory, 1991 Gale Research Inc. 835 Penobscot Building Detroit, Michigan 48226-4094, U.S.A. Telephone: 313-961-2242 Telefax: 313-961-6815	Guide to university-related and other nonprofit research organizations
International Research Center Directory, 1994-95 Gale Research Inc. 835 Penobscot Building Detroit, Michigan 48226-4094, U.S.A. Telephone: 313-961-2242 Telefax: 313-961-6815	A world guide to government, university, independent nonprofit, and commercial research and development centers, institutes, laboratories, bureaus, test facilities, experiment stations, research parks, data collection and analysis centers, foundations, and councils
Encyclopedia of Associations, 1995 Gale Research Inc. 835 Penobscot Building Detroit, Michigan 48226-4094, U.S.A. Telephone: 313-961-2242 Telefax: 313-961-6815	A guide to national and international organizations including trade, agricultural, environmental, engineering, technological, and governmental
Ag Retailer Magazine Agricultural Retailers Association 11701 Borman Drive, Suite 110 St. Louis, Missouri 63146, U.S.A. Telephone: 314-567-6655 Telefax: 314-567-6808	Fertilizer plant equipment list (published yearly)
Fertilizer Focus Magazine FMB Publications Ltd., FMB House 6 Windmill Road, Hampton Hill Middlesex TW12 1RH, England Telephone: (+44 81) 979 7866 Telefax: (+44 81) 979 4573	1. Directory of bulk materials handling directory equipment suppliers (published yearly) 2. Directory of bag and bagging machinery suppliers (published yearly) 3. Directory of shipbrokers (published yearly)

1.9 Resource Publications

1. International Fertilizer Development Center & United Nations Industrial Development Organization. December 1979. *Fertilizer Manual*, IFDC Reference Manual R-1, Edited by T. P. Hignett.
2. UNIDO. 1967. *Fertilizer Manual*, Vienna, Austria.
3. Incitec Limited. 1990. *Fertilizer Handbook*, Morningside, Queensland, Australia, Edited by J. S. Glendinning.
4. IFDC. 1993. *Farm Servicing Handbook*, IFDC A-3, prepared by C. C. Yaptenco, Jr.
5. Association of American Plant Food Control Officials, Inc. 1994. *Official Publication No. 47*, West Lafayette, IN, U.S.A.
6. Meister Publishing Company. 1995. *Farm Chemicals Handbook*, Willoughby, OH, U.S.A.
7. The Fertilizer Institute. 1976. *The Fertilizer Handbook*, Washington, D.C., U.S.A.
8. International Organization for Standardization. 1983. *Fertilizers and Soil Conditioners* – Classification; ISO 7851, Geneva, Switzerland.
9. International Organization for Standardization. 1984. *Fertilizers and Soil Conditioners – Vocabulary*; ISO 8157, Geneva, Switzerland.
10. International Organization for Standardization. 1989. *Fertilizers and Soil Conditioners – Vocabulary, Addendum 1*; draft addendum ISO 8157, Geneva, Switzerland.
11. Standards and Industrial Research Institute of Malaysia. 1980. *Malaysian Standard – Glossary of Terms Used in the Fertilizer Trade and Industry*, Selangor, Malaysia.
12. Chemical Fertilizer Control Act – Mauritius. 1981.
13. Fertilizer and Pesticide Authority of the Philippines. 1975. FIA Brand Resolution No. 2-75 (Philippine Fertilizer Regulatory Law), Makati, Metro Manila, Philippines.
14. Ministry of Agriculture, Agricultural Regulatory Division. 1975. *Fertilizer Act*, Bangkok, Thailand.
15. Order Concerning the Admissibility of Fertilizer Types (Fertilizer Order). 1963. Federal Republic of Germany.
16. The National Institute of Agro-Environmental Sciences, Ministry of Agriculture, Forestry, and Fisheries. *Fertilizer Control Law of Japan*, Tsukuba-shi, Ibaraki-ken, Japan.
17. Fertiliser Association of India. 1993. *The Fertilizer Control Order*, New Delhi, India.

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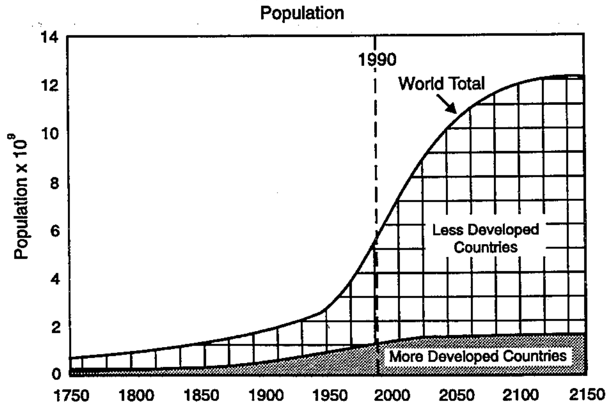
Chapter 2. The Role of Fertilizers in Agriculture

2.1 Demand for Agricultural Products and Plant Nutrients

The rapid increase in the world's population is the main driving force for the growing demand for agricultural products in the form of food and fiber. As this demand has increased, so has the demand for nutrients to support plant growth. Since there is little scope for opening more land for crop production, future demand can be met mainly by increased production on existing cropland. The essence of all but subsistence agriculture, in which the farm family consumes practically all of the produced food, is that commodities produced on the land are consumed at another locale, mainly by the rapidly growing urban populations. As products flow to sites of consumption, so flow the plant nutrients or elements contained in the products. By 2050 world population will be approximately 11.5 x 10^9; likewise, the outflow of nutrients from farmers' fields will continue to increase (Figure 2.1). The rapid population rise has been supported mainly by the increased use of nutrients by farmers and movement of plant nutrients to population centers.

Soil nutrients removed in farm products must be replenished or the soil becomes impoverished of those nutrients, and plant growth and production from succeeding crops is decreased. From the very beginning of sedentary agriculture, farmers have recognized the basic problem of nutrient depletion. On all continents slash and burn techniques have been used to replenish nutrients that have been depleted by cropping. Slash and burn is still practiced in many developing countries and relies on the slow, natural processes of nutrient release from soil organic matter and soil minerals and on biological nitrogen fixation (BNF) to accumulate nutrients in the form of biomass. If the native vegetation can be left for periods (termed fallow) of 15-20 years, the accumulated biomass will release enough nutrients after it has been slashed and burned to support crops for possibly 2-4 years. After the soil becomes impoverished of nutrients, the process of revegetation must be repeated. Besides containing nutrients, the ash has a beneficial effect of raising soil pH. This liming increases the availability of nutrients and provides a better rooting medium.



Source: [9].

Figure 2.1. World Population Growth Trends, Fueling the Need for More Food and Nutrients.

The failure to maintain soil nutrients has led to the downfall of many ancient societies [1]. When nutrients are not replenished to soils, sometimes even the growth of native vegetation cannot be supported. Currently, food demands in some impoverished areas of developing countries that have high population densities are causing farmers to use shorter fallow periods. With decreased soil cover from both native vegetation and crops, severe soil erosion occurs, less nutrients are accumulated in the biomass, and the areas are left totally unproductive and environmentally degraded. The Mayan culture of Central America supposedly declined for this reason. In addition to slash and burn practices, ancient societies strived to replenish soil nutrients by applying animal and human manures and by growing legumes (BNF) that can capture nitrogen from the air by means of symbiotic bacteria attached to their roots. Residues from the legume crops provide N for succeeding crops.

As population pressures restricted land availability and prohibited long fallow periods, farmers were forced to spend more time transporting and applying whatever organic forms of nutrients they could find. Until the introduction of commercial fertilizers, the maintenance of plant nutrients in farmers' fields was a major occupation of farmers. Medieval European farmers spent approximately two-thirds of their time in transporting and spreading organic materials. In North America, farmers moved west to undisturbed lands after depleting the nutrients of lands in the east.

Agriculture is commonly perceived to have functioned well before World War II without commercial fertilizers; however, this was not the case. Farming was inefficient because large segments of the population had to be involved to produce enough food; the systems were not sustainable in nutrients even with the use of fallows and legumes in crop rotations. There were many periods of mass starvation and deprivation [2], and the farming systems, which consisted of poor soil conservation practices and low nutrient inputs, caused great damage to the environment. Because an extensive area of land was required for such agriculture, marginal land was cultivated and the soils ultimately were degraded. At the time of the Dust Bowl years (1930-33), one-third more land was being cultivated in the United States than currently. The scars left on the land as a result of these practices are still evident throughout the world.

2.2 The Soil Resource

In addition to water and sunlight, the soil covering the earth's surface is a basic support system for all terrestrial life. While human activities have impacted hydrologic cycles and, to some extent, sunlight, their primary consequences, both to the detriment of the life support system and to the enhancement of its ability to support human populations, have been caused by manipulation of soils. Soils are the loose, unconsolidated materials covering the earth, which are derived from rock materials, either in place or carried by wind or water from another location, and they serve to physically support plants and provide water and nutrients for growth. However, soils are not simply the mineral materials derived from rock; they also contain populations of microorganisms and soil fauna that are integral to soil development, nutrient and water dynamics, weathering of rock materials, and the physical characteristics of soils. In general, soils are about 48% by volume inorganic materials, 4% organic material, and 48% open space, about one-half of which is occupied by water.

If soils are to be cultivated for crop production, other conditions must be present that are conducive to plant growth, i.e., a favorable climate, adequate water and rooting depth, absence of excessive flooding or seawater intrusions, favorable terrain, and sufficient cultivatable area. Arable or cultivatable land, therefore, consists of only about 24% of the earth's land surface. Another 27% is suitable only for grazing, and 47% of the earth's land surface will not support any agricultural activity [3].

In a natural state, the availability of nutrients in soils depends on the nutrient contents of the parent materials (the rocks or naturally imported materials) and on processes that degrade the minerals to make the nutrients available to plants, recycle nutrients between the soil and vegetation, and remove them from the soil-plant system. The processes that form soils, particularly weathering of rocks to smaller particles, break down the mineral structures; thereby, their contained nutrients are released to soil solution and made available for plant uptake. As the mineral structures are broken down and new ones are formed in response to a climatic regime, particularly moisture and temperature, soils change in character, generally at slower speeds during dry or cold periods and at faster speeds under warmer or moister conditions. Young soils contain a storehouse of undegraded minerals that can release nutrients. Therefore, a soil's age is a relative rather than a chronological characteristic. In soils that have been subjected to warmer temperatures and more moisture for longer periods, the minerals are changed in form, the weatherable minerals are degraded, and nutrients are lost to the sea. Glacial deposition areas of temperate regions contain fertile soils formed from ground rock materials, which are of recent origin and located in temperate climates. Because most tropical soils are exposed to longer periods of weathering, higher temperatures, and more moisture, they undergo more weathering. Recently formed volcanic soils and soils in river valleys, which receive sediment from flooding events, are essentially the only tropical soils that have not been weathered enough to have had much of their weatherable minerals degraded and most of their nutrients removed. As with organisms, soils go through transitions of aging, and the rate of the process depends on the environment.

Younger soils still contain a storehouse of nutrients in the mineral fraction; however, most of the nutrients of warm and moist tropical soils are stored only in the accumulated biomass growing on the soils. The recycling of the nutrients under most native vegetation is very efficient in maintaining the nutrients in the system, but losses still occur as evidenced from the low nutrient status of many tropical soils that have always been covered by native vegetation. This efficient cycling is drastically changed by removal of the native vegetation and cultivation of the soil, which increase the rates of organic material breakdown and expose the soil to water and wind erosion, both of which increase the rates of nutrient removal. While many tropical soils can support large amounts of biomass production, they are rapidly depleted of nutrients under cultivation. European colonialists had a difficult time recognizing the large differences between temperate soils and tropical soils. Their practices caused rapid removal of nutrients under cultivation. They also failed to understand how much more important the maintenance of soil organic matter was to store and supply nutrients in tropical soils relative to the temperate soils.

Productivity of soils is quite different from soil fertility. If a soil is to be productive for crop production, it must have a suitable climate, sufficient but not excessive water-supplying ability, and available plant nutrients for crop growth. A droughty soil may be fertile (contain nutrients) but not productive; however, it could become productive with irrigation. An infertile soil can support a large biomass of natural vegetation but be unproductive for cultivated crops, which require higher amounts of plant nutrients in short periods of time. Most of the population growth in the past 50 years has occurred in tropical areas; these same areas have soils that are poorly endowed in plant nutrients and climates that make the soils susceptible to nutrient loss and degradation.

2.3 Concepts of Soil Fertility

As animals require specific amounts of proteins, carbohydrates, vitamins, and minerals for proper growth, plants require nutrients in the form of ions derived from the soil. Insufficient quantities of protein, or even specific amino acids of proteins, can limit growth or specific biological processes in animals. Similarly, each nutrient plays a specific role in the structure of plant cells and the enzyme and energy transfer molecules that carry out the metabolic processes of plants. Because of the unique chemical characteristics of these nutrients, other elements cannot be used as substitutes for them.

The amounts of nutrients needed by crops varies both with the crop and the yield attainable. Table 2.1 presents the approximate amounts of nutrients that various crops actually take up to achieve the yields indicated. These yields are not exceptionally high, but are normally attainable in areas well suited for growth of these crops. The amounts of nutrients listed do not mean that these are the amounts of nutrients that must be added as fertilizers. In many cases, much of the nutrients come from the soil when adequate reserves of the nutrients are present. In other cases, because of very low fertility, much more than the listed amount of fertilizer nutrients might have to be added, from inorganic or organic nutrient sources, to achieve the indicated yields. In addition, nutrients can be internally cycled in crop production, and only the amounts of nutrients removed in the harvested crop must be replenished. Much of the potassium contained in wheat, for instance, may be left in the field in straw residues, or it may be removed if the farmer takes the straw for some purpose.

Basic understanding of plant nutrients evolved from developments in chemistry in the 19th century. An important concept of plant nutrition developed by the German chemist Justus von Liebig in about 1840 was "The Law of the Minimum." According to this concept, illustrated by a wooden barrel with staves of different lengths (Figure 2.2), plant growth is limited by a particular growth factor that is in the shortest supply to the plant. The staves (representing the sufficiency of various growth factors), and particularly the shortest stave, determine how much liquid (total growth) the barrel can hold. Growth factors include water, light, genetic potential, and soil-derived nutrients. Different factors could potentially control the rate of plant growth at different times during crop growth. For example, temperature might limit early spring growth, moisture during a droughty period, and nitrogen supply during another phase when these factors do not limit growth. Obviously some factor

Table 2.1. Approximate Amounts of Nutrients Taken Up by Crops

Crop	Yield	N	P_2O_5	K_2O	S
	(t/ha)	---------(kg/ha)-------			
Rice	6	100	50	160	10
Wheat	6	170	75	175	30
Maize	6	120	50	120	25
Cassava	40	150	70	350	20
White potato	40	175	80	310	20
Banana	40	250	60	1,000	15
Cotton	1	120	45	90	20

Source: *Better Crops International*, December 1988, Potash and Phosphate Institute, Atlanta, Georgia, U.S.A., 51 pp.

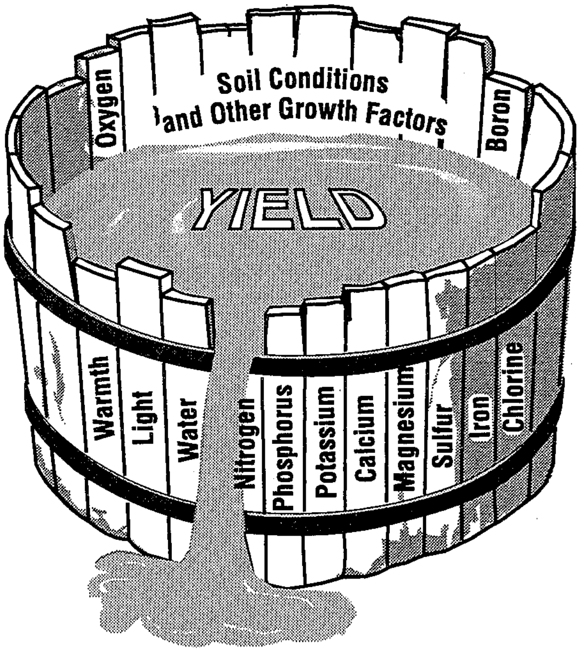


Figure 2.2. Liebig's "Law of the Minimum" Illustrated by Barrel Staves of Varying Lengths Representing Growth Factors.

always limits plant growth, ultimately genetic capability. By manipulating the soil-related factors over which he has some control, the farmer tries to lengthen the limiting stave or staves to increase crop yield and profit. He lengthens the growth-limiting staves by using such practices as irrigation, nutrient additions, weed control, and suitable crop varieties.

The analogy of the barrel illustrates some useful concepts:

1. If other factors, e.g., moisture or day length, limit growth, there is no benefit to increasing plant nutrient levels above those that can be used by the crop.
2. When a limiting factor is removed by irrigation or nutrient addition, other nutrients or factors become limiting.
3. It is not a useful practice to raise the available level of one nutrient far above that of others. The nutrients should be added to supply those crop needs that the soil does not provide. Many people refer to this practice as "balanced" fertilization; it does not mean that fertilizers must be added in a specific nutrient ratio but that the nutrient-supplying capacities are maintained in relative balance to the crop needs.

2.3.1 Classifications of Soil Nutrients

Only a few forms of nutrients are taken up by plants (Table 2.2). Concentrations of these forms of nutrients are normally low in soils, but soils have the ability to store nutrients in many organic and inorganic molecules. They are transformed to the soluble plant-available forms at rates defined by the environmental conditions for the biotic and abiotic reactions, amounts of the different nonavailable forms, their rates of conversion, and removal of various nutrient forms from soil solution. Thus, all of the plant nutrients have ionic forms that are plant-available, and soils contain an assortment of less-available forms that became available to plants through chemical and biological reactions.

The nutrients supplied from soils have been classified in different ways: by their functions in plants, by whether they generally need to be added to soils to optimize growth, or by their mobility in the plant. For agricultural production, nutrients are classified by the quantities of the nutrients needed by plants and whether they are

Table 2.2. Classification, Available Forms, and Concentrations of Nutrients in Plants

	Chemical Symbol	Principal Forms Taken Up by Plants	Approximate Concentrations in Soils	Approximate Concentrations of Element in Plants (%)
Macronutrients[a]				
Primary (Major)				
Nitrogen	N	NH_4^+ and NO_3^-	0.3%-1%	1.5
Phosphorus	P	$HPO_4^{=}$ and $H_2PO_4^-$	0.02%-0.5%	0.2
Potassium	K[b]	K^+	0.05%-3.8%	1
Secondary (Minor)				
Calcium	Ca	Ca^{++}	0.7+%	0.5
Magnesium	Mg	Mg^{++}	0.6+%	0.2
Sulfur	S	HSO_4^- and $SO_4^{=}$	30-500 ppmw	0.1
Micronutrients[c]				(ppmw)
(Trace Elements)				
Boron	B	H_3BO_3, $H_2BO_3^-$	4-100 ppmw	20
Copper	Cu	Cu^{++}, $Cu(OH)^+$	1-100 ppmw	6
Chlorine	Cl	Cl^-	7-50 ppmw+	35-2,000
Iron	Fe	Fe^{++}, $Fe(OH)_2^+$, $Fe(OH)^{++}$, Fe^{+++}	1%-6%	100
Manganese	Mn	Mn^{+2}	120-6,000 ppmw	50
Molybdenum	Mo	$MoO_4^{=}$, $HMoO_4^-$	0.1-40 ppmw	0.1, 1.6
Zinc	Zn	Zn^{++}	10-130 ppmw	20
Cobalt	Co	Co^{++}	1-40 ppmw	0.1
References		Brady, 1984 [3]	Jackson, 1965 [10]; Mitchell, 1965 [11]; Brady, 1984 [3]	Epstein, 1972 [12]; Brady, 1984 [3]

a. Carbon, hydrogen, and oxygen are furnished from CO_2 and water and are not considered "nutrients" in the normal agricultural sense.

b. From the Latin "*kalium.*"

c. Other elements, such as sodium, fluorine, iodine, barium, strontium, nickel, vanadium, and silicon may be essential to particular plant species.

normally present in sufficient quantities in soils to optimize the growth of a crop.

2.3.1.1 Macronutrients – The elements nitrogen (N), phosphorus (P), and potassium (K) are the nutrients that most often limit crop growth, and they are called "macronutrients." The soil factors affecting the availability of each of these nutrients are discussed separately in this chapter. Since N, P, and K are the nutrients most widely deficient in soils, they are also called the "major," "primary," or the "fertilizer" nutrients. Sometimes S is also considered a major nutrient because deficiencies are becoming more widespread. As discussed in Chapter 1, both synthesized and organic fertilizers are applied to cropland principally to supply N, P, and K. This is not to say that they are deficient in all soils and for all crops. For instance, many soils have sufficient weathering clays so that K is not deficient, and K may become deficient only after many years of cropping. Nitrogen may not be limiting for a crop that is planted after a good legume crop, or the soil may be able to release sufficient P to maximize the growth of a grass crop but not nearly enough to grow a good crop of white (Irish) potatoes. As explained earlier, soils ultimately become depleted of any plant nutrient unless the supply is replenished either from the atmosphere, added soil materials, or organic or synthesized fertilizers.

Calcium, Mg, and S are called the "secondary" nutrients of the macronutrients because they are not as widely deficient as N, P, and K. They may also have been considered secondary in that they are often contained in materials that are applied to supply another nutrient or need. For instance, Ca and Mg are supplied in large amounts in dolomitic limestones that are applied to raise the pH of acidic soils. Similarly, S fertilizers are not usually applied simply as S sources but are "secondary" to another nutrient, e.g., in P fertilizers such as single superphosphate, or in the N fertilizer ammonium sulfate. One should not be misled by the term "secondary" – deficiencies of Ca, Mg, or other nutrients can be as serious as more common deficiencies of N, P, K, or S. They can also very severely limit plant growth.

2.3.1.2 Micronutrients – Other elements that are needed by plants in much lower amounts than the macronutrients are called micronutrients or trace elements (Table 2.2). They are as essential to plant growth as the macronutrients because they perform very essential and specific roles, particularly in molecules involved with energy transfer processes, hormones, and enzymes. When deficiencies of micronutrients are properly diagnosed and corrected, spectacular growth increases can occur by making small amounts of the limiting element available to the crop.

Plant species vary in their susceptibility to micronutrient deficiencies. For instance, zinc deficiencies normally become evident in maize or sorghum crops before they appear in other crops. Crucifers, leafy vegetables, and forage legumes are susceptible to boron deficiencies. Certain tree species and shrubs will first show iron deficiencies. Legumes will respond to molybdenum before most other crops; and manganese deficiencies generally are observed on soybeans and small grain crops before they are seen in other plants.

A characteristic of micronutrients is that they can become toxic to plants more readily than the macronutrients. Iron toxicities are fairly common in flooded rice, and boron has a narrow range between deficiency and toxicity. Therefore, the proper diagnosis of the cause of toxicity or deficiency and application of the proper element, form, and amount are needed to alleviate micronutrient deficiencies. Molybdenum might be added at 35-70 g/ha to correct a deficiency, whereas 3 or 4 kg/ha of this element may cause toxicity. Fortunately, soils form many relatively insoluble compounds with most of the micronutrients, which limit the amounts of the elements in soil solution at any one time. In addition, plants have considerable capacity to discriminate between wanted and unwanted elements. In many cases, plants are adversely affected by excess nutrients that interfere with the uptake of some other nutrient, rather than from toxicity of the nutrient per se.

Deficiencies and toxicities of micronutrients are usually related to the content of the soils' parent materials. Oxides, hydroxides, and sometimes sulfides of micronutrients precipitate in soils after they have been released by weathering of silicate clays. The organic material in soils is very important in supplying micronutrients not only by releasing nutrients as the organic material is degraded by microbial action but also by solubilizing micronutrients by chelation. Soil pH and cation exchange capacity of soils are important aspects that greatly affect the availability of both macronutrients and micronutrients.

2.3.2 Factors Affecting Nutrient Availability

As mentioned earlier, all species of plants need practically the same nutrients, but they differ both in the amounts of particular nutrients needed for growth and their ability to use nutrients that are available in the soil. Soil factors such as soil pH, cation exchange in soils, organic matter in soils, and cropping interactions influence nutrient availability and are important considerations in fertilizer use.

2.3.2.1 Soil pH – Soil pH is conceptually the same as solution pH, the negative logarithm of the H^+ ion activity (understood to mean effective concentration). Soils of humid regions tend to become more acidic with time, whereas soils of arid regions remain more neutral or alkaline. Soil pH can sometimes be changed significantly in only a few years. The amounts of N addition, soil weathering, and the types of vegetation can affect the rate at which soil pH decreases. Soil pH greatly affects the solubility of nutrient compounds in soils, biological reactions that release nutrients, and the development of toxicities from particular elements.

Soil pH is measured by using a permeable glass electrode or litmus paper after adding water or a dilute soluble salt solution to a soil sample. Protons (H^+ ions) in the water phase are a measurement of acidity or basicity as in solution pH. Soils are pH buffered by organic and inorganic weak acids and clays that can adsorb and desorb H^+. Soils in their normal state have pHs from about 3.8 to 9 (Figure 2.3), depending on the parent material, weathering, and vegetation. The main effect of soil pH on plant growth is due to the effects of pH on the ionic forms of compounds in the soil and on the solubilization of minerals. Soil pH affects the availability of all the nutrient elements but has the greatest effect on P and several micronutrients. Most of the nutrients are more available at pHs from 6 to 7.5 (Figure 2.4). The mineralogy and total amounts of nutrients greatly affect the nutrient availability; thus, Figure 2.4 serves illustrative purposes only. For instance, it is certainly possible to have P deficiencies on a soil with pH of 6.2 even though P is normally most available at pH 6.2.

Besides the effects on nutrient availability, toxicities of aluminum and manganese occur at low pHs, below about 4.6. The solubility of compounds of these elements increases dramatically as the pH decreases below 4.6. Aluminum toxicity is particularly important on acidic tropical soils that may have low pH in their subsoils, which limits root development into these layers. Aluminum toxicities decrease the permeability of root cells and reduce root growth; thus, the plant's ability to take up water and nutrients is decreased. This effect can be much more detrimental to the plant than P deficiencies because of low pH and high Al concentrations per se [4]. In addition to nutrient availability due to solubility effects, mineralization of N from organic matter is decreased, and BNF by the rhizobia of legumes is decreased at low pHs.

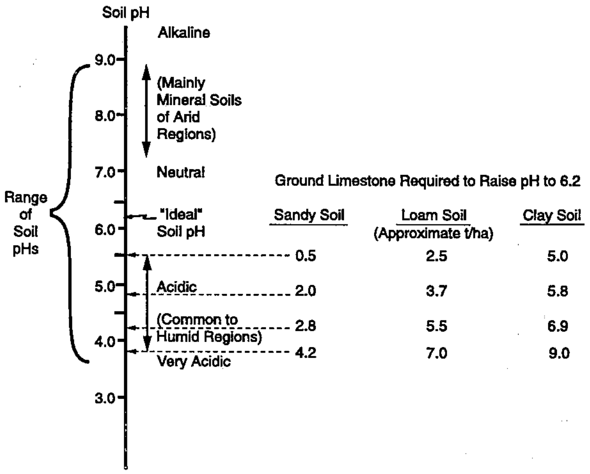


Figure 2.3. Soil pHs and Approximate Calcium Carbonate Required to Increase pH to 6.5.

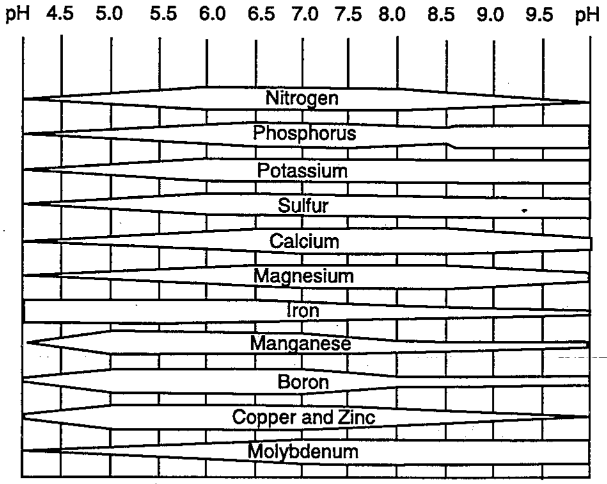


Figure 2.4. Relative Availabilities of Nutrients at Various Soil pHs.

Soils become more acidic with soil weathering, which depends on the climatic regime. Wetter climates cause soils to become acidic more rapidly than drier climates because the base cations are leached from the soil and clays are degraded. Nitrification, the microbial conversion of ammonium to nitrate, also acidifies soils. The ammonium may be of organic or synthetic (chemical fertilizer) origin; the effect on soil pH is the same. Cropping, which speeds organic matter decomposition, nitrification, and the application of ammonium-N fertilizer sources (including urea) are therefore inevitable and important causes of soil acidification. Nitrate additions cause no acidification, but the use of organic-N materials and ammonium sources will ultimately necessitate the addition of liming materials to readjust the soil pH. This will be discussed more fully in the section on N.

Liming materials are either bases or conjugate salts of weak acids. Wood ashes and basic slag are used as liming materials as are other basic waste products. However, the most common liming agents are carbonates such as limestones, oyster shells, and marls. They neutralize soil acidity by displacing protons from cation exchange sites (discussed in the next section) with Ca or Mg, and forming carbonate species that ultimately form water and CO_2 (Figure 2.5). The dissolution of carbonates is slow; therefore, materials must be finely ground and well incorporated into the soil to hasten the reactions. In addition to reducing the acidity of soils, liming materials contain the important macronutrient Ca, and dolomitic limestones contain Mg as well.

Liming of acidic soils is normally done by applying tonne-per-hectare quantities of liming materials to raise the pH to about 6.0. However, very impressive results have been achieved on tropical soils by adding smaller quantities, 500-600 kg ha^{-1}, which raise the pH only 0.3-0.5 pH units. This increase in pH is enough to greatly reduce Al toxicities and/or furnish growth-limiting Ca and Mg. The amount of liming material needed to raise the soil pH to a particular level depends not only on the initial pH but also upon the amount of protons held on exchange sites, termed residual acidity (illustrated in Figure 2.5).

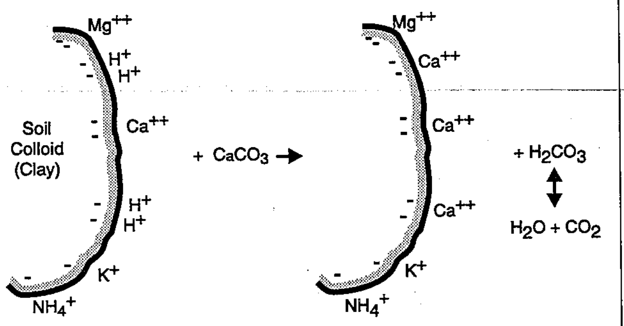


Figure 2.5. Neutralization of Soil Acidity by Carbonate Liming Materials.

As important as soil pH is to maintaining favorable plant growth conditions, it is somewhat incongruous that the subject receives so little attention in many farming systems. Often agricultural lime is sold only through assistance from governmental subsidy programs. The benefits of liming are often difficult for farmers to observe until very severe toxicities or deficiencies develop. Many of the concepts of soil liming developed for temperate climates, such as the desired pH, appropriate fineness of grind, etc., may not have been properly applied to wet tropical soils, and more liming materials will be needed to keep these soils productive. Fertilizers alone cannot maintain the soils of many regions in a productive state. The practice of liming deserves much more attention than it traditionally receives.

2.3.2.2 Soil Cation Exchange – Next to photosynthesis, many plant scientists consider the ability of soil materials to exchange cations to be the most important phenomenon that enables soils to support plant growth. Minerals and organic materials have permanent negative charges that give them the ability to adsorb and desorb cations by exchange. This phenomenon reduces susceptibility of these ions to leaching and buffers their concentrations in soil solution to provide ions for growth and to reduce the possibility of toxic concentrations. Cation exchange in the mineral clay or colloidal fractions of soils is developed by the substitution of similar-sized cations for silicon (Si) atoms in the silicate layers of clay minerals. Aluminum, Mg, and other elements of lesser valence than Si occupy positions in the silicate lattices. This gives the clay a net negative charge that must be satiated by cations on the edges or between the layers of the clay particles. Most often K occupies interlayer positions, while any cation, including H and Al ions, can occupy the negatively charged sites at the edges of the clays to maintain electroneutrality (as illustrated for soil acidity, Figure 2.5). There are also hydroxide clays of Fe and Al, which have no negative charges and thus no cation exchange capacity.

A clarification of terminology may prevent some confusion. Clay can mean the smallest size of solid particles of soils or less than 0.002-mm diameter. "Clays" can also refer to the clay minerals, which are layered silicates, such as vermiculite, montmorillonite, kaolinite, illite, etc., that have the substitution in the silicate layers that give them net negative charges, and layers of base cations holding the silicate layers together.

After being degraded by biological activity, organic materials form stable materials called humus. These organic materials can be colloidal but are largely bound to minerals in the soil. These organics have weak acid groups that can absorb cations. These weak acids, such as phenolic, carboxylic, and enolic groups, are very affected by soil pH. At very low pHs, protons are held so tightly on the groups that there is little potential for exchange with other cations. As the soil pH is increased, exchange can then occur, and at more neutral pHs, organic materials have much higher exchange capacity per unit weight than clay minerals. Sandy soils have little clay to provide cation exchange capacity; therefore, the organic matter is very important. If the soil pH is very low, these soils have practically no exchange capacity and no nutrient-holding ability.

Cation exchange can be thought of as the formation of a complex salt, with the amount of a particular salt formed being dependent on the dissociation constants of the salts and concentrations of ions in solution. Cations are interchanged on and off the negatively charged sites, but the sites are always occupied by cations. The retention and release of Ca^{++}, Mg^{++}, K^{+}, NH_4^{+}, and many of the micronutrients give soil with adequate cation exchange capacity (CEC) the ability to maintain nutrient ion concentrations in the soil solution at levels conducive to plant growth. This ability obviously depends on the amounts and types of clays, the amount of stable organic matter in soils, and soil pH. Clays and organic matter are the most important fractions of soils because of their high specific area, their CEC, and their ability to bind soil particles together to form larger, stable aggregates. They affect the nutrient and water-holding characteristics of soils and the physical handling characteristics of a soil or tilth. It is more difficult to maintain nutrient levels in soils with little clay or organic matter content; sandy soils with low CEC have more tendency to leach nutrients; their pH can be decreased quickly; they have low water-holding capacity and develop wide ranges of nutrient deficiencies.

2.3.2.3 Soil Organic Matter - Soil Life – As mentioned earlier, soils are not simply inorganic storehouses of chemicals in various forms; they are also very active biological entities that have microbial and macrofauna populations upon which plant growth, soil fertility, and soil development all depend. Comprising perhaps only 0.03% of the total weight of soil, the living biomass decomposes organic materials for recycling nutrients and CO_2, transforms molecular forms of nutrients, and affects many soil physical properties that are important to plant growth. The amount of soil biomass depends on the amounts and types of organic materials added to soils and the conditions that affect microbial growth. The organic matter content of soils, fresh additions of organic material, and the climatic regime determine how much soil life and activity can be supported.

In addition to CEC and nutrient storage and release, organic matter causes aggregation of soil particles, which helps to develop large soil pores that facilitates water infiltration, gas movement, root penetration, and resistance to soil erosion. Soil tilth, or the characteristic of soils to be physically manipulated, is improved with organic matter, and the water-holding capacity of soils is increased by organic materials. Organic materials make heavy clay soils less sticky and much easier to till, while increasing the CEC and water-holding ability of sandier or light soils. Organic matter also reduces Al and Mn toxicities in acidic soils.

In temperate climates, organic material degradation slows during cold months, whereas in warm climates the organic matter is degraded throughout the year. The amount of organic matter that accumulates in soil is not simply a matter of temperature, however. Very dry soil conditions can limit biological activity and organic matter degradation. Saturated soil conditions also reduce the activity by limiting the supply of oxygen that is needed for the more rapid aerobic degradation. Organic soils such as peats develop under conditions in which soils are flooded during much of the year. The amount and characteristics of organic matter returned to the soil obviously also affect the organic matter content of soils. Lighter (sandier) soils tend to have less organic matter than soils with more clay content in a given context of temperature, cropping, etc., because of better aeration and less ability to form organic-clay complexes that protect the humus material from degradation.

Under natural conditions, essentially the only way to remove organic material other than by microbial degradation is by fire. However, when land is cleared and the soil is tilled for planting crops, the mixing action exposes the organic material to oxygen, and degradation rates are greatly increased, regardless of the climatic conditions. The organic matter content then declines with cropping and reaches a new equilibrium depending on the climate, crop rotations, biomass production, and amount of crop residue returned to the soil (Figure 2.6). Note that as a generality temperate soils start with more organic matter than tropical soils and tend to maintain a higher level of organic matter than tropical soils. As discussed previously, the weathering of clays is more rapid under tropical conditions; therefore, organic matter becomes an even more important component of tropical soils than temperate soils in maintaining soil physical properties and CEC.

2.3.2.4 Cropping Interactions – It should be self-evident that crop response to nutrients is highly interactive with other growth conditions. Nutrient problems can be caused by adverse weather conditions, or the response to nutrient additions can be nil or even negative. Similarly, insect pests and weeds reduce the effect of fertilizer additions. As conceptualized by the "Law of the Minimum," growth is dependent on the most limiting factor, but rarely does only one factor limit growth. Several different factors may influence growth at various times during the growing season. Because the strong interactions between nutrient availability, weather, and pests, confound the interpretation of the effect of a particular nutrient, fertilizer experiments are normally conducted under conditions in which the researcher tries to eliminate all of the controllable limitations to yield. Thus, N experiments would normally be conducted on soils fertilized with P, K, and other nutrients at an optimum level, and pests would also be controlled as much as possible. This is quite different from the situation of farmers who make highly complex decisions on the

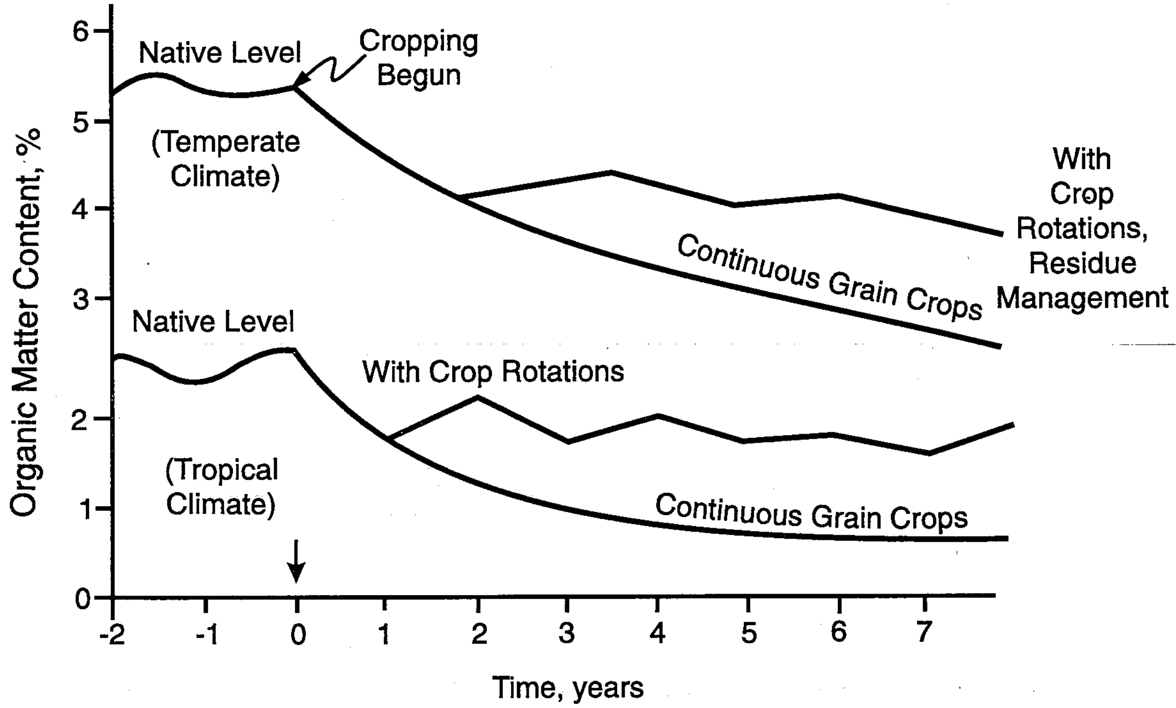


Figure 2.6. Illustration of the Decrease of Soil Organic Matter Following Land Cultivation.

investment of limited amounts of money, labor, time, or land under multiple constraints.

One of the consequences of this approach is that the actual benefits of fertilizers are over-estimated in fertility trials relative to when they are used by farmers. In addition, the results from adverse years when no or poor response to fertilizer occurs are usually not reported because weather caused no response to the nutrient. Unfortunately, farmers cannot make decisions under a similar lack of constraints; they must make investment decisions regarding seed, pesticides, labor, and fertilizer inputs in a total farm management context. To maximize the benefits from management factors, the limiting factors should be in balance with each other, e.g., the crop variety must be able to benefit from the fertilizers used. Weed and insect control, plant density, water availability, tillage, and other management practices should be adequate for the farmer to realize a profit from fertilizer use.

2.4 Fundamentals of N, P, and K

Soil factors that affect the plant availability of the primary or fertilizer nutrients (N, P, and K) are quite complex, and different from one another. The available forms, mechanisms of becoming plant-available, forms of stored nutrients in soils, and timing of plant uptake are different not only between the nutrients but also for individual fertilizer sources of each nutrient. A basic understanding of the reaction of nutrients in soils and the factors that affect the response of crops to fertilizers is essential for people in the fertilizer industry so that they can make informed production and marketing decisions based on what can increase the profit from using fertilizers.

2.4.1 Soil Nitrogen

Nitrogen is a component of amino acids, which make up proteins, chlorophyll (the molecule that captures the sun's energy), enzymes, and the genetic material, nucleic acids. Therefore, this nutrient is needed in large amounts by all plants. Plants that do not have adequate N are yellowish, have yellowing and browning older leaves, are stunted, and have poor root systems. Without additions of N, the nutrient is practically uniformly deficient for all grasses and cultivated crops. The only exceptions are the leguminous crops that have symbiotic bacterial colonies growing within the plant, which have the ability to meet N needs through fixation of atmospheric N_2. Excess N can cause excessive vegetative growth, delayed maturity, and stalk breakage in small grains. The other macronutrients do not have direct detrimental effects when applied to excess.

The availability of N to plants is largely controlled by soil microbial processes. The N cycle in soils is complex, and under certain conditions large amounts of plant-available N can be lost from the soil in drainage water or to the atmosphere (Figure 2.7). In this way, N is different from the other nutrients, which are not as readily lost from soils. The rates of conversion between forms of N and the direction (immobilization and mineralization) depend principally on the growth conditions of the microorganisms, i.e., temperature, moisture, oxygen availability, and composition of organic substrates, etc., rather than simply abiotic reactions.

Nitrogen uptake depends on the relatively small amount of available N forms in soil solution, the soil's ability to replenish the available forms, and the growth conditions for the plant. Of course, any condition that inhibits plant growth such as other nutrient deficiencies, poor rooting conditions, poor weather, etc., will reduce N uptake.

Nitrate (NO_3^-) is the main form of N available to upland crops, whereas ammonium (NH_4^+) is the main form taken up by plants growing under flooded conditions, notably rice. Nitrate moves through soils with the soil water, since soils have little anion-absorbing capacity. Therefore, NO_3^- can move with water to plant roots for uptake. Nitrate is also eligible for leaching into groundwater. To reduce NO_3^- pollution, it is therefore important that the amounts of NO_3^- stored in the soil be minimized during periods in which water percolates through the soil. Fertilizer-N applications can be made more efficient by applying the N shortly before it is needed by the crop.

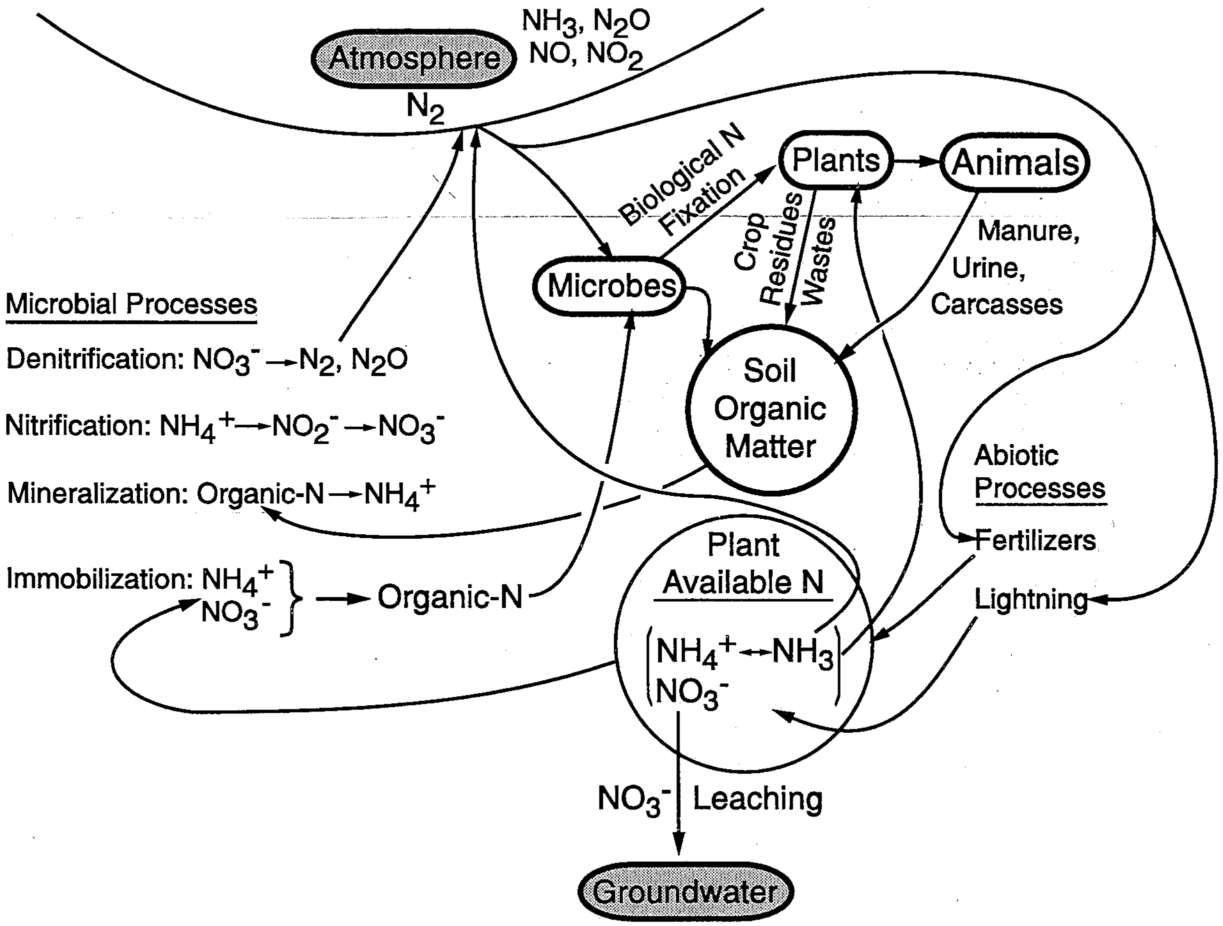


Figure 2.7. The Nitrogen Cycle in the Atmosphere-Biosphere.

Nitrate-N is also subject to loss from the soil through microbial processes when soils become highly anaerobic due to water saturation, which inhibits oxygen movement. When soils become anaerobic, certain microbes use NO_3^- as a terminal electron acceptor, and the NO_3^- is converted to N_2 and N_2O, forms of N that cannot be used by plants. This loss of plant-available N, called denitrification, therefore precludes NO_3^- use in flooded rice culture. When soils are flooded to grow rice, the NO_3^- accumulated from organic matter transformations during the period of dry season fallow is lost through denitrification. Upland soils, which become very wet for a week or more because of poor internal drainage or weather conditions, can lose NO_3^- through denitrification, particularly if there is readily degradable organic material in the soil. The organic material causes O_2 to be consumed more rapidly and provides growth substances for the denitrifying organisms.

While the denitrification process is lamented by agronomists as a loss of plant-available N from the soil system, it is the only way that N is recycled back to the atmosphere as N_2. Without this process, lower soil layers and groundwaters would become large reservoirs of NO_3^-, and the oxygen-enriched atmosphere would support continual conflagrations and, thus, make life difficult. Therefore, the N cycle is just as important as the carbon and the hydrologic cycles to the life support system of the earth.

Ammonium-N is a plant-available form in addition to NO_3^-, but in normal upland soils it is converted fairly rapidly to NO_3^- by a series of microbial reactions collectively called nitrification (Figure 2.7). Most NH_4^+ fertilizers are converted to NO_3^- within a few weeks, but this period can vary with soil temperature, moisture, O_2 availability, soil pH, and the manner in which NH_4^+ or NH_3 was applied. Soils of pH of less than 5.0 nitrify more slowly than more neutral soils. Concentrated zones of NH_4^+ can also reduce the rate of its conversion to NO_3^-. As a cation, NH_4^+ can be absorbed onto cation exchange sites and is therefore normally not subject to leaching as is NO_3^-. In addition, NH_4^+ can move into the interior of clay lattice structures and be protected from nitrification or plant uptake; this is called ammonium fixation. While not significant on most soils, fixation can be appreciable on certain clayey soils. Since NH_4^+ is absorbed on exchange sites, it also does not move with water to plant roots like NO_3^-; therefore, it is normally not as important a form of available N for upland crops as NO_3^-.

As illustrated (Figure 2.7), N in organic forms is the major storehouse of N in soils and since the biological conversions occur fairly rapidly, plants rely mainly on N derived from organic material to meet their N needs. When NH_4^+ and NO_3^- are added to soils, the soil microorganisms make the major decisions as to what happens to the N, that is, whether the N is put into the organic-N pool by their assimilation of the N or is converted to other forms of N either usable or unusable by plants. When a carbonaceous material, for instance straw, is added to soils, NO_3^- or NH_4^+ (termed mineral N) will be used by the microbes to utilize the carbon energy source, and there will be net immobilization or incorporation of the plant-available N into unavailable organic forms. This organic N can then be converted back to NH_4^+- and then to NO_3^- after only a few weeks and become available to the crop. This organic pool of N is therefore the most important aspect of N nutrition, and 70%-80% of the N taken up by crops is normally from this pool rather than directly from mineral fertilizer additions. Synthesized fertilizer-N sources not only increase the available mineral N status of soil but also temporarily increase the amount of N in soil organic matter as well.

2.4.1.1 Application of N Fertilizers – Because N applied to soils can enter the large organic pool or be lost from the soil by the several mechanisms illustrated in Figure 2.7, N efficiency, or how efficiently the applied N is taken up by the crop, is normally only 40%-50%. Efficiencies of 90% are also possible under conditions when the crop is growing rapidly and takes up more of the applied N before other processes occur. Since the amounts of N fertilizers used are normally more than other nutrients and losses are variable and high, methods to improve N efficiencies have been of considerable interest. Judicious timing of applications, coatings to control the release of N, improved application methods, nitrification inhibitors, and urease inhibitors have all been demonstrated to improve efficiencies, but considerable scope still remains to increase N use efficiencies.

There is considerable evidence that plants respond better to having both NH_4^+ and NO_3^- present in soils. For this reason and to reduce losses of fertilizer N through leaching and denitrification, there has been considerable work on developing organic compounds that specifically block the nitrification processes. Currently the compounds dicyandiamide (DCD), which is both an N source and a nitrification inhibitor, and 2-chloro-6-(trichloromethyl) pyridine (trade named N-serve) are marketed as nitrification inhibitors.

Efficiency can be affected by the form of N used, either nitrate, ammonium, ammonia (either in solution or anhydrous), or urea. There have been scores of experiments to compare N sources, improve N efficiency, and establish the reasons for poor efficiencies. This research has shown that generally there is little difference in crop response to different N sources provided the fertilizers are applied appropriately. This means that anhydrous ammonia is placed below the soil surface to avoid losses, and urea is incorporated, etc. Under a specific condition, one form may produce slightly better results than another, but under another condition the results might be reversed, depending on the susceptibility of the particular N form to the major loss mechanisms under particular weather and soil conditions. An exception to this generality is the ill-advised use of nitrate sources on flooded soils.

2.4.1.1.1 Urea Reactions in Soils – Urea requires more specific discussion because it is neither an ammonium nor nitrate form, but it can be considered an ammonium source. Urea is the main form of N excreted by animals. Because of the importance of available N sources, microorganisms and higher plants have developed an enzyme capable of hydrolyzing urea to be able to utilize the N from urea. The enzyme, urease, was the first enzyme to be crystallized in a pure state. All enzymes are protein catalysts of biological origin, but urease can exist extracellularly in organic matter-clay complexes. This extracellular enzyme gives soils an intrinsic lower-limit of urease activity, mainly related to the amounts of clay in the soil. Since urease is of biological origin and it is also contained in microbial cells, urease activity is also related to the biological activity of soils, which is a function of the organic matter content and other microbial growth factors.

Urease catalyzes the following reaction:

$$CO(NH_2)_2 + 2\,H_2O + H^+ \xrightarrow[\text{urease}]{} 2\,NH_4^+ + HCO_3^- .$$

The reaction is written to illustrate the formation of the ionic species most prevalent at soil pHs. While urea is extremely stable at ambient conditions, soil urease converts urea rapidly; often urea fertilizer additions are completely hydrolyzed in 2 to 3 days, a very rapid reaction in soil terms. The rate of hydrolysis depends on the soil temperature, moisture, how dispersed the urea is, and the amount of urease present. Very cold or dry soils hydrolyze urea more slowly than warmer or moist soils. The enzyme activity can be significantly different in different zones of a particular soil. High enzyme activities can develop on a moist soil surface because of algal and other microbial growth on the soil surface.

For a given urea distribution, the faster the urea hydrolysis, the higher the ammoniacal and carbonate concentrations can become. The ammonia/ammonium equilibrium (pKa = 9.3) at the soil surface determines how much ammonia is lost to the atmosphere, but the loss is also related to soil moisture, wind turbulence across the soil, soil CEC, and possibly solar energy input. In addition to producing high pH conditions conducive to ammonia volatilization losses from surface-applied urea, the pH is also buffered by the carbonate produced. Therefore ammonium sulfate, diammonium phosphate, and ammonium nitrate, which lack this buffer, are less susceptible to NH_3 volatilization losses than urea when surface applied. After urea hydrolysis, the ammoniacal forms are nitrified like any ammonium source.

The loss of NH_3 to the atmosphere of surface-applied urea can be extreme; loss of 50% within 7 days of application has been measured for both flooded rice and moist upland soils. Losses can be greatly decreased by incorporation shortly after application, by banding, by point placement of large granules of urea at a depth of 5 to 10 cm, or if water additions shortly after the urea application wash the urea into the soil. Urea is very soluble in water, and it is not absorbed by soil particles and therefore moves freely with water in soils. The effect of urea granule size on urea hydrolysis and subsequent N losses can vary. Smaller urea particles facilitate more rapid urea hydrolysis but also provides more access to cation exchange sites for NH_4^+ absorption. It is possible to leach urea when large granules are applied to soils with high percolation rates and low urease activities, i.e., sandy soils. If urea is incorporated shortly after application, its efficiency is the same as any other source. For topdress applications to pastureland, efficiency would average perhaps 70%-90% that of other N sources, with the amounts of ammonia volatilization loss being very dependent on weather conditions following application.

2.4.1.1.2 Adverse Effects of Nitrogen Transformations – Leaving out several intermediate reactions, the microbiological process of nitrification can be simplified to the following:

$$NH_4^+ \xrightarrow{2\,O_2} NO_3^- + 2\,H^+ + H_2O + \text{Energy}.$$

This illustrates that the process is aerobic (requires O_2) and yields energy for the microbes. Most importantly to soil productivity, it is acidifying. Ammonium, whether originating from organic matter mineralization, urea, or ammonium salts, goes through the same process and, as a result acidifies soils, while addition of nitrate does not cause acidification. Therefore, it is an unfortunate aspect of crop cultivation that large amounts of N are needed to grow crops, and N additions, either as NH_4^+ or organic forms, acidify soils. The N compounds in organic and legume residues also acidify soils since they are ammonium sources following mineralization of the N-containing compounds. The amount of acidification, in equivalents of pure calcium carbonate needed for its neutralization, varies with the carrier anion of the material, ammonia volatilization losses, and secondary reaction products (Table 2.3). The choice of N products can therefore be based not only on the price per unit of N but also on the cost of counteracting the acidification

Table 2.3. Acidification Caused by Various N Products

Material	% N	kg Pure $CaCO_3$ to Neutralize[a] Per kg of N	 Per kg of Material
Ammonium sulfate	20.5	5.35	1.10
Ammonium nitrate	33.5	1.75	0.59
Urea	46.6	1.80	0.84
Anhydrous ammonia	82.2	1.80	1.48
Monoammonium phosphate	11.0	5.00	0.55
Potassium nitrate	13.0	0[b]	0[b]
Calcium ammonium nitrate	20.5	0	0
Dried blood	13.0	1.75	0.23
Sewage sludge product[c]	7.0	1.70	0.12
Peruvian guano	13.8	0.95	0.13

a. $CaCO_3$ needed to neutralize material after nitrification in soil, assuming no N losses.
b. Actually base forming.
c. Milorganite, from Milwaukee, WI (U.S.A.).

Source: Based on Tisdale et al. [5].

caused by the product. Additions of N fertilizers in excess of plant needs will cause soils to acidify more quickly.

Additions of N fertilizers in excess of crop uptake or if applied at inappropriate times can cause another problem – contamination of groundwaters with nitrate. During different periods of a crop season, the amount of nitrate in the soil varies with the rates of mineralization, ammonification, and nitrification and the counteracting processes of plant uptake, leaching, and denitrification (Figure 2.7). Nitrate leaching is generally not a problem during periods of active crop growth except on very sandy soils that receive excess amounts of water. At the end of cropping seasons there is normally very little N in mineral (available) forms since healthy crops are effective at taking up N in these forms.

2.4.2 Soil Phosphorus

Phosphorus compounds are important in energy transfer and storage reactions since electrons are moved via adenosine di- and triphosphate in most biochemical reactions. Phosphorus is also a constituent of nucleic acids, which make up genetic encoded strands of DNA and RNA used for protein synthesis. Flowering, fruiting, seed formation, and early plant development therefore rely heavily on P supplies, as do root development and several other processes. Even though the P content of plant tissues is about 0.1%-0.4%, which is about one-half of the amounts of N or K, P is a critical component of particular compounds basic to life. Phosphorus is fairly mobile in plants and is therefore moved to the youngest tissues if plants are P deficient. Deficiencies of P are not as readily observed as those of N, or even K, although the effects on growth and yield are often dramatic. Some plant species exhibit a purple or red coloration when they are deficient in P; all will show overall stunting.

The orthophosphate form $H_2PO_4^-$ predominates as the form of P taken up by plants although there are also a few organic compounds that have been shown to be taken up directly by plants. The solubility of orthophosphate compounds in the soil largely controls the availability of P to plants. At any time during a growing season, the P concentrations in soil solution may vary from 0.05 to 3 ppmw. Unlike N, which is supplied as NO_3^- by mass flow of water to plant roots, only a fraction of the P needed by plants is supplied by mass flow with soil water. Diffusion is a much more important mechanism by which plant roots are supplied with P, and the amounts of P in solution and its replenishment are determined by the dissolution of relatively insoluble P compounds or minerals. However, plant roots are not totally passive sinks for P; the exudation of organic materials provides substrates for microbial populations, which produce various acids that help to dissolve P compounds in soils. Zones around plant roots, called the rhizosphere, support colonies of microorganisms that are essential to the growth of many species of plants.

Essentially all native soil P originates from apatitic minerals. As apatites weather, new minerals are formed, which are relatively soluble, and make up the labile P pool, which replenishes P in soil solution. Many less soluble forms are also formed that comprise a nonlabile pool, which is a large but fairly inert storehouse for P.

The P moves between the various pools of varying solubilities in response to changing phosphate and cation concentrations. The distribution of these compounds depends principally on the Ca, Fe, Mn, and Al concentrations and the soil pH. Organic forms of P can also be of importance in soils. Young soils, which contain weatherable apatites, are better endowed with available-P than older, more weathered and acidified soils.

2.4.2.1 P Fixation – When water-soluble sources of P are added to soils, the orthophosphate forms are converted to many different compounds, depending on the above elements and soil pH. In soils of moderate pH, Ca phosphates dominate, whereas Fe and Al compounds become more important in more acidic soils. An incomplete list of over 60 compounds or mineral forms of phosphates has been identified as being formed in a P fertilizer reaction zone [5]. These compounds then revert to even more stable or insoluble compounds with time. Various sorption reactions onto metal oxides, hydroxides, and carbonate mineral surfaces also occur; these reactions are either reversible or relatively irreversible and affect phosphate solubilities and supply. These relatively irreversible reactions of phosphate are collectively called P fixation and are very dependent on the chemical constituents of soils. Soils that are of near neutral reaction and sandy texture have little fixation; next would come other neutral soils with lower levels of soluble Fe and Al. Soils with the highest fixation are acidic, clayey soils high in Fe and Al. Younger soils tend to have more available-P and lower fixation capacity although some young volcanic soils have colloidal amorphous materials that fix large amounts of P. The response of crops to added water-soluble phosphate fertilizers is very dependent on P fixation capacity since the amount of P which is actually available depends on the P fixation capacity (Figure 2.8).

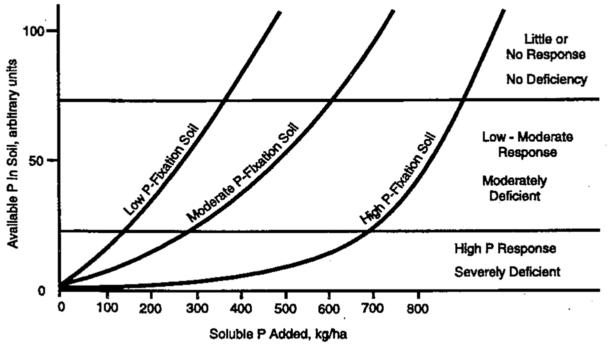


Figure 2.8. Illustration of Phosphorus Availability in Soils of Different P Fixation Capacity as Soluble P Fertilizers Are Added.

Figure 2.8 attempts to illustrate several points: (1) crop response to P fertilizer is very dependent on the fixation capacity of the soil that is fertilized; (2) response to P can change dramatically with P fertilization after the fixation capacity is satisfied; (3) after P fixation is satisfied and the available P level is raised to the no-response zone, further P additions are only needed to replenish P removed by the crop; and (4) the efficiency of P applications will be different on the same soil, depending on the amount of soluble P fertilizers that have been previously applied.

A favorable aspect of the mechanisms by which P is held and released in soils is that there is little P lost from a soil except through harvested crop removal and soil erosion. The P lost through erosion is contained in clay particles and organic matter. There generally is little movement of P through soils with percolating water since soils contain Ca, Fe, and Al in sufficient quantity to precipitate the forms of P. However, extremely P-fertile soils can leach small amounts of orthophosphate. Organic-P forms are more mobile in soils than mineral forms. Soils that have had large amounts of animal manures added can have organic-P compounds leached into relatively shallow water tables. The P added in animal manures can move perhaps twice as far as similar amounts of inorganic P.

In fortunate contrast to N, the formation of P compounds of limited solubilities in soils allows P fertility to increase through P additions, and P applied in one year can furnish P to succeeding crops. This is called a residual fertilizer effect. The P not used by the crop remains mainly in the nonlabile or plant-unavailable pool, but it still contributes to the P nutrition of crops for many years. From solely an agronomic perspective, it is most beneficial to build P fertility rapidly by fairly large additions, then apply only the amounts needed to maintain the P status, which can be done every other year or every third year.

While fixation of P largely controls the efficiency of P fertilizer use, even under the best of conditions the uptake of added fertilizer P by the first year's crop is normally only 10%-15%, even lower than for N which is readily lost from soils. This low amount of uptake of applied P fertilizer results from the formation of nonlabile and fixed compounds, which contribute little to uptake in a specific cropping season. An interesting example of an extreme in P fixation occurs in the Cerrados area of Brazil. In early fertilizer trials in the region, little response to P was found even though the soils were extremely P deficient. It was thought that crop production on these soils would not be economic because of the severe P fixation. Scientists showed that large amounts of P (400-800 kg P_2O_5/ha) could be added to satisfy the P fixation of the soils, and amounts added above this amount produced a typical P response found for less fixing soils. When the P needed to satisfy P fixation of the soils was treated as a capital investment in the land, important land areas in the Cerrados region became major suppliers of soybeans to the world market. Although liming can reduce P fixation considerably by reducing the formation of insoluble Fe and Al compounds, additions of other materials besides phosphate do not reduce P. fixation.

2.4.2.2 Dissolution and Water Solubility of P Fertilizers – An important question regarding P fertilizers is how much water solubility is desirable to furnish P to crops. The main issues are (1) the expense of making apatite more water soluble by treatment with strong acids or by heating and (2) if much of the water-soluble P is rapidly fixed or made insoluble, what is gained by adding a soluble source? Answering these questions is not easy because soil characteristics, P application method, P fertilizer particle size, crop P demand, the value of the residual P, and even the weather influence the answers [6]. Obviously the addition of ground apatite (phosphate rock or PR), with limited solubility, would not meet the needs of crops with high and rapid demand. They have the greatest benefit on highly acidic soils and must be applied in larger amounts than more concentrated and soluble P sources. Fertilizer particle size and the proximity of particles to each other affect dissolution of P fertilizers and the rate of fixation (precipitation, occlusion, etc.) that occurs around the materials, since P movement is controlled by solubilities and diffusion mechanisms.

Phosphate fertilizers are analyzed by various methods in different countries to establish their value as fertilizers. Using the U.S. system, for example, P fertilizers are analyzed for water-soluble P, citrate-soluble P (soluble in 1N ammonium citrate after water extraction), and total P. Plant-available P is considered to be the sum of the water- and citrate-soluble P. In actuality, of course, plant availability is not only a function of forms of P in the fertilizer but the soil environment into which the fertilizer is placed. The uptake pattern of the plant, particularly how rapid the P uptake is, determines to a large extent how suitable different sources are for different crops. Fertilizers of low solubility are more suitable for long-term crops on low fixation soils, whereas higher solubilities are required for short-season crops with high P requirements. Thus, cassava or tree crops would respond better to less-soluble P sources than would white potatoes. Not only are their demand rates for P different (slow versus fast, respectively) but also the soil temperatures under which the crops are grown are much different. Potatoes therefore require large amounts of soluble P; cassava requires little.

In some cases crops may have similar P requirements and uptake patterns, but the soil environment defines the response. For example, flooded rice and wheat may need similar amounts of P, but under flooded reduced soil conditions, Fe phosphates and other minerals become very soluble. Even small amounts of total P in the soil can meet the rice requirements, while wheat grown on the same field under upland conditions may be severely P deficient. In another example, ground PR might supply a wheat crop with adequate P on a soil with a pH of 5.0, but on a soil of pH 6.0 the same amount of PR would have little effect.

The diammonium and monoammonium phosphates are completely water soluble, as are potassium phosphates. Acidified PR products (nitric phosphates, single superphosphate, and triple superphosphate) and heated or calcined products can differ in their available P content depending on the degree of acidification, the extent of the reaction, or the degree of calcination.

Phosphate rocks can be applied directly to soils to furnish P, and they have been used for the past century. With their limited solubility, however, they are most beneficial on very acidic soils (pH below about 5.2). Most PR must be ground to a fairly fine state to improve its reactivity in soils, which make it less convenient to handle than granulated fertilizers. There are large differences in the reactivity of PRs, which increases with the amount of substitution of carbonate for phosphate in the apatitic mineral structure. Warm climates with adequate soil moisture and acidic soils have the potential for PR to be competitive with other P sources under certain conditions, particularly for slow growing crops, and if transportation costs are low.

With the exception of PRs used for direct application, there normally is a negligible difference in crop response between sources of the common P fertilizers, which indicates in itself that differences in water solubility is not a major factor in determining P availability. A possible exception to this generalization is that N-P sources are sometimes more efficiently used in banded applications because of N-P interaction created by increased root proliferation in the fertilizer zone and anion/cation effects. The effect of placing ammonium sources with water-soluble P has been shown to be the most beneficial.

It is generally accepted that 80% water solubility is sufficient for most crops, and 60% water solubility is often sufficient for long season crops or extensively rooted crops like forage legumes or grasses. Low water solubility products are less effective on calcareous (free calcium carbonate, pH above 7.5) soils. High water solubility is also desirable on cooler soils and for crops with high P demand or with limited rooting zones. Partial acidulation of PRs can supply some water soluble P and is also an alternative.

2.4.2.3 Effects of Placement and Particle Size on P Efficiency – The efficiency of P fertilizer use can be affected more than other fertilizer nutrients by the method of placement and the size of particles. On soils with high P fixation, the placement of P fertilizers in concentrated zones can greatly improve efficiencies of uptake by reducing the exposure of the soluble phosphate forms to precipitation as insoluble "fixed" forms and by inducing plant root proliferation in the zone. Banding of P fertilizers has become common practice to improve efficiency, but it requires soil openers and fertilizer hoppers on the planter or drill equipment. Manual band application is laborious. Bands often increase P efficiency threefold over broadcast incorporated applications, but the efficiency can actually be reduced on dry soils because nutrient uptake ceases when the soil in the fertilizer zone becomes dry. Bands are therefore most efficient if they are at a depth where there is good soil moisture and yet readily reached by plant roots. Band applications can be done with the seed, called a pop-up application in the United States; beneath and to the side of the seed, called a starter application; or between the crop rows. Starter or pop-up applications are most beneficial on cold, wet soils.

Similarly to bands, the size of individual granules can affect the amount of P fixation that occurs. Large granules of P sources are therefore more efficiently used on many soils than smaller particles. Obviously there are limits to this generalization since the particles cannot be so large that access by roots is limited. Surface applications are generally not as efficiently used as applications within the plow layer since plant roots do not normally grow near the soil surface. Surface banding before plowing, however, can also improve P efficiency. An exception to improving P efficiencies with concentrated zones of fertilization is with insoluble sources such as PR, which requires soil contact for dissolution.

2.4.3 Soil Potassium

Potassium is considerably different than the other fertilizer nutrients, both in its function within plants and in the way it becomes available to plants. Unlike most nutrients, K in plants does not become part of structural components of plants nor elements of proteins, carbohydrates, etc., but it remains as an ion, mainly in cellular liquids. It functions to control turgidity of cells, helps in the transport mechanisms of starches and sugars, acts in protein synthesis, and activates enzymes. It encourages root growth, makes plant stalks healthy and strong, and is very important in reducing the effects of drought. Frequently, the most important benefits of good K nutrition are not only in yield but also from the reduction of fungal diseases, and improved quality of harvested products. Since K is very mobile in plants, deficiency symptoms are seen in older leaves first, usually as yellowing or browning of the leaf margins, or in some crops as brown spots on the older leaves. Deficiency symptoms are not as readily observable as those of N, even though K is needed in almost the same amounts as N. Overall slow growth, lodging (the plant falls over from stalk weakness), and poor grain or fruit quality are often indicators of K deficiencies. Potassium is important to crops in root and grain development, and many other aspects of plant growth and development.

As a cation, K enters soil solution from cation exchange sites of clays and organic materials. The exchangeable K originates from the weathering of the minerals contained in the rocks from which soils are formed. Potassium feldspars are very large natural reserves of available K in young soils; however, they are rapidly weathered and thus are essentially absent from moist tropical soils. Various micas, orthoclase, and microcline are primary silicate minerals that contain K. These primary minerals degrade to illite, clay chlorite, and vermiculite with release of K^+ contained as layers in the clay lattices. Vermiculite and its degradation product montmorillonite (smectite) are 2:1 layer clays, meaning that two tetrahedral silica sheets around one octahedral alumina sheet comprise the basic structure. These clays have the ability to expand and contract with changes in soil moisture, an important characteristic because they can affect water movement and storage, K release and absorption, and soil structure.

Young soils with appreciable clay content commonly contain large amounts of K, and some of these soils can be cropped for years without development of substantial K deficiencies. Weathered, sandy, and organic soils are primarily in need of K additions. Sandy and weathered soils, particularly under warm, wet climatic conditions under which organic matter degrades rapidly, have low CEC, which means they can retain only small quantities of K. They also lack clays that can fix K within the clay lattices. Potassium added to such soils can be leached as can other base cations, particularly when other nutrients such as N and S are added, which add concomitant anions to maintain electroneutrality in the leachate.

The leaching of K^+ tends to be more dependent upon the amount of percolate passing through the soil than on soil texture. Sandy soils, however, can infiltrate more water than heavier soils, so less runoff occurs than with a heavier soil on a similar slope and rainfall intensity. Leaching losses of K^+ can vary from essentially nil to somewhat more than 100 kg K ha^{-1} yr^{-1}. Losses from sandy irrigated soils can be particularly high. Soil liming generally decreases the amount of K leached from soils; in one case it reduced losses to about one-half [7], and this is an important aspect of liming in maintaining soil fertility.

Losses of K through erosion of clays from the soil surface can be very substantial. Few measurements of runoff loss have apparently been done, but these losses are certainly important. Since K can be lost from soils and fixed in clay minerals, yearly additions of K are more efficient than larger, infrequent applications on some soils although few crops respond to split applications of K in the same season as they do to N.

Plants need large amounts of K, which is removed in harvested plant parts. Plant residues left in the field can return some K back to the soil. Animal manures are important sources of K because they often contain as much K as N. Applied K salts, as KCl or K_2SO_4, give the same K response, but in some cases the crops may respond to either the Cl or S carriers.

Because 100 kg K per hectare is often removed annually through cropping, even soils that have adequate amounts of K in their clay materials will ultimately develop K deficiencies. The Hungarian Plain, for example, became deficient in many nutrients through centuries of cropping although the soils were relatively fertile in their native state. Many countries have not conducted adequate extension and demonstration work to convince farmers to use adequate K, and more effort is needed in this area.

2.4.4 Soil Sulfur

Sulfur is needed by plants in amounts similar to those of P. It is an essential constituent of three amino acids, the building blocks of proteins and enzymes. It cycles in the soil-plant-atmospheric system similarly to N, with reduced sulfide forms (H_2S, pyrites), oxidized sulfate, and organic S forms existing in soils, while sulfur dioxide and organic sulfur compounds exist in the atmosphere. As with nitrogen, organic forms of S comprise the major storehouse for soil S. A notable difference between N and S is that gypsum ($CaSO_4 \bullet 2H_2O$), a relatively insoluble mineral, can form in soils to maintain S in more arid soils. Insoluble sulfates also form in wetter soils and accumulate S in subsoils. Obviously the atmosphere does not contain elemental S as it does N_2.

Sulfur deficiencies in plants look similar and are often confused with those of N. Both deficiencies are manifest as yellowing of the plant; yet, there are clear distinctions. Deficiencies of S are seen in the younger leaves, whereas those of N are seen mainly in the older leaves. Sulfur deficiencies result in small, spindly plants and severely reduced nodulation for BNF in legumes. Seed and fruit maturation is also delayed.

Sulfur deficiencies can readily develop, particularly in humid areas and areas that do not receive S from the atmosphere or from S-containing fertilizers. Atmospheric sources of S are organic S compounds emitted from marine plankton and inorganic S from oil and coal combustion. Because enforcement of environmental laws and better technologies have reduced the amount of S that soils receive through acid rain, this source has decreased. In addition, since higher analysis fertilizers have largely replaced S-containing single superphosphate and ammonium sulfate, incidental contributions of S to soils are reduced. Sulfur deficiencies are therefore expected to increase, and sulfur-containing fertilizers will probably be needed, particularly in moist tropical areas and especially for legume and vegetable production.

2.4.5 Other Nutrient Deficiencies

As stated earlier, deficiencies of the micronutrients (needed in small amounts by plants) and other nutrients such as Ca and Mg (needed in large amounts) can all cause extreme reductions in plant growth and yield. In some cases, additions of small amounts of micronutrients can correct a deficiency and may be added to NPK fertilizers to alleviate the problem. Larger amounts of Ca and Mg are needed. Deficiencies of micronutrients are often caused by unavailability of the nutrients even though they may be present in large amounts in the soil. This phenomenon occurs most notably on soils that have a high pH, and the addition of the nutrient to the soil only causes precipitation of the nutrient as insoluble forms. The high pH could be lowered to alleviate the deficiency, or the nutrient could be supplied efficiently by foliar application of soluble nutrient forms to the plants. Many nutrient problems can be alleviated or avoided by application of organic materials and by maintaining the organic matter content of soils.

While an in-depth discussion of these deficiencies is beyond the scope of this chapter, there are a few generalizations. Problematic soils are normally the very acidic and the very basic soils. Sandy soils, particularly those that are deficient in organic material, are especially problematic, particularly after fertilizers have been used and new deficiencies are created because of the increased removal of nutrients in harvested crops. Inefficient and excessive use of fertilizers can also induce nutrient deficiencies or soil problems; for example, Zn deficiencies can be caused by excessive P use, and soil acidification can be caused by ammonium fertilizers. New, and often unexpected, nutrient problems can develop with cropping, which can only be adequately diagnosed and addressed by trained agronomists. There are numerous interactions of factors that may be important besides pH, organic matter, and fertilizer use. Crops vary substantially in the amounts of micronutrients that they require and how efficiently they use what is available. Many problems with nutrients can be avoided by good land management, particularly controlling soil erosion, maintaining the soil organic matter content and the soil pH.

2.4.6 Non-Nutrient Soil Problems

Productive soils can be rendered unproductive through mismanagement. The most common mismanagement is that the soil is not adequately protected from wind and water erosion by plants or crop residues. Erosion preferentially removes the organic matter and clays from soils, the two most important constituents to soil productivity. Materials eroded from soil have higher nutrient concentrations than the original soils by factors of 3 to 12. Soils naturally concentrate nutrients in the surface or topsoil layer, which also is a much better physical growth medium than undeveloped subsoil layers. As the topsoil is eroded, soils become less productive. Loss of gross national product (GNP) because of soil erosion has been estimated to be from 1.5% to 10% per year in several tropical countries.

Soil productivity can also be lost through poor irrigation management and poor water quality, which cause the accumulation of soluble salts in the soil. Irrigation waters contain soluble salts that remain in the soil after the large amounts of water are transpired by crops, particularly in hot, arid areas. The salts can be leached from the rooting zone if adequate water is added and the soil permits water movement. However, some soils do not allow enough water movement through them to remove the salts, and the salts reduce soil productivity. Expansion of irrigated areas has been a major driving force of increasing world crop production. Unfortunately, poor irrigation techniques, poor water quality, and unsuitable soils have caused many irrigated areas to become saline and waterlogged. Current estimates are that the areal extent of irrigated areas being created is about equal to the areas being permanently destroyed by salinity and high water tables.

Salinity raises the osmotic pressure of the soil water, which inhibits water uptake by plants. In addition, if the irrigation water contains high amounts of Na relative to Ca and Mg, the soil clays can be deflocculated or dispersed as Na comes to occupy a higher proportion of cation exchange sites relative to Ca and Mg. As the clays are dispersed, the aggregation of soil particles is destroyed, and the soil becomes practically impermeable to water. This makes the removal of salts very difficult if not impossible. Although it is extremely difficult, sodium-affected (sodic) soils can be ameliorated by the addition of Ca (usually gypsum), by the selection of deep-rooted plants, and by careful water management. The best solution is to avoid the problem by monitoring the Na content relative to the other cations, good water management, use of crop rotations, and application of Ca sources.

Because chemical fertilizers are salts, the over-application of soluble fertilizers can cause the soil solution to have high osmotic pressure and inhibit water uptake by seeds or plants. For this reason, soluble fertilizers (mainly the N and K forms) cannot be applied in large amounts with seeds or close to plants. A "salt index" was developed years ago to provide relative guidance as to the effect of the fertilizers on the osmotic pressure of soil solution. While the concept is reasonable, the application of it has not been very useful since the type of soil, rainfall, and moisture content largely determine the salt effects on germinating seeds. The salt index therefore has been of limited value in developing application rates and techniques, and agronomists have developed more specific recommendations as to how much fertilizer can be placed with the seed or banded next to the seed. Often ammonia toxicities to germinating seeds from urea or an ammonium fertilizer cause germination problems rather than a salt effect.

The salt effect of fertilizers and soil salinity developed in irrigated systems have led to recommendations and policies regarding fertilizer use in certain countries. This has been largely an unfortunate outcome based on poor understanding of the origin of salts and the possible effect of fertilizers. The amount of salts contained in even good quality irrigation water is much greater than the amount of salts added at normal rates of fertilization. The calculation of salt buildup with different quality waters is fairly simple and readily shows that the salt addition from fertilizers, such as potash (KCl), is inconsequential. Texts on soil salinity do not even discuss the issue since the salts from fertilizers are not significant in the development of soil salinity.

2.5 Diagnosis of Nutrient Problems

Trained, experienced agronomists can often look at the leaves of crops and diagnose deficiency symptoms and other soil problems. Because of the large number of interactions, such as crop, variety, growth stage, weather conditions, tillage, land history, and other factors, this is often successful only if the agronomist can personally observe the crop. However, in some cases deficiency symptoms are difficult to diagnose in the field. The crop may not show sufficient symptoms to diagnose the problem, called "hidden hunger" in fertilizer promotions, or have multiple nutritional problems. Herbicide damage and diseases may make it difficult to clearly determine deficiencies and toxicities. Tissue sampling and analysis can be used to establish the deficiency or toxicity. The concentrations of nutrients in specific leaf tissues, response to nutrient addition, and crop yields have been shown to be highly related.

2.5.1 Plant Tissue Analysis

The analysis of tissues can be used to identify observed nutrient deficiencies, to survey geographical areas for possible problems, and to distinguish between nutrient problems and herbicide damage or other problems. Since plant symptoms are a manifestation of a lack or a buildup of particular compounds in plants, which may result from a variety of causes, the measurement of nutrient concentrations is a much clearer indication than the symptoms, and use of tissue analysis began as early as 1926 in the United States. Generally the youngest fully developed leaf of plants gives the largest range between sufficiency and deficiency. At early growth stages, whole plants can be used. Nutrient deficiencies may occur and then disappear at various stages of growth, but the most critical period to developing yield is the time of flowering and very early fruiting stage.

Scientists have developed indices of concentrations of nutrients in specific plant parts at certain growth stages. A system called the Critical Nutrient Range (CNR) establishes ranges of concentrations of nutrients for many crops, which delineate sufficiency, deficiency, and toxicities. This approach works quite well when one nutrient is mainly limiting. Occasionally, however, excesses of one nutrient, or deficiencies of several nutrients, cause the CNR to give misleading indications. This has prompted scientists to use nutrient concentration ratios to determine antagonisms between nutrients, such as N/S, K/Mg, K/Ca, N/P, and others. Comprehensive consideration of the many possible nutrient interactions is needed. In addition, it should be noted that nutrient concentrations may be high because nutrient deficiencies cause metabolic processes and growth to decrease. If one of the deficient nutrients is added, growth may then increase and other nutrients are shown to be deficient because their concentrations are essentially diluted in the tissue.

A system called DRIS (Diagnosis and Recommendation Integrated System) was developed by a South African researcher to overcome these limitations. The system compares ratios of the nutrient concentrations and can help determine when nutrients are in balance relative to each other. This gives a better indication of which nutrients are deficient [8].

The analysis of plants gives a reliable indication of what nutrients are actually available and recovered by the crop. However, in many cases, that knowledge comes too late to apply fertilizer to affect the growth of the current crop; it is likely useful for succeeding crops or for perennial crops. Tissue analyses also require fairly sophisticated instrumentation and a knowledge base for the interpretation. To maximize the benefits of money spent on fertilizers and to avoid crop nutritional problems and environmental problems, farmers need the techniques of soil testing and tissue analysis to determine which nutrients are needed and in what quantities.

2.5.2 Soil Testing

Adjacent fields having the same soil but different fertilization and cropping histories develop different levels of soil fertility over time. This fertility level greatly affects the crop response to particular nutrients and obviously the most profitable fertilizer rate. If the farmer has a good estimate of the fertility status for each nutrient, anticipated crop growth conditions, and the relation of nutrient addition and crop yield, he could fertilize at a rate that maximizes his profit given the prices for the fertilizer and the crop. This is difficult for most farmers to do, but soil testing can remove some of the guesswork.

Soil testing (often called somewhat inappropriately "analysis") is a process of taking a representative soil sample from a field and testing it for available nutrients. From this test, expected yield, and prices, a recommendation is made of how much fertilizer should be applied to maximize the profit for the farmer. Although not an exact science, the process has proved its worth in the past 50 years. Soil testing becomes more important after fertilizers are used for some years since large differences in fertility between fields in an area will develop, and P and K levels increase in the soil. It is therefore very cost-effective to establish more accurately the necessary rates and monitor the soils for other potential problems.

Soil testing uses quite rudimentary analytical procedures; the problem is to select the correct extractants and measure parameters that are indices of the availability of each nutrient. This requires a chemical extraction or other method that gives numbers for the fertility status of each nutrient or other characteristics that relate well to expected crop response. Normally categories of (1) very deficient, (2) deficient, (3) sufficient, and (4) high are satisfactory. The test is analogous to a blood test. Knowing that your red blood cell count is 1,252/cc is not particularly useful unless you know if that number is considered normal, high, or low. Similarly, is an extractable P level of 15 ppmw P high or low? Is 150 kg K per hectare sufficient or deficient? Some agronomists spend their careers conducting experiments that allow them to relate the numbers of the tests to the most profitable use of fertilizers, and a great amount of information exists on soil tests and expected fertilizer response for different crops.

Soil testing procedures are used to measure soil pH and in places where they might be problematic, soil salinity and alkalinity (in soil science terms this refers to the Na content, not pH). This can be used to suggest management procedures, selection of crop, and liming recommendations and providing information on irrigation and drainage problems. The soil test recommendations give farmers guidelines for not only rates of each nutrient but also advice on the most efficient methods of application and timings of fertilizers. A major problem that occurs when soil testing is not used with fertilizer use is that soils become too fertile in certain nutrients. This not only causes inefficiencies but also can cause new nutrient problems to occur, excess acidity, contamination of water resources by nutrients, and excess leaching losses of other nutrients.

Testing for N is problematic because of the rapid fluctuations in available N that can occur. However, if the soils, climate, and crops are well known, agronomists can make good recommendations based on past cropping and yield potential. In some cases they may additionally base it on a soil organic matter test. In recent years, more accurate N recommendation procedures have been developed by testing the soil for nitrate before N fertilizer topdressings to small grains or sidedressings on row crops. Chlorophyll meters, which measure the intensity of the green color of leaves, have also been used successfully.

The measurement of P availability in soils requires very good application of the art of soil testing because the soil extractant must remove P from many minerals of different solubilities in amounts proportional to the amount of P that will become available to the crop during growth. The P extractants are therefore chosen depending on prevalent soil characteristics of the area to give the best possible relationship between extractable P and crop response. The P test is one of the more valuable tests since it is a relatively expensive nutrient that can build to excess levels and cause deficiencies of other nutrients, such as Zn. Information on the most profitable application rate and the best method of applying P at particular soil test levels and with particular crops is valuable information for farmers.

The test for K is more straightforward and universal than that for the other nutrients. This test measures the amount of K^+ on cation exchange sites by displacing the K^+ with an excess of another cation. However, knowledge of K fixation and release of exchangeable K^+ on specific soils is very important to the interpretation. On a sandy soil, 150 kg K ha^{-1} may be quite sufficient, whereas on a clayey soil, profitable responses to additional applied K up to tests of 350 kg K ha^{-1} may be found. Similar tests for Ca and Mg may be conducted on soils suspected of having these deficiencies.

The availability of other nutrients, such as S, Zn, B, Cu, Cl, Mo, Mn, and Fe, can be measured in soils, but these tests are far more difficult to conduct. Plant tissue testing is often used more successfully to diagnose these deficiencies (or toxicities).

Despite its limitations, soil testing is a very valuable tool to improve the efficiency of fertilizer use and to avoid many soil management problems. In addition, it gives a scientific basis for fertilizers to be sold to farmers. Most agronomists believe fertilizers should not be used over a long period without a small investment in soil testing. The possibilities for creating new problems and the inefficiency of use require that soil testing be used.

2.6 Profitable Fertilizer Use

From the previous discussions on the basics of plant growth and soil nutrients, the following tenets should be clear: (1) response is not simply a function of fertilizer additions but may be affected by many other growth and management factors, (2) new deficiencies and/or problems develop over time, (3) response can be changed drastically by the timing and method of fertilizer application, and (4) fertilizer response depends on the fertility of the soil. Soils in a native state normally are responsive to N and P, and many also respond to K and other nutrients. As fertilizers are used, P and K status increases, and yield response to those nutrients decreases, whereas the response to N may increase because of the soil's higher P and K fertility. For example, 100 kg P ha^{-1} may be the agronomically optimum amount to fertilize a soil initially, but this would decrease to rates required to simply replenish the removed P after 20 years of fertilization (Figure 2.9).

2.6.1 The Economics of Fertilizer Use

An initial assumption is that the goal of fertilizer use is to maximize the farmer's profit. For some farmers this assumption may not be true or only partially true. Although higher profit is usually the main motivation for fertilizer use, farmers' decisions about fertilizer use are affected by biophysical, economic, and social constraints and by risk and other motivations, which are difficult to assess. Economic analysis is based on a per-hectare or area basis because farmers normally have a specific area of land to plant to crops. In a typical response curve, because of diminishing returns, the addition of the first few kilograms of fertilizer has the largest effect on yield or largest incremental effect, but these very low fertilizer rates will not maximize the benefits to the farmer.

In Figure 2.10, familiar response curves of crop yield to fertilizer are used in conjunction with prices to derive revenue and cost curves and graphically illustrate the changes in total revenue and costs associated with the use of fertilizers. Curves are shown for fields with high (Field A) and low fertility (Field B). Total revenue curves TR A and TR B represent changes in values of crop output as a result of additions of fertilizer, and fertilizer use costs include the cost of fertilizer plus all other costs that vary with the use of fertilizers, for example, labor required for additional weeding and the harvesting of additional output. These curves show that (1) without fertilizer use, crop yields and total revenues are higher in soils with high initial fertility levels; (2) fertilizer use has a greater impact on crop yield, total revenues, and profits in soils with low initial levels of soil fertility; and (3) the fertile Field A requires less fertilizer to maximize profit than Field B. In general, soils with high soil fertility

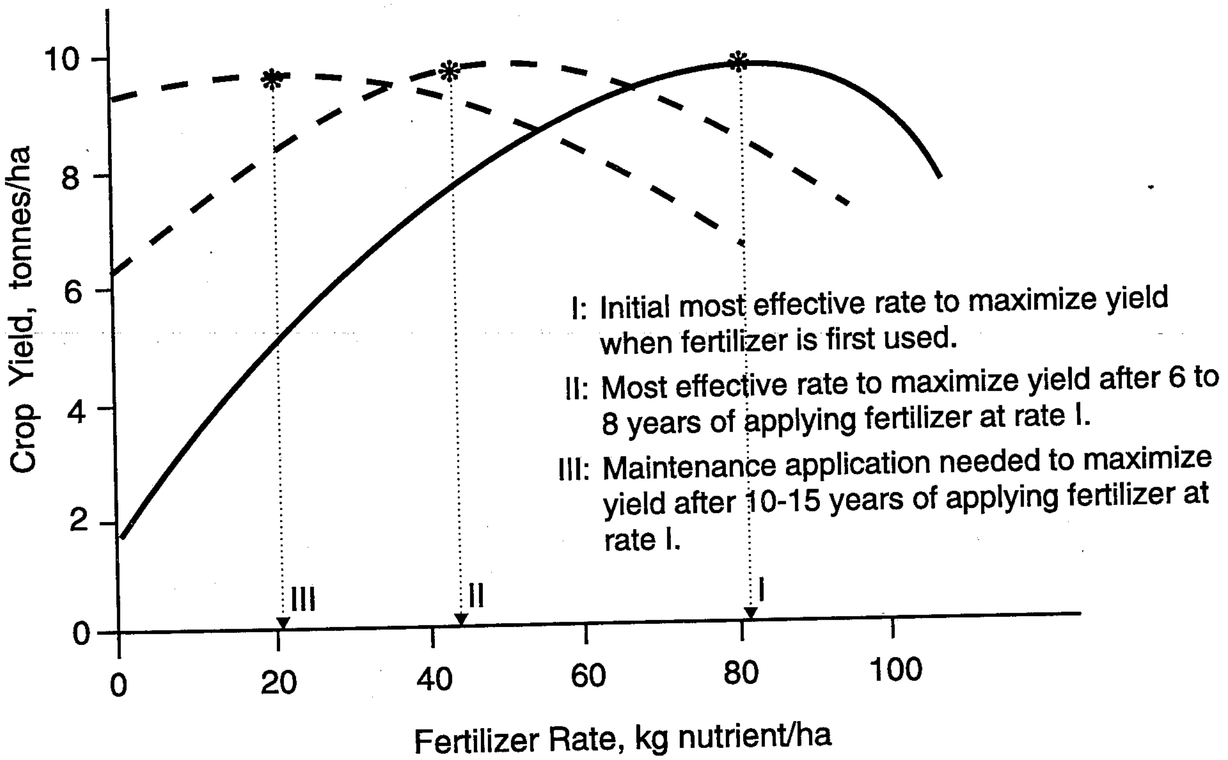


Figure 2.9. Expected Changes in Fertilizer Response to P or K as Fertilizers Are Used.

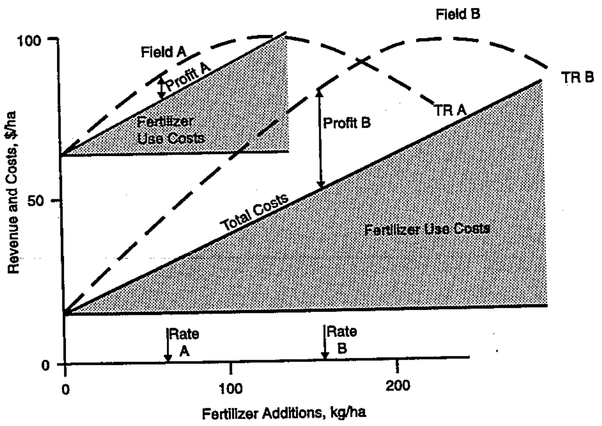


Figure 2.10. Benefits and Costs to Fertilizer Use at Different Initial Fertility Levels.

levels are more productive and can provide higher crop yields, revenues, and profits to farmers even if fertilizers are not used. Only the additions to profit derived from fertilizer use are depicted in Figure 2.10. The two curves (Figure 2.10) illustrate the reasons why farmers should try to raise the soil fertility for nutrients such as P to a state at which relatively small amounts can be added to maintain soil fertility. A similar situation between fields could occur for N if a legume crop were grown the season before on field A. Generally, however, there is little residual effect from N, thus these response differences to N between fields would not occur except in the case of the legume. Although this analysis appears straightforward on the surface, how does the farmer know, before fertilizing the field, if the response will be like that of field A or field B? He cannot conduct response trials in each of his fields. Soil testing is needed to maximize the benefits from fertilizer use.

Because of variability in climatic and other factors, a single response curve for a field of a given fertility does not exist. Rather, there is essentially a continuum of response curves, bounded by the limits of the climate and other growth factors (Figure 2.11). Similarly, with variations in prices the revenues and profit can change substantially. More variability and uncertainty in prices and weather result in larger differences in revenues and profits between good and poor years. Remote locations may be less favored because of volatile prices and poor marketing capabilities. Unfortunately, when the weather is favorable, it is favorable to many farmers, then local production increases, and prices drop unless there are wide marketing capabilities for the produce. Under more

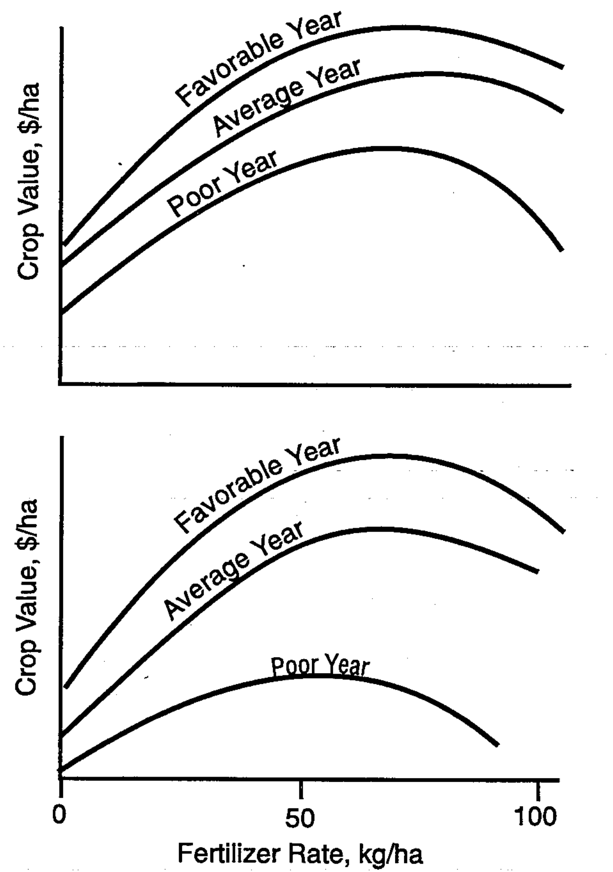


Figure 2.11. Crop Response Curves Under Favorable and Unfavorable Conditions of Production and Prices.

favorable and stable conditions for agricultural production and marketing, farmers can more easily predict the revenues and profits from fertilizers. Figure 2.11 could also contrast developed versus less developed agricultural production systems and marketing capabilities.

Various mathematical models or algebraic equations can be used to estimate fertilizer response curves such as those shown in Figures 2.10 and 2.11. Mathematical models selected for this purpose are equations that properly represent agricultural production-fertilizer relationships that can be estimated using statistical methods. A quadratic function model is commonly used to estimate fertilizer response functions that properly represent agricultural output increasing at a decreasing rate as a result of increased fertilizer application rates. A quadratic response function model may be written as:

$$Y = A + BF + CF^2; \quad B > 0,\ C < 0;$$

where Y is crop yield, F is fertilizer rate, and A, B, and C are coefficients of the response function, which are usually estimated using ordinary least square procedures and experimental data. The actual yield for a given year, of course, is affected by many other factors besides fertilizer rate, such as weather, diseases, and insect or weed infestations.

The economic optimum rate of fertilizer is the rate that provides maximum profit-maximum addition to profit as a result of fertilizer use. This rate, say F*, is determined by imposing the condition for profit maximization

$$\frac{\partial Y}{\partial F} = \frac{P_f}{P_y} \text{ and solving for F;}$$

where P_f and P_y are the prices of fertilizer and crop output, respectively. Thus, for the case of the quadratic response function model presented above

$$F^* = \left(\frac{P_f}{P_y} - B\right) \Big/ 2C.$$

The main indicators of profitability used in the economic evaluation of fertilizer use are (Figure 2.12):

1. The magnitude of added profit due to fertilizer use expressed in monetary value per unit of area, for example, US $/ha.
2. The value:cost ratio (VCR), which is the value of the increased crop output produced as a result of fertilizer use divided by the cost of fertilizer. The VCR changes with the rate of application and should be evaluated at optimum rates of fertilizer use.

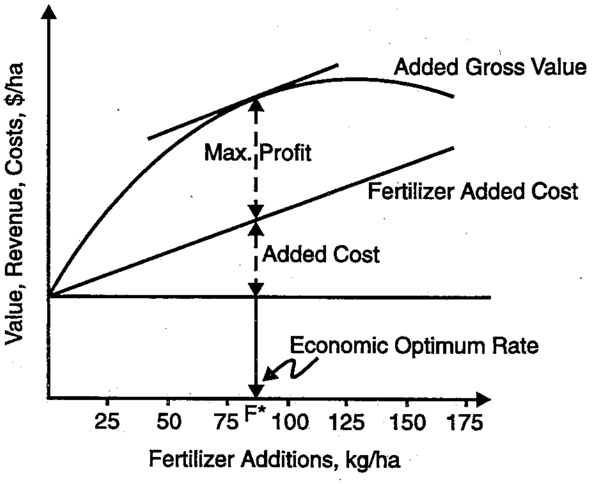


Figure 2.12. Benefits and Costs of Fertilizer Use.

In addition, the fertilizer:crop price ratio is often used to measure the price of fertilizer in terms of units of crop output, i.e., how many kilograms of crop output will be needed to buy a kilogram of fertilizer.

For most farmers, the impact of fertilizer on profit is the key determinant of their decision to use fertilizers. The VCR measures the economic return of fertilizers to expenditures. The VCR is an important indicator in the context of risk and uncertainty associated with fertilizer use in rainfed agriculture. Usually the risk of fertilizer use is associated with the uncertainty of crop yield due to weather variations and also uncertainty about prices for the produce.

For a farmer who has the advantage of reliable weather or irrigation, a VCR of 2 may be acceptable, whereas a farmer with less reliable weather and less control over prices often requires a VCR of more than 3 to justify investment in fertilizer. Risk aversion by farmers in well-developed agricultural systems is somewhat different because they have price subsidy programs, less variation in weather and prices, crop insurance, good access to credit, and a low share of fertilizer cost relative to total costs. The more resource-favored farmers of developed countries view risk of fertilizer use in terms of trying to ensure that they apply enough fertilizer, particularly N, to maximize the benefit when favorable growth conditions occur. Whereas poorer farmers tend to apply smaller amounts, the more affluent farmers tend to apply more because they hope to maximize profit and achieve high crop yields in the best years.

Farmers of the less-developed regions tend to be very sensitive to fertilizer price increases, whereas farmers who pay less for fertilizer relative to their total expenses tend to be relatively insensitive. For these reasons increasing fertilizer prices tend to decrease use disproportionately for farmers who can least afford the reduced production caused by lower fertilizer use.

Despite the inherent uncertainties of crop production, risks can best be avoided by maintaining fertilizer use in balance with the farmer management skills and soil productivity, which involves average weather conditions. A cartoon frequently used in fertilizer promotion shows two farmers talking across the fence. The one with obviously poor crops says to the other with good crops, "I would fertilize too if I had good soil like you." Farmers with good management skills risk less in using fertilizers than farmers who are poor managers.

2.6.2 Site-Specific Management

In the late 1980s and early 1990s, land management systems were developed in the United States which can be used by farmers and fertilizer dealers to provide more exact fertilizer application and management of other inputs. Called "Precision Agriculture" or "Site-Specific Management," it became possible when computer and satellite technologies enabled accurate knowledge of location in fields and the management of large amounts of data. The two necessary tools are the Global Positioning System (GPS) and a Geographical Information System (GIS). The GPS is a small (7 x 10 x 20 cm) locator device which communicates with a system of satellites in orbit around the earth, originally established for U.S. military purposes. The GIS is a computer-based information management system that manages the data from each of the unit mapping areas, called pixels, and allows the interfacing of the database with other equipment. The pixels are delineated in a uniform grid, and may be from 1 to 3 hectares in size. Individual characteristics of each pixel for nutrient level, yield, or any other parameter can be managed by the GIS.

Using the GPS locator, soil samples can be taken from within the small areas on a grid system, and accurately identified in the GIS. Similarly, harvesting equipment is equipped with "on the go" yield monitoring devices which are linked to the locator and the GIS of a computer system. Fertilizer spreaders use the GPS in conjunction with the soil fertility test data stored in the GIS to apply needed nutrients to individual areas using variable rate spreading equipment. Planting machinery can be equipped to change seeding rates in response to soil parameters in the GIS. Herbicide applications can be made in accord with soil organic matter content or weed infestations. Irrigation equipment can be linked to the GIS to apply water in response to soil infiltration rates or water-holding capacity.

The systems are, of course, expensive, but provide a much better recordkeeping system for farmers. It helps them to identify yield differences in fields and the likely reasons for those differences. Corrective actions can be taken to improve production on lower yielding areas with the variable rate systems, and farmers can integrate and visualize soil, yield and other parameters with the GIS. Pesticides, water, and fertilizers can be managed to reduce costs and very importantly, reduce the adverse environmental impacts of their use. The systems provide an extremely valuable set of tools that give farmers the ability to more carefully manage their land.

Site-specific management or precision agriculture is an exciting and valuable tool that allows farmers to manage land and crop production more efficiently and more environmentally responsibly. The technology is continuing to develop, and farmers and farmer advisers are developing their capabilities to use the technology. Many in the fertilizer industry believe the technology is as revolutionary as the development of high-yielding varieties or the mechanization of agriculture.

2.7 Soil Productivity and Sustainability

In the early 1980s, the concept of what agriculturists called "sustainability" started to gain attention. In the late 1970s the term was used by Lady Eve Balfour to describe "regenerative" agriculture or agricultural production systems that rely very little on external inputs to a farm, but use internal and efficient organic matter recycling and crop rotations for nutrient maintenance, use less pesticides, less energy, and have other attributes that are beneficial to society as a whole. Its original connotations were of low-input organic agriculture.

The concept, however, was broadened and redefined by more "conventional" or "production" agriculturists who saw great merit in the underlying principles of what is now considered sustainable agriculture. These agriculturists came to believe that essentially all agriculture could be greatly improved to better meet both short- and long-term societal needs. Modern or conventional high-external input agriculture did not adequately address environmental concerns, rapid depletion of resources, equity concerns of society, and the ability of future generations to have reasonable standards of living. The concept of sustainability has become an overriding philosophical and ethical approach to address problems in the agricultural sector and the problems originating from agriculture. Agriculture cannot function responsibly as a part of society with the sole purpose of profit maximization for the current land user because of environmental, resource depletion, and intergenerational concerns.

Sustainability addresses farming holistically rather than by each component (e.g., fertility, erosion, weed control, etc.) and considers the entire enterprise, the farming family, soils, plants, and animals, and agriculture's role in meeting societal needs. Farming viewed from narrow disciplines lacks ability to solve one problem without causing another. Sustainability attempts to address causes of problems, not treat the symptoms, and to be more in accord with and use natural processes as much as possible, rather than to dominate nature. For example, natural systems recycle and retain nutrients well, maintain soil cover, and are biologically diverse. The diversity makes the system more resilient to weather and other types of adversity, and reduces the buildup of pest populations. The converse and what makes "modern" agriculture less sustainable and in need of better approaches are the monoculture crop systems and poor integration of crop and livestock practices. This causes pollution from manures, wastes valuable nutrients, the soils are not protected from erosion, and there is excessive reliance on pesticides and inorganic fertilizers. The concepts were initially scoffed at by traditional agricultural people until they realized that the extremely narrow, single-discipline approach to meeting the needs of agricultural production were indeed, in most cases, wasteful, despoiling, and did not address farmer problems nor develop solutions based on farmers' needs and perspectives.

The concept became widely accepted as it was realized that the conventional methods of production are not meshed well and that sustainability does not mean going back to the horse-drawn days but taking the best scientific knowledge to approach farming differently. The economic viability of farmers must obviously be maintained, but farming must meet the needs of future generations and society as a whole, not just the profit maximization for the current land user.

More sustainable practices always require a higher level of management intensity, i.e., better, more knowledgeable management. Most practices that are judged more sustainable than an alternative have synergistic or several benefits not only to farming but also to the environment and resource conservation. Examples are organic matter recycling (soil protection from erosion, nutrient cycling, less water contamination, better soil tilth and water-holding capacity, weed suppression) and greater crop diversification (reduced weed and insect infestations, less susceptibility to adversities of weather and prices, better soil protection); systems that reduce runoff from fields decrease erosion and furnish more water to the crop and protect surface waters from contamination. Whereas the more sustainable practices have multiple benefits, they require more knowledge, better management, and possibly more time and different farm equipment. Integrated pest management (IPM), which relies on very specific targeting of insects and use of pesticides in conjunction with other methods to control harmful insects, is considered more sustainable than the more conventional practices of relying only on pesticides. It provides multiple benefits, such as better use of natural predation, and it is less environmentally objectionable because it requires less pesticides, but it requires a higher level of management and understanding.

It should be obvious that more sustainable does not mean low-external input. Low-input agricultural systems are in many ways much less sustainable than higher external input systems because they do not meet current farmer and societal needs, degrade soils through erosion and nutrient depletion, and have additional adverse impacts, such as requiring more land to be cultivated. There are numerous examples of how low-input systems have become much more sustainable by use of greater external inputs.

As far as fertilizers and nutrients are concerned, greater sustainability means increasing fertilizer efficiency, reducing excess applications, avoiding losses of nutrients by runoff and leaching, using practices for organic matter maintenance through careful management of crop residues, animal manures and other available sources, and decreasing energy use in manufacturing, distribution, and application of fertilizers. Soil testing, band applications of fertilizers, efficient use of on-farm resources, use of legumes, and split applications and proper timing of N are viewed as more sustainable than their alternatives.

Each farm unit has unique problems, constraints, and capabilities; therefore, sustainability requires a very site-specific approach. Sustainability requires adaptability because what is deemed to be "more sustainable" today may put the farmer out of business tomorrow. Some of the largest problems of modern agriculture are the loss of livestock and cropping integration, loss of populations from rural areas, the large amount of capitalization required in modern agriculture, and the extent to which the farmer or the government controls the management of land. These questions are arising more and more in protection of water, biodiversity, and land resources as societies develop consciousness of the importance of the interrelationships of the natural world, societal needs, and farming activities.

The term "sustainability" may lose favor, but the underlying concepts of societal, environmental, and intergenerational responsibility will be issues as long as man continues to live on the planet. These issues will become more complicated with time. Understanding of the complexities of agricultural processes at both global and micro scales continues to grow as do the human population and demands on resources.

2.8 References

1. Ponting, C. 1990. "Historical Perspectives on Sustainable Development," *Environment*, 32(9):4-9, 31-33.
2. Dando, W. A. 1980. *The Geography of Famine*, John Wiley and Sons, Inc., New York, NY, U.S.A.
3. Brady, N. C. 1984. *The Nature and Properties of Soils*, Ninth Edition, Macmillan Publishing, New York, NY, U.S.A.
4. Black, C. A. 1968. *Soil-Plant Relationships*, Second Edition, John Wiley and Sons, Inc., New York, NY, U.S.A.
5. Tisdale, S. L., W. L. Nelson, and J. D. Beaton. 1985. *Soil Fertility and Fertilizers*, Fourth Edition, Macmillan Publishing, New York, NY, U.S.A.
6. Kilmer, V. J., and J. Webb. 1968. "Agronomic Effectiveness of Different Fertilizers," IN *Changing Patterns in Fertilizer Use*, L. B. Nelson (Ed.), pp. 33-65, Soil Science Society of America, Madison, WI, U.S.A.
7. Bertsch, P. M., and G. W. Thomas. 1985. "Potassium Status of Temperate Region Soils" IN *Potassium in Agriculture*, R. L. Munson (Ed.), pp. 131-162, American Society of Agronomy, Madison, WI, U.S.A.
8. Munson, R. D., and W. L. Nelson. 1990. "Principles and Practices in Plant Analysis," IN *Soil Testing and Plant Analysis*, Third Edition, R. L. Westerman (Ed.), pp. 377-82, Soil Science Society of America, Madison, WI, U.S.A.
9. Bongaarts, J. 1994. "Global and Regional Population Projections to 2025," Paper presented at the IFPRI Round Table on Population and Food in the Early 21st Century, Washington, D.C., U.S.A.
10. Jackson, M. L. 1965. "Chemical Composition of Soils," IN *Chemistry of the Soil*, Second Edition, F. E. Bear (Ed.), pp. 71-141, Reinhold Publishing, New York, NY, U.S.A.
11. Mitchell, R. L. 1965. "Trace Elements in Soils," IN *Chemistry of the Soil*, Second Edition, F. E. Bear (Ed.), pp. 320-368, Reinhold Publishing, New York, NY, U.S.A.
12. Epstein, E. 1972. *Mineral Nutrition of Plants: Principles and Perspectives*, John Wiley and Sons, Inc., New York, NY, U.S.A.

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Chapter 3. Status of the Fertilizer Industry

3.1 Short History of Fertilizer Development

The history of the world fertilizer industry can be traced to the earliest agriculture when man began cultivation of plants to produce food. Prior to cultivation of plants and domestication of animals, man was a hunter and gatherer of whatever sources of food he could find in his local environment. The early farmers soon learned that some soils were more productive than others; they also learned that continuous cultivation of the same land resulted in reduced yields. Some learned that the addition of manures, composts, fish, ashes, and other substances would sometimes increase yields or apparently restore productivity to fields that were considered to be "worn out." Most of these soil amendments (the first fertilizers) were discovered by trial and error, and results were unpredictable.

Agriculture and the use of soil amendments appear to have started through independent developments in Mesopotamia (now Iraq) in the river basins of the Tigris and Euphrates, in the Nile Valley, in the Orient, and possibly other parts of the world. By Graeco-Roman times, the art of farming and fertilizer use was being documented by Plato (428-348 B.C.), Aristotle (384-322 B.C.), and other scholars of the day. These Greek and (later) Roman observations dominated agricultural practices and philosophies well into the eighteenth century.

Some of the early theories were later proven to be wrong, primarily because the scientific method had not yet been developed; theories were based on speculation and reasoning by the most learned philosophers of that era. It must be remembered that soil science and chemistry did not develop very far until late in the eighteenth century. Aristotle, for example, believed that organic matter was the source of all plant nutrition. Empedocles (490-430 B.C.) thought that everything, organic or inorganic, was composed of four elements – earth, air, fire, and water. In spite of flaws in this scientific base, some useful textbooks or agricultural practices were developed during the middle ages (12th through 16th century) by the Romans, Arab scholars, and others. But soil fertility and soil amendment practices remained much the same in the year 1800 as were described by the Greek scholars in 300 B.C. The major "fertilizer materials" were animal manures, composts, sewage, sea sand, seaweed, fish, bones, and liming materials, particularly marl. Crop yields remained low: wheat, for example, sown at 2 to 2½ bushels per acre returned seed-yield ratios of 1:3 or slightly higher, with 1:6 occurring only under the most favorable conditions.

One of the first true experiments with a living plant appears to have been conducted by Van Helmont (1577-1644), a Flemish physician and chemist, in his classical "willow experiment."

> I took an earthen vessel into which I put 200 pounds of soil dried in an oven, then I moistened it with rainwater and pressed into it a shoot of willow tree weighing 5 pounds. After exactly 5 years the tree had grown up and weighed 169 pounds and 3 ounces. But the vessel had never received anything but rainwater or distilled water to moisten it when necessary. At the end I dried the soil once more and got the same 200 pounds I started with, less about 2 ounces. Therefore, the 164 pounds of increased weight of wood, bark, and root came from the water alone.

Van Helmont considered the 2-ounce loss in the weight of the soil to be within experimental error, and his conclusion was erroneous. However, his simple, direct approach and use of quantitative measurement paved the way for future experimentation that led to an understanding of plant nutrition, which led to a scientific approach to fertilizer development [1].

3.1.1 Foundation for the Modern Fertilizer Industry

Justus Von Liebig (1803-73) is generally considered to be the father of the world fertilizer industry. Von Liebig stressed the value of mineral elements derived from the soil in plant nutrition and the necessity of replacing those elements to maintain soil fertility. He recognized the value of nitrogen but believed that plants could derive their nitrogen from the air. He envisioned a fertilizer industry with nutrients such as phosphate, lime, magnesia, and potash prepared in chemical factories. He recommended treatment of bones with sulfuric acid to render the phosphate more readily available.

Von Liebig was a philosopher and a scientist. His philosophy was as follows:

> Perfect agriculture is the true foundation of all trade and industry – it is the foundation of the riches of nations. But a rational system of agriculture cannot be formed without the application of scientific principles for such a system must be based on an exact acquaintance with the means of vegetable nutrition. This knowledge we must seek through chemistry.

Liebig propounded the "Law of the Minimum," which is still a useful concept despite its lack of quantitative exactness. This law states that, if one of the nutrients from the soil or air is deficient or lacking in availability, growth will be poor even when all other elements are abundant. If the deficient element is supplied, growth will be increased in proportion to the amount supplied up to the point where the supply of that element is no longer the limiting factor. Increasing the supply beyond this point is not helpful since some other element is now in minimum supply and becomes the limiting factor.

The concept of the law of the minimum has been modified as additional elements have proved to be essential in plant nutrition and has been extended to include other factors such as moisture, temperature, insect control, weed control, light, plant population, and genetic capacities of plant varieties. In fact, modern advances of crop production have consisted mainly of identifying successive limiting factors and correcting them.

3.1.2 Phosphate Fertilizers

The first phosphate fertilizer as such – ground bones – was used widely in Europe during the early part of the 19th century. When the supply of animal bones was short, human bones were gathered from battlefields or burial places. Treatment of bones with sulfuric acid began about 1830 and soon became a common practice. Dilute acid was used, and the product was a slurry, which was distributed in wooden casks. Potash salts and sulfate of ammonia or nitrate of soda sometimes were added; thus, the first liquid mixed chemical fertilizers were produced.

In about 1840 treatment of phosphate rock with sulfuric acid yielded an effective phosphate fertilizer, which was called superphosphate. The first successful commercial superphosphate production was started by Lawes in England in 1842. Others followed, and by 1853 there were 14 manufacturers in the United Kingdom and several in other countries. By 1870, 80 factories were operating in the United Kingdom.

Many of the early factories were primitive; ground rock and sulfuric acid were mixed in kettles or vats by manual labor with paddles or hoes. However, by 1862, Lawes was using a continuous mixer with a 100-tpd capacity. Some modern plants produce 1,000 or more tonnes per day, but smaller plants serving local areas generally are favored since it is seldom economical to ship the low-analysis material long distances.

The history of production of concentrated or triple superphosphate is associated with the production of phosphoric acid. The first known commercial production occurred in the 1870s in Germany where the objective was to use a low-grade phosphate rock that had a high content of iron and aluminum. A very dilute phosphoric acid was produced by batch extraction and filtration of the rock, and this was concentrated by evaporation. The acid was used to acidulate more phosphate rock. Other plants were soon built in Europe and America. However, most of them were small, and much of the product was used in sugar clarification rather than for fertilizer.

Triple superphosphate did not become an important fertilizer until the 1950s. In contrast with ordinary superphosphate, triple superphosphate has a higher content of phosphate than the phosphate rock from which it is made; thus, it should be produced near the source of the rock in large plants, with shipment of the product to local mixing plants or to farmers.

Although ammonium phosphate had long been known to be an effective fertilizer and small quantities had been produced in several countries from time to time, it did not become a popular fertilizer until the 1960s. Ammonium phosphates (diammonium phosphate and monoammonium phosphate) are now the leading form of phosphate fertilizer in the world.

Development of nitrophosphate fertilizer was started in Europe in the 1930s. Several processes were developed, and subsequent improvements have added to their efficiency and improved the quality of the products. The popularity of nitrophosphates in Europe has continued, and several plants have been built in other continents. Many of the plants are quite large and produce 1,500 or more tonnes of product per day.

Direct application of raw, finely ground phosphate rock has been practiced to a substantial extent in the United States, Russia, and China and to some extent in other countries. The practice has almost disappeared in the United States. However, recent information indicates that the value of raw phosphate varies widely with variations in the character of the ore and the crop and soil on which it is used. There are indications that reactive rocks may be useful sources for at least part of the phosphorus requirement of many crops grown on acid soils.

Early sources of phosphate rock were small deposits in England, Ireland, Spain, France, Germany, and the United States (South Carolina). Most of these deposits are no longer mined because of their low grade or because they have been virtually exhausted. Present supplies are mainly from other areas of the United States, Russia, and Morocco with smaller outputs from the Near East, Egypt, Tunisia, Algeria, South Africa, Brazil, Togo, Senegal, and the Pacific Islands. New discoveries have been found, and several new deposits appear to be very large and capable of producing a good grade of rock.

To name a few, deposits in Australia, Peru, Arabia, Venezuela, Colombia, Iran, and India have interesting possibilities, and some are being exploited at this time.

3.1.3 Nitrogen Fertilizers

For many years the need for supplying nitrogen in fertilizers was considered to be of secondary importance although the essential role of nitrogen in crop production was recognized. Natural supplies and a system of crop rotation were deemed adequate. Fixed nitrogen is supplied in rainwater (about 5 kg/ha), and atmospheric nitrogen is fixed by certain leguminous crops that were included in the rotation. Return of crop residues and waste materials helped to conserve the nitrogen supply. These natural supplies were supplemented by small amounts of fertilizer nitrogen from guano, Chilean nitrate of soda, and various organic wastes.

Coal contains about 1% nitrogen, about half of which is evolved as ammonia in byproduct coke ovens or some types of gas producers. Starting in the latter part of the 19th century, this nitrogen became an increasing source of fertilizer nitrogen. Most of it was in the form of ammonium sulfate; smaller amounts were supplied as gas liquor, a dilute solution of ammonia.

As a growing population made it evident that world food needs could be met only by an increased supply of fixed nitrogen, research in several countries was concentrated on the fixation of atmospheric nitrogen. Three commercially successful processes emerged. In 1903 the arc process was introduced commercially in Norway. Nitrogen and oxygen were combined to form nitric oxide (NO) at a very high temperature (about 3250°C) in an electric arc; at lower temperatures the nitric oxide reacted with more oxygen to form nitrogen dioxide (NO_2), which was hydrated in the presence of excess air to form nitric acid. The nitric acid was converted to the end product, calcium nitrate, by reaction with limestone.

At about the same time the calcium cyanamide process was perfected. Calcium carbide, produced by reaction of lime with coke in an electric furnace, was converted to calcium cyanamide ($CaCN_2$) by reaction with pure nitrogen extracted from the air. The product could be used directly as a fertilizer, or it could be hydrolyzed to form ammonia.

The economics of the arc and cyanamide processes depended on low-cost electricity; at best, both were costly.

Direct synthesis of ammonia from nitrogen and hydrogen was first carried out successfully on a commercial scale in Germany in 1913. Plants were built in several other countries after World War I. Most of these plants derived their hydrogen-nitrogen synthesis mixtures from the reactions of coke with steam and air.

The first ammonia plants were quite small, 25-50 tpd, and costs remained high. Much of the ammonia was used to produce explosives or industrial chemicals. Fertilizer use remained small because chemical nitrogen was too expensive for liberal use on farm crops other than those of high cash value. Even as late as 1950 many agriculturists advocated that principal reliance for nitrogen supplies be placed on legumes grown in rotation with other crops.

During the latter half of the 20th century, successive improvements in ammonia production have lowered the cost to the point that its liberal use in crop production is economically attractive. Notable among these improvements was perfection of processes for reforming natural gas or naphtha to supply the hydrogen-nitrogen synthesis gas and to increase the scale of operation.

The use of centrifugal compressors, starting in the 1960s, made possible large, single-train ammonia plants of 1,000- or even 1,500-tpd capacity. These large ammonia plants are capable of producing ammonia much more economically than the older, smaller plants that used reciprocating compressors.

At first the final products – ammonium sulfate, calcium nitrate, sodium nitrate, and calcium cyanamide – were all low-analysis materials (15%-21% N). Ammonium nitrate (34% N) began to be an important fertilizer material in the 1940s and became the leading form in the 1960s. More recently, urea production (46% N) has grown rapidly and is now the world's leading form. Direct application of ammonia (82% N) to the soil, either in anhydrous form or in aqueous solution, is popular in the United States, Canada, and Australia and has been introduced into other countries.

The popularity of urea-ammonium nitrate solutions (28%-32% N) has increased in North America and parts of Europe during the 1980s and 1990s. Much of the popularity is due to ease of handling plus the ease of mixing herbicides with nitrogen solution for simultaneous on-farm application.

3.1.4 Potash Fertilizers

Early sources of potash were wood ashes, sugar beet wastes, and saltpeter. The salt deposits in Germany were opened in 1860 and dominated the world market for 75 years. Low-grade, unrefined ores such as manure salts (20%-25% K_2O) and kainite (19% K_2O) were the first products. The development of refining methods gradually increased the grade of commercial products. High-grade potassium chloride (60%-62% K_2O) is now the main product. Potassium sulfate, sulfate of potash-magnesia, and potassium nitrate are the principal nonchloride potash fertilizers. They are more expensive and hence are used primarily on crops or soils for which the chloride is unsuited. Important potash deposits were found in other countries, and production was started in France (1910), Spain (1925), Russia (1930), United States (1931), and Canada (1960). Large deposits occur elsewhere and may be used in the future.

3.1.5 Other Nutrients

One of the important early fertilizers was gypsum, which supplied sulfur and calcium. Its use evidently originated when a German plasterer observed that small amounts of plaster, which spilled from his wheelbarrow, made the grass along the pathway lush and green. In any event, gypsum for agricultural use became known as "land plaster."

Later, superphosphate and ammonium sulfate supplied adequate amounts of sulfur even though their primary purpose was to supply phosphorus and nitrogen. Likewise, basic slag has been widely used in Europe and the United States for its phosphorus, calcium, and micronutrient content. In most industrial countries, millions of tonnes of sulfur from fuel combustion escape to the atmosphere and subsequently return to Earth in rainfall. In most such areas the deliberate addition of sulfur to fertilizer has not proved necessary, but there are important exceptions. As the removal of sulfur from stack gas becomes widespread for the prevention of atmospheric pollution, more sulfur may need to be added to fertilizers. In many less industrial areas the need for sulfur is already well known.

Limestone and dolomite are widely used to supply calcium and magnesium when these nutrients are needed. Other magnesium materials include magnesium silicate, calcined brucite (MgO), magnesium sulfate, and langbeinite ($K_2SO_4 \bullet 2MgSO_4$).

The importance of most micronutrients in crop production was not recognized until the 20th century. Iron is an exception: Gris (France) discovered in 1844 that chlorosis of some plants can be corrected by spraying them with iron salts. Liebig noted the presence of manganese in plant ash but doubted that it was a nutritive element. It was not until 1905 that manganese was recognized as essential to plant growth; then copper and boron followed in the 1920s before zinc (about 1930), molybdenum (1939), and chlorine (1954). Still other elements that are not strictly essential may, in some cases, be economically important in increasing crop yields or improving quality. Silicon, sodium, and cobalt are examples.

3.1.6 Compound Fertilizers

Most of the early experimenters in chemical fertilizers, such as Murray and Liebig, worked with mixtures that contained several nutrients. However, as the European fertilizer industry developed, the usual practice was the separate production of straight fertilizers – each containing only one primary nutrient.

In contrast, the early development of the U.S. fertilizer industry was primarily devoted to providing compound fertilizer. Starting from these extremes, the practices of the two areas converged and compound fertilizers are now relatively more important in Europe than in the rest of the world. The trend is toward supplying most of the phosphate and potash and smaller proportions of the nitrogen in compound fertilizer, which also may contain secondary or micronutrients. Much of the nitrogen is supplied as a straight material.

The reason for the popularity of compound fertilizer is that farmers in industrialized nations no longer have the time or inclination to apply several fertilizers separately, nor do they have facilities to mix them. In addition, formulations are becoming more and more complex as farmers strive for higher yields and greater productivity. However, nitrogen is often applied separately because timing is important, and supplemental applications of nitrogen during the growing season are often needed for best results. Some straight nitrogen materials, such as anhydrous ammonia, are much cheaper than the same amount of nitrogen in compound fertilizers.

At first, compound fertilizers were made by simple mixing of low-grade materials – guano, superphosphate, ammonium sulfate, potassium chloride, and waste organic materials. Limestone often was added as a filler and to neutralize the acidity of superphosphate. Ammoniation of superphosphate became popular in the 1930s because it supplied nitrogen economically and improved the physical properties of the superphosphate. Light ammoniation in batch mixers characterized the early practice. Gradually, the various waste organic materials were eliminated, often because a better use was found for them. For example, cottonseed meal became more valuable for animal feed. Analyses of products rose as fillers were eliminated.

With the higher analyses came increased caking problems. Increased use of mechanical application equipment by farmers called for dependably free-flowing material; thus, granulation became popular starting in the 1950s.

Analyses of compound fertilizer rose further as triple superphosphate replaced ordinary superphosphate, and ammonium nitrate or urea replaced ammonium sulfate or sodium nitrate. Later, still higher analyses were attained by the liberal use of phosphoric acid and ammonia in the formulations. Compound fertilizer preparation was no longer a simple mechanical task but a complex chemical engineering operation. As such, its economics depended on large-scale operation. Some small local mixers expanded to large regional manufacturers; others became bulk blenders or went out of business.

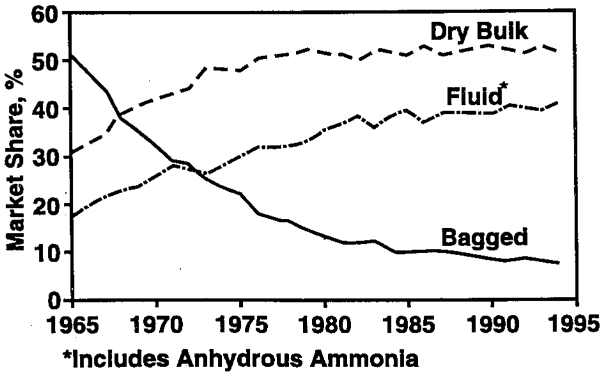
Bulk blending became popular in some countries as a method by which a local mixer could supply whatever mix the farmer needed in simple equipment at a low cost. Granular materials such as diammonium phosphate, muriate of potash, and ammonium nitrate or urea were produced by large companies that had the facilities and capabilities for chemical manufacture and granulation and favorable raw material costs. These products were shipped in bulk to blenders offering prescription mixing, custom application, and many other services to the farmers. The success of this system largely depends on dependable, low-cost transportation. Covered, hopper-bottom railcars protect the material from the weather, minimize spillage, and simplify unloading. Barge transport or ocean shipment is also suitable between points on waterways.

3.1.7 Fluid Mixed Fertilizers

Manufacture of liquid mixed fertilizers began in the United States during the 1920s. However, liquids did not expand beyond California and a few other western States until the 1950s when technology, largely developed by the Tennessee Valley Authority (TVA), resulted in rapid expansion in the fluid segment of the fertilizer industry. By the 1990s, fluid mixtures (liquids plus suspensions) comprised approximately 20% of multinutrient fertilizer sales in the United States. To a lesser extent, fluid mixtures have been introduced into Europe, North America, and South America. Popularity of fluid fertilizers is greatest in areas of high labor costs; fluids are easily handled with pumps. A common practice is the combined application of fluid fertilizers and herbicides.

3.1.8 Trend Away From Bagged Fertilizers

Because farm size has increased in most developed countries, farmers have switched from bagged fertilizers to bulk or liquid products. This trend is most pronounced in the United States and is illustrated in Figure 3.1. In 1965 bagged fertilizers comprised more than one-half of the fertilizers used by U.S. farmers; by 1994 less than 10% was sold in bags. Increased farm size, increased mechanization, lower labor costs for bulk application of fertilizers, and lower production and distribution costs have all contributed to the trend away from bagged products.



Source: Derived from TVA data.

Figure 3.1. Fertilizer Use by Class in the United States, 1965-94.

3.1.9 More Intensive Agriculture

Changes in agriculture have been no less dramatic than developments in fertilizer technology, and these have played a large part in increasing the demand for fertilizers.

When the world population was relatively small and when land and labor were plentiful, there was little need for increasing yields per hectare. For example, at the beginning of the 20th century, about one-half of the farms in the original 13 colonies of the United States had been abandoned. Farmers and immigrants moved on to new, richer lands in the Ohio and Mississippi Valleys. Chemical fertilizers were so expensive that they were used only on high-value cash crops such as cotton and tobacco. Abandoned farmland in some cases regained a part of its native fertility through natural processes; trees reached mineral elements deep in the subsoil, and fallen leaves deposited these nutrients in the topsoil. Rocks weathered and released their mineral elements in a more available form. Natural fixation processes – meteorological and microbiological – increased the nitrogen content of the fallow soil. In other cases, severe erosion caused more damage than nature could repair.

The richer soils of the Mississippi Valley were farmed for 75-100 years without fertilizer. Farms of those days and even 50 years ago were, to a large extent, subsistence farms. Draft animals supplied the motive power for farm machinery and transportation. Farm animals supplied meat, eggs, milk, and butter. Grain, vegetables, and fruit raised on the farm supplied the family's food. A large part of the nutrients in farm crops was returned to the soil as crop residues and manure. Legumes such as clover or alfalfa were grown in rotation and plowed under to supply nitrogen to cereal crops.

Cyril Hopkins, in his popular book *The Farm That Won't Wear Out* (1913), recommended a farming system that conserved soil nutrients through the return of crop residues, animal wastes, and green manure. Since phosphorus and sometimes lime were often deficient, he recommended the application of ground phosphate rock at 5- to 10-year intervals and limestone when necessary. Nitrogen was furnished by legumes in rotations. The soil's supply of potash was considered adequate for the foreseeable future. He warned against use of chemical fertilizers because of their high cost and transitory effect. For example, at that time the delivered cost of superphosphate was four times that of ground phosphate rock.

Hopkins gave examples of how his system increased the profits of a farm's operation. The system was indeed profitable under the conditions existing 80 years ago, and yields were much better than the national average but still low by present-day standards.

Many countries have passed through this stage when low yields, utilization and conservation of native soil fertility, and bringing new land under cultivation were adequate and economical methods for supplying food needs. Today the rapidly growing population leaves few countries that choice. Yields per hectare must be greatly increased in many developing countries as they have been in developed (and some developing) countries. Increased fertilizer use is a necessary requirement for intensive agriculture. More of the farm produce now leaves the farm to feed workers in the cities. Decreased use of draft animals releases more food for people, but less manure is available. These factors mean that less of the nutrient content of crops is returned to the soil. On the other hand, higher yields mean more crop residues and increased importance of returning crop residues to the soil.

An important landmark in the intensification of agriculture is the development of high-yielding varieties of cereal crops. Starting in the 1930s, the development of hybrid corn played a primary role in increasing yields and fertilizer use. In addition, the varieties adapted to climatic conditions (drought-resistant or early-maturing, for example) extend the area in which this crop can be grown. Improved varieties of wheat and rice followed, and improvement is continuing with these and other crops. These improved varieties are much more responsive to fertilizer and have been a large factor in increased fertilizer use.

Dr. B. L. Bumb of the International Fertilizer Development Center analyzed FAO's fertilizer production and consumption yearbooks and data tapes in 1994 and developed Tables 3.1 – 3.16 and Figures 3.2 – 3.9 which appear in this chapter. Data are presented to show global production and consumption trends; trends by geographic region; and trends by developed and developing countries. Data are also presented to describe fertilizer production and consumption in the reforming markets of Eastern Europe and Eurasia. Chapter 4 includes data for 1994 and 1995, and fertilizer production and consumption projections are extended through the year 2005.

3.2 Statistical Overview of Fertilizer Production, 1960-95

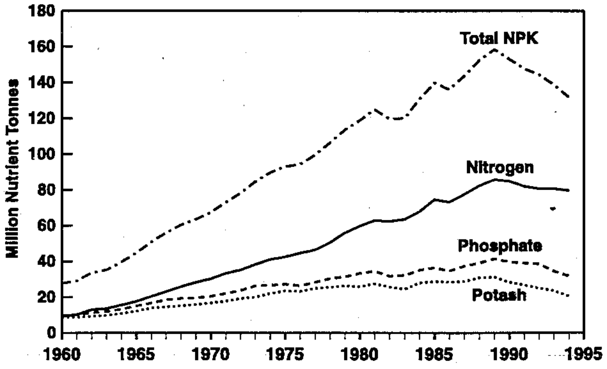


Figure 3.2. World Nitrogen, Phosphate, Potash, and Total NPK Production, 1960-94.

World fertilizer production increased steadily from 28 million nutrient tonnes in 1960 to a peak of 158 million tonnes in 1989 as shown in Figure 3.2. (Throughout this chapter, statistical data are reported for the split year ending June 30 of the year stated; for example, 1985 refers to the period July 1, 1984, through June 30, 1985.) Production increases averaged almost 4.5 million tonnes per year during this 29-year period. However, world production totals declined by an average of about 5 million tonnes per year during the next 5 years to a low of 132 million tonnes in 1994. A steep decline in production in the reforming economies of Eastern Europe and Eurasia was primarily responsible for this decrease in global fertilizer production. Production trends were similar for all three primary plant nutrients. Between 1980 and 1990 nitrogen production increased by 26 million tonnes and phosphate and potash production by 8 and 5 million tonnes, respectively.

Statistics showing annual fertilizer production by economic class of countries (developed and developing) for the years 1960 through 1995 are shown in Table 3.1. Other data, presented in Table 3.2, show recent production trends within developed markets, developing markets, and the reforming markets of Eastern Europe and Eurasia.

At the regional level, all regions except Western Europe and Oceania registered an increase in fertilizer production during the 1980s. In contrast, only North America, Africa, and Asia registered increases during the early 1990s (Table 3.2).

Several factors affected fertilizer production during the 1979/80 to 1994/95 period. Depressed fertilizer prices, economic and political reforms, structural adjustment programs, raw material shortages, and depressed demand were some of the important contributory factors.

Table 3.3 provides data on fertilizer production in different markets and regions. The growth experiences of the three market groups are not uniform. The developed

Table 3.1. World Fertilizer Production — Historical Data, 1960-95

Year	Developing Countries[a]				Developed Countries[b]			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
	(millions of nutrient tonnes)				(millions of nutrient tonnes)			
1960[c]	0.74	0.44	0.18	1.19	8.49	9.34	8.69	26.52
1965	2.07	1.10	0.60	3.22	15.58	13.97	12.13	41.68
1970	3.87	2.17	0.87	6.13	26.36	18.19	16.57	61.12
1975	7.82	4.24	3.01	12.36	34.62	22.94	23.10	80.66
1980	17.72	6.20	0.40	23.96	41.90	27.06	25.81	94.78
1981	19.69	7.69	0.43	27.42	43.09	26.83	27.41	97.33
1982	20.61	7.46	0.48	28.12	41.68	24.23	25.61	91.51
1983	22.16	7.81	0.56	30.03	41.26	24.30	24.36	89.93
1984	23.65	8.59	2.20	32.46	44.17	26.51	27.68	98.36
1985	26.77	9.02	3.47	36.13	47.74	27.47	28.33	103.55
1986	26.92	8.90	5.70	36.39	46.18	25.74	27.72	99.63
1987	29.16	10.34	6.97	40.20	48.26	27.03	28.06	103.36
1988	31.94	11.48	7.97	44.21	50.34	27.66	30.02	108.03
1989	34.06	13.01	8.90	47.96	51.66	28.37	30.27	110.29
1990	35.46	12.17	9.76	48.60	49.19	27.56	27.35	104.11
1991	35.90	12.87	9.57	49.72	46.00	26.11	25.75	97.87
1992	36.49	13.67	10.54	51.22	44.13	24.94	23.93	93.00
1993	37.73	13.26	10.60	52.04	42.21	21.56	22.45	86.22
1994	38.02	12.42	11.53	51.60	41.35	19.34	19.34	80.04
1995	40.30	14.01	13.28	55.64	40.10	18.77	21.92	80.79

a. Developing countries include Latin America, Asia (except Japan and Israel), Africa (except South Africa), and Oceania (except Australia and New Zealand).

b. Developed countries include North America, Europe, Eurasia, Japan, South Africa, Australia, and New Zealand.

c. Yearly data represent production for the period July 1 through June 30, i.e., 1960 data are for the period July 1, 1959, through June 30, 1960.

Source: Data compiled by IFDC from various issues of FAO *Fertilizer Yearbooks* and fertilizer data tapes.

markets experienced a steady decline and the developing markets a steady increase in fertilizer production between 1979/80 and 1992/93. The reforming markets had a contrasting experience. Fertilizer production increased in these markets in the 1980s and decreased in the early 1990s.

3.2.1 Developed Markets

Fertilizer production decreased from 60.9 million tonnes in 1979/80 to 54.9 million tonnes in 1992/93. Decreases in fertilizer production in Western Europe and Oceania contributed mostly to this trend. Depressed demand and low prices caused many fertilizer plants to be unprofitable and unsustainable in these regions.

In contrast to Western Europe and Oceania, North America registered an increase in production. Most of the increase in production occurred after 1984/85 partly in response to increased domestic prices after the drought of 1988 and partly in response to increased demand for phosphate fertilizers, especially diammonium phosphate (DAP), from the developing markets in Asia. Domestic availability of fertilizer raw materials such as phosphate rock, sulfur, natural gas, and potash ore helped North America to sustain its production. Unlike North America, Western Europe and Oceania depended on imported raw materials and therefore were unable to compete with cheap fertilizers imported from the regions endowed with raw materials. Environmental regulations, especially those dealing with the disposal of phosphogypsum, also affected fertilizer production in Western Europe.

Most of the decrease in total fertilizer production resulted from the decrease in phosphate and potash production. Nitrogen production decreased in the early 1980s but recovered and increased after the mid-1980s; after 1988/89, however, it again decreased.

Table 3.2. Annual Growth in Regional Fertilizer Production, 1979/80-1992/93

Region	1979/80–1988/89	1988-89–1992/93
	(%)	
Developed Regions	**0.3**	**(2.4)**
North America	1.1	1.4
Western Europe	(0.1)	(8.4)
Oceania	(2.6)	(10.5)
Reforming Regions	**4.6**	**(12.4)**
Eastern Europe	1.3	(20.6)
Eurasia	5.6	(10.6)
Developing Regions	**6.6**	**2.0**
Africa	8.0	1.4
Asia	6.5	2.5
Latin America	5.9	(2.0)
World	**3.2**	**(3.3)**

( ) = decrease.

Source: Derived from FAO data.

3.2.2 Reforming Markets

Fertilizer production increased from 30.0 million tonnes in 1979/80 to 45.2 million tonnes in 1988/89 and decreased rapidly thereafter to reach 27.7 million tonnes in 1992/93. Production of all three nutrients, namely, nitrogen, phosphate, and potash, followed a similar trend. However, potash production decreased by a lower amount than nitrogen production partly because increased costs of energy (natural gas) had a smaller impact on potash production than on nitrogen production in Eurasia.

Most of the increase in production occurred during the 1979/80-1984/85 period and was contributed by growth in fertilizer production in Eurasia. Economic and political reforms are responsible for the recent decline in production. Specifically, depressed demand, removal of subsidies, the high cost of energy and raw materials, and low capacity utilization resulting from outdated technology and poor maintenance have contributed to decreased production. Sudden withdrawal of governmental support without the provision of an alternative and adequate financial and institutional support also contributed to this process.

Nevertheless, devaluation of domestic currencies has created some incentives for the enterprises to continue

Table 3.3. World: Fertilizer Production by Regions, 1979/80-1992/93

Region/Market	1979/80	1984/85	1988/89	1992/93
	(million tonnes)			
Developed Markets	**60.9**	**60.3**	**61.3**	**54.9**
North America	32.0	32.8	35.0	36.0
Western Europe	27.3	26.3	25.1	18.0
Oceania	1.6	1.2	1.3	0.9
Reforming Markets	**30.0**	**39.2**	**45.2**	**27.7**
Eastern Europe	8.4	9.2	9.4	4.7
Eurasia	21.6	30.0	35.9	23.0
Developing Markets	**27.9**	**40.2**	**51.7**	**55.7**
Africa	2.0	3.4	4.7	4.9
Asia	22.8	32.4	41.9	46.2
Latin America	3.1	4.4	5.1	4.6
World	**118.7**	**139.7**	**158.3**	**138.3**

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

production and export fertilizer products to earn hard currency. Consequently, many countries in Eurasia and Eastern Europe have sold products in the international markets at low prices. This practice, however, will not be sustainable in the long term.

In Eurasia, fertilizer production, like fertilizer use, is heavily concentrated in Russia. In 1990, Russia accounted for over one-half of the total fertilizer production – ranging from 43% of K_2O to 56% of P_2O_5. Ukraine and Belarus are other dominant producers. Over one-half of the potash production occurred in Belarus, and about one-fifth to one-fourth of phosphate and nitrogen production took place in Ukraine (Table 3.4).

Although fertilizer production has decreased drastically in recent years, these markets, especially Eurasia, are rich in raw materials such as natural gas, potash ores, and phosphate rock. Therefore, they will continue to play an important role in supplying nitrogen and potash fertilizers in the global markets. Because Eastern Europe is not as rich in energy resources and raw materials, increased energy costs may reduce its comparative advantage in world fertilizer markets.

3.2.3 Developing Markets

Fertilizer production nearly doubled in the developing markets – from 27.9 million tonnes in 1979/80 to 55.7 million tonnes in 1992/93 (Table 3.5). Although all three regions experienced increases in fertilizer production, Asia contributed over 80% to this increase. Likewise, nitrogen production contributed the most to the increase in total fertilizer production.

In Asia fertilizer production increased by 23.4 million tonnes – from 22.8 million tonnes in 1979/80 to 46.2 million tonnes in 1992/93. All three subregions registered growth in fertilizer production. Availability of raw materials, growing fertilizer demand, conducive policy environment, and governmental support contributed to this rapid increase in production.

Compared with fertilizer production in Asia, Latin America's fertilizer production increased by a small amount of 2 million tonnes between 1979/80 and 1988/89. Both South America and Central America contributed to this increase. After 1988/89, fertilizer production decreased in both subregions – relatively more in South America. Macroeconomic instability, decrease in demand, and changes introduced under structural adjustment programs have contributed to the observed decrease in fertilizer production in Latin America in the early 1990s. It is likely that fertilizer production may decrease further due to privatization and subsidy removal programs in the 1990s, as inefficient units are closed under competitive market pressures.

Africa registered an increase of 2.9 million tonnes in its fertilizer production from 1980 to 1993. Most of this increase occurred in phosphate production in North Africa. Sub-Saharan Africa experienced a modest increase and South Africa a small decline. Sub-Saharan

Table 3.4. Fertilizer Production in Eurasia, 1990

State/Region	Total '000 tonnes	Total %	Nitrogen '000 tonnes	Nitrogen %	Phosphate '000 tonnes	Phosphate %	Potash '000 tonnes	Potash %
Azerbaijan	205	0.7			166	1.9	39	0.4
Belarus	5,996	19.4	747	5.7	257	2.9	4,992	55.3
Estonia	216	0.7	106	0.8	110	1.2	0	0.0
Georgia	130	0.4	130	1.0	0	0.0	0	0.0
Kazakhstan	1,181	3.8	431	3.3	737	8.3	13	0.1
Latvia	180	0.6	41	0.3	139	1.6	0	0.0
Lithuania	480	1.6	312	2.4	168	1.9	0	0.0
Russian Fed.	15,845	51.1	7,054	53.9	4,943	55.8	3,848	42.6
Tajikistan	73	0.2	73	0.6	0	0.0	0	0.0
Turkmenistan	192	0.6	55	0.4	137	1.5	0	0.0
Ukraine	4,726	15.3	3,022	23.1	1,561	17.6	143	1.6
Uzbekistan	1,762	5.7	1,113	8.5	649	7.3	0	0.0
Eurasia	**30,987**	**100.0**	**13,084**	**100.0**	**8,867**	**100.0**	**9,035**	**100.0**

Note: Totals may not add due to rounding.

Source: FAO.

Table 3.5. Developing Markets: Fertilizer Production, 1979/80-1992/93

Region/Market	1979/80	1984/85	1988/89	1992/93
	(million tonnes)			
Africa	**2.0**	**3.4**	**4.7**	**4.9**
North	0.9	2.2	3.3	3.6
Sub-Saharan	0.2	0.2	0.5	0.5
South	0.9	1.0	0.8	0.8
Latin America	**3.1**	**4.4**	**5.1**	**4.6**
Central	1.1	1.7	2.2	2.1
South	2.0	2.7	2.9	2.5
Asia	**22.8**	**32.4**	**41.9**	**46.2**
East	16.2	20.6	24.4	27.3
South	3.8	7.0	11.1	12.2
West	2.8	4.8	6.4	6.7
Developing Markets	**27.9**	**40.2**	**51.7**	**55.7**

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

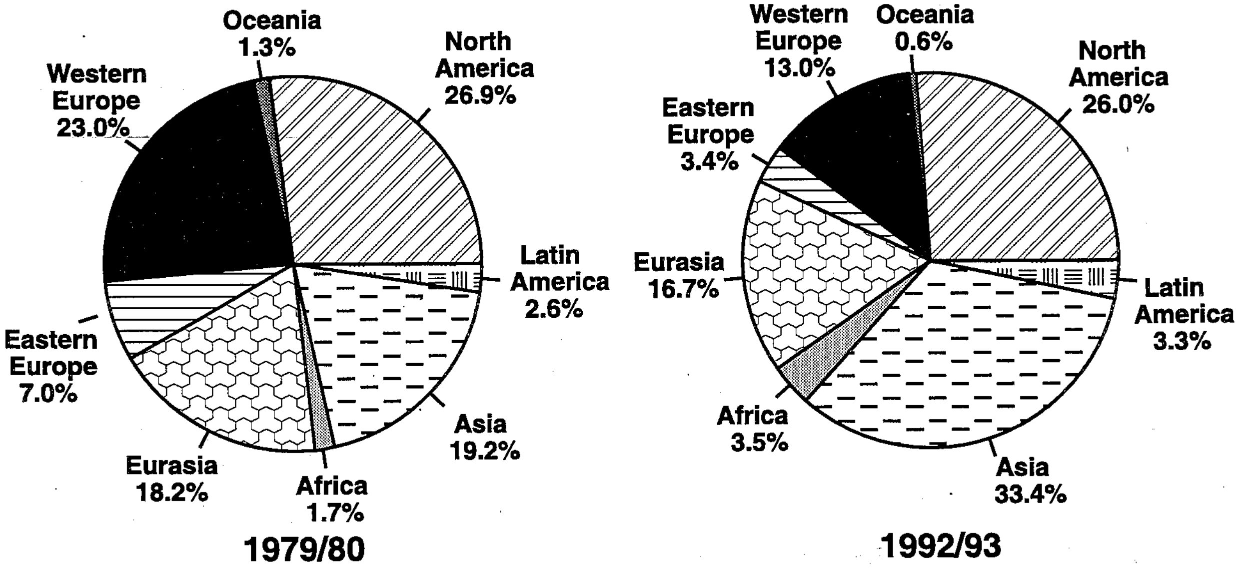
Africa's increase was created by the commissioning of a large ammonia-urea plant in Nigeria in 1988.

3.2.4 Regional Shares

Asia increased its share from 19% in 1979/80 to 33% in 1992/93 (Figure 3.3). In contrast to its decreased share in fertilizer use, North America maintained its share in fertilizer production at about one-fourth of the world production. The major loser was Western Europe; its share in global fertilizer production dropped from 23% to 13%. Africa and Latin America made small gains, and Eastern Europe and Eurasia lost their shares by small percentage points.

3.3 Statistical Overview of Fertilizer Consumption, 1960-95

World fertilizer consumption increased from approximately 28 million nutrient tonnes in 1960 to a peak of 146 million tonnes in 1989 as shown in Figure 3.4.



Source: Derived from FAO data.

Figure 3.3. Global Fertilizer Production: Regional Shares, 1979/80 and 1992/93.

Annual consumption increases averaged about 3.9 million nutrient tonnes during this 30-year period. During the next 4 years, consumption declined by an average of 4.9 million tonnes per year and reached a level of 126 million tonnes in 1993. Most of this recent decline occurred in the reforming markets of Eastern Europe and Eurasia.

Annual fertilizer consumption by economic class of countries (developed and developing) for the years 1960 through 1995 is shown in Table 3.6.

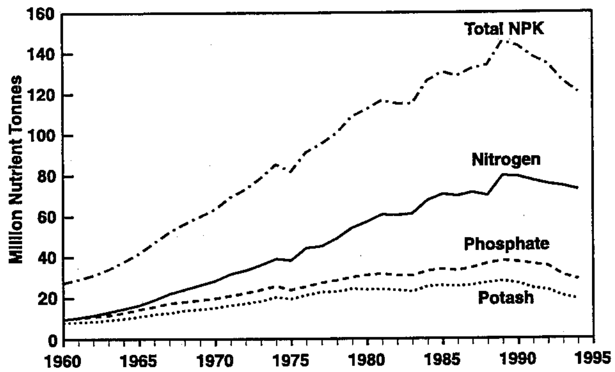


Figure 3.4. World Nitrogen, Phosphate, Potash, and Total NPK Consumption, 1960-94.

Different markets had different experiences. Fertilizer use decreased steadily in the developed markets and increased significantly in the developing markets during the 1980s and the early 1990s. However, in the reforming markets, it increased until 1988/89 and decreased rapidly thereafter. A steep decrease in fertilizer use in these markets resulted from the economic reforms introduced after the demise of communism. Western Europe contributed the most to the trends in the developed markets, whereas Asia dominated those in the developing markets.

Nitrogen (N), phosphate (P_2O_5), and potash (K_2O) use also increased during the 1980s and decreased during the early 1990s (Table 3.7). N use increased by higher amounts than did K_2O and P_2O_5 use in the 1980s. Higher growth in N use resulted from two factors: First, the developing markets of Asia, Africa, and Latin America continued to experience higher growth in N use, and second, because of residual phosphorus and potassium in the soils and unfavorable crop prices, the developed markets experienced declines in P_2O_5 and K_2O use. Between 1988/89 and 1992/93, potash use decreased by a much higher amount than did phosphate and nitrogen use.

The annual growth in fertilizer use slowed considerably during the 1980s. Total fertilizer use grew at 2.8% per annum during the 1980s. This growth was about one-half of the annual growth in the 1970s and one-third of the growth in the 1960s [2]; it was also about two-thirds of the projected growth for the 1980s (projections made by the FAO/UNIDO/World Bank Fertilizer Working Group, June 1980). Because investments for production capacity were made on the basis of the projected growth in demand, slower growth in fertilizer use led to excess production capacity and lower fertilizer prices in the 1980s. The slow growth in fertilizer use produced near stagnation in per capita fertilizer use.

The slow growth of the 1980s converted into a rapid decline in the early 1990s. Between 1988/89 and 1992/93, global fertilizer use decreased at an annual rate of 3.6%. This led to an increased surplus in the market, depressed fertilizer prices, and forced closure of some fertilizer plants.

In the 1980s, Asia and Eurasia registered over 5% annual growth in their fertilizer use. However, during the early 1990s, Eurasia's fertilizer use decreased at an annual rate of over 18%, whereas Asia's use increased by 3.6% per annum. Few other regions experienced significant growth in their fertilizer use during the early 1990s (Table 3.8). After 1988/89, fertilizer use in Western and Eastern Europe decreased at an annual rate of 7% and 35%, respectively.

Several factors have contributed to the slow growth of the 1980s and steep fall of the 1990s. These factors, which are discussed in more detail while analyzing the trends in developed and developing markets, are briefly summarized below.

1. Economic reforms in Eastern Europe and Eurasia had a tremendous effect on fertilizer use in these regions. During a short period of time, fertilizer use decreased by 30%-70% in many countries.
2. Debt crises, foreign exchange shortages, and balance-of-payment difficulties led to restricted fertilizer supplies and therefore decreased fertilizer use in many developing countries, especially in Africa and Latin America.
3. Policy reforms introduced under structural adjustment programs such as the devaluation of domestic currency, subsidy removal, and privatization (sudden withdrawal of governmental organizations) have had a negative impact on fertilizer use in several developing countries.
4. Depressed crop prices resulting from grain surpluses and acreage reduction programs in the developed markets have contributed to a decline or stagnation in fertilizer use.

Table 3.6. World Fertilizer Consumption — Historical Data, 1960-93

Year	Developing Countries[a]				Developed Countries[b]			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
	(millions of nutrient tonnes)				(millions of nutrient tonnes)			
1960	1.67	0.76	0.30	2.73	7.87	8.99	7.83	24.68
1961	1.97	0.92	0.41	3.30	8.51	9.31	8.01	25.83
1962	2.19	1.06	0.41	3.67	9.39	9.87	8.25	27.51
1963	2.65	1.19	0.44	4.27	10.49	10.42	8.79	29.71
1964	3.11	1.44	0.55	5.10	11.64	11.48	9.45	32.58
1965	3.66	1.61	0.58	5.84	12.82	12.88	10.34	36.04
1966	4.42	1.93	0.65	7.00	14.67	13.87	11.46	40.00
1967	5.69	2.48	0.78	8.95	16.49	14.93	11.96	43.38
1968	5.71	2.48	0.96	9.16	18.50	15.66	12.96	47.12
1969	6.51	2.61	1.22	10.33	19.74	16.43	13.31	49.48
1970	7.52	3.08	1.28	11.88	20.95	16.72	13.93	51.60
1971	8.82	3.52	1.45	13.79	22.94	17.60	14.99	55.52
1972	9.44	4.02	1.54	15.00	24.10	18.41	15.80	58.31
1973	10.74	4.65	1.82	17.21	25.41	19.36	16.72	61.49
1974	11.63	5.45	2.22	19.31	27.58	20.42	18.18	66.17
1975	10.93	5.34	2.29	18.55	27.50	18.65	17.25	63.39
1976	13.68	5.73	2.16	21.57	30.74	19.87	19.21	69.83
1977	13.94	6.20	2.34	22.49	31.32	21.12	20.51	72.95
1978	17.51	7.31	2.87	27.70	31.61	21.24	20.07	72.91
1979	20.68	7.40	3.29	31.37	33.57	22.64	21.17	77.39
1980	22.54	8.28	3.64	34.46	34.68	22.91	20.41	78.01
1981	25.06	9.68	4.03	38.76	35.72	22.02	20.22	77.96
1982	25.25	9.34	3.82	38.40	35.21	21.61	19.93	76.75
1983	26.62	10.07	3.79	40.48	34.57	20.79	19.20	74.56
1984	29.58	10.84	4.07	44.49	38.09	22.24	21.48	81.81
1985	31.92	11.92	4.61	48.45	38.73	22.11	21.29	82.12
1986	31.36	11.01	4.37	46.74	38.47	22.22	21.19	81.88
1987	32.34	11.96	5.06	49.36	39.15	22.70	21.04	82.89
1988	36.06	13.78	5.98	55.82	39.54	22.91	21.32	83.77
1989	39.78	15.12	6.60	61.51	39.82	22.87	21.44	84.13
1990	40.70	15.23	6.30	62.23	38.49	22.16	20.59	81.24
1991	41.97	16.21	6.92	65.10	35.27	20.06	17.61	72.95
1992	42.47	17.54	7.37	67.38	33.00	17.75	16.20	66.95
1993	44.29	16.93	6.98	68.21	29.34	14.59	13.79	57.73

a. Developing countries include Latin America, Asia (except Japan and Israel), Africa (except South Africa), and Oceania (except Australia and New Zealand).

b. Developed countries include North America, Europe, Eurasia, Japan, South Africa, Australia, and New Zealand.

Source: Data compiled by IFDC from various issues of FAO *Fertilizer Yearbooks* and fertilizer data tapes.

5. Environmental concerns associated with fertilizer use, such as nitrate leaching, eutrophication, and greenhouse gas emissions, have resulted in regulations on fertilizer use and thereby induced decreases in fertilizer use in the developed markets.
6. Agronomic factors such as residual phosphorus in the soil reduced the need for additional phosphate application, especially during the 1980s when crop prices were falling.
7. Climatic factors such as droughts and floods also contributed to decreased fertilizer use.

Table 3.9 provides data on total fertilizer use in different markets and regions.

3.3.1 Developed Markets

Total fertilizer use steadily decreased from 47.2 million tonnes in 1979/80 to 40.1 million tonnes in 1992/93. Annual decreases were much higher between 1988/

Table 3.7. World: Fertilizer Use by Nutrients, 1979/80-1992/93

Year/Period	N	P_2O_5	K_2O	Total
Fertilizer Use (million tonnes)				
1979/80	57.2	31.2	24.1	112.8
1984/85	70.1	34.0	25.9	130.6
1988/89	79.6	38.0	28.4	145.6
1992/93	73.6	31.5	20.8	125.9
Annual Growth (%)				
1980-89	3.5	2.2	1.8	2.8
1989-93	(2.0)	(4.3)	(7.3)	(3.6)

( ) = decrease.

Source: Derived from FAO data.

Table 3.8. Annual Growth in Regional Fertilizer Use, 1979/80-1992/93

Region	1979/80–1988/89 (%)	1988/89–1992/93 (%)
Developed Markets	**(0.6)**	**(2.6)**
North America	(1.5)	1.3
Western Europe	0.3	(7.0)
Oceania	0.1	(1.1)
Reforming Markets	**3.7**	**(22.1)**
Eastern Europe	(0.2)	(35.4)
Eurasia	5.5	(18.4)
Developing Markets	**5.3**	**2.7**
Africa	2.1	0.3
Asia	6.0	3.6
Latin America	3.4	(2.9)
World	**2.8**	**(3.6)**

( ) = decrease.

Source: Derived from FAO data.

89 and 1992/93 than those between 1979/80 and 1988/89. During the 1980s, fertilizer use in Western Europe and Oceania decreased by modest amounts, whereas in North America, it decreased by 2.8 million tonnes. During the early 1990s, however, the situation reversed. North America and Oceania increased their fertilizer use by small amounts, whereas Western Europe experienced a 24% decline. Decreased prices, acreage reduction programs and production quotas under the Common Agricultural Policy of the European Union, and drought contributed to this decline in fertilizer use. Economic reforms and restructuring in the former East Germany (now the eastern part of the unified Germany) also contributed.

Depressed crop prices and acreage reduction programs seem to have contributed to an annual decline of 2.8% in fertilizer use in North America during the 1980s. Residual phosphorus in the soils may have also allowed farmers to reduce phosphate consumption without adversely affecting crop yields. Phosphate use decreased in all three regions of the developed markets (Table 3.10).

3.3.2 Reforming Markets

The reforming markets of the 1990s are basically the centrally planned economies of the 1980s. In these markets, total fertilizer use increased in the 1980s and decreased rapidly in the 1990s (Figure 3.5).

During the 1980s, total fertilizer use in these markets increased from 27.5 million tonnes in 1979/80 to 37.3 million tonnes in 1988/89. Most of this increase was contributed by an increase in fertilizer use in Eurasia. Eastern Europe experienced little increase in its fertilizer use. The 5.5% annual growth in fertilizer use in Eurasia resulted from government commitment to increasing fertilizer use to achieve food security in the former Soviet Union [3].

After 1988, many of the countries of Eastern Europe and Eurasia initiated political and economic reforms, which led to the demise of communism and movement toward the establishment of democratic polities and market-based economies. A series of economic reforms were introduced, under which domestic currencies were allowed to float in the open markets. Consequently, the currencies of these countries depreciated rapidly. Such devaluations followed by deregulation and liberalization resulted in rapid increases in the prices of many commodities. Sudden withdrawal of the government from agriculture, industry, and trade also resulted in the disruption of marketing and distribution channels. Hence, fertilizer prices increased, and fertilizers were not available to the farmers on time. Further, farmers were unable to sell their agricultural produce and have adequate financial resources to purchase fertilizers. Inflationary pressures, inadequate credit arrangements, and poor technical support to new private farmers also adversely affected fertilizer use.

Rapid devaluation of domestic currency increased the cost of imported fertilizers. Foreign exchange shortages and the dissolution of barter trade among the former communist countries affected fertilizer supplies and use in these countries. Between 1988/89 and 1992/93, fertilizer use decreased by 55% in Eurasia and 71% in

Table 3.9. World: Fertilizer Use by Markets and Regions, 1979/80-1992/93

Market/Region	1979/80	1984/85	1988/89	1992/93
	(million tonnes)			
Developed Markets	**47.2**	**45.8**	**44.0**	**40.1**
North America	22.7	22.1	19.9	21.2
Western Europe	22.7	22.0	22.4	17.0
Oceania	1.8	1.8	1.7	1.9
Reforming Markets	**27.5**	**33.1**	**37.3**	**15.0**
Eastern Europe	10.1	10.1	10.1	2.9
Eurasia	17.4	23.1	27.2	12.2
Developing Markets	**37.8**	**51.6**	**64.4**	**70.8**
Africa	2.8	3.5	3.7	3.8
Asia	28.3	40.8	51.9	59.2
Latin America	6.7	7.3	8.7	7.9
World	**112.5**	**130.6**	**145.6**	**125.9**

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

Table 3.10. Developed Markets: Annual Decline in Phosphate Use, 1979/80-1992/93

Region	Annual Decline 1979/80–1988/89	Annual Decline 1988/89–1992/93
	(%)	
North America	2.8	(1.0)
Western Europe	1.7	8.9
Oceania	1.7	2.0
Developed Markets	**2.2**	**3.7**

( ) = growth.

Source: Derived from FAO data.

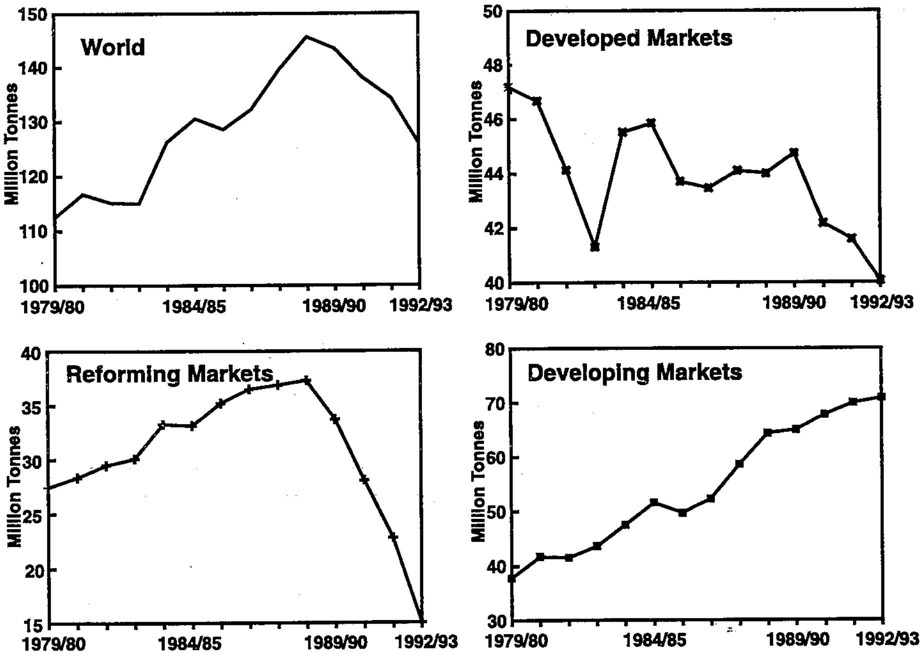
Eastern Europe (Figure 3.6). In 1993/94, Russia, a major user in Eurasia, reported another 40% decrease in its fertilizer use [4].

About one-half of the fertilizer use in Eurasia is concentrated in Russia (officially known as Russian Federation). In 1990, Russia used 11.1 million tonnes of fertilizer nutrients. Ukraine and Belarus were two other states accounting for a relatively large share. These three states accounted for about 81% of total fertilizer use in Eurasia (Table 3.11).

The developments in Eurasia during the 1980-93 period can be divided into three phases [3]. Phase I consists of the period, 1980-88, when the old communist government ruled and the rules of the centrally planned economy applied. During this period, fertilizer use increased rapidly. Phase II consists of the period, 1988-91, when reforms under *perestroika* were introduced by the Gorbachev government. During this period, controls on prices remained effective, but allocation rules of the planned economy were relaxed. Enterprises were given freedom to sell their products as they wished. Consequently, "disorganization" rather than privatization of distribution channels occurred during this period. This resulted in decreased fertilizer use. The last phase started when the former Soviet Union ceased to exist and its republics became independent states. The disintegration also resulted in further disorganization and disruption of supply and distribution channels. Economic reforms led to devaluation, deregulation, and liberalization of prices and supply arrangements. Because these changes were not accompanied by well-developed institutional infrastructures and management skills, they contributed to a rapid collapse of agricultural and fertilizer markets.

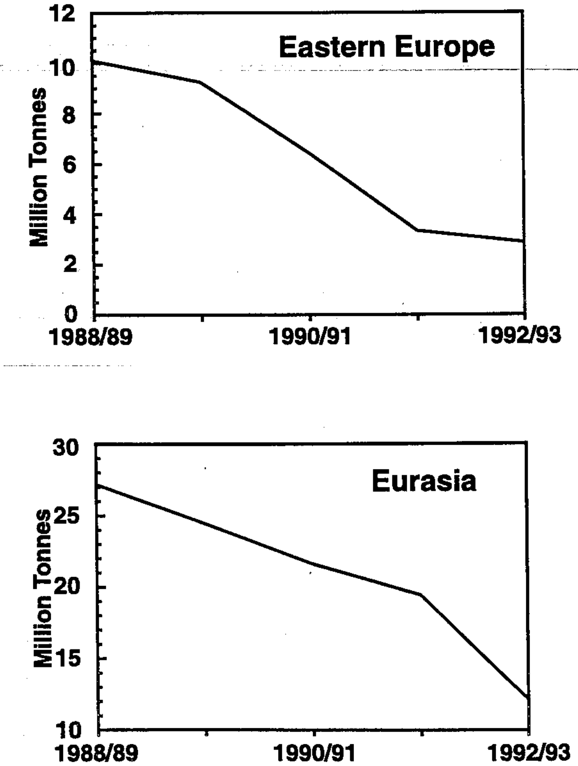
3.3.3 Developing Markets

Unlike the developed and reforming markets, the developing markets registered significant increases in their fertilizer use. Total fertilizer use increased by 87% – from 37.8 million tonnes in 1979/80 to 70.8 million tonnes in 1992/93 (Table 3.12). Asia contributed about 94% to this growth.



Source: Derived from FAO data.

Figure 3.5. Global Fertilizer Use by Markets, 1979/80-1992/93.



Source: Derived from FAO data.

Figure 3.6. Fertilizer Use in Eastern Europe and Eurasia, 1988/89-1992-93.

Asia's total fertilizer use increased from 28.3 million tonnes in 1979/80 to 40.8 million tonnes in 1984/85 and 59.2 million tonnes in 1992/93. All three subregions, namely East Asia, South Asia, and West Asia, registered growth in fertilizer use. A conducive and stable policy environment was the most important factor in maintaining growth in fertilizer use. Whether Asia will be able to keep this tempo of growth in the future is not clear. In 1992/93, India introduced several ad hoc policy changes that affected fertilizer use and production adversely. For example, the removal of subsidy on P_2O_5 and K_2O led to 14% and 31% decreases in their use, respectively [5].

Compared with Asia, Africa experienced a small increase in its fertilizer use between 1979/80 and 1992/93. North Africa and sub-Saharan Africa registered increases, whereas South Africa experienced continuous decline in the 1980s. In sub-Saharan Africa, fertilizer use increased from 0.7 million tonnes in 1979/80 to 1.2 million tonnes in 1988/89 and 1.5 million tonnes in 1992/93. In spite of this 50% increase, per hectare fertilizer use in sub-Saharan Africa is still very low at 11 kg/ha.

Foreign exchange shortages, structural adjustment programs, and drought have induced slow growth in many African countries. Debt crisis and balance-of-payment difficulties have made many nations in sub-Saharan Africa dependent on foreign aid for fertilizer supplies. About two-thirds of the countries in sub-Saharan Africa

Table 3.11. Fertilizer Use in Eurasia, 1990

State/Region	Total '000 tonnes	Total %	Nitrogen '000 tonnes	Nitrogen %	Phosphate '000 tonnes	Phosphate %	Potash '000 tonnes	Potash %
Armenia	47	0.2	26	0.3	12	0.2	9	0.2
Azerbaijan	143	0.7	88	1.0	49	0.6	6	0.1
Belarus	2,151	9.9	682	7.9	483	6.2	986	19.2
Estonia	205	1.0	71	0.8	53	0.7	81	1.6
Georgia	119	0.6	89	1.0	26	0.3	4	0.1
Kazakhstan	589	2.7	237	2.7	342	4.4	10	0.2
Kyrgyzstan	176	0.8	87	1.0	79	1.0	10	0.2
Latvia	382	1.8	117	1.4	104	1.3	161	3.1
Lithuania	661	3.1	214	2.5	175	2.2	272	5.3
Moldova Rep.	244	1.1	101	1.2	108	1.4	35	0.7
Russian Fed.	11,051	51.1	4,334	50.0	4,339	55.4	2,378	46.2
Tajikistan	205	1.0	111	1.3	82	1.1	12	0.2
Turkmenistan	245	1.1	135	1.6	91	1.2	19	0.4
Ukraine	4,352	20.1	1,836	21.2	1,457	18.6	1,059	20.6
Uzbekistan	1,074	5.0	541	6.2	430	5.5	103	2.0
Eurasia	**21,644**	**100.0**	**8,669**	**100.0**	**7,830**	**100.0**	**5,145**	**100.0**

Note: Totals may not add due to rounding.

Source: FAO.

Table 3.12. Developing Markets: Fertilizer Use, 1979/80-1992/93

Region	1979/80	1984/85	1988/89	1992/93
	(million tonnes)			
Africa	**2.8**	**3.5**	**3.7**	**3.8**
North	1.1	1.5	1.7	1.5
Sub-Saharan	0.7	1.0	1.2	1.5
South	1.0	1.0	0.8	0.8
Latin America	**6.7**	**7.3**	**8.7**	**7.9**
Central	2.1	2.7	3.0	2.5
South	4.7	4.6	5.8	5.4
Asia	**28.3**	**40.8**	**51.9**	**59.2**
East	19.1	27.0	34.0	38.8
South	7.0	10.6	14.0	15.7
West	2.2	3.3	3.9	4.6
Developing Markets	**37.8**	**51.6**	**64.4**	**70.8**

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

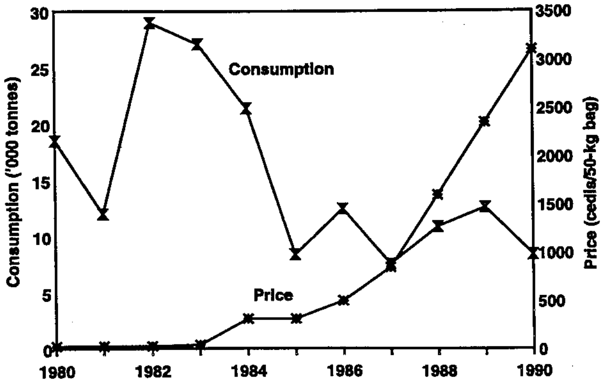
depended on donor support to meet over 50% of their fertilizer requirements (Table 3.13). Devaluation of currency, removal of subsidies, and sudden withdrawal of government from fertilizer markets also adversely affected fertilizer use in many African countries including Ghana, Senegal, and Zambia. Figure 3.7 vividly indicates that the structural adjustment program introduced in 1984 had a negative impact on fertilizer use in Ghana.

Latin America's fertilizer use increased from 6.7 million tonnes in 1979/80 to 8.7 million tonnes in 1988/89. Thereafter, it decreased by 9% to 7.9 million tonnes. Both Central and South America contributed to these trends.

Table 3.13. Sub-Saharan Africa: Distribution of Countries by the Ratio of Fertilizer Aid to Fertilizer Imports, 1985-90

Ratio (%)	1985	1987	1990
0	7	8	6
1-20	3	4	3
20-50	2	1	2
50-80	3	5	7
80-99	2	2	0
100	23	20	22
Total	**40**	**40**	**40**

Source: FERTECON, Unpublished data.

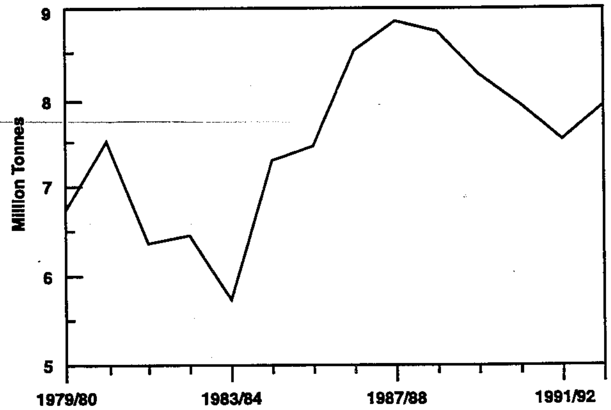


Source: [10].

Figure 3.7. Ghana: Fertilizer Consumption and Price, 1980-90.

Although Latin America recorded a 3.4% average annual growth in its fertilizer use during the 1980s, its fertilizer use fluctuated widely from one year to another (Figure 3.8). Having reached 7.5 million tonnes in 1981, it decreased to 5.7 million tonnes in 1984, recovered to 8.8 million tonnes in 1988, and decreased again thereafter. The 1992/93 level was marginally higher than that in 1981. Partly, these fluctuations were caused by the removal (1981), reintroduction (1984), and removal again (1988) of fertilizer subsidy in Venezuela and the removal of credit subsidies in Brazil.

Unlike Asia, Latin America experienced considerable policy instability and an unfavorable policy environment. Ad hoc policy changes were introduced in several countries. Debt crisis, currency depreciation, and declining crop prices also contributed to fluctuations in fertilizer use. Mexico, Brazil, and Venezuela have removed fertilizer subsidies. Because these changes were not met by the availability of increased credit funds for farmers and dealers, they had an adverse impact on fertilizer use. However, it is expected that improved incentives and better financial arrangements may accelerate growth in fertilizer use in the 1990s [6].

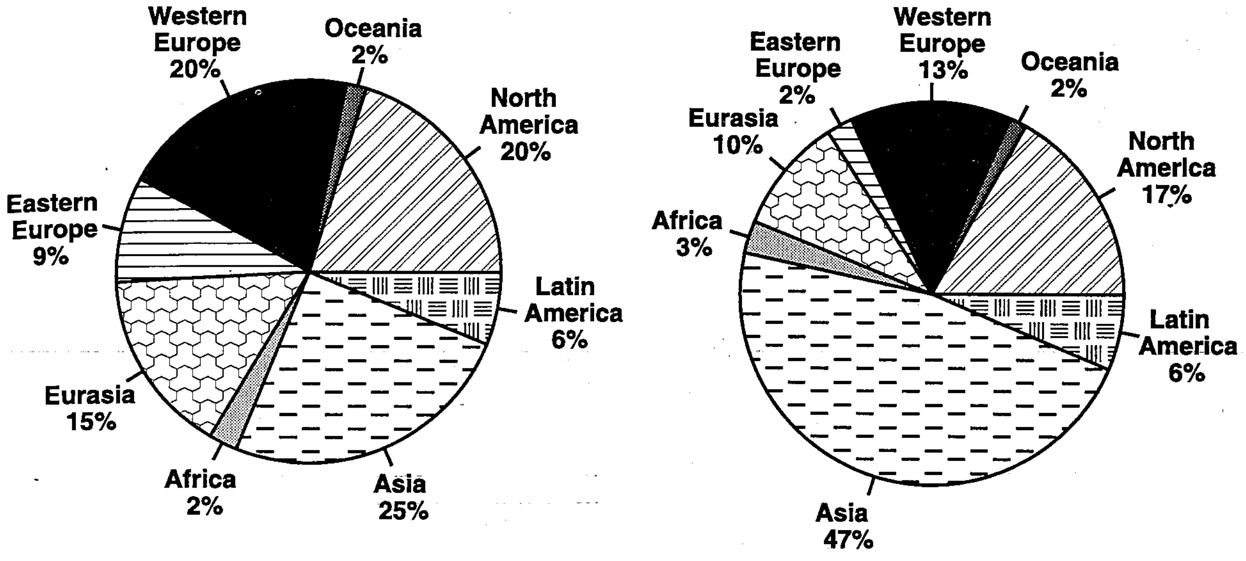


Source: FAO.

Figure 3.8. Latin America: Fertilizer Use, 1979-80-1992/93.

3.3.4 Regional Shares

Due to relatively higher growth in fertilizer use, Asia increased its share in global fertilizer use from 25% in 1979/80 to 47% in 1992/93 (Figure 3.9). Latin America maintained its share, and Africa increased its share by one percentage point – from 2% in 1979/80 to 3% in 1992/93. Asia's gains were at the cost of Western Europe, Eastern Europe, and Eurasia who lost their shares by 5-7 percentage points each. North America also decreased its share by 3 percentage points. Thus Asia has become the dominant region in the global fertilizer market.



1979/80

1992/93

Source: Derived from FAO data.

Figure 3.9. Global Fertilizer Use: Regional Shares, 1979/80 and 1992/93.

3.4 Trends in Fertilizer Trade

3.4.1 Global Trends

Global fertilizer imports increased at 3.9% per annum—from 34.0 million tonnes in 1979/80 to 48.5 million tonnes in 1988/89 – and stagnated after 1988/89 (Table 3.14). The share of imports in consumption also increased from 30.1% in 1979/80 to 33.3% in 1988/89 and 38.8% in 1992/93. Likewise the ratio of exports to production also increased from 29% in 1979/80 to 34.4% in 1992/93. These trends suggest that fertilizer trade has become an important source of fertilizer supply in several countries. Because of low global fertilizer prices, many developing countries including India and China have relied more on imports to meet their domestic fertilizer requirements and less on investments in capacity building for achieving fertilizer self-sufficiency. Increased exports from the reforming markets have also contributed to this process.

Imports of N increased by a higher amount than did K_2O imports. Foreign exchange shortages and perceptions about K_2O requirements for crop production in many developing countries kept K_2O imports to a minimum.

3.4.2 Regional Trends

Table 3.15 provides data on net imports at the regional level. Net imports are defined as the difference between imports and exports. Because net imports data exclude intraregional trade among countries within a region, they indicate whether a particular region is deficit

Table 3.14. World: Import and Export of Fertilizers, 1979/80-1992/93[a]

	1979/80	1988/89	1992/93
	------ (million tonnes)------		
Imports			
N	12.6	19.8	21.2
P_2O_5	5.8	9.6	10.5
K_2O	15.5	19.1	17.1
Total	**34.0**	**48.5**	**48.8**
Ratio of Imports to Fertilizer Use (%)	**30.1**	**33.3**	**38.8**
Exports			
N	11.9	19.5	20.8
P_2O_5	6.8	10.3	10.5
K_2O	15.6	18.5	16.3
Total	**34.4**	**48.3**	**47.6**
Ratio of Exports to Production (%)	**29.0**	**30.5**	**34.4**

a. In theory, at the global level, fertilizer imports should be equal to fertilizer exports. In reality, they differ slightly due to in-transit shipments, losses, and recording errors.

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

Table 3.15. World: Net Fertilizer Imports,[a] 1979/80-1992/93

Region/Market	1979/80	1988/89	1992/93
	(million tonnes)		
Developed Markets	**(9.4)**	**(8.6)**	**(5.0)**
North America	(6.7)	(8.1)	(7.6)
Western Europe	(3.0)	(1.2)	1.4
Oceania	0.3	0.7	1.2
Reforming Markets	**(1.5)**	**(4.8)**	**(10.8)**
Eastern Europe	1.5	1.2	(1.4)
Eurasia	(3.0)	(6.0)	(9.3)
Developing Markets	**10.5**	**13.6**	**17.0**
Africa	0.9	(0.8)	(1.0)
Asia	6.0	10.6	14.6
Latin America	4.6	3.8	3.4
World	**(0.4)**	**0.1**	**1.2**

( ) = net exports.

a. Imports minus exports.

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

Table 3.16. Developing Markets: Net Fertilizer Imports,[a] 1979/80-1992/93

Region/Market	1979/80	1988/89	1992/93
	(million tonnes)		
Africa	**0.9**	**(0.8)**	**(1.0)**
North	0.2	(1.5)	(2.1)
Sub-Saharan	0.6	0.8	1.0
South	0.1	(0.0)	0.1
Latin America	**3.6**	**3.8**	**3.4**
Central	1.0	0.8	0.4
South	2.7	2.9	3.0
Asia	**6.0**	**10.6**	**14.6**
East	3.2	10.5	12.1
South	3.1	2.5	4.1
West	(0.4)	(2.4)	(1.6)
Developing Markets	**10.5**	**13.6**	**17.0**

( ) = net exports.

a. Imports minus exports.

Note: Totals may not add due to rounding.

Source: Derived from FAO data.

or surplus in fertilizer nutrients. On this basis, the developed and reforming markets had a surplus, and the developing markets had a deficit in their fertilizer trade balance sheets; that is, the developed and reforming markets were net exporters and the developing markets net importers. However, net exports decreased in the developed markets by about 50% and increased over sevenfold in the reforming markets. In the developed markets, North America improved its position, but Western Europe reversed its position from being a net exporter in 1979/80 to being a net importer in 1992/93. Oceania remained a net importer, and its net imports increased from 0.3 million tonnes in 1979/80 to 1.2 million tonnes in 1992/93. Reduced domestic production induced increased imports in Oceania.

Eurasia also improved its position as a net exporter by increasing net exports from 3.0 million tonnes in 1979/80 to 9.3 million tonnes in 1992/93. A drastic fall in domestic use has further strengthened its position. Eastern Europe's net imports decreased over time, and as a result of a drastic reduction in domestic use, it has become a net exporter in the world fertilizer market.

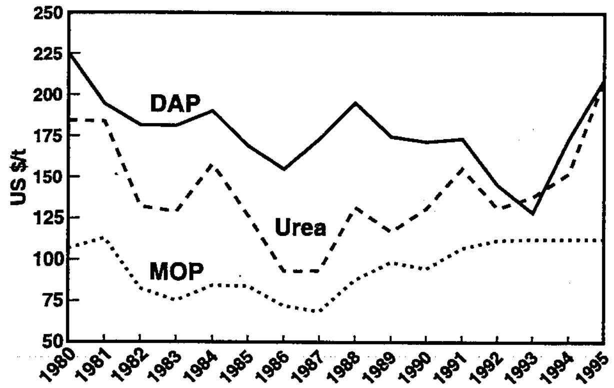
Among the developing markets, both Asia and Latin America remained net importers, whereas Africa changed its position from that of a net importer to that of a net exporter. In 1979/80 Africa was a net importer of about 0.9 million tonnes of fertilizer nutrients, but in 1992/93 it became a net exporter of 1 million tonnes of fertilizer nutrients. North Africa alone contributed to this switchover in Africa's trading position (Table 3.16); exports of phosphate fertilizer from Morocco, Jordan, and Tunisia dominated the African exports. Sub-Saharan Africa remained a net importer. Both South America and Central America remained net importers although Central America's dependence on fertilizer imports was modest.

Similarly, East and South Asia remained net importers, and net fertilizer imports increased nearly fourfold in East Asia. Achieving food security through increased fertilizer use was the main force behind such a spectacular increase in net imports of fertilizer nutrients in East Asia. On the other hand, West Asia increased its net exports from 0.4 million tonnes in 1979/80 to 2.4 million tonnes in 1988/89. The availability of cheap natural gas encouraged investments in production capacity for exports in West Asia. After 1988/89, its exports decreased because relatively cheaper exports were available from the reforming markets.

3.5 Trends in Fertilizer Prices

Fertilizers prices tend to be cyclical and are often quite volatile; recent history is no exception. Prices (in US $) of urea, diammonium phosphate (DAP), and muriate of potash (MOP) for the period 1980-95 are shown in Figure 3.10. Prices of all three products declined during the period 1980-87 but have recovered since that time.

The 1980-87 declining trend in prices was induced by both the demand-side and the supply-side factors.



Source: Green Markets.

Note: Current urea and DAP prices are f.o.b. bulk, U.S. Gulf, and MOP price is f.o.b. bulk, Vancouver.

Figure 3.10. Fertilizer Prices, 1980-95.

On the demand side, low crop prices and acreage reduction programs resulting from grain surpluses of the mid-1980s reduced demand for fertilizer use in the developed markets; slow growth in demand for grain and other crop exports also affected demand for fertilizer use. In the developing countries, the devaluation of domestic currencies and subsidy removal programs led to rapid increases in prices and therefore reduced fertilizer demand. The availability of residual phosphorus in the soils of developed markets contributed to a decrease in phosphate use. All these factors reduced demand for fertilizer use. This reduced demand was matched by excess supply in the markets because production capacity was not reduced in response to decreased demand. As a result, fertilizer supply exceeded demand by a significant margin. Such excess supply created downward pressures on fertilizer prices.

Price recovery during the early 1990s was interrupted by a drastic fall in fertilizer use in the reforming markets, which created excessive supplies in the global market. However, record imports by China and strong North American markets absorbed much of the excess supply and led to near record level prices in 1995. Urea prices climbed from the $93/tonne level in 1986 and 1987 to more than $230 during the spring of 1995. DAP prices increased from $155 in 1986 to $240 during the fall of 1995, and MOP prices increased from $69 in 1987 to $112 in 1995.

Supply-demand balance estimates suggest that fertilizer markets during the late 1990s will be dominated by "surpluses" under most scenarios and therefore will continue to put downward pressures on prices. However, in any given year, price may increase due to unexpected changes in the supply-side/demand-side factors, as happened in 1994 and 1995.

In spite of low international fertilizer prices in the 1980s, many developing countries were not able to reap the benefits of increased fertilizer use because the domestic fertilizer prices increased rapidly due to subsidy removal and devaluation of domestic currency. In Mexico, Zambia, and Turkey, fertilizer prices increased by over 2,000%-5,000% during the 1980-90 period [7]. This created a paradoxical situation of declining fertilizer prices in the world market and increasing domestic prices in several developing countries.

3.6 Emerging Centers of Fertilizer Production

Close proximity of production facilities to markets is desirable; however, the world's ratio of imports to fertilizer use increased from 30.1% in 1979/80 to 38.8% in 1992/93. This indicates that location of basic (N, P, and K) production capacity is increasingly dictated by availability of low-cost raw materials. Some of the reasons for new, emerging centers of production of nitrogen, phosphate, and potash fertilizers are discussed below.

3.6.1 Nitrogen

Essentially all nitrogen fertilizers are based on ammonia, and natural gas is a major item of cost for producers of ammonia. Production cost surveys by The Fertilizer Institute (TFI) show that natural gas costs comprised almost 70% of total ammonia production costs for North American producers. Thus, it is not surprising that world ammonia production has shifted toward the regions with abundant, low-cost natural gas. Synthetic gas from coal gasification is technologically feasible and is an alternative to natural gas in some regions with high natural gas costs and an abundant coal resource. Many of the new ammonia plants under construction in 1995 are in China and India where both natural gas and synthetic gas from coal gasification will be used as feedstock. New natural gas-based plants are also planned or under construction in Venezuela, Trinidad, Indonesia, and the Middle East. The China and India plants will produce for domestic markets; most of the other expansions are aimed at export markets.

Projected increases in nitrogen fertilizer production capacity by region are discussed in Chapter 4 of this manual. Most expansions will occur in Asia and Latin America; North America, Eastern Europe, and Oceania will see little change in capacity, whereas Eurasia and Western Europe are expected to reduce capacities by small amounts.

3.6.2 Phosphate

Phosphoric acid is used in the production of most phosphate fertilizers. According to TFI's 1994 production cost survey of North American producers, phosphoric acid represented about 60% of the total production costs for DAP, 74% of costs of producing MAP, and 62% of costs of producing TSP. Cost of phosphate rock comprised 47% and sulfur 30% of total costs of producing phosphoric acid. Therefore, the production of phosphoric acid-based phosphate products will continue to be concentrated in the regions with low-cost phosphate rock and sulfur. Acidulation of phosphate rock with nitric acid is a competitive technology, particularly in Europe.

At the global level, phosphoric acid capacity is expected to increase to about 39 million tonnes P_2O_5 by the year 2000; mostly in the developing markets. The developed markets and the reforming markets will register little change.

Beginning near the year 2000, production in Florida (U.S.A.) is expected to decline due to environmental pressures and increased production costs. However, the United States is expected to be a major producer and exporter well into the 21st century. More detailed projections of changing phosphate production capacity are included in Chapter 4 of this manual.

3.6.3 Potash

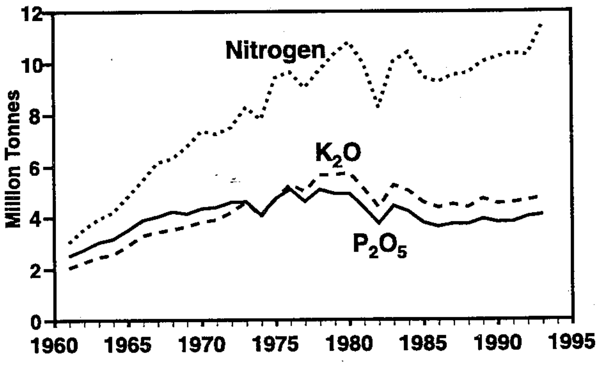
Excess production capacity troubled the world potash industry during the 1980s and 1990s; existing capacity was underutilized and little new capacity has been developed. Because market conditions improved somewhat in 1994 and 1995, capacity expansions are again receiving consideration.

Unlike ammonia capacity, potash capacity is restricted to a few countries because potash mines are mostly concentrated in North America and Eurasia. These two regions account for over 90% of the existing potash capacity. Canada, Russia, and Belarus are dominant producers.

Compared with the increases in ammonia and phosphoric acid capacity, the increase in potash capacity will be very small. The main reason for this small increase is that, during the 1980s, slow growth in demand left considerable excess capacity. The decrease in demand in the early 1990s further added to the excess capacity and created surpluses in the global markets. More detailed projections of global potash production capacity are described in Chapter 4 of this manual.

3.7 Industry Restructuring in Older Producing Areas

The older fertilizer-producing regions of Europe and North America are undergoing major structural changes as the world approaches its 21st century. West European and North American markets are considered to be mature; low growth or declining growth in consumption is forecast by most analysts. To illustrate the level of maturity, plant nutrient consumption in the United States for the period 1960-95 is shown in Figure 3.11. These data show that consumption of nitrogen peaked in 1980 and did not again reach this level until 1994; consumption of phosphate and potash declined slightly during the period 1980-94. Application rates changed little; therefore, most of the peaks and valleys in plant nutrient consumption were caused by changes in the area devoted to crop production [8].

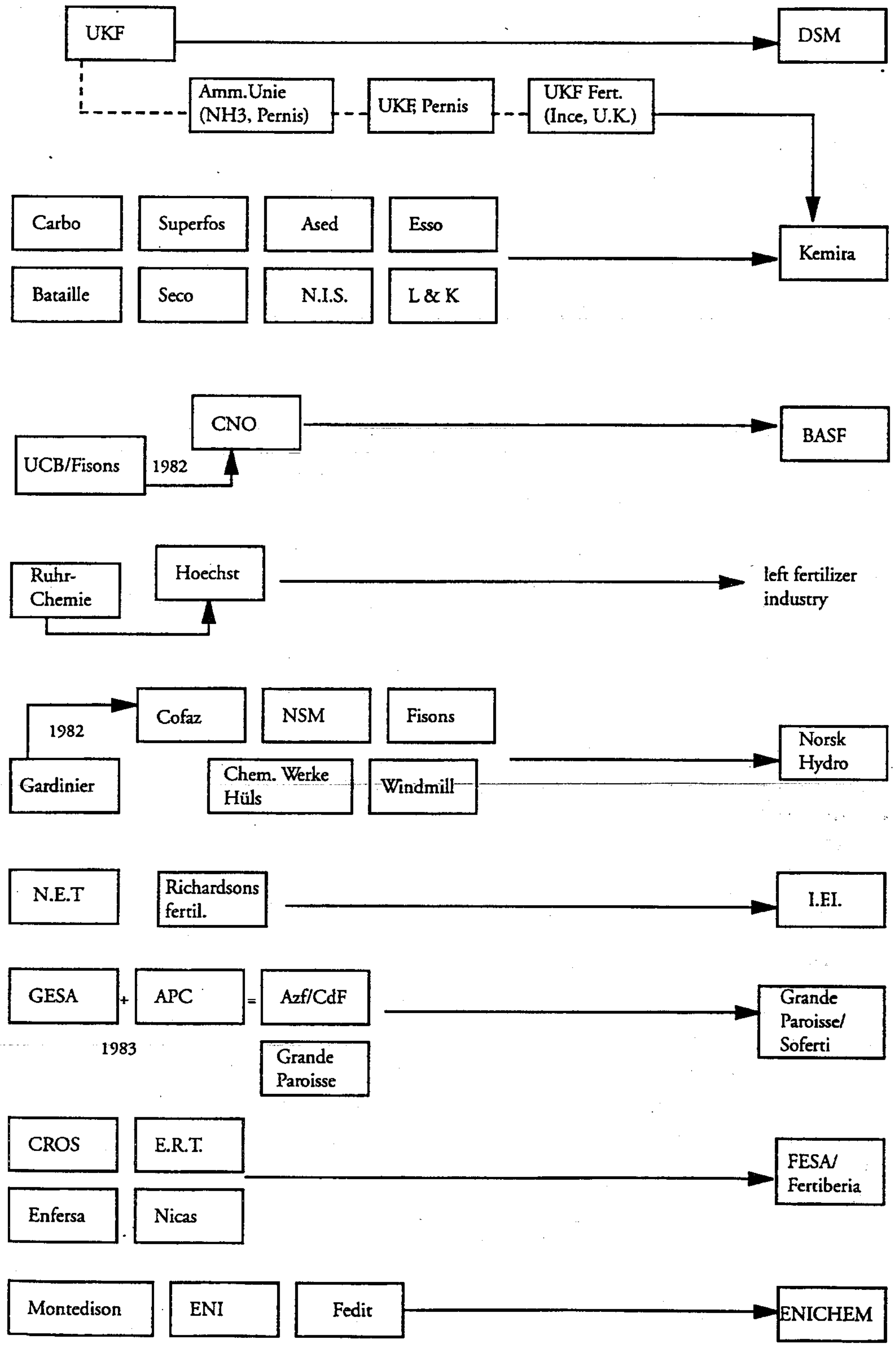


Source: Derived from TVA data.

Figure 3.11. Plant Nutrient Consumption in the United States.

No new phosphate plants were built, and no major new potash mines were opened in North America or Europe during the period 1980-95. One new nitrogen fertilizer complex (SASFERCO in Canada) was constructed during that time period.

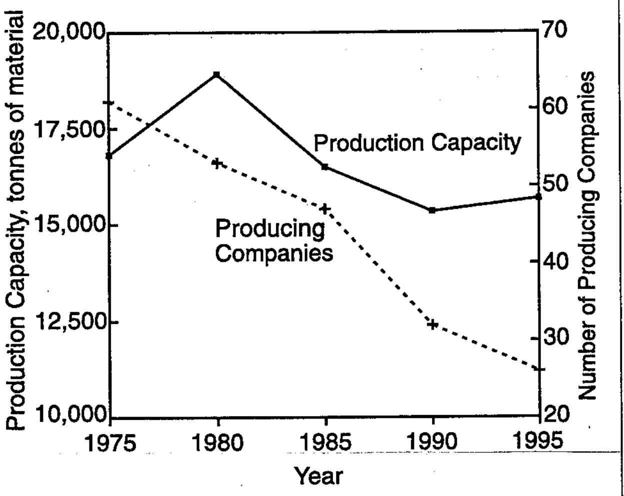
The European fertilizer industry has experienced several mergers and plant closings since 1980 as depicted in Figure 3.12. In 1992 it was estimated that eight major companies owned 80% of the European fertilizer production capacity. The European fertilizer industry employed about 110,000 people in 1983, but by 1992 the number of employees was reduced to only 40,000. In the 10-year period leading up to 1990, the number of ammonia plants decreased from 74 to 41 and production capacity declined by 12%. The number of phosphoric acid plants was halved during the 1980s, and capacity was reduced by 35%. In 1977 there were 11 phosphoric acid plants in the United Kingdom. Now there are none in the United Kingdom, which is considered by historians as the cradle of the phosphate industry [9].



Source: EFMA. 1994. *The Fertilizer Industry of the European Union.*
Note: Those companies which did not undergo fundamental changes in ownership and/or name are not included.

Figure 3.12. Restructuring of the Fertilizer Industry of the European Union, 1980-93.

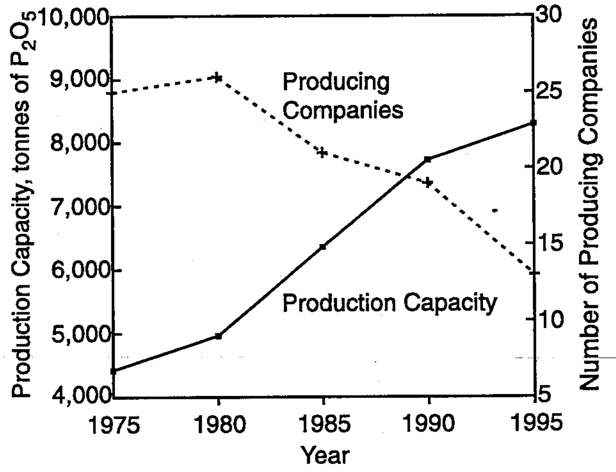
The U.S. fertilizer industry has also experienced rationalization. In 1975, 61 different companies operated 93 ammonia plants with a combined capacity of about 16.8 million tonnes per year. In 1995, 26 companies operated 39 ammonia plants with a combined capacity of 15.7 million tonnes per year (Figure 3.13). The average age of U.S. ammonia plants was 22 years in 1995; however, these old plants have generally been well maintained and were operated at more than 100% of design capacity in recent years.



Source: Data for 1975 through 1990 derived from various reports by TVA's National Fertilizer Environmental Research Center; 1995 data derived from International Fertilizer Development Center report: North American Fertilizer Capacity, June 1996.

Figure 3.13. Ammonia Production Capacity in the United States, Number of Producing Companies, 1975-95.

The United States continues as the world's largest producer of phosphate fertilizers and expanded ammonium phosphate production capacity by 87% between 1975 and 1995 (Figure 3.14). However, maturity of the domestic market has forced U.S. phosphate producers to become more dependent on exports. In 1995, the United States exported more than 10.5 million tonnes of ammonium phosphate; these exports accounted for about 63% of the U.S. production of ammonium phosphate.



Source: Data for 1975 through 1990 derived from various reports by TVA's National Fertilizer and Environmental Research Center; 1995 data derived from International Fertilizer Development Center report: North American Fertilizer Capacity, June 1996.

Figure 3.14. Ammonium Phosphate Capacity in the United States, Number of Producing Companies, 1975-95.

Canada has become the world's largest producer of potash and is the largest exporting country in the world. In 1995, 6 companies operated Canada's 12 potash mines with a combined production capacity of about 12.3 million tonnes of K_2O per year.

Globalization is the term that most aptly describes the current restructuring of the world fertilizer industry. Mature domestic markets and relatively high gas costs have forced nitrogen producers in older producing areas to seek joint venture partners or form strategic alliances with firms in the regions of the world that have low-cost natural gas. U.S. and European companies now own ammonia plants in Trinidad and have plans for nitrogen plants in Venezuela, Argentina, Chile, and other countries. Japan is investing in nitrogen production facilities in Jordan and Canada; whereas, India is investing in nitrogen production in Jordan, United Arab Emirates, and Oman. Major phosphate-importing countries are seeking joint ventures in countries that have high-quality phosphate rock reserves and/or phosphate plants. China has invested in phosphate production facilities in the United States; India is considering similar investments in the United States and Morocco.

3.8 References

1. Nelson, L. B. 1990. *History of the U.S. Fertilizer Industry*, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.
2. Bumb, B. L. 1989. *Global Fertilizer Perspective, 1960-95: The Dynamics of Growth and Structural Change*, T-34 and T-35, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
3. Aleinov, D. P. 1993. "The Russian Nitrogen Industry," Paper presented at the 1993 IFA Regional Conference for Europe, Vienna, Austria.
4. *FERTECON, Ltd., London, U.K.*
5. Narayan, P. 1993. "Recent Developments in Indian Fertilizer Sector," Paper presented at World Bank/ IFA Roundtable Meeting, Washington, D.C., U.S.A.
6. Puggina, W. A. 1993. "Fertilizer Demand in Brazil: Evolution, Present Situation and Perspectives," Paper presented at the Sixty-First IFA Annual Conference, New Orleans, LA, U.S.A.
7. Bumb, B. L. 1995. *Global Fertilizer Perspective, 1980-2000: The Challenges in Structural Transformation*, T-42, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
8. Brummitt, W. C. 1995. "Structure and Trends Within the United States Fertilizer Industry," Paper presented at Management Staff Training for Hubei (China) Phosphate Project, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
9. Maene, L. M. 1992. "Fertilizer Industry Restructuring: West and East Europe," Paper presented at the Fertilizer Industry Round Table Meeting, Baltimore, MD, U.S.A.
10. Bumb, B. L., J. F. Teboh, J. K. Atta, and W. K. Asenso-Okyere. 1994. *Ghana: Policy Environment and Fertilizer Sector Development*, T-41, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

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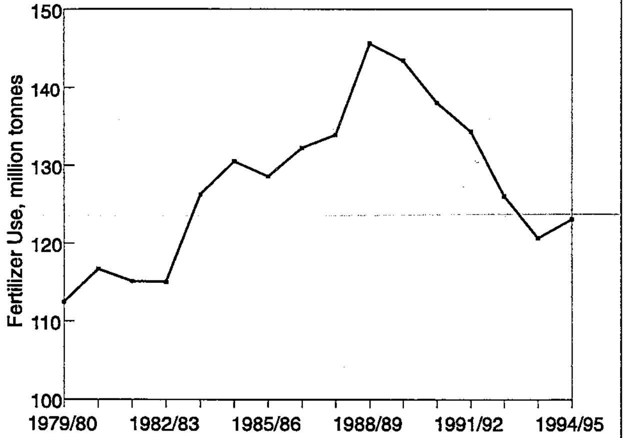
Chapter 4. Outlook for the Fertilizer Industry, 1995-2005

4.1 Introduction

The year 1994/95 has a special importance in the history and future outlook of the fertilizer industry. Having peaked at 145.6 million tonnes in 1988/89, global fertilizer use has been decreasing ever since; it reached 120.7 million tonnes in 1993/94 (Figure 4.1). The year 1994/95 is the first year when global fertilizer use registered about 2% increase over the previous year. Although the recorded increase of 2%, or 2.4 million tonnes, per se is not large enough to outweigh the previous decreases, it is significant because it marks the beginning of a new era in the global fertilizer industry. It signifies the turning point of the downward trend of the late 1980s and the early 1990s.



Source: FAO [1].

Figure 4.1. Global Fertilizer Use, 1979/80-1994/95.

Several factors including political and economic reforms in Eastern Europe and Eurasia (former Soviet Union) have had a negative influence on fertilizer use and production. The negative impact of these factors (explained below) counterbalanced the positive impact of growth in fertilizer use in the Asian markets. The net result was a continuous decline in global fertilizer use. On average, global fertilizer use decreased by 5 million tonnes per annum during the 1988/89-1993/94 period. The upturn in global fertilizer use indicates that the fertilizer industry may expect growth in fertilizer use in the future.

This upturn in fertilizer use is caused mainly by two factors. First, the declining trend in Eastern Europe has reversed; fertilizer use increased by 2% in 1994/95. It is expected that fertilizer use may start increasing in Eurasia beginning in 1996/97. Second, several regions including Asia, Latin America, Oceania, and Western Europe experienced significant increases in fertilizer use (Table 4.1). Asia alone registered about 10% increase in its fertilizer use. This increase of 5.5 million tonnes in Asia was large enough to compensate for declines in fertilizer use in North America, Eurasia, and Africa. This setting provides the background for assessing the future outlook of the fertilizer industry.

Table 4.1. Fertilizer Consumption, 1993/94 and 1994/95

Region/Market	1993/94	1994/95	Change
	('000 nutrient tonnes)		(%)
Developed Markets	**42,179**	**41,651**	**-1.3**
North America	22,709	21,514	-5.3
Western Europe	17,313	17,832	3.0
Oceania	2,157	2,305	6.9
Reforming Markets	**10,702**	**7,689**	**-28.2**
Eastern Europe	3,067	3,124	1.9
Eurasia	7,635	4,565	-40.2
Developing Markets	**67,934**	**73,912**	**8.8**
Africa	*3,952*	*3,532*	*-10.6*
North	1,643	1,420	-13.6
Sub-Saharan	1,465	1,280	-12.6
South	844	832	-1.4
Latin America	*8,418*	*9,289*	*10.3*
Central	2,404	2,375	-1.2
South	6,014	6,914	15.0
Asia	*55,564*	*61,091*	*9.9*
East	35,174	39,963	13.6
South	15,933	17,279	8.4
West	4,457	3,849	-13.6
World	**120,815**	**123,252**	**2.0**

Note: Totals may not add due to rounding.
Source: FAO [2].

4.2 Recent Economic and Political Developments and Their Impact on the Fertilizer Industry

In the late 1980s and the early 1990s, many countries experienced profound political and economic changes. The most notable among these changes are the collapse of communism and centrally planned economies in Eastern Europe and Eurasia and the implementation of structural adjustment programs in developing countries, especially Africa and Latin America. As a result of the political and economic changes in the former centrally planned economies, many policy changes, such as devaluation of domestic currency, subsidy removal, and privatization of production, marketing, and distribution facilities, were introduced. Most importantly, the governmental interference in economic activities was drastically reduced. These changes had an adverse effect on both fertilizer use and production in these regions. Both devaluation and liberalization of prices including subsidy removal resulted in high prices for fertilizers. Nominal and real prices increased severalfold. Increased prices reduced fertilizer demand drastically. Between 1988/89 and 1993/94, fertilizer use decreased by 69%-72%. Reduced demand also had an adverse impact on fertilizer production, albeit with a lag. Fertilizer production decreased in these regions by over 50%.

Initially, decreased domestic demand in these countries created production surpluses, which were diverted to international markets and depressed fertilizer prices. Between 1991 and 1993, urea prices decreased by about 40%. Prices of other products also decreased significantly. Such depressed prices made fertilizer production unprofitable in Western Europe and North America and forced plant closures.

These catastrophic effects were further compounded by the adverse impact of policy changes in the developing countries. Devaluation and subsidy removal in many developing countries resulted in increased fertilizer prices and reduced demand. Ad hoc privatization of marketing and distribution facilities also affected fertilizer use adversely. As a result, there was little growth in fertilizer use in Africa and Latin America in the early 1990s. All these factors produced a declining trend in global fertilizer use in the late 1980s and the early 1990s.

4.3 Future Outlook for Fertilizer Demand

The experience of the late 1980s and the early 1990s indicates that it is difficult to assess the future outlook of the fertilizer industry. Many uncertainties surround the industry. Uncertainty introduced by the weather leads to wide fluctuations in crop prices. In addition, uncertainty introduced by policy reforms leads to changes in fertilizer subsidies and organizational arrangements and makes it difficult to forecast fertilizer demand and supply more accurately. Recent changes in the U.S. Farm Bill, which give freedom of farming to farmers, and environmental regulation and common agricultural policy reforms in Europe add further uncertainty to forecasting demand and supply. However, by considering various factors, the World Bank/FAO/UNIDO/Fertilizer Industry Working Group (referred to as the Working Group hereafter) has developed supply and demand projections. The Working Group's projections are used to provide an assessment of the future outlook for the fertilizer industry.

4.3.1 Global Fertilizer Demand Projections

The demand projections developed by the Working Group are presented in Table 4.2. Global fertilizer demand is projected to increase at 2% per annum – from 123.3 million tonnes in 1994/95 to 137.5 million tonnes in 1999/2000 (referred to as 2000 hereafter) and 149.9 million tonnes in 2004/05. The demand is projected to grow at a higher rate during the first half than the second half of the projection period. This results from two factors, namely higher growth in North America and recovery in the reforming regions. The

Table 4.2. Global Fertilizer Demand Projections, 1994/95-2004/05

Nutrient	1994/95 (Actual)	1999/2000[a]	2004/05	1994/95 - 2004/05 Absolute Change (million nutrient tonnes)	1994/95 - 2004/05 Annual Change (%)
	(million nutrient tonnes)				
N	73.6	82.1	88.9	15.3	1.9
P_2O_5	29.7	33.6	36.4	6.7	2.0
K_2O	20.0	21.8	24.6	4.6	2.1
Total	**123.3**	**137.5**	**149.9**	**26.6**	**2.0**

a. Referred to as 2000 hereafter.

Source: FAO [2] for actual consumption and World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995 for projections.

need to feed the growing population in Asia will continue to exert pressures for increased but environmentally sound fertilizer use.

The demand for all three nutrients is expected to increase at 1.9% to 2.1%/year. A relatively higher growth for potash is a result of the impact of recovery in the reforming regions on potash use. Nitrogen demand is projected to increase from 73.6 million tonnes in 1994/95 to 88.9 million tonnes in 2004/05. Phosphate and potash demand is projected to increase from 29.7 and 20.0 million tonnes in 1994/95 to 36.4 and 24.6 million tonnes in 2004/05, respectively. Of the projected increase of 26.6 million nutrient tonnes in global fertilizer use, over half of the increase will be contributed by an increase in N demand, and about one-fourth by an increase in phosphate demand. Increased demand for potash will account for less than one-fifth of the projected increase.

The developing markets will account for nearly two-thirds of the projected growth in global fertilizer use during the 1994/95-2004/05 period (Table 4.3). The reforming markets will account for one-fourth of the projected growth. Most of the growth in this region is basically a recovery of the steep declines in fertilizer use experienced during the 1988/89-1994/95 period. The developed markets will record modest growth, primarily in North America. Growing demand for grain exports and freedom to farm acreage is expected to give a slight boost to fertilizer use in the United States.

At the regional level, Asia will continue to dominate the global fertilizer scene. Nearly half of the projected increase in fertilizer use will occur in Asia. Both East Asia and South Asia will increase their fertilizer use by 5-6 million nutrient tonnes each. In West Asia, fertilizer use is expected to increase by over 1 million tonnes. In Latin America, both Central and South America, are

Table 4.3. Fertilizer Demand Projections by Regions, 2000 and 2004/05

Region	1994/95[a]	2000	2004/05	1994/95-2004/05 Absolute Change	 Annual Growth
	('000 nutrient tonnes)			('000 nutrient tonnes)	(%)
Developed	**41,651**	**42,610**	**43,450**	**1,799**	**0.4**
North America	21,514	24,020	24,750	3,236	1.4
Western Europe	17,832	16,140	16,000	-1,832	-1.1
Oceania	2,305	2,450	2,700	395	1.6
Reforming	**7,689**	**11,200**	**14,450**	**6,761**	**6.3**
Eastern Europe	3,124	4,800	5,700	2,576	6.0
Eurasia	4,565	6,400	8,750	4,185	6.5
Developing	**73,912**	**83,700**	**92,000**	**18,088**	**2.2**
Africa	*3,532*	*4,910*	*5,650*	*2,118*	*4.7*
North	1,420	1,970	2,160	740	4.2
Sub-Saharan	1,280	1,840	2,240	960	5.6
South	832	1,100	1,250	418	4.1
Latin America	*9,289*	*10,510*	*12,150*	*2,861*	*2.7*
Central	2,375	3,055	3,650	1,275	4.3
South	6,914	7,455	8,500	1,586	2.1
Asia	*61,091*	*68,280*	*74,200*	*13,109*	*1.9*
East	39,963	42,850	46,200	6,237	1.5
South	17,279	20,000	22,000	4,721	2.4
West	3,849	5,430	6,000	2,151	4.4
World	**123,252**	**137,510**	**149,900**	**26,648**	**2.0**

a. Actual.

Source: FAO [2] for actual consumption and The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995 for projections. Demand projections for subregions in Africa are from Bumb [3].

expected to increase fertilizer use by over 1 million tonnes each. In Africa, total fertilizer use is projected to increase by 2.1 million tonnes – 0.7 million tonnes in North Africa, 0.4 million tonnes in South Africa, and 1.0 million tonnes in sub-Saharan Africa (SSA). Although fertilizer use is projected to increase at 5.6% per annum in SSA, overall fertilizer use levels of 2.2 million tonnes will remain inadequate to meet the nutrient requirements of the countries in the region. During the 1984/85-1994/95 period, fertilizer use increased at an annual rate of 3.4% – from 1.0 million nutrient tonnes to 1.4 million nutrient tonnes. It is expected that with increased focus on food security and policy reforms in place, SSA may experience a higher growth in the future.

4.3.2 Fertilizer Demand Projections by Nutrients and Regions

Fertilizer demand projections by nutrients at the regional levels are presented in Table 4.4.

Nitrogen Demand – The developed markets are expected to increase their N demand by 1.6 million tonnes and the reforming markets by about 4 million tonnes. North America will increase its N use by over 2 million tonnes, whereas Western Europe is expected to decrease its N use by less than 1 million tonnes. Growing demand for grain exports and replenishment of the depleted grain stocks are expected to enhance N use in North America and Oceania. In Western Europe, increased environmental concerns and reduced farm subsidies are the main factors responsible for reducing N use in that region.

In the developing markets, N use is projected to increase by about 9.8 million tonnes. Over 70% of the projected increase is expected to occur in Asia. East Asia and South Asia will account for a larger share. In these regions, N use will increase by 3.4 and 2.6 million tonnes, respectively. The need to increase food production is expected to enhance nitrogen use in these regions. In contrast to Asia, N use is projected to increase by 1.2 and 1.6 million tonnes in Africa and Latin America. In sub-Saharan Africa, N use will increase by about 0.6 million tonnes during the 1995-2005 period.

Table 4.4. Fertilizer Demand Projections by Nutrients, 2000 and 2004/05

Region/Market	Nitrogen 1994/95[a]	Nitrogen 2000	Nitrogen 2004/05	Phosphate 1994/95[a]	Phosphate 2000	Phosphate 2004/05	Potash 1994/95[a]	Potash 2000	Potash 2004/05
	--- ('000 nutrient tonnes) ---			---- -('000 nutrient tonnes) ---			---- -('000 nutrient tonnes)- - -		
Developed Markets	**22,436**	**23,590**	**24,000**	**9,655**	**9,520**	**9,750**	**9,560**	**9,500**	**9,700**
North America	11,935	13,700	14,000	4,623	5,000	5,250	4,956	5,320	5,500
Western Europe	9,784	9,000	9,000	3,785	3,300	3,200	4,263	3,840	3,800
Oceania	717	890	1,000	1,247	1,220	1,300	341	340	400
Reforming Markets	**4,833**	**6,800**	**8,800**	**1,304**	**2,000**	**2,450**	**1,552**	**2,400**	**3,200**
Eastern Europe	2,035	2,800	3,300	590	1,000	1,200	499	1,000	1,200
Eurasia	2,798	4,000	5,500	714	1,000	1,250	1,053	1,400	2,000
Developing Markets	**46,331**	**51,680**	**56,150**	**18,698**	**22,075**	**24,200**	**8,883**	**9,945**	**11,650**
Africa	*2,023*	*2,820*	*3,250*	*1,026*	*1,480*	*1,700*	*483*	*610*	*700*
North	987	1,300	1,400	329	520	580	104	150	180
Sub-Saharan	641	1,000	1,250	390	560	670	249	280	320
South	395	520	600	307	400	450	130	180	200
Latin America	*3,960*	*4,710*	*5,550*	*2,884*	*3,195*	*3,600*	*2,445*	*2,605*	*3,000*
Central	1,600	2,010	2,350	506	645	800	269	400	500
South	2,360	2,700	3,200	2,378	2,550	2,800	2,176	2,205	2,500
Asia	*40,348*	*44,150*	*47,350*	*14,788*	*17,400*	*18,900*	*5,955*	*6,730*	*7,950*
East	25,558	27,500	29,000	9,866	10,600	11,500	4,539	4,750	5,700
South	12,417	13,500	15,000	3,624	4,750	5,000	1,238	1,750	2,000
West	2,373	3,150	3,350	1,298	2,050	2,400	178	230	250
World	**73,600**	**82,070**	**88,950**	**29,657**	**33,595**	**36,400**	**19,995**	**21,845**	**24,550**

a. Actual.

Source: FAO [2] for actual and The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995 for projections. Demand projections for subregions in Africa are from Bumb [3].

subjective judgments about both quantifiable and nonquantifiable parameters. The wave of privatization and deregulation that followed the collapse of the Soviet Union is having, and will continue to have, profound effects on the global supply of fertilizers and their raw materials. The obligation to survive within the framework of private solvency, or at least with a sharply increased regard for normal entrepreneurial behavior, is governing an increasing proportion of the industry. This phenomenon is occurring not only in Eurasia and Eastern Europe but also in the large developing markets of Asia and Latin America. At the same time, these areas are becoming subject to the same environmental pressures, which involve the same additional investment expenses, constraints, and obligations as in the Western market economies even though these vary in ways and degrees. Moreover, the trend toward the reduction or elimination of subsidies on fertilizer use has already had dramatic effects in numerous countries; thus, it is especially difficult to forecast future consumption, particularly in those countries such as India, where existing large subsidies are in extreme dispute. This situation makes it more difficult than ever to forecast the future development of fertilizer supply; however, on the basis of the available information and informed judgments, the Working Group has developed estimates of fertilizer capacities and supply potential for the 1994/95-2000 period. These estimates are derived from announcements about closures, expansions, and new projects. Because it requires only 2-3 years to bring new ammonia or phosphoric acid capacity on stream, plans about future capacity beyond a 3-year period are mostly uncertain; changes in conditions can delay or postpone the implementation of the planned projects. Nevertheless, these are the most reliable estimates and therefore are used in developing supply forecasts and supply-demand balances in the future.

4.4.1 Global Fertilizer Supply Projections

The estimates of capacity and supply potential prepared by the Working Group are presented in Table 4.5. Nitrogen capacity is based on ammonia capacity because ammonia is the main source of nitrogen fertilizers. Phosphoric acid capacity is used for estimating capacity for producing phosphate fertilizers; phosphoric acid generally accounts for over two-thirds of the phosphate fertilizers. Since potassium fertilizers are mainly derived from potash ores or sea brines, potash capacity is the main source of potassium fertilizers. Supply potential is derived from capacity by considering operating rates, nonfertilizer uses, conversion and distribution losses, and fertilizers available from nonammonia and nonacid sources. Although nonammonia sources are insignificant, nonphosphoric acid sources, such as SSP, and phosphate rock used in the production of TSP and NPKs and for direct application, account for about one-third of phosphate fertilizers and therefore add significantly to the supply of phosphate fertilizers available from phosphoric acid sources.

Table 4.5. World: Fertilizer Capacity and Supply Potential, 1994/95-2000

Nutrient	Capacity 1994/95	Capacity 2000	Supply Potential 1994/95	Supply Potential 2000
	(million nutrient tonnes)		(million nutrient tonnes)	
N	114.4	123.5	74.6	83.3
P_2O_5	34.1	36.6	32.5	34.7
K_2O	36.1	35.0	27.0	25.4
Total	**184.6**	**195.1**	**134.1**	**143.4**

Source: The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995.

Global nitrogen capacity is projected to increase from 114.4 million tonnes in 1994/95 to 123.5 million tonnes in 2000 – at a rate of 2 million tpy. In contrast, P_2O_5 capacity is projected to increase by only 2.5 million tonnes. The existing excess capacity does not make investment in new capacity profitable. Despite this small increase, no shortages of phosphate fertilizers are expected in the 1990s. Likewise, the existing excess potash capacity may lead to closure of some of the potash capacity – from 36.1 million tonnes in 1994/95 to 35.0 million tonnes in 2000.

Overall, fertilizer supply potential is projected to increase from 134.1 million tonnes in 1994/95 to 143.4 million tonnes in 2000. Most of this increase will be contributed by an increase in nitrogen supply potential, which is projected to increase from 74.6 million tonnes in 1994/95 to 83.3 million tonnes in 2000. Because demand is projected to increase from 73.6 million tonnes to 82.1 million tonnes during the same period, nitrogen supply will be adequate to meet the projected demand and will leave about a 1 million tonne surplus over demand. Phosphate supply potential is projected to increase by over 2 million tonnes, whereas potash supply potential is projected to decrease by a little less than 2 million tonnes. However, because the projected demand for these two nutrients is less than the projected supply, no shortages are expected in the year 2000. On the contrary, the industry will have a surplus of 1.1 million tonnes of P_2O_5 and 3.6 million tonnes of K_2O (see section 4.5 for details).

4.4.2 Fertilizer Supply Potential by Nutrients and Regions

Nitrogen – The projected N capacity and supply potential by markets and regions are presented in Table

4.6. Modest growth in N capacity and supply potential is expected in the developed markets. The reforming markets are expected to register a slight decline due to closure of old plants in Russia and other countries. Of all the regions in these market groups, only North America is expected to increase its capacity by a modest amount.

Table 4.6. N Capacity and Supply Potential, 1994/95 and 2000

Region	N Capacity 1994/95	N Capacity 2000	N Supply 1994/95	N Potential 2000
	(million nutrient tonnes)		(million nutrient tonnes)	
Developed	**28.2**	**29.0**	**20.0**	**20.5**
North America	16.5	17.2	12.2	12.6
Western Europe	11.1	11.2	7.5	7.6
Oceania	0.6	0.6	0.3	0.3
Reforming	**29.5**	**28.3**	**16.6**	**15.2**
Eastern Europe	8.3	8.1	4.3	4.4
Eurasia	21.2	20.2	12.3	10.8
Developing	**56.7**	**66.2**	**38.0**	**47.6**
Africa	*3.8*	*4.1*	*2.3*	*2.5*
North	2.6	2.6	1.5	1.5
Sub-Saharan	0.4	0.7	0.3	0.5
South	0.8	0.8	0.5	0.5
Latin America	*5.4*	*6.9*	*4.4*	*5.3*
Central	3.5	4.2	3.1	3.7
South	1.9	2.7	1.3	1.6
Asia	*47.5*	*55.2*	*31.3*	*39.8*
East	29.6	33.1	18.7	23.1
South	12.4	15.3	8.9	11.5
West	5.5	6.8	3.7	5.2
World	**114.4**	**123.5**	**74.6**	**83.3**

Source: The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995. Data for subregions in Africa are from Bumb [3].

The developing markets are expected to increase their N capacity by 9.5 million tonnes. Most of this increase is expected to occur in East and South Asia. Africa and Latin America are expected to register modest increases in capacity; thus, most of the projected increase in global N capacity is expected to occur in Asia. Both the need for satisfying the growing food demand in East and South Asia and the availability of natural gas in West Asia make Asia the dominant region in the global market. In Asia, N capacity is expected to reach 55.2 million tonnes in 2000. With Asia contributing most of the increase in global N capacity, its share in global N capacity will increase from 41% in 1995 to 45% in 2000, whereas Eurasia's share will decrease from 18% to 14% during the same period. Other regions will register modest changes in their shares.

What is true for capacity is also true for supply potential. The developed markets are expected to register a marginal increase and the reforming markets a modest decrease. The developing markets will expand their N supply potential by approximately 10 million tonnes. Of this, 8.5 million tonnes will be in Asia and 1 million tonnes in Latin America. Africa will increase its supply potential by only 200,000 tonnes N in Nigeria. By 2000, East Asia will be supplying twice as much nitrogen fertilizer as North America will, or as much as North America and Eurasia combined. South Asia will be supplying 11.5 million tonnes of N – more than Eurasia's supply potential but marginally less than North America's.

Phosphate –The projected P_2O_5 capacity and supply potential are presented in Table 4.7. Modest increases in P_2O_5 capacity and supply potential are projected for

Table 4.7. P_2O_5 Capacity and Supply Potential, 1994/95 and 2000

Region	P_2O_5 Capacity 1994/95	P_2O_5 Capacity 2000	P_2O_5 Supply 1994/95	P_2O_5 Potential 2000
	(million nutrient tonnes)		(million nutrient tonnes)	
Developed	**14.0**	**14.3**	**12.2**	**12.5**
North America	12.1	12.4	10.2	10.4
Western Europe	1.9	1.9	1.4	1.5
Oceania	0.0	0.0	0.6	0.6
Reforming	**8.1**	**8.2**	**5.0**	**5.1**
Eastern Europe	1.9	1.9	1.7	1.8
Eurasia	6.2	6.3	3.3	3.3
Developing	**12.0**	**14.1**	**15.3**	**17.1**
Africa	*5.4*	*5.7*	*5.0*	*5.3*
North	4.2	4.3	3.9	4.0
Sub-Saharan	0.4	0.4	0.3	0.3
South	0.8	1.0	0.8	1.0
Latin America	*1.4*	*1.4*	*1.6*	*1.6*
Central	0.7	0.7	0.5	0.5
South	0.7	0.7	1.1	1.1
Asia	*5.2*	*7.0*	*8.7*	*10.2*
East	2.1	3.3	6.1	7.0
South	0.8	0.8	1.1	1.1
West	2.3	2.9	1.5	2.1
World	**34.1**	**36.6**	**32.5**	**34.7**

Source: The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995. Data for subregions in Africa are from Bumb [3].

both the developed and reforming markets. Thus, none of the regions in these markets are expected to realize any significant change in P_2O_5 capacity. The developing markets are expected to increase their P_2O_5 capacity by about 2 million tonnes. Most of this increase will occur in East and West Asia. Limited availability of phosphate rock in South Asia does not allow any increase in capacity in this region. South Africa is expected to increase its capacity by 200,000 tonnes. No capacity increase is projected for Latin America. Excess capacity and the low prices of the past do not encourage investment in new capacity.

No growth is projected in P_2O_5 supply potential in most regions. Only North America, East Asia, South Africa, and West Asia are expected to register modest increases.

Potash – Potash capacity is concentrated in a few regions in the world. North America (Canada) and Eurasia (Russia and Belarus) account for 33 million tonnes of the existing 36 million tonnes of global potash capacity (Table 4.8). Existing surpluses do not permit further expansions. Western Europe and Eurasia have plans to close some capacity. About 0.6 million tonnes of capacity expansion is expected in South America (Brazil) and East Asia (China). Because of closures, global K_2O supply potential is expected to decrease by about 2 million tonnes K_2O. Western Europe and Eurasia will account for most of this decrease. Both East Asia (China) and South America (Brazil) will increase their supply potential by 200,000 tonnes each. One potential project, not included in these estimates, is the potash project in Thailand. This project has a potential to supply 600,000 additional tonnes of K_2O, most likely after the year 2000.

Table 4.8. K_2O Capacity and Supply Potential, 1994/95 and 2000

Region	K_2O Capacity 1994/95	K_2O Capacity 2000	K_2O Supply Potential 1994/95	K_2O Supply Potential 2000
	(million nutrient tonnes)		(million nutrient tonnes)	
Developed	**21.1**	**19.9**	**17.5**	**16.2**
North America	14.0	13.8	11.6	11.4
Western Europe	7.1	6.1	5.9	4.8
Oceania	0.0	0.0	0.0	0.0
Reforming	**12.0**	**11.5**	**7.0**	**6.1**
Eastern Europe	0.0	0.0	0.0	0.0
Eurasia	12.0	11.5	7.0	6.1
Developing	**3.0**	**3.6**	**2.5**	**3.1**
Africa	*0.0*	*0.0*	*0.0*	*0.0*
North	0.0	0.0	0.0	0.0
Sub-Saharan	0.0	0.0	0.0	0.0
South	0.0	0.0	0.0	0.0
Latin America	*0.4*	*0.7*	*0.3*	*0.5*
Central	0.0	0.0	0.0	0.0
South	0.4	0.7	0.3	0.5
Asia	*2.6*	*2.9*	*2.2*	*2.6*
East	0.1	0.4	0.0	0.2
South	0.0	0.0	0.0	0.0
West	2.5	2.5	2.2	2.4
World	**36.1**	**35.0**	**27.0**	**25.4**

Source: The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995.

4.5 Fertilizer Supply-Demand Balances

Fertilizer supply-demand balances are derived from projected demand and estimated supply potential. Because capacity projections are not available for 2004/05, supply-demand balances for 2004/05 are based on the projected demand for 2004/05 and the estimated supply potential for 2000. This is done for two reasons: First, to estimate how much additional capacity will be needed between 2000 and 2005 to meet the projected demand and in what regions. Second, what are the chances that the required additional capacity will be brought on stream?

4.5.1 Global Fertilizer Supply-Demand Balances

The estimated supply-demand balances indicate that for all three nutrients, supply will exceed the projected demand by 1.2 to 3.5 million tonnes in 2000 (Table 4.9). For nitrogen and phosphate, supply will exceed demand by about 1 million tonnes each and for potash by 3.5 million tonnes. In spite of decreases in projected capacity and supply potential, there will be a surplus of potash fertilizers although the surplus is expected to decrease from 7.0 million tonnes in 1994/95 to 3.5 million tonnes in 2000. As indicated above, this is due to existing excess capacity. Nitrogen surplus is expected to remain at 1 million tonnes, and phosphate surplus is

Table 4.9. World: Fertilizer Supply-Demand Balances, 1994/95-2004/05

Nutrient	1994/95	2000	2004/05[a]
	(million nutrient tonnes)		
N	1.0	1.2	(5.6)
P_2O_5	2.8	1.1	(1.7)
K_2O	7.0	3.5	0.9
Total	**10.8**	**5.8**	**(6.4)**

Note: ( ) = Deficit.

a. Derived from the projected demand in 2004/05 and the estimated supply potential in 2000.

expected to decrease from 2.8 million tonnes to 1.1 million tonnes. Overall, fertilizer surplus is expected to decrease from 10.8 million tonnes in 1994/95 to 5.8 million tonnes in 2000.

Unless additional capacity is brought on stream, both N and P_2O_5 will be in short supply in 2005. There will be a deficit of 5.6 million tonnes of N and 1.7 million tonnes of P_2O_5. For potash, there will be a surplus of 1 million tonnes of K_2O. Because several companies are planning to build ammonia/urea plants in Asia and Latin America, it is unlikely that nitrogen fertilizers will remain in short supply. Some of the planned plants include India-Oman and India-Iran joint ventures, an Arcadian plant in Trinidad, and plants in China, Indonesia, Venezuela and Argentina. Some additional capacity is also expected in North America (Table 4.10). However, it must be stressed that the planned new capacity estimates included in Table 4.10 are based on announced intentions rather than firm commitments. If prices do not remain attractive or finances are not available, especially in developing and reforming markets, some of this planned new capacity may not materialize. Nevertheless, under normal circumstances, adequate additional capacity may come onstream to bridge the gap between demand and supply. Moreover, arrangements should also be made for replacing old capacity. During the 1993-95 period, about 4 million tonnes of N capacity was closed annually. With growing demand, such replacement may generally occur, but in Eurasia and other reforming countries, such a scenario is not automatically guaranteed. All national and international efforts should be made to revitalize the fertilizer sector in the reforming markets. Similarly, China, Morocco, Jordan, and Egypt have plans to build additional phosphate capacity. Although there is adequate potash capacity to meet the demand in 2004/05, some planned projects, such as one in Thailand and another in Argentina, may add additional potash capacity. The fluctuations in prices may affect the realization of these projects. However, as fertilizer supply becomes limited, prices may increase to justify additional investment. As the supply-demand forecasts suggest, unless additional capacity is brought on stream, nitrogen and phosphate shortages will develop by 2004/05 and put pressure on prices. Additionally, continued growth in population in Asia, especially in countries like India and China, may create pressure to invest in fertilizer production for food security reasons. Further increased prices may improve capacity utilization currently averaging at about 81% at the global level. Every 1% point increase in capacity utilization can add an additional 1 million tonnes of N. Thus, chances seem reasonable that required additional supply will be forthcoming to meet the projected demand in 2004/05.

Table 4.10. Planned N Capacity Increases After 2000 (million tonnes)

Region	Planned N Capacity
North America	3.3
Eastern Europe	0.5
Eurasia	0.5
Africa	0.8
Latin America	1.6
Asia	5.2
Total	**11.9**

4.5.2 Supply-Demand Balances by Nutrients and Regions

Supply-demand balances by nutrients and regions are presented in Table 4.11.

Nitrogen – Both developed and developing markets will remain deficit in nitrogen, whereas reforming markets will continue to have substantial surpluses (6-8 million tonnes). In the developed markets the nitrogen deficit will increase from 2.4 million tonnes in 1994/95 to 3.5 million tonnes in 2004/05. All three regions – North America, Western Europe, and Oceania – are expected to remain deficit in nitrogen. The N deficit in Western Europe is expected to decrease from 2.3 million tonnes in 1994/95 to 1.4 million tonnes in 2004/05, whereas in North America, it is expected to increase from a surplus of 0.3 million tonnes in 1994/95 to a deficit of 1.4 million tonnes in 2005. In the reforming markets, as demand recovers, N surplus is expected to decrease in both regions – Eastern Europe and Eurasia.

In the developing markets, as new capacity comes on stream after 1994/95, the nitrogen deficit will decrease from 8.4 million tonnes in 1994/95 to 4.1 million tonnes in 2000 but will increase again to 8.6 million tonnes in 2005. All three regions, namely, Africa, Latin America, and Asia, are expected to have a deficit in nitrogen supply. However, West Asia, North Africa, and Central America will have a surplus. East Asia, South Asia, South America, and sub-Saharan Africa will have a deficit. Because of a rapidly growing demand, in spite of planned large increases in capacity, South and East Asia will continue to depend on imports. Due to import dependence, macroeconomic policy, especially exchange rate stability and foreign exchange allocations, will play a crucial role in meeting the future demand in these subregions. In the past, fertilizer aid played an important role in satisfying the fertilizer requirements of sub-Saharan Africa. Increasingly, fertilizer aid is being reduced by donors; therefore, countries in this region may have to make additional efforts to ensure fertilizer supplies.

Table 4.11. Regional Fertilizer Supply-Demand Balances, 1994/95-2004/05

Region	Nitrogen			Phosphate			Potash		
	1994/95	2000	2004/05	1994/95	2000	2004/05	1994/95	2000	2004/05
	- - (million nutrient tonnes)- -			- - (million nutrient tonnes) - -			- - (million nutrient tonnes) - -		
Developed	**-2.4**	**-3.1**	**-3.5**	**2.6**	**3.0**	**2.8**	**7.9**	**6.7**	**6.5**
North America	0.3	-1.1	-1.4	5.6	5.4	5.2	6.6	6.1	5.9
Western Europe	-2.3	-1.4	-1.4	-2.4	-1.8	-1.7	1.6	1.0	1.0
Oceania	-0.4	-0.6	-0.7	-0.6	-0.6	-0.7	-0.3	-0.3	-0.4
Reforming	**11.8**	**8.4**	**6.4**	**3.7**	**3.1**	**2.7**	**5.4**	**3.7**	**2.9**
Eastern Europe	2.3	1.6	1.1	1.1	0.8	0.6	-0.5	-1.0	-1.2
Eurasia	9.5	6.8	5.3	2.6	2.3	2.1	5.9	4.7	4.1
Developing	**-8.4**	**-4.1**	**-8.6**	**-3.5**	**-5.0**	**-7.1**	**-6.3**	**-6.7**	**-8.4**
Africa	*0.3*	*-0.3*	*-0.8*	*4.0*	*3.8*	*3.6*	*-0.4*	*-0.7*	*-0.7*
North	0.5	0.2	0.1	3.6	3.5	3.4	-0.1	-0.2	-0.2
Sub-Saharan	-0.3	-0.5	-0.8	-0.1	-0.3	-0.4	-0.2	-0.3	-0.3
South	0.1	0.0	-0.1	0.5	0.6	0.6	-0.1	-0.2	-0.2
Latin America	*0.4*	*0.6*	*-0.3*	*-1.3*	*-1.6*	*-2.0*	*-2.2*	*-2.1*	*-2.5*
Central	1.5	1.7	1.4	0.0	-0.1	-0.3	-0.3	-0.4	-0.5
South	-1.1	-1.1	-1.6	-1.3	-1.5	-1.7	-1.9	-1.7	-2.0
Asia	*-9.1*	*-4.4*	*-7.6*	*-6.2*	*-7.2*	*-8.7*	*-3.7*	*-4.1*	*-5.3*
East	-6.9	-4.4	-5.9	-3.8	-3.6	-4.5	-4.5	-4.6	-5.5
South	-3.5	-2.0	-3.5	-2.5	-3.7	-3.9	-1.2	-1.8	-2.0
West	1.3	2.0	1.9	0.1	0.0	-0.3	2.0	2.2	2.2

Note: Totals may not add due to rounding.

Source: The World Bank/FAO/UNIDO/Industry Fertilizer Working Group Meeting, August 1995.

Phosphate – Both developed and reforming markets are expected to have phosphate surpluses – with a heavy concentration in North America and Eurasia. Although North America has traditionally been a major producer and exporter of phosphate fertilizers, a surplus in Eurasia results from a drastic reduction in fertilizer use during the reform process. In both regions, surpluses will range between 2 and 5 million tonnes and will gradually decrease during the 1995-2005 period. Western Europe will continue to have a deficit.

In developing markets, deficits are forecast to increase from 3.5 million tonnes in 1994/95 to 7.1 million tonnes in 2004/05. Except North Africa (Morocco), all regions and subregions are expected to increase their deficits. In Asia, deficits will reach 8.7 million tonnes in 2004/05. Obviously, fertilizer imports will remain crucial for these regions to satisfy the domestic phosphate fertilizer requirements. Additional capacity of about 2 million tonnes P_2O_5 will be needed by 2004/05. Projects in Morocco, Senegal, and Egypt may come on stream to balance the situation.

Potash – Like phosphate surpluses, potash surpluses will be concentrated in the developed and reforming markets. North America and Eurasia will account for most of the surpluses in these markets. The developing markets will remain in deficit (6-8 million tonnes). Except West Asia, all regions in this group will be in deficit. East Asia will have the highest deficit of 5.5 million tonnes in 2004/05. Canada, Russia, and Belarus will remain major exporters; Israel and Jordan will also export potash fertilizers to Asian markets.

4.6 Summary

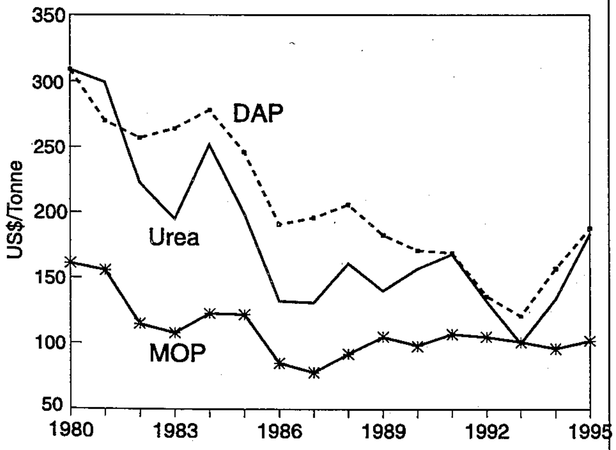
The year 1994/95 provides a turning point in the history and future outlook of the fertilizer industry. Since 1988/89, global fertilizer use had been declining due to the drastic reduction in fertilizer use in the former centrally planned economies. The year 1994/95 is the first year after the fall of the Berlin wall in 1988 when global fertilizer use registered a 2% increase. During the 1994/95-2004/05 period, fertilizer demand is projected to increase by 2%/year – from 123 million nutrient tonnes in 1994/95 to 150 million nutrient tonnes in 2004/05. The demand for all three nutrients is projected to increase at 1.9%-2.1% per annum. Nitrogen demand is projected to increase from 74 million nutrient tonnes in 1994/95 to 89 million nutrient tonnes in 2004/05. Phosphate and potash demand is projected to increase from 30 and 20 million nutrient tonnes in 1994/95 to 36 and 25 million nutrient tonnes in 2004/05, respectively. Fertilizer supply is expected to be adequate to meet fertilizer demand in the year 2000, but additional capacity will be needed to meet the projected demand for nitrogen and phosphate in 2004/05. No serious difficulties are expected in sustaining growth in fertilizer supply. However, most developing countries will remain deficit in fertilizer supplies and will have to depend on imports. Hence, macroeconomic policy will play an important role in meeting the future requirements of fertilizer-deficit countries.

To sustain growth in fertilizer demand and supply, a conducive policy environment should be maintained. Policy reforms should be properly sequenced and phased, and adequate human and institutional capacity should be developed. Every reasonable effort should be made to continue to improve the environmental effects of production and use of fertilizers.

4.7 Price Outlook

Since the early 1980s, fertilizer prices (in 1990 constant U.S. dollars) have been decreasing with occasional increases caused by short-term changes (Figure 4.2). In 1991, the Gulf War created temporary shortages and allowed all fertilizer prices to increase. However, a drastic fall in fertilizer use in Eastern Europe and Eurasia in the early 1990s created a surplus in the global market and reduced urea prices drastically. In some months in 1993, urea was selling for US $80/tonne (f.o.b. Black Sea), as compared with over US $150/tonne in the previous year. However, fertilizer prices increased sharply in 1994 and 1995. Increased demand in the United States, reduced urea supplies from Eurasia, and increased imports from India and China created an upward surge in fertilizer prices. In 1995 urea prices averaged $184/tonne (1990 dollars) – over 80% higher than the 1993 level. These increases in prices are not justified by the structural parameters of the price equation. It is expected that in the late 1990s prices may decrease to normal levels due to improved grain supplies leading to lower grain prices. Improvements in market conditions in Eurasia and Eastern Europe may also generate stable supplies. However, it must be stressed that, in the long term, several factors may contribute to keep fertilizer prices higher than those prevailed in 1986/87 or 1992/93 after the collapse of the former Soviet Union. Some of these factors are elaborated below.

First, very little idle capacity exists in the developed markets; low and unremunerative prices of the mid-1980s and early 1990s had already led to permanent closures of many idle plants in North America and Western Europe. Most of the existing plants have been operating at or near full capacity. Second, removal of subsidies on fertilizer production in reforming economies is resulting in increased cost of production. This coupled with increased energy prices and investment for revamping and rehabilitation is likely to increase the cost of fertilizer supplies from Eastern Europe and Eurasia. Third, restructuring of fertilizer sector leading to subsidy removal and privatization in developing markets may lead to higher cost of production. Fourth, as the gap between demand and supply narrows and surpluses reduce, additional investment will be needed to satisfy the growing demand. Because of high capital investment requirements of new plants, fertilizer supplies coming from new plants will be available at higher prices. In a new ammonia-urea complex, capital recovery cost accounts for about 60%-70% of the total cost, whereas, in nearly fully-depreciated old plants, capital cost accounts for only 10%-20% of the total cost. Higher capital cost will naturally result in higher cost of production and price. Thus, fertilizer prices may be relatively higher in the long run. Nevertheless, to the extent fertilizer capacity continues to be built for food-security reasons without due regard to cost of production in large countries, such as India and China, and global grain surpluses rise and fall, short-term prices may fluctuate considerably from one year to another.



Note: Urea prices are f.o.b. bagged Western Europe, and DAP and MOP prices are f.o.b. U.S. Gulf and Vancouver (Canada) respectively. All prices are in 1990 US$.

Source: The World Bank [4].

Figure 4.2. World: Fertilizer Prices, 1980-95.

4.8 References

1. FAO (1996a). *Fertilizer Yearbook*, Rome, Italy.
2. FAO (1996b). *Fertilizer Data*, Computer files.
3. Bumb, B. L. 1995. *Global Fertilizer Perspective, 1980-2000: The Challenges in Structural Transformation*, T-42, International Fertilizer Development Center (IFDC), Muscle Shoals, AL, U.S.A.
4. The World Bank. 1996. *Commodity Markets and the Developing Countries: A World Bank Quarterly*, February, Washington, D.C., U.S.A.

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Chapter 5. Fertilizer Raw Materials and Reserves

5.1 Availability and Sources of Raw Materials

The primary raw materials for nitrogen fertilizers are natural gas, naphtha, fuel oil, and coal. The manufacture of phosphate fertilizers most often requires sulfur and phosphate rock. Naturally occurring potassium salts form the basis of the production of most potash fertilizers.

Natural gas, naphtha, fuel oil, and sulfur are substances or mixtures to which clearly definable specifications can be applied; compositions may vary little regardless of where they are obtained or produced. Potash ores vary greatly in composition from locality to locality; however, the end products of mining, beneficiation, and processing generally have relatively constant compositions. Phosphate rock and coal are products that can vary significantly in composition and other characteristics. These variations can have significant effects on the processes used to upgrade the as-mined ores or on the processes in which they are used to manufacture fertilizers from beneficiated products.

A fertilizer plant or power plant may be designed to use a particular phosphate rock or coal. Changes in the sources of raw materials may adversely affect processing and lead to lower efficiency, the loss of output, and/or serious operational difficulties. Coal and phosphate rock supplies are generally secured with medium- to long-term contracts. Test programs and trials of alternative supplies are in order if changes in supply sources are necessary. Plant designs should allow for variations in the quality of both phosphate rock and coal even when the feedstocks are to be procured from single sources over the projected life of a facility. It is desirable to construct production facilities with sufficient flexibility to accept feedstocks from several sources to benefit from competitive situations and/or to account for the possibility that the intended source of supply may be terminated.

Information is presented in this chapter concerning the physical characteristics, geology, geographic distribution, reserves and resources, processing, and production of fertilizer raw materials. This chapter is based on several chapters from the previous edition. Considerable effort was expended in developing more comprehensive overviews of the geologic, mineralogic, and processing characteristics of fertilizer raw materials.

As in previous editions, the difficulties in establishing the amount of resources/reserves for fertilizer raw materials on a global basis are recognized. A review of resource/reserve terminology is given in Section 5.3.8.2, World Phosphate Rock Reserves and Resources. Resource/reserve data for specific raw materials are presented in each section.

It is impossible to present more than gross estimates of world resources of fertilizer raw materials for several reasons. Although man continues to explore his environment and many areas of the globe have been explored in detail, particularly in the last 30 years, there are areas of the globe that have not been surveyed or have been surveyed inadequately. When deposits are known to exist, the extent and quality of information on the quantity or quality of material in the deposit may vary greatly. Reasonably good data may only exist when considerable effort and funds have been spent to develop deposits. Detailed exploration and evaluation of a deposit is an expensive process only undertaken when commercial exploitation is probable.

Estimators may also use different criteria for categorizing reserves and resources. Some estimators may take an optimistic approach, whereas others may be more pragmatic. Data may be gathered from many sources both public and private. Producers may not wish to divulge reserves for competitive reasons. In general, public sources of information may be much more optimistic than private sources.

5.2 Nitrogen Feedstocks

Ammonia is a basic building block for most nitrogen fertilizers with the exception of some naturally occurring nitrates. In ammonia manufacture, nitrogen is actually fixed from the earth's atmosphere. At about 78%, nitrogen is the most common gas in the earth's atmosphere. The amount of nitrogen in the earth's atmosphere is not considered a limiting factor in nitrogen fertilizer production.

Hydrocarbon and coal feedstocks for ammonia manufacture perform a dual role as sources of both hydrogen and energy. The relative amounts of hydrogen and energy that are actually supplied for the manufacture of ammonia depend on the type of feedstock and type and efficiency of a process. An average figure for the contribution to each category may be 60% hydrogen and 40% energy. Water also contributes a portion of the hydrogen needed for ammonia manufacture.

5.2.1 Origins of Hydrocarbons and Coal

Natural gas, oil, and coal are associated with sedimentary rocks. Natural gas and oil are produced from sedimentary rocks ranging in age from Precambrian

(+600 million years) to Cenozoic (60 million years to the present).

It is widely accepted that plankton living in ocean waters were the sources of nearly all petroleum. Fine-grained muds rich in planktonic remains are deposited offshore in low-energy, oxygen-poor environments. Slow decomposition by anaerobic bacteria turns the planktonic remains into an amorphous material called sapropel. As the muds are buried and form shales and mudstones, the sapropel is converted to petroleum compounds by biologic, chemical, and physical processes, which are not fully understood. Young petroleum tends to have compounds of higher molecular weight and produces heavy crudes. With deeper burial, increased temperature and pressure break down the organic structures into lighter and simpler hydrocarbon compounds. At great depth, methane may be the only remaining hydrocarbon.

Several criteria must be met before petroleum hydrocarbons can accumulate to form a field:

1. Sapropelic source beds must be formed.
2. With burial, heat and pressure conditions must exist to bring the source beds to maturity and generate petroleum compounds.
3. Migration from source beds to reservoir rocks must be possible.
4. Suitable porous reservoir beds must exist.
5. Traps (stratigraphic and structural) must exist so that accumulations can form.
6. A suitable seal or cap rock must exist to prevent the oil and gas from escaping.

Perhaps 60% of the world's petroleum reserves are associated with sandstones, whereas about 40% are associated with limestones. Gas migrates undip of (above) the liquid fraction, may form separate fields, or may cap the oil zone.

Significant oil and gas fields are mainly associated with large basins located on continental margins, on former continental margins, or in intercontinental basins where significant sediment accumulations have occurred. These accumulations may be currently located onshore or offshore. Areas devoid of petroleum accumulations include areas of igneous rocks or sedimentary rocks that have been subjected to very high levels of heat and pressure.

Crude oils are separated into components such as gasoline, naphtha, and fuel oils by distillation. Higher weight petroleum compounds may be broken down to lighter fractions by heat in a process called thermal cracking or under the influence of catalysts (catalytic cracking). Lighter fractions may be processed to higher weight hydrocarbons by a process called reforming. Sulfur is generally removed from natural gas near the wellhead, and sulfur is removed in the process of refining crude oils.

Liquid petroleum fractions are more easily transported and stored than gases, which require high-pressure compression and transportation in special vessels. In areas where there is no market for petroleum gas or developed infrastructure to transport natural gas, the use of natural gas to produce ammonia and solid nitrogen fertilizers may be the only and/or most lucrative option for development.

Coals are formed in swamps under warm climatic conditions that promote rapid vegetative growth. Coal deposits are generally associated with mountain-building events and deltaic environments. Coals can be traced to the Devonian period, when woody plants first evolved, about 370 million years before the present.

To be preserved, vegetative matter must accumulate quickly in an anaerobic environment. After deposition, anaerobic bacteria cause biochemical changes that slowly transform the vegetative matter into peat. As the peat deposits become buried beneath increasing thicknesses of younger sediments, the peat is subjected to increases in temperature and pressure. Water and volatile compounds are expulsed, and crosslinking occurs between carbon atoms.

Under the effects of increasing temperature and pressure, peat acquires the solidity, color, and chemical composition of coal. These changes are the basis for a progressive increase in the rank of coal. Coal is characterized or ranked by four groups although the boundaries between groups are arbitrary. Peat is more or less spongy decomposed plant debris with a high water content. Brown coals and lignite have high water contents and 40%-55% volatile contents. Bituminous coals are the best known coals; those with 30%-45% volatiles are widely used for steam-raising and general combustion, while those with 20%-30% volatiles may be suitable for coking. Anthracites or hard coals contain up to 95% carbon and less than 5% volatiles.

Coals contain impurities such as sulfur (mostly between 0.5% and 3.0%) and clays, which lead to varying amounts of ash and clinker. As coals increase in rank, calorific values increase to the anthracite level at which, due to expulsion of most volatiles, calorific values may decrease somewhat. The calorific content and impurity content of coals dictate the design of coal-burning or gasifying facilities and associated pollution control equipment.

Commercial coal beds are generally extensive and thick, have minimal partings, and have acceptable calorific contents. Coal is mined by both opencast and underground methods that are very similar to the methods used to mine phosphate rock. If the coal is mined underground, suitable roof rock conditions must exist. The thickness and character of overburden and other site-specific conditions determine the use of opencast methods.

Power generation using coal requires significant amounts of water and coal. Coal-fired power generation units and/or fertilizer production units are often located near the mine site.

5.2.2 World Ammonia Production and Feedstock Reserves

Table 5.1 presents an estimate of energy requirements and natural gas equivalents for ammonia manufacture through the year 2000/01. This forecast indicates that world ammonia production will be increasing at slightly over 3% per year. These energy requirements may be met by natural gas, oil, naphtha, or coal depending on the regions of the world where the ammonia will be produced. Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are used as feedstocks in some regions that produce little oil or natural gas. Table 5.2 shows the production of natural gas and petroleum for the year 1995 and the reserves at the end of 1995.

The cost of feedstocks will vary from region to region depending on supply, reserves, etc. In the past, there has been some credibility to pricing natural gas, naphtha, oil, and coal on an energy content basis. However, in recent times extensive pipeline construction in developed countries has given the end user more options in obtaining supplies of feedstock so that price is driven more by competition than energy content. This principle also applies to refinery capacity, i.e., the region that has the most excess capacity will normally have the lowest cost oil and naphtha. Generally, coal has been priced much lower than natural gas or liquid feedstocks on an energy-content basis.

Since the energy crisis of 1977/78 in the United States, there has been a movement for deregulation of pipelines/transportation. The various components of moving natural gas from the wellhead to the end user have been priced separately, e.g., gathering, storage,

Table 5.1. Forecast of World Ammonia Production ('000 tonnes nitrogen)

	1997/98	1998/99	1999/2000	2000/01
Developing Regions				
Africa	3,848	3,848	4,445	4,445
Latin America	6,368	7,483	8,969	9,462
West Asia	5,123	5,489	5,489	5,489
East Asia	26,308	27,035	29,487	30,513
China	27,277	28,221	28,465	28,465
Total	**68,924**	**72,076**	**76,855**	**78,374**
Developed Regions				
North America	18,291	18,425	18,	
Western Europe	11,446	11,537	11,537	11,537
Eastern Europe	8,067	8,067	8,067	8,067
Former Soviet Union (FSU)	20,965	21,372	21,279	21,279
Oceania	566	566	566	566
Total	**59,335**	**59,967**	**59,874**	**59,874**
World Total	**128,259**	**132,043**	**136,729**	**138,248**
Ammonia Equivalent ('000 tonnes)	155,743	160,338	166,028	167,873
Natural Gas Required (10^9 m^3)	176.54	181.75	188.20	190.29
Energy Required (MMBtu x 10^6)	6,228	6,413	6,641	6,715
Energy Required (Gcal x 10^6)	1,573	1,619	1,677	1,696

Source: International Fertilizer Development Center, unpublished data.

Notes: 1. Ammonia equivalent based on average of 10.1 Gcal/tonne (40 MMBtu/tonne).
2. Natural gas assumed to contain 0.14 Gcal/m^3 (1,000 Btu/ft^3).

Table 5.2. World Production and Reserves of Natural Gas and Petroleum

	Natural Gas		Petroleum	
	Production 1995	Reserves 1995 End	Production 1995	Reserves 1995 End
	(10^9 m^3)	(10^9 m^3)	(10^9 bbl/d)	(10^9 bbl)
Developing Regions				
Africa	84.40	9,400	6.97	73,100
Latin America	78.00	5,700	5.65	78,900
West Asia	179.70	46,700	20.84	665,300
East Asia	114.40	5,700	2.92	12,700
China	17.60	1,700	2.99	24,000
Total	**474.10**	**69,200**	**39.37**	**854,000**
Developed Regions				
North America	713.30	8,400	13.74	86,600
Western Europe	208.20	4,600	5.94	13,700
Eastern Europe	34.70	900	0.67	4,000
Former Soviet Union (FSU)	659.70	56,000	7.23	57,000
Oceania	29.60	600	0.58	1,600
Total	**1,645.50**	**70,500**	**28.16**	**162,900**
World Total	**2,119.60**	**139,700**	**67.53**	**1,016,900**
Energy Equivalent (MMBtu x 10^9)	74.84	4,933	411.96	6,203,000
Energy Equivalent (Gcal x 10^9)	18.86	1,243	104	1,562,000

Source: [1].

Notes: 1. Energy content of natural gas assumed at 8.9 MMcal/m^3 (35,310 Btu/m^3).
2. Energy content of petroleum assumed at 1.54 Gcal/bbl (6.1 MMBtu/bbl).
3. 3.9685 MMBtu equivalent to 1 Gcal.

and transportation. This has allowed the end user to purchase those services needed, and the price of the natural gas is adjusted accordingly. This also permits the end user to purchase feedstock directly from the producer and have it transported to the plant site. Other countries are moving in this direction.

During the 1977/78 energy crisis, the natural gas reserve/production ratio indicated a 12-year supply, and forecasts indicated that natural gas would reach a price of over $10.00 per million British thermal units (MMBtu). This did not occur, and some 17 years later, the United States still has a reserve/production ratio indicating a 8.5- to 9.0-year supply. The price of natural gas in the 1990-96 timeframe has ranged from as low as $0.25 per Gcal ($1.00 per MMBtu) to as high as $1.13 per Gcal ($4.50 per MMBtu).

Feedstocks in developing countries will vary depending on not only availability but also the ability to move the feedstock to the plant site. Coal is used as a feedstock where natural gas is not readily available. Table 5.3 shows world production and reserves of coal for 1995 and the end of 1995 [1].

China is a large producer of nitrogen and probably is the world's largest ammonia producer using coal as a feedstock. Because of vast reserves of coal and the lack of a pipeline infrastructure for transporting natural gas, the feedstock used is generally coal, naphtha, or oil. Accordingly, many of the nitrogen plants in China are equipped to use dual feedstocks, and recent reports indicate that retrofits are being installed to allow plants to switch between feedstocks and use gasification more efficiently. Chinese news releases indicate that additional nitrogen plants are being planned using natural gas from the Hainan Islands. It is expected that as pipeline transportation infrastructure is developed, more of the Chinese nitrogen plants will switch to natural gas as a feedstock.

In south central Asia, primarily India, several new nitrogen plants are in the planning stage, but the lack of in-country natural gas reserves requires the use of oil or naphtha as a feedstock. Feasibility studies on pipelines from the Middle East to India are in progress, but when this will result in natural gas sources for Indian nitrogen plants is conjectural. LNG as a feedstock is another consideration for India, but this is an expensive alternative.

Table 5.3. World Production and Reserves of Coal, 1995

	Production (million tonnes oil equivalent)	Reserves (million tonnes coal)
Developing Regions		
Africa	113.3	61,672
Latin America	26.2	10,196
West Asia	133.4	72,360
East Asia	74.8	33,766
China	655.5	114,500
Total	**1,003.2**	**292,494**
Developed Regions		
North America	593.7	250,392
Western Europe	139.3	104,419
Eastern Europe	156.9	52,248
Former Soviet Union (FSU)	203.8	241,000
Oceania	128.2	91,057
Total	**1,225.1**	**739,116**
World Total	**2,225.1**	**1,031,610**
Energy Equivalent (MMBtu x 10^9)	97.7	30,659
Energy Equivalent (Gcal x 10^9)	24.6	7,723

Source: [1].

Notes:
1. Energy content of oil assumed at 6.1 MMBtu/bbl.
2. Energy content of coal assumed at 29.7 MMBtu/tonne.
3. 3.9685 MMBtu equivalent to 1 Gcal.
4. 7.2 bbl of oil/tonne.
5. Includes anthracite, bituminous, and lignite coals.

Other east Asian countries, the Koreas, and Japan have little natural gas and use naphtha or LNG for ammonia production. Indications are that several southeast Asian countries (Thailand, Malaysia, and Indonesia) have large reserves of natural gas and oil, and significant oil and gas exploration is underway in this region. LNG is a large export from this area, much of which goes to Japan.

The former Soviet Union (FSU) has large reserves of oil and natural gas, but adequate pipeline capacity to supply internal regions and eastern and western Europe is lacking. Considering the pipeline construction that is already underway and the planned pipeline construction, assuming that capital is available, it is expected that this problem will be solved in the next few years. Additional pipelines from the North Sea are to bring natural gas into western Europe, which will put competitive pressure on prices in this region.

Proven oil and natural gas reserves in Latin America, with natural gas prices well below average, make this a logical location for additional nitrogen production for export. Negotiations are in progress between Venezuela and large nitrogen producers to construct new nitrogen plants in Venezuela.

5.2.3 Ammonia Feedstock Outlook

While reliable data are not readily available on feedstock use by type, e.g., natural gas, oil, naphtha, and coal, a look at world reserves of natural gas, oil, and coal by region indicates that natural gas will be the dominant feedstock. Coal use will decline because of environmental aspects and high plant costs. Oil and naphtha will continue to be used as feedstocks primarily in those regions or areas that do not have natural gas reserves and are unable to receive natural gas by pipeline. Review of reserve data covering all feedstocks indicates no shortage of feedstock material through the year 2000.

Barring any world conflicts and with some exceptions, feedstock prices are not expected to dramatically increase through the year 2000. Natural gas reserves appear to be holding or gaining slightly on production, and oil reserves in OPEC and non-OPEC countries are such that production will control price. Oil prices have been relatively stable since the energy shortage of the late 1970s and early 1980s. Coal prices have also been relatively stable over this same period and are expected to remain stable in the short-term future.

5.3 Phosphate Rock

"Phosphate rock" is an imprecise term that includes both unprocessed rocks and beneficiated concentrates. Practically all production of phosphate fertilizers is based on phosphate rocks containing some form of the mineral apatite.

5.3.1 Geological Origin and Characteristics of Phosphate Rock

There are two main types of phosphate rock deposits – sedimentary and igneous. Sedimentary phosphate deposits are exploited to produce more than 80% of the total world production of phosphate rock.

Igneous phosphate deposits are often associated with carbonatites and/or alkalic (silica deficient) intrusions. Igneous phosphate rock concentrates are produced from deposits that are mainly exploited in Russia, the Republic of South Africa, Brazil, Finland, and Zimbabwe. Igneous phosphate ores are often low in grade (less than 5% P_2O_5) but can be upgraded to high-grade products (from about 35% to over 40% P_2O_5).

Sedimentary phosphate rocks occur throughout the geological time scale. Most sedimentary deposits were apparently formed in offshore marine conditions on continental shelves. They exhibit a wide range of chemical compositions and great variations in physical form. Economic deposits usually occur as one or more thick high-grade beds that are unconsolidated and have a uniform granular texture and composition, shallow overburden, and a minimum of structural deformation.

Insular deposits are a type of sedimentary deposit associated with oceanic islands. Insular deposits have been an important source of phosphate rock for more than 100 years. However, intensive exploitation has caused several deposits to be totally depleted or to have short projected lifetimes (Ocean Island, Christmas Island, and Nauru, to name a few).

Depending on their origin (igneous or sedimentary), phosphate rocks have widely differing mineralogic, textural, and chemical characteristics. Furthermore, entire deposits or portions of deposits have been influenced by near-surface conditions that alter their original mineralogic, textural, and chemical characteristics. Indeed, many igneous apatite deposits are composed of loose residual materials. In these cases the apatite has survived weathering and has become concentrated due to the fact that it is more resistant to this process than are associated minerals.

Many important sedimentary phosphate deposits owe their present character to surface or near-surface processes. For instance, the Florida deposits have been reworked in the past under surface conditions. Several cycles of deposition and reworking have concentrated the phosphate, and weathering has removed most of the carbonates from the upper (near the surface) portions of the deposits.

While each general type of phosphate deposit (sedimentary and igneous) would seem to have its own general set of characteristics, widely differing characteristics are found within sedimentary and igneous deposits as groups. Some igneous phosphate deposits, such as the Kola deposit in Russia, are hard-rock deposits. Apatite crystals are found within a hard crystalline fabric of other igneous minerals. With intense weathering, the fabric of igneous phosphate rocks can be destroyed; soft soil-like residual deposits, such as those found at Sukulu Hills, Uganda, are produced. The character of such soil-like material is more like an unconsolidated sedimentary rock than a hard-rock igneous deposit. Weathering of igneous deposits may also be at an intermediate stage, between an unaltered hard rock and soft soils.

Sedimentary phosphate rocks can range from loose unconsolidated materials, to weakly cemented materials, to highly indurated rocks. In general, younger sedimentary phosphate rocks that have not been subjected to deep burial and that contain significant amounts of phosphate particles, sands, and clays tend to be in the unconsolidated category. Phosphate rocks of varying ages have been deposited simultaneously with carbonates. Such carbonate-containing phosphate rocks can range from weakly indurated to highly indurated, depending on the postdepositional history and degree of carbonate cementation. As previously mentioned, exposure to near-surface conditions may result in the leaching of carbonates from the rock.

When sedimentary phosphate rocks have been subjected to varying levels of burial and heat, profound mineralogical and textural changes can occur. In general, the rock becomes less porous, more compact, and more highly indurated. Crystal growth occurs, and individual phosphate particles can become highly interlocked. Mineral compositions can change as strata come to equilibrium under new temperature/pressure regimes. Sedimentary phosphate rocks that have been subjected to extremely deep burial (high pressure and perhaps shearing forces and/or heat) may be further categorized as a third type of phosphate rocks, metamorphic phosphate rocks. Igneous rocks may also be subjected to heat and pressure to form metamorphic phosphate rocks. In extreme cases, metamorphosed sedimentary phosphates may be very difficult to differentiate from igneous rocks. Metamorphic phosphate rocks will not be dealt with separately in this section except to say that metamorphic examples of both sedimentary and igneous phosphate deposits can be found.

5.3.2 Phosphate Rock Mineralogy

Phosphate rock mineralogy can be highly variable, depending primarily on the origin of the rock (igneous or sedimentary), its formational or postdepositional history, and the type and degree of near-surface processes that the rock has been subjected to. Sedimentary apatites are formed near the surface of the earth under low temperature and pressure in a variety of environments that can range from freshwater to marine to hypersaline conditions. Igneous apatites, on the other hand, are formed under very high temperature and pressure. Although these apatites have similar formulas and crystal structures, they are distinctly different when analyzed in depth and may be separated into groups based on common characteristics.

Minerals associated with the various types of phosphate rocks are fairly distinctive. High-temperature igneous minerals are associated with hard-rock and mildly weathered igneous phosphate deposits. Clastic sedimentary minerals such as quartz and clays or biological or chemical precipitates such as carbonates are associated with sedimentary phosphate rocks.

Under conditions near the surface of the earth, a wide spectrum of secondary minerals can form that may be common to both igneous and sedimentary phosphate rocks. These minerals include iron and aluminum phosphates, clays, and iron oxides.

5.3.2.1 Sedimentary Apatites – Most sedimentary deposits contain varieties of carbonate-fluorapatite that are collectively called francolite. Francolite is defined as an apatite that contains significant CO_2 with >1% fluorine [2]. In establishing a series of systematic relationships among francolites, McClellan and Lehr [3] and McClellan [4] used x-ray diffraction (XRD), chemical analysis, and statistical methods to show that the contents of Ca, Na, Mg, P, CO_2, and F can adequately describe most francolites (Table 5.4). McClellan and Van Kauwenbergh [6] used similar methods, reconfirmed earlier findings, and included SO_4 as a minor component in the francolite structure. Studies of francolite in commercial phosphate rock concentrates show that the replacement of Ca^{2+} by Na^+ and Mg^{2+} is systematic although limited. Thus, at least a part of the Na^+ and Mg^{2+} in a commercial concentrate can be substituted within the francolite structure and cannot be removed by beneficiation. Most importantly, carbonate substitutes for phosphate in a 1:1 ratio. The maximum amount of substitution is between 6% and 7% CO_2. Net charge imbalances are compensated by both cation and anion substitutions (primarily Na^{+1} and F^{-1}). The incorporation of CO_2 into the francolite structure is accompanied by increased fluorine contents. In this section, these carbonate apatites are referred to as excess-fluorine francolites.

One of the most important results of these studies was the recognition that francolite compositions and properties can be estimated by x-ray and optical measurements. In excess-fluorine francolites, the unit-cell a dimension (a value) decreases from 9.369 ± 0.001Å to approximately 9.320 ± 0.001Å with maximum carbonate substitution. The index of refraction also decreases with increasing carbonate substitution (Table 5.4).

Table 5.4. Varieties of Apatite and Selected Crystallographic and Optical Properties

Variety	Formula	Unit-Cell a-Value (Å)	Refractive Index (N_D^{25})
Francolite[a]	$Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_2F_{0.4z}$	9.320-9.369	1.595-1.633
Francolite[b]	$Ca_{10-a-b}Na_bMg_b(PO_4)_{6-c}(CO_3)_cF_2F_{0.185c}$	9.318-9.369	1.597-1.633
Carbonate-hydroxylapatite	$Ca_{10}(PO_4,CO_3)_6OH_2$	9.420	1.630
Fluorapatite	$Ca_{10}(PO_4)_6F_2$	9.370	1.629-1.633
Hydroxylapatite	$Ca_{10}(PO_4)_6OH_2$	9.420	1.651
Chlorapatite	$Ca_{10}(PO_4)_6Cl_2$	9.640	1.667

a. [3,4].
b. [5].

Sedimentary phosphate rocks that are obtained from insular and cave deposits often contain carbonate apatites that have a lower F content than that of stoichiometric fluorapatite and, according to calculations, contain significant amounts of hydroxyl in their structures. Although some of these carbonate apatites may meet the francolite definition, they have crystallographic, chemical, and other physical properties that differ substantially from those of francolites that contain excess fluorine [7]. These carbonate apatites form a series with end members that contain almost no fluorine (carbonate-hydroxylapatite) (Table 5.4) and end members that are very close in composition to pure fluorapatite and francolites that have almost no carbonate substitution. Members of this series are referred to as hydroxyl-fluor-carbonate apatites in this section. Table 5.5 shows the a-values of some phosphate rocks containing hydroxyl-fluor-carbonate apatites in this series.

Table 5.5. Unit-Cell a-Dimension of Some Hydroxyl-Containing Carbonate Apatites in Some Sedimentary PRs

PR Source	Length of a-axis (Å)
Naura Island[a]	9.375
Christmas Island[a]	9.389
Lumphun, Thailand[a]	9.434
Mejillones, Chile[b]	9.332
Sechura, Peru[b]	9.337

a. Samples from insular or cave deposits. These apatites are part of a hydroxyl-fluor-carbonate apatite series.

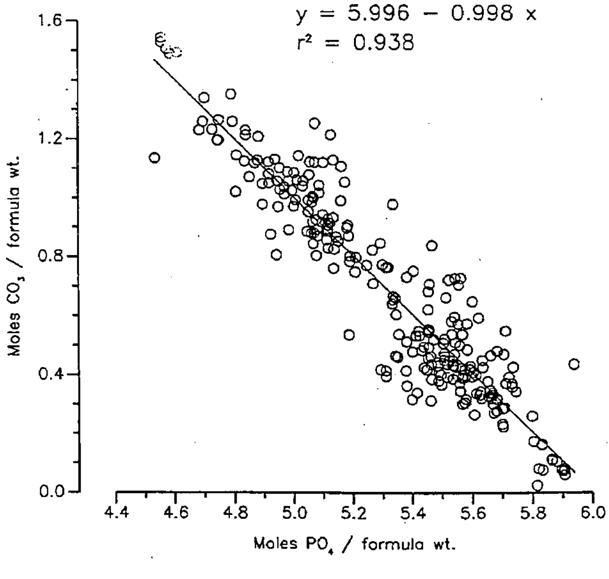
b. Calculations indicate these samples are fluorine-deficient and may contain significant hydroxyl. Unit-cell a-dimensions are similar to those of excess-fluorine francolites, but other properties vary.

Continuing studies of sedimentary apatite mineralogy have indicated that some minor revisions of previous francolite models are warranted [5]. In studies conducted at IFDC, data from approximately 1,200 phosphate rock samples were sorted into groups from predominantly marine deposits, insular or guano-derived deposits, and igneous deposits. The samples from sedimentary deposits were further screened, and all samples with less than 28% P_2O_5 were removed from further consideration. This P_2O_5 level is the approximate level to which most phosphate ores are concentrated for further chemical processing to fertilizers although the data base contains many naturally occurring phosphate samples with high P_2O_5 contents. These data were also carefully screened to remove any samples that had to be subjected to heat treatments, contained iron and/or aluminum phosphates, or contained free carbonates. Many of the samples were extracted with neutral ammonium citrate (NAC) or other mild extraction media to remove all detectable free carbonates. This resulted in a data base that included samples from most of the major deposits in the world.

Screening by this method resulted in a data base containing approximately 260 samples from predominantly marine deposits. The francolites in these samples were mainly of the excess-fluorine type as described by McClellan and Van Kauwenbergh [6]. The number of samples from insular or guano-derived deposits was much more limited. Screening by this method resulted in a data base containing approximately 30 samples.

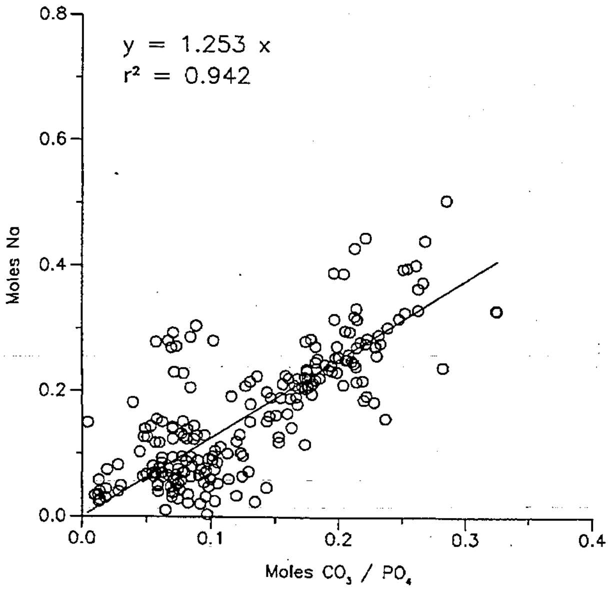
It is practically impossible to find pure samples of sedimentary apatites. This fact has plagued apatite mineralogists since apatite studies were first performed. In order to evaluate these sedimentary apatites, each chemical analysis was recalculated to a 100% apatite basis. Based on previous studies, it was assumed that the excess-fluorine francolites contained CaO, Na_2O, MgO, P_2O_5, CO_3, SO_4, and F.

Some of the results of the analysis of the data from excess-fluorine francolites are portrayed in Figures 5.1-5.6. The results of this analysis reconfirm previous



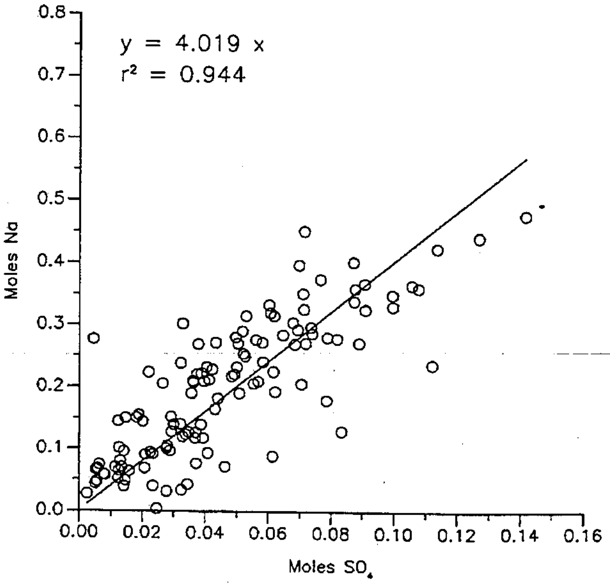
Source: [6].

Figure 5.1. Excess-Fluorine Francolites, Correlation of Moles of CO_3^{-2} Per Formula Weight With PO_4^{-3} Per Formula Weight.



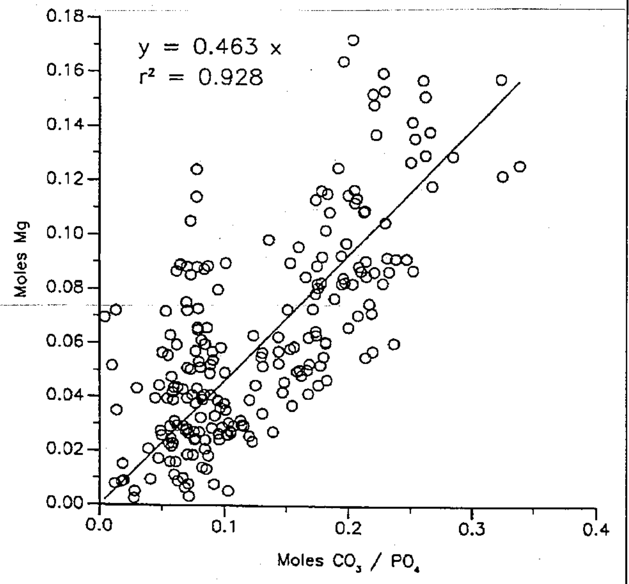
Source: [6].

Figure 5.2. **Excess-Fluorine Francolites, Correlation of Moles of Na^{+1} With Increasing CO_3^{-2} for PO_4^{-3} Substitution.**



Source: [6].

Figure 5.4. **Excess-Fluorine Francolites, Correlation of Moles of Na^{-1} With SO_4^{-2} for 120 Samples.**



Source: [6].

Figure 5.3. **Excess-Fluorine Francolites, Correlation of Moles of Mg^{+2} With Increasing CO_3^{-2} for PO_4^{-3} Substitution.**

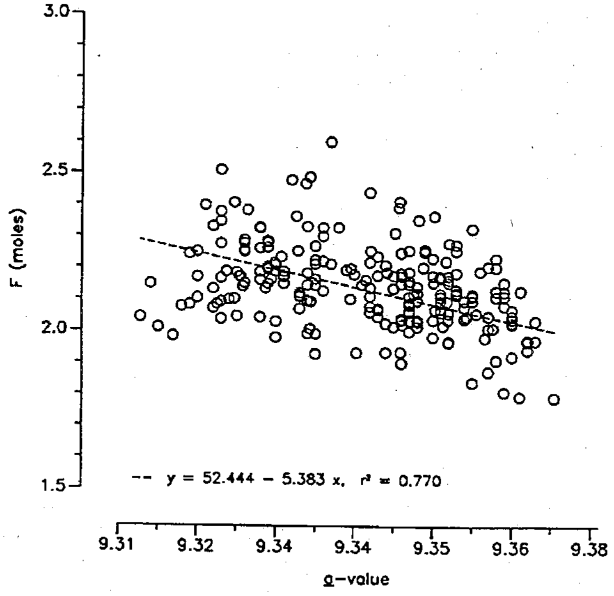
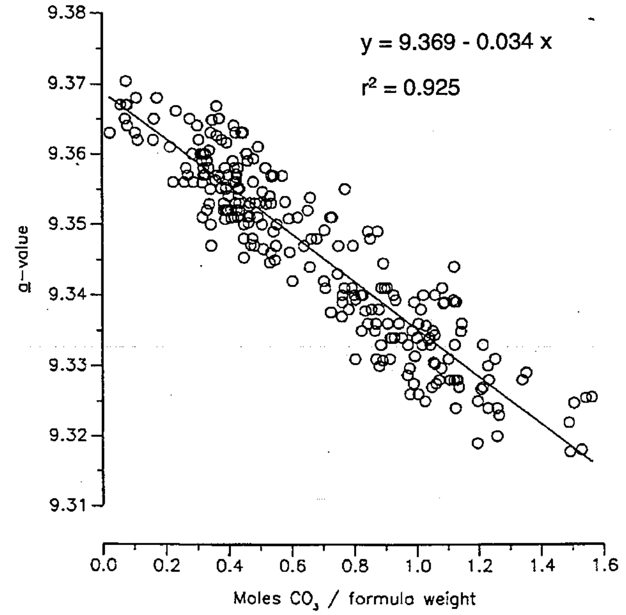


Figure 5.5. **Correlation of Moles of F^{-1} with the Unit-Cell a Value, Excess-Fluorine Francolites.**



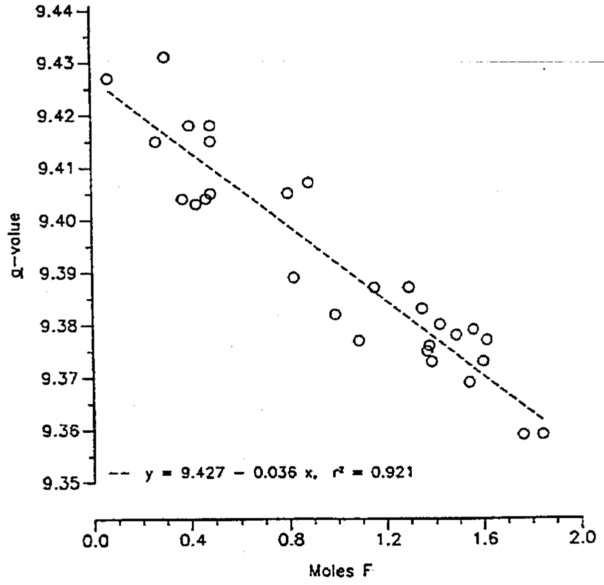
Source: [6].

Figure 5.6. Excess-Fluorine Francolites, Correlation of Moles of Mg^{+2} With Increasing CO_3^{-2} for PO_4^{-3} Substitution.

findings and refine the previous francolite models. According to this model, excess-fluorine francolites derived from sedimentary phosphate rocks can range from a minimum P_2O_5 content of about 33.3 wt % with a maximum CO_2 substitution of about 6.9 wt %, to a maximum P_2O_5 content of 42.2 wt % P_2O_5 with no CO_2 substitution.

Perhaps the most significant deviation of this model from previous models is an apparent reduction in the amount of fluorine in the theoretical francolite formula. According to previous francolite formulae, carbonate substitution (z) is accompanied by 0.4 z increased fluorine substitution. The regression line comparing fluorine content to a-values (Figure 5.5) in the present model is drawn through a veritable cloud of data although the correlation coefficient (r^2) is acceptable (0.77). Fluorine values as high as 2.4 to 2.5 moles per unit cell, as determined by previous models, are certainly possible based on the data used to drive the present model. However, statistical analysis indicates that the excess-fluorine francolite model formula should be revised to $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-c}(CO_3)_cF_{2+0.185c}$.

Analysis of samples containing apatites in the hydroxyl-fluor-carbonate apatite series indicates that the best correlation that can be obtained between any chemical, crystallographic, or physical properties is the F content (moles) versus the a-value (Figure 5.7). Significantly, the simultaneous plotting and analysis of data from the excess-fluorine francolite data set and the hydroxyl-fluor-carbonate apatite data set clearly separate these carbonate apatites into two distinct groups or series (Figure 5.8). Whereas carbonate substitution is the dominant



Source: [7].

Figure 5.7. Relationship of the Fluorine Content of Hydroxyl-Fluor-Carbonate Apatites to the Unit-Cell a Value.

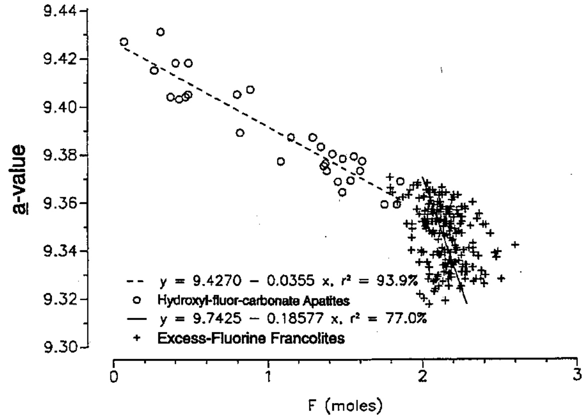


Figure 5.8. Correlation of the Unit-Cell a Value With the Moles of F^{-1} in Hydroxyl-Fluor-Carbonate Apatites and Excess-Fluorine Francolites.

factor influencing the chemical, crystallographic, and physical characteristics of excess-fluorine francolites, the carbonate contents of hydroxyl-fluor-carbonate apatites clearly cannot be correlated to the a-value (Figure 5.9).

Apatites in the hydroxyl-fluor-carbonate apatite series that are only slightly fluorine deficient have a-dimensions in the upper range of excess-fluorine francolites (≅9.360-9.370Å). The carbonate apatites in this series that are assumed to be highly OH^- substituted have a-dimensions similar to those measured for pure igneous hydroxylapatite (9.410-9.430Å) or carbonate-hydroxylapatites (9.430Å). Perhaps due to a limited sample base, other systematic chemical variations that are well established in francolites (Na, Mg, and CO_2 contents versus unit-cell a-dimensions) cannot be definitively established within the hydroxyl-fluor-carbonate apatite series at this time. It is presently impossible, by current analytical methods, to determine the hydroxyl content of these apatites. All estimations of hydroxyl contents must be based on the relative lack of fluorine or calculated based on charge imbalances. Based on charge balance calculations, it is assumed that hydroxyl-fluor-carbonate apatites contain excess hydroxyl in their structures that is associated with carbonate substitution similar to the excess fluorine associated with carbonate in excess-fluorine francolites.

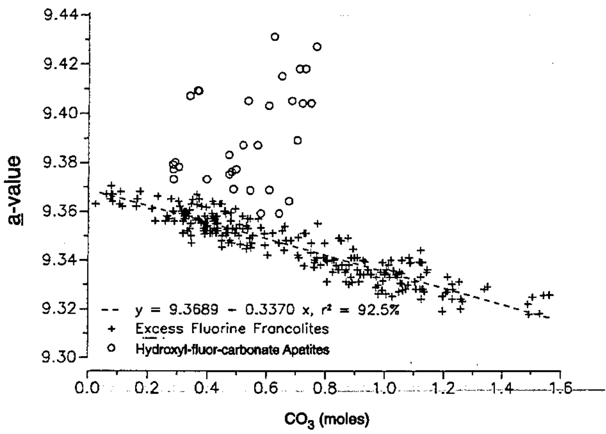


Figure 5.9. Correlation of the Unit-Cell a Value With the Moles of CO_3 in Excess-Fluorine Francolites and Hydroxyl-Fluor-Carbonate Apatites.

Some carbonate apatites do not fit well within either the excess-fluorine francolite series or the hydroxyl-fluor-carbonate apatite series and perhaps belong in an intermediate class (Table 5.5). Phosphate rocks from the deposits in Sechura, Peru, and Mejillones, Chile, might be placed in this category. The carbonate apatites in these rocks have unit-cell a-dimensions that fall plainly into the range of the francolite series (≅9.320-9.370Å). However, samples from these deposits, which have been extracted for free carbonates, exhibit higher carbonate contents and chemical reactivities than calculations based on excess-fluorine francolite models would indicate. Calculations indicate that the carbonate apatites from these deposits have lower fluorine contents than expected and may contain significant hydroxyl substitution.

Phosphate rocks from the same sedimentary deposit may contain apatites with widely differing properties due to geologic conditions and postdepositional alterations [8]. Francolites are metastable with respect to fluorapatite and can be systematically altered through the combined effects of weathering, metamorphism, and time [4]. Older sedimentary rocks generally contain francolites with a limited amount of carbonate substitution, whereas younger sedimentary phosphate rocks may have compositions that span the francolite model (Figure 5.10) [9].

The determination of the type and amount of apatite in a phosphate rock is very important. Sedimentary phosphate rocks containing the most highly carbonate-substituted apatites can only be beneficiated to maximum grades of 33-34 wt % P_2O_5. Depending on the amount of carbonate substitution, the grade can increase to a maximum of about 42 wt % P_2O_5 for sedimentary apatites with essentially no substitution. In order to reach

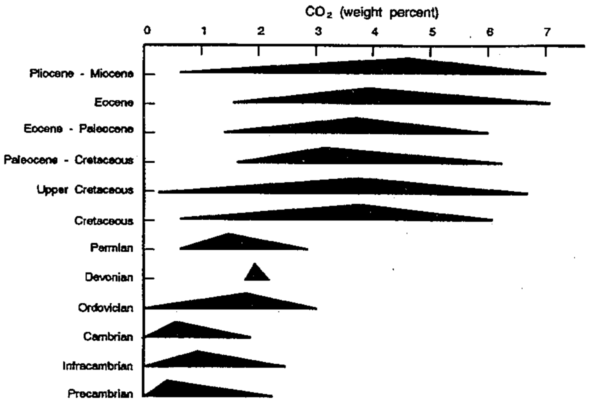


Figure 5.10. Variation in CO_2 Contents in "Excess-Fluorine" Francolites of Varying Geologic Ages (472 Samples, 165 Deposits; Peak of Triangle Represents Average CO_2 Content).

comparable concentrate grades, increasing amounts of gangue minerals must be removed from sedimentary phosphate rocks containing highly carbonate-substituted apatites (Table 5.6).

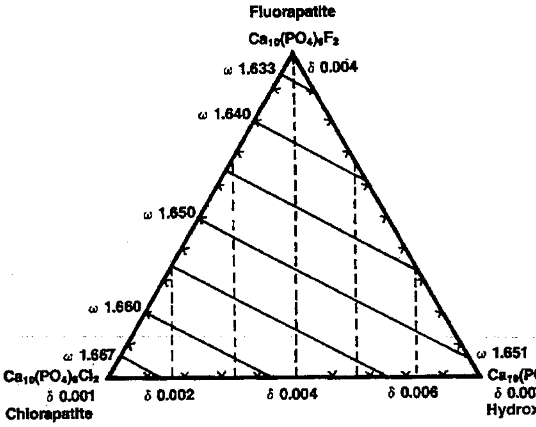
5.3.2.2 Igneous Apatites – The apatite associated with igneous source rocks may be of a primary magmatic, hydrothermal, or secondary origin. Primary igneous apatite crystals are generally well formed and found in association with high-temperature minerals or the weathering products of high-temperature minerals. Apatite may also form in the last stages of hydrothermal alteration of phosphate-bearing igneous bodies. Evidence from phosphatic pegmatites [10] suggests that apatite may form at temperatures as low as 50°-100°C. Secondary apatite is common in the weathered and supergene-enriched zones of igneous deposits. Such apatites are generally microcrystalline and may have some degree of carbonate substitution.

Table 5.6. Mineral Composition of Selected Sedimentary Phosphate Rocks

Source	Apatite[a]	Gangue Minerals
	(wt %)	
Western U.S.A.	79.8	20.2
Tennessee, U.S.A.	82.7	17.3
Sechura, Peru	86.4	13.6
Florida, U.S.A.	86.3	13.7
Morocco	88.2	11.8
North Carolina, U.S.A.	90.7	9.3
Tunisia	92.2	7.8

a. Wt % apatite = actual P_2O_5/theoretical P_2O_5 (100% apatite). Assumes all samples contain 32% P_2O_5.

Primary apatite from igneous sources may be of fluorapatite, hydroxylapatite, or chlorapatite varieties (Table 5.4). A continuous series exists between the fluorapatite and hydroxylapatite end members. Examples of fluorapatite and hydroxylapatite mixing with chlorapatite are limited. Statistical models have been established to equate the wide range of crystallographic, chemical, and physical properties of sedimentary apatites; however, models equating these properties in igneous apatites are generally lacking although optical and crystallographic properties do vary (Table 5.4) (Figure 5.11). Perhaps the most clearly recognized effect of anion substitution in igneous apatites is that of the variation of the average refractive index (N_D^{25}) [11,12] (Figure 5.11). Pure apatites from igneous deposits contain slightly over 42% P_2O_5.



Source: [11].

Figure 5.11. Optical Properties of Fluor-, Chlor- and Hydroxylapatites.

5.3.2.3 Aluminum and Iron Phosphates – A total P_2O_5 analysis of a potential ore is not a dependable criterion for evaluation of a phosphate deposit. With the weathering of apatitic phosphates and associated minerals, a suite of other secondary phosphate minerals may form (Table 5.7). These minerals are most commonly aluminum- and iron-containing phosphates. These minerals cannot be processed by the methods used to beneficiate apatitic calcium phosphates. Aluminum and iron phosphate minerals may form in both sedimentary and igneous deposits.

Probably the most common secondary phosphate minerals produced by weathering are members of the crandallite series. Wavellite is also a common aluminophosphate weathering mineral. Iron phosphates

Table 5.7. Common Secondary Phosphate Minerals Formed During the Weathering of Phosphate Deposits

Crandallite Series	
Crandallite	$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$
Goyazite	$(Sr,Ca)Al_3(PO_4)_2(OH)_5 \cdot H_2O$
Gorceixite	$(Ba,Ca)Al_3(PO_4)_2(OH)_5 \cdot H_2O$
Wavellite	$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$
Varisite	$AlPO_4 \cdot 2H_2O$
Strengite	$FePO_4 \cdot 2H_2O$
Dufrenite	$Fe^{+2}Fe^{+3}(PO_4)_3(OH)_5 \cdot 2H_2O$
Beraunite	$Fe^{+2}Fe_5^{+3}(PO_4)_4(OH)_5 \cdot 4H_2O$

such as dufrenite, strengite, or beraunite may also form. Table 5.7 provides a list of only the most common phosphates found in these deposits. There are over 300 currently valid names for species of phosphate minerals [13].

Aluminophosphate ores with high P_2O_5 contents can be calcined at low temperatures (550° to 600°C) to remove waters of hydration and alter the crystallinity of the aluminophosphate minerals. This treatment results in marked improvements in the availability of P_2O_5 as measured by common extraction procedures.

In Senegal, approximately 300,000 tpy (1994/95) of product called Phos-Pal is produced by calcination of aluminophosphate ores. The Phos-Pal product contains 34% P_2O_5, and 26%-27% P_2O_5 is soluble in ammonium citrate (Joulie test).

Two calcined aluminophosphate products, Calciphos (coarse product) and Citraphos (fine product), were produced by calcining Christmas Island C grade ore. The products had a total minimum P_2O_5 content of 30%; a minimum of 20% P_2O_5 was soluble in neutral ammonium citrate, and approximately 10% P_2O_5 was soluble in 2% citric acid or 2% formic acid. These products are not currently being produced.

5.3.2.4 Other Minerals in Phosphate Rocks – The most common nonphosphatic accessory minerals associated with sedimentary phosphate rocks are quartz, clays, and two carbonates: dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$). Carbonate-cemented phosphate rocks are particularly noteworthy because of their abundance. McClellan and Gremillion [14] estimated that there are 3 tonnes of carbonate-cemented phosphate rock for every tonne of ore that could be handled by conventional milling and flotation processes (quartz- and clay-containing phosphate rocks).

Quartz can occur as detrital grains or as chalcedony cement. Chalcedony cement or particles in samples can be particularly difficult to detect using optical microscopy because the material is anisotropic in nature and similar in appearance to microcrystalline francolite. Quartz can also occur as opaline varieties in sedimentary phosphate rocks.

Other tectosilicates found in sedimentary phosphate rocks include the various feldspars. Orthoclase is probably the most common feldspar variety, although many other types have been detected in samples from various localities. The high-temperature potassium feldspar, sanadine, has even been detected in sedimentary phosphate rocks from geologic provinces where volcanic activity was occurring during deposition. Micas (biotite and muscovite) can also be found in sedimentary phosphate rocks.

The clays found in sedimentary phosphate rocks include illite, kaolinite, smectites, and magnesium-rich clays such as palygorskite and sepiolite. Illite often appears to be a detrital mineral. Kaolinite, smectites, and magnesium-rich clays often appear to occur in zones within phosphate deposits. This zonation may be related to weathering and the general alteration of deposits under surface or near-surface conditions [15,16]. Clay-like minerals such as the zeolite clinoptilolite occasionally are found in phosphate rock.

Apatite of igneous origin is preferentially associated with alkaline intrusions and carbonatites. Common minerals associated with apatite-bearing alkaline igneous intrusions include nepheline, alkali feldspars, micas, pyroxenes, and amphiboles. Commonly the pyroxenes and amphiboles are Mg- or Fe-rich varieties, and the micas are biotite or phlogopite.

Carbonatites may or may not be associated with alkaline igneous complexes. Calcite and/or dolomite can be present in these carbonatites. Magnetite is very commonly associated with igneous apatite in carbonatite deposits.

Weathering of carbonatites has played an important part in producing some igneous apatite deposits. Weathering leaches and removes the more soluble carbonates and silicates, leaving resistant minerals such as apatite, magnetite and other iron oxides, pyrochlore, and zircon in the residuum over the deposit.

During igneous phosphate rock weathering, a wide variety of secondary phosphate minerals and clays may form. These phosphate minerals and clays include all the minerals previously mentioned in conjunction with sedimentary deposits. The residuum over such deposits is typically very rich in iron and contains significant proportions of hematite and goethite.

5.3.3 Apatite Reactivity

Several methods can be used to measure apatite reactivity. All these methods are empirical methods; that is, they depend on standardized procedures and specific extraction media. Common extraction media include neutral ammonium citrate (NAC), 2% citric acid, and formic acid. It is not the purpose of this section to discuss the relative merits or disadvantages of different methods. A discussion of these methods can be found in McClellan and Van Kauwenbergh [7]. All discussions in this section are based on extraction with NAC (AOAC method).

Lehr and McClellan [17] studied a suite of sedimentary phosphate rocks and an igneous phosphate rock concentrate and concluded that carbonate substitution in apatite was the dominant factor influencing reactivity measurements. This study also concluded that reactivity measurements with NAC resulted in the highest correlations with various apatite physical and chemical properties. McClellan and Van Kauwenbergh [7] and Van Kauwenbergh and McClellan [18] have further characterized sedimentary phosphate rock reactivity according to the separation of excess-fluorine francolites and insular or guano-derived apatites (hydroxyl-fluor-carbonate apatites). Excess-fluorine francolites have NAC solubilities ranging from about 1.3% P_2O_5 at 0% carbonate substitution to about 7% P_2O_5 at 6-9 wt % CO_2 substitution (Figure 5.12).

Apatites from insular or guano-derived deposits exhibit NAC solubilities which range from about 3.5% to 7% P_2O_5. While the CO_2 content of hydroxyl-fluor-carbonate apatites cannot be correlated with unit cell a-values, the unit cell a-values of these apatites do appear to be related to the NAC solubility (Figure 5.13) and the fluorine content can be clearly related to solubility (Figure 5.14).

Igneous apatites have essentially no carbonate in their structures although at times traces of CO_2 are picked up in chemical analyses of igneous apatite crystals. The reactivities of igneous apatites as measured with NAC are very low (Table 5.8), corresponding to values obtained from excess-fluorine francolites with essentially no carbonate substitution.

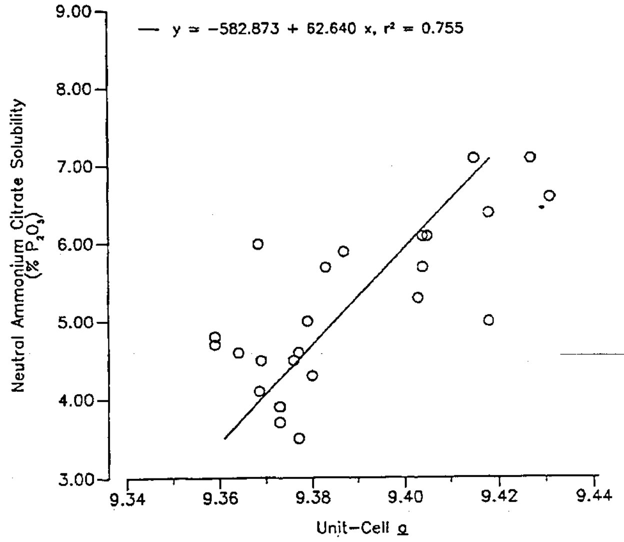


Figure 5.13. Unit-Cell a Dimension Versus Neutral Ammonium Citrate Solubility (% P_2O_5) of Hydroxyl-Fluor-Carbonate Apatites.

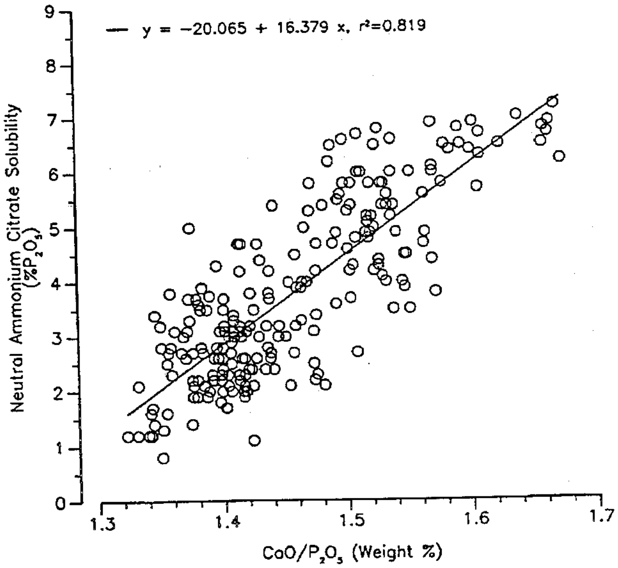


Figure 5.12. Relationship of CaO/P_2O_5 Weight % Ratio to Neutral Ammonium Citrate Soluble P_2O_5, "Excess-Fluorine" Francolites.

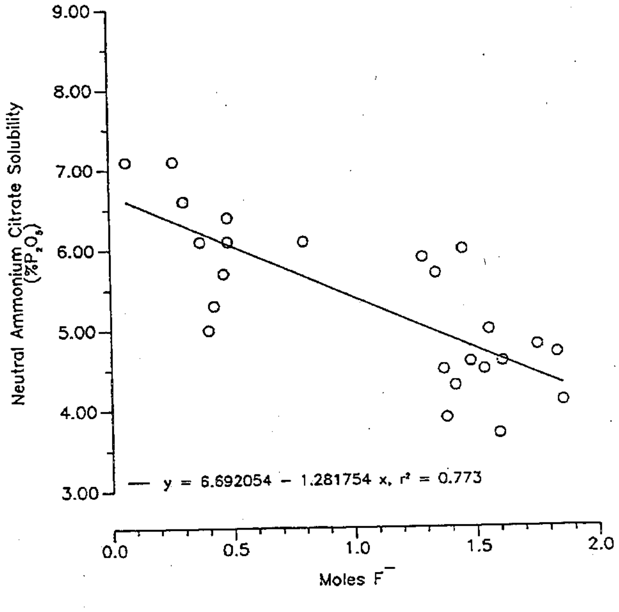


Figure 5.14. Relationship of the Fluorine Content of Hydroxyl-Fluor-Carbonate Apatites to Neutral Ammonium Citrate Solubility.

Table 5.8. Neutral Ammonium Citrate Solubility (AOAC Method) of Some Igneous Apatite Concentrates

Deposit, Country	Total P_2O_5 (wt %)	NAC P_2O_5 (% P_2O_5)
Phalaborwa, S. Africa	36-41	0.4-1.5
Dorowa, Zimbabwe	33.1	0.8
Tapira, Brazil	35.4	0.8
Matongo, Burundi	39.6	1.3
Araxa, Brazil	36.1	1.4
Martison, Canada	37.8	1.5
Sukulu Hills, Uganda	41.0	1.6

As previously mentioned in the discussion of excess-fluorine francolites, samples from the same deposits can have widely varying francolite a-values, CO_2 contents, and compositions. Samples from all types of sedimentary deposits, including those from the same deposits or from deposits within the same country, exhibit widely varying NAC solubilities due to compositional differences (Figure 5.15).

The type of apatite and/or degree of carbonate substitution largely determines the reactivity (as independently measured by reactivity tests) and suitability for direct application. The most highly carbonate-substituted sedimentary apatites have the highest reactivity and highest potential. Reactivity of sedimentary apatites decreases with decreasing carbonate substitution to a level where reactivities are essentially the same as those of igneous apatites. Igneous apatites have the lowest potential for direct application of all the apatites.

While determination of the type of apatite and reactivity of a phosphate rock may give an indication of the potential for direct application, many other factors are involved. These factors include type of crop (long or short term), soil pH and other soil characteristics, and climatic factors. Agronomic testwork is needed to determine the potential for direct application under specific conditions or a range of conditions.

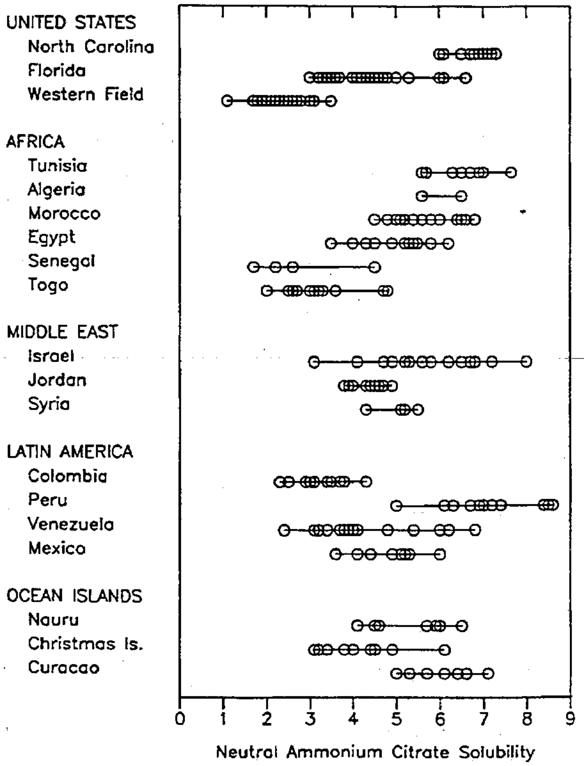


Figure 5.15. Neutral Ammonium Citrate Solubilities of Sedimentary Phosphate Rocks From Various Countries.

5.3.4 Effect of Mineralogy on Further Processing

The texture and mineralogic contents of phosphate rocks can have a profound effect on the possibilities for beneficiation. Phosphate rocks that contain large well-defined apatite crystals or phosphate grains that break cleanly from enclosing crystals or cements usually have good liberation characteristics and typically can be further processed. Phosphate rocks containing small apatite crystals or grains that may be well-intergrown with enclosing crystals or cements require finer grinding for liberation; further processing of such rocks usually results in high phosphate losses and lower grade concentrates. Sedimentary phosphate rocks containing phosphate grains or a microcrystalline phosphate matrix with significant amounts of occluded gangue are typically very difficult to beneficiate to levels suitable for fertilizer processing.

The type of rock, the grain or crystal size, and the amount of gangue minerals determine possible beneficiation routes. Fine clays or Fe and Al phosphates in unconsolidated sedimentary phosphate rocks can often be removed by simple water washing and size classification methods (screening or hydrocyclones). Plate-like micas can also be removed by hydraulic methods. For weathered igneous phosphate rocks, attrition scrubbing may be required to remove Fe and Al phosphates and fine iron oxides from the surface of apatite grains. Magnetic or paramagnetic minerals can be removed by magnetic fields.

Chemical ratios and the level of certain chemical constituents can be important considerations in deposit assessment, beneficiation, and processing for use as fertilizers. One of the most useful criteria in the mineralogical and metallurgical evaluation of phosphate deposits is the CaO/P_2O_5 ratio. The CaO/P_2O_5 ratio of pure igneous apatite is approximately 1.32. For excess-fluorine francolite, CaO/P_2O_5 ratios can range from 1.66 to 1.32. In an unbeneficiated phosphate rock sample, this ratio may be influenced by the presence of other phosphate and nonphosphate minerals. The presence of calcium-aluminum, aluminum, and iron phosphates decreases the CaO/P_2O_5 ratio below that of the apatite that is present. Crandallite minerals have a CaO/P_2O_5 ratio of approximately 0.39. Wavellite and many iron phosphates contain no calcium ($CaO/P_2O_5 = 0$). If the CaO/P_2O_5 ratio of a phosphate rock is below the ratio predicted for the variety of apatite present, significant amounts of nonapatite phosphates may be present. Based on CaO/P_2O_5 ratios, mineralogic determinations, and beneficiation testwork, portions of or entire phosphate deposits may be deemed unsuitable for further processing.

Carbonate substitution in the apatite lattice increases the CaO/P_2O_5 ratio. The presence of other calcium-bearing minerals will also raise the CaO/P_2O_5 ratio above 1.32. In both sedimentary and igneous phosphate deposits, these calcium-bearing minerals often are calcite and dolomite. Calcium-bearing silicates such as augite, feldspars, and clays also may raise the ratio.

Many fertilizer processing calculations are based on CaO levels and/or CaO/P_2O_5 ratios. Acid consumptions in acid attack processing are primarily related to CaO contents, and the relative yield of P_2O_5 is closely related to the CaO/P_2O_5 ratio. The presence of carbonates results in the increased consumption of costly acids. Ca-bearing silicates may be highly resistant to acid attack and are relatively inert.

The characteristics of potential ores from a deposit are critical in the evaluation of the deposit. For instance, low CaO/P_2O_5 ratios and elevated Fe_2O_3 and Al_2O_3 contents may be indicative of undesirable ore zones. Knowledge of these factors can guide further planning and exploration. Chemical analysis (and expenses for analyses) can be limited to those analyses that are actually needed to adequately define potential ore zones. Portions of deposits with unsuitable ore types may be eliminated from resource/reserve calculations. Portions of deposits may be determined to have slightly different characteristics and may require different processing methods. The first evaluation of a phosphate deposit should probably include some type or level of characterization studies. Many aspects of phosphate characterization that initially may seem minor to nonspecialists may be critical at some point in later studies.

5.3.5 Phosphate Rock Mining

The most successful phosphate mining operations in the world generally involve high-volume removal of waste and ore, low or reasonable costs for upgrading, ore suitable for upgrading to prevailing market-grade specifications, and large annual concentrate output. Successful export-oriented mining operations are also generally located within 200 km of the coast and a port, or there is a well-developed transportation network to a port or markets.

A wide variety of techniques and many types of equipment are used to mine and process phosphate rock. Phosphate rock is mined by both surface (open cast or strip mining) and underground methods. In the following sections, several examples of mining operations illustrate the diversity of mining methods and equipment that may be employed.

5.3.5.1 Surface Methods – Surface mining can take many forms, from manual methods employing picks and shovels to highly mechanized operations. Surface mining is by far the most popular method for phosphate deposits.

In Burkina Faso at the Kodjari Mine, perhaps a maximum of a few thousand tonnes of phosphate rock is produced per year. After less than 1 m of overburden waste is removed, jackhammers are used to excavate the relatively hard but thin-bedded sedimentary phosphate rock from the surface; front-end loaders are used to load the rock into trucks. The Kodjari phosphate rock is transported about 40 km to the site of the crushing, grinding, and bagging facility at Diapaga. The ground Kodjari rock is distributed throughout Burkina Faso as a direct-application phosphate source (≅25% P_2O_5).

In Tanzania at the Minjingu Mine, power shovels, bulldozers, front-end loaders, and dump trucks are used to strip overburden and produce up to 22,000 tpy from flat-lying soft phosphate beds about 1 m thick that gently dip off Minjingu Hill. The phosphate beds may range in P_2O_5 content from less than 20% P_2O_5 to about 25% P_2O_5. A dry beneficiation process results in a concentrate containing about 30% P_2O_5. Minjingu phosphate rock has been trucked to Kenya where it is used as a direct-application phosphate source; it is also used to make single superphosphate (SSP) in Kenya. Up to about 20,000 tpy of Minjingu concentrate was trucked to Arusha (about 90 km) and then railed to a phosphoric acid/triple superphosphate (TSP) plant at Tanga on the coast until the plant was closed in the late 1980s.

At the Riecito Mine in Venezuela, dozer/rippers (Cat D8), large front-end loaders (5 m^3), and large mine trucks (35 t) are used to strip overburden and mine over 100,000 tpy of phosphate rock from beds up to about 20 m thick. Crushed and screened Riecito phosphate rock (27%-28% P_2O_5) is transported by truck (35 t) about 90 km to the PEQUIVEN fertilizer complex at Moron where it is used to produce phosphoric acid. A rail line to the mine has been under construction for several years.

Small diesel draglines and power shovels were used to mine soft phosphate deposits at the surface in the Tennessee phosphate district of the United States. In this area, mining sites could be as small as 5 acres and located at considerable distances (up to about 150 km) from processing plants. Small, over-the-road dump trucks were used for transport. Mobility of equipment was important in this case. The phosphate ore is a residual deposit remaining from the dissolution of limestones. The subsurface in these areas is composed of irregular limestone pinnacles and solution features; small buckets on the draglines ($\cong 1$ m^3) and power shovels were essential in this situation to maximize recovery. Tennessee ores were washed and screened and mainly used in the production of elemental phosphorus in electric arc furnaces.

Mining methods similar to those used in Tennessee are employed on the island of Nauru. On Nauru, the soft phosphate ore is developed over a highly irregular limestone karst sub-surface where limestone pinnacles may be over 12 m in height. Prior to World War II, the island was mined by labor-intensive methods. After World War II, laborers were still used in the pits where small clamshell excavators could not extract the ore and for a final cleaning of the pinnacles. Due to safety considerations, workmen were removed from the pits in 1978. Phosphate is currently mined using a backshovel and several small clamshell digger cranes. Ore is transported to the primary crusher by 10- to 20-tonne trucks. Crushed and sorted ore is transported to the drying plant and storage facilities on the coast by a narrow-gauge railway.

In Idaho, U.S.A., at the Henry Mine (Monsanto Corporation), the producing beds of the Meade Peak Member of the Phosphoria Formation are very soft and dip at angles of 50°-60°. Bulldozers with vertical scraper blades peel off layers of ore; then earthmovers scrape up the ore and move it to storage piles according to grade. The high wall is benched approximately every 50 ft with 10- to 15-ft benches. The ore is transported by truck to the plant on a special road where it is used for elemental phosphorus manufacture.

In Florida (U.S.A.), large electric walking draglines are used to both strip soft overburden and mine the essentially flat-lying soft phosphate beds. Typical bucket sizes may range from 40 m^3 to 70 m^3. The draglines must have a relatively flat and stable surface to work from and walk on. Bulldozers, dump trucks, graders, earthmovers, power shovels, and various other equipment are used for site preparation. This type of equipment is also used for land reclamation once an area is mined-out.

Each Florida mine uses a minimum of two draglines. While one dragline is mining ore, the other dragline strips overburden. In this way the beneficiation plant is constantly fed without a stockpiling and reclaiming step in the process. One of the advantages of using draglines is that they can mine wet or moist ore from a bench above the ore horizon. Indeed, although losses may be high and the practice is not recommended, ore can be mined from underwater. Ore is dumped from dragline buckets into ore pits where water is sprayed at high velocity from "pit guns" to break up the ore. A grizzly is used to screen out large debris, and the ore is transported to the beneficiation plant hydraulically via pipes. In Florida up to 15 tonnes of water may be used to produce 1 tonne of concentrate although most of this water is recycled.

One operation in Florida does not use draglines to remove overburden or mine the ore. The Wingate Creek Mine in Manatee County uses one dredge to mine overburden and another to remove ore, which is pumped to the beneficiation plant.

Most of the phosphate rock produced in Florida is used in Florida to produce fertilizer. Phosphate rock concentrate is moved mainly by railroads. Some rock is exported through terminals in the Tampa area.

Large draglines are used to remove overburden at the Kingisepp Mine in Russia. Up to 23 m of hard limestone overburden is blasted and removed by the draglines. Smaller scale equipment is used to selectively remove the approximately 2.5-m-thick ore bed, which is friable and does not require blasting. Large dump trucks are used to transport the ore to the beneficiation plant, which is located within an integrated fertilizer production complex.

In the initial phase of mining at the Lee Creek Mine (currently owned by PCS Phosphates) near Aurora, North Carolina (U.S.A.), a dredge was used to remove a portion of the overburden. The dredged section of the mine development was pumped out, and conventional earthmoving equipment was used to prepare the pad (a shell bed) that the draglines walked on. Two draglines were used to remove a final thickness of overburden and the ore zone. The overburden and ore thicknesses in North Carolina are much thicker than those in Florida. In the Aurora Phosphate District, the overburden and ore zones may be from 10 to 15 m thick. Use of the dredge at Lee Creek has been discontinued, and currently a portion of the overburden is removed with large bucket wheel excavators. The Lee Creek ore (@14% P_2O_5) is mined and stockpiled next to the washer pit, fed into the washer pit, disaggregated, and transported hydraulically to the beneficiation plant. Much of the rock is used internally at the site to produce a variety of products. Phosphate rock is also transferred by barge to the ocean port facility at Morehead City.

Large bucket wheel excavators are very suitable for open pit operations when the overburden and ore are soft and dry. In Togo the first several meters of overburden, containing tree roots and other debris, are extracted using bulldozers, front-end loaders, power shovels, and large dump trucks. Large bucket wheel excavators remove the remaining overburden (from 7 to 30 m) in two benches. The overburden is transferred to mined-out areas by conveyors and offloaded by transloaders. In Togo bucket wheel excavators are also used to mine the ore zones, which can be as much as 6 m thick. Conveyors move the ore to a transfer point where it is loaded into railcars for shipment to the beneficiation plant on the coast. Beneficiated concentrate is conveyed to an offshore loading platform.

5.3.5.2 Underground Methods – There are several underground phosphate rock mining operations in the world and, just as with surface mining, the methods used range from labor intensive to highly mechanized.

In India, mining of the Mussoorie deposit was entirely by hand in the initial stages of development (1960s and 1970s). The deposit lies within the Himalayas, and the beds can be highly contorted. Over the years underground mining has become mechanized and highly sophisticated, employing methods such as block caving, inclined room and pillar, shrinkage stoping, and sublevel caving. Mussoorie rock is crushed, ground, and bagged to produce a direct-application product.

In Baja California, Mexico, at the San Juan de la Costa Mine of Roca Fosforica Mexicana (ROFOMEX), a moderately well cemented, relatively flat lying, sedimentary bed is mined. A room and pillar method in a herringbone configuration is used to extract about 65% of the ore. Continuous miners mine a bed approximately 1 m thick. The continuous miners feed ore to shuttle cars, which in turn transfer the ore to feeder stations and conveyor belts that transport the ore to one of several mine entrances. Conveyors and/or trucks move the rock to a beneficiation plant stockpile. Beneficiated rock (about 30% P_2O_5) is stockpiled to air dry. The dock is located adjacent to the beneficiation plant. Conveyors load the air-dried rock onto ships.

Underground methods have been used in Morocco for many years. Ore has been produced by a combination of mechanized and classical methods. Conventional room and pillar methods were used with the aid of short-wall drum shearers. Underground methods are also used in Tunisia and Egypt to mine gently sloping sedimentary beds. Long-wall techniques similar to the techniques used to mine coal have been used in Tunisia.

A combination of open pit and underground mines is used in Russia to produce the phosphate ores of the Khibiny Complex. As surface deposits have been exhausted, underground mines have been developed at several sites; there are plans to achieve depths of over 2,500 m.

5.3.6 Beneficiation of Phosphate Rock

Increasing world fertilizer demand in the 1960s and 1970s and the need for phosphate feedstocks stimulated efforts to develop techniques to upgrade low-grade ores and remove impurities. Among the common impurities (gangue minerals) associated with phosphate ores are clays (kaolinite, illite, smectites, and attapulgite), quartz and other silicates (usually feldspars), carbonates (mainly calcite and dolomite), secondary phosphates (iron- and aluminum-bearing phosphates), and iron oxides (goethite, hematite, and magnetite). It is highly desirable, for both economic and technical reasons, to remove as much of these impurities as possible and thus to increase the apatite content and the grade of phosphate feedstocks and improve the chemical quality. Phosphate ores can be beneficiated by many methods, and usually a combination of methods is used.

5.3.6.1 Beneficiation Techniques – In phosphate rock beneficiation, the availability of water is of prime importance and may dictate the process or processes used. The total lack of water or lack of availability of freshwater may exclude deposits from development or restrict capacity. In areas where water availability is severely restricted, such as at several locations in North Africa and the Middle East, dry screening may be an effective way to produce preconcentrates or concentrates if ore characteristics are suitable. Seawater or brackish water may be used for washing and size classification such as in Togo, West Africa. Seawater may also be used for flotation such as at the ROFOMEX mine in Baja California, Mexico. Where seawater or brackish water is used for beneficiation, a freshwater final rinse is needed to remove as much chloride as possible from the final concentrate. In other areas of the world, freshwater availability is not such a problem. In Florida from 8 to 15 tonnes of freshwater is used to produce each tonne of phosphate rock. Water is carefully managed in Florida, and most of this water is recycled.

Clays, fine-grained iron-aluminum phosphates, and fine-grained iron oxides can often be removed from phosphate ores fairly simply by using combinations of comminution, scrubbing, water washing, screening, and/or hydrocyclones. The disposal of fine ore constituents can be problematic. In some areas of the world, fines may be disposed of at sea or in mined-out areas. In other situations, environmentally suitable disposal of fine waste is mandated. In Florida about 1 tonne of fines (slimes) is generated for each tonne of concentrate produced. The slimes leave the beneficiation plants in Florida as slurries at approximately 3% solids. These slimes contain clays that do not readily flocculate and settle. Vast aboveground areas are required for slimes settling ponds in Florida. The earth dams for slimes storage may range from 20 to 60 ft tall, and up to 70% of the mined acreage may be set aside for slimes storage. The Florida slimes consolidate very slowly, preventing any type of reclamation for long periods of time after mining. The failure of earthen slimes dams in Florida is also a problem. Significant efforts by private companies and governmental organizations in Florida have been aimed at developing reasonable economic methods of slimes disposal while maintaining acceptable environmental standards and producing multi-use land forms in reclaimed areas. Disposal of fine waste produced by the beneficiation of phosphate ores in other areas of the world may not be so problematic. Slimes generated by the operations of PCS Phosphates in North Carolina (formerly Texasgulf) settle much more quickly than do Florida slimes and are slurried with flotation tailings and gypsum to mined-out areas.

The beneficiation technique of froth flotation is widely used within the world phosphate industry. Froth flotation is generally employed with silicious ores when other less expensive or less complicated techniques fail to produce phosphate concentrates suitable for chemical processing. Of course, these other techniques are often employed to prepare the feed for froth flotation. Prior to conditioning for flotation, flotation feed is deslimed. Fine particles have high surface to volume ratios and cause excessive consumption of relatively expensive reagents. Also, very fine particles are undesirable because they may become entrained in the various streams of the flotation process.

In the flotation of phosphate ores, apatite particles are generally directly transferred to the froth fraction (direct flotation) by using anionic collectors such as fatty acids. The anionic collectors selectively attach to the phosphate particles, rendering them hydrophobic, and the particles attach and are lifted to the surface by air bubbles and formation of the froth. The mineral-bearing froth may simply overflow the cells or it may be skimmed off by paddles. Quartz or other silicates are typically removed from the bottom of the flotation cells as tailings. A second stage of flotation may be added to remove silica from the phosphate-rich float through the use of cationic collectors (usually amines). In this case the silica is floated, and the phosphate particles report to the underflow. Tailings from the flotation process, due to their size, dewater easily and are pumped to storage areas or directly back to mined-out areas.

The removal of carbonates from phosphate rock has been the focus of significant research efforts for several reasons. Many countries have large deposits of phosphate rock that contain significant amounts of calcite ($CaCO_3$) and dolomite ($CaMg[CO_3]_2$). Many of these deposits are not exploitable using existing beneficiation technology. Carbonates in phosphate concentrates consume valuable acid in any acid-attack processing scheme and lower the grade of resulting products. High magnesium contents, from the dissolution of dolomite and other impurities, can contribute to poor chemical and physical characteristics in fertilizer products. Although carbonate, to varying degrees, is part of the crystal structure of the apatite typically found in sedimentary phosphate ores, it is desirable to reduce the free carbonate contents of phosphate ores and concentrates as much as possible.

Several treatments have been proposed for the removal of free carbonates from phosphate ores including flotation [19,20], acid washing [21], calcination [22], magnetic separation [23], and heavy media separation [19]. Heavy media separation can be utilized when the phosphate grains are liberated from the associated gangue minerals at relatively coarse sizes. Magnetic separation may be possible when the carbonates are contaminated with iron oxides.

Calcination of phosphate ores to remove carbonates is expensive because of the high costs of energy used to attain the temperatures necessary to thermally disassociate carbonates (approximately 780° to 835°C). Calcination is a very satisfactory method for removing organic matter. Calcination is practiced commercially at several phosphate mines around the world, mainly to improve final product quality by removing minor amounts of carbonates and organic matter. Calcination is also used where the cost of natural gas is very low. The oxides (CaO and MgO) produced by calcination of significant amounts of carbonates can be removed by slaking with water. The slaking process adds a size classification step and a drying step to the beneficiation process, further increasing costs.

Flotation of calcareous and dolomitic phosphate ores seems to be the most economically viable technical alternative. However, selective flotation of carbonates from phosphate is rather difficult due to the similarity in the physico-chemical properties of carbonate and phosphate minerals. Carbonate/phosphate separation by flotation is commercially used in Finland and Brazil to treat igneous phosphate ores.

Despite the fact that significant research has been conducted on the selective flotation of carbonate-containing phosphate ores, carbonate flotation has not been commercially adopted for the treatment of sedimentary phosphate ores. Both direct and reverse phosphate and carbonate flotation techniques have been tested for effectiveness in upgrading sedimentary phosphate ores with high carbonate contents. In carbonate flotation processes, the phosphate minerals may be depressed by using an aluminum sulfate/sodium potassium tartrate mixture [24], sodium tripolyphosphate [25], diphosphonic acid [26], hydrofluosilicic acid [27], sodium silicate, or sulfuric or phosphoric acid in slightly acidic pulps (pH 5.-6.0) and simultaneously floating the carbonate by using fatty acids or their sulfonated salts [28]. Related methods have been developed for anionic flotation of both carbonate and phosphate followed by selective deoiling of the phosphate surface using sulfuric acid at pH 5.3 and then floating the carbonate fraction [29]. Direct cationic phosphate flotation uses a tallow amine acetate/fuel oil mixture while depressing carbonate using acetic or hydrofluoric acids [30]. Some of these methods show promise and may be utilized in the future.

Many phosphate ores have high iron contents that render them undesirable for chemical processing into fertilizers. Iron minerals are often present as iron oxides coating the surface or interlocking with the phosphate grains. Complex iron-containing silicates (such as amphiboles, micas, and clays) are another major source of iron in most phosphate ores. Iron may also be present as iron phosphates.

Various methods have been developed for the removal of iron gangue minerals from phosphate rocks, including scrubbing and size classification [31], magnetic separation [32], and flotation [33]. Quite often combinations of two of these methods are used to reduce the iron content of concentrates to acceptable levels. Attrition scrubbing to remove iron minerals coating the surface of phosphate particles is generally recommended for igneous ores with well-formed competent apatite crystals. Attrition scrubbing of sedimentary phosphate rocks containing soft phosphate grains usually results in high phosphate losses as fines. Gravity separation of iron-bearing minerals from phosphate ores can sometimes be achieved by using heavy media. Good separation efficiencies can usually be obtained with coarsely liberated particles or closely sized feeds. Low-intensity magnetic separation can be used to separate iron minerals with high magnetic susceptibilities such as magnetite, and wet high-intensity magnetic separation can be used to separate feebly magnetic minerals such as hematite and goethite. Flotation of iron oxides from phosphate ores by using anionic and cationic collectors has been studied by many investigators. The effects of organic and inorganic electrolytes on the activation and depression of iron oxides in flotation systems have been reported. Starches and sodium silicate have been proven to be effective depressants for iron minerals [34].

5.3.6.2 Examples of Beneficiation Processes – The design of the beneficiation processes can vary widely depending on the characteristics of the ores being processed. For sedimentary phosphate ores, beneficiation flowsheets can be as simple as washing and size classification. Beneficiation flowsheets can also be very complicated when several size classification steps, several stages of flotation, or other processing steps are used. The following examples illustrate beneficiation schemes for two sedimentary phosphate ores (Togo and Florida) and two igneous phosphate ores (Sukulu and Siilinjarvi).

The Hahotoé and Kpogamé phosphate mines lie to the north of Lake Togo in the coastal area of southern Togo. Ore is transported to the beneficiation plant on the coast by a narrow- gauge railway. The beneficiation plant common to both mines comprises five processing trains resulting in an overall design capacity of 3.5 million tpy (Figure 5.16). The raw ore feed is scrubbed with seawater and wet screened at between 0.8 and 3 mm depending on the characteristics of the ore. The next processing stage involves slurrying with seawater and using a series of primary and secondary hydrocyclones. Fines (approximately minus 44 µm), which include clays, constitute approximately 40% of the composition of the feed and are removed by hydrocycloning. The wet ore concentrate is dewatered using 430-mm hydrocyclones and then passes through centrifuges where it is given a freshwater rinse to reduce the chloride content. A large-diameter rotary dryer with low airflow is used to reduce moisture from 17% to less than 2%. The dry product can be passed through a vibrating screen to remove particles over 400 mm, and ferrous material can be removed by an optional electromagnetic separation step. The Togo phosphate rock concentrate is marketed at a P_2O_5 content of over 36%.

The ores from the land pebble phosphate deposits of central Florida typically consist of about equal portions of phosphatic grains, quartz sands, and clays. Florida beneficiation plants usually include a washer section (Figure 5.17a) and a flotation section (Figure 5.17b). In the following descriptions and figures, the size classifications are approximate and depend on the equipment used at specific installations. In the washer section, the ore slurry (matrix) is processed using log washers, trommel screens and inclined screens to remove large-scale contamination (tree roots, large particles, etc.), break up clay balls, free and clean the phosphate particles, and classify the material. The minus 50 mm to plus 9.5 mm and minus 9.5 mm to plus 1.0 mm fractions may be separated as phosphate pebble products if they are of suitable grade and quality. The minus 1.0 mm fraction is deslimed in hydroseparators or hydrocyclones. The minus 0.1 mm fraction (slimes) is pumped to clay storage ponds. The minus 1.0 mm plus 0.1 mm fraction (flotation feed) is pumped to the flotation section.

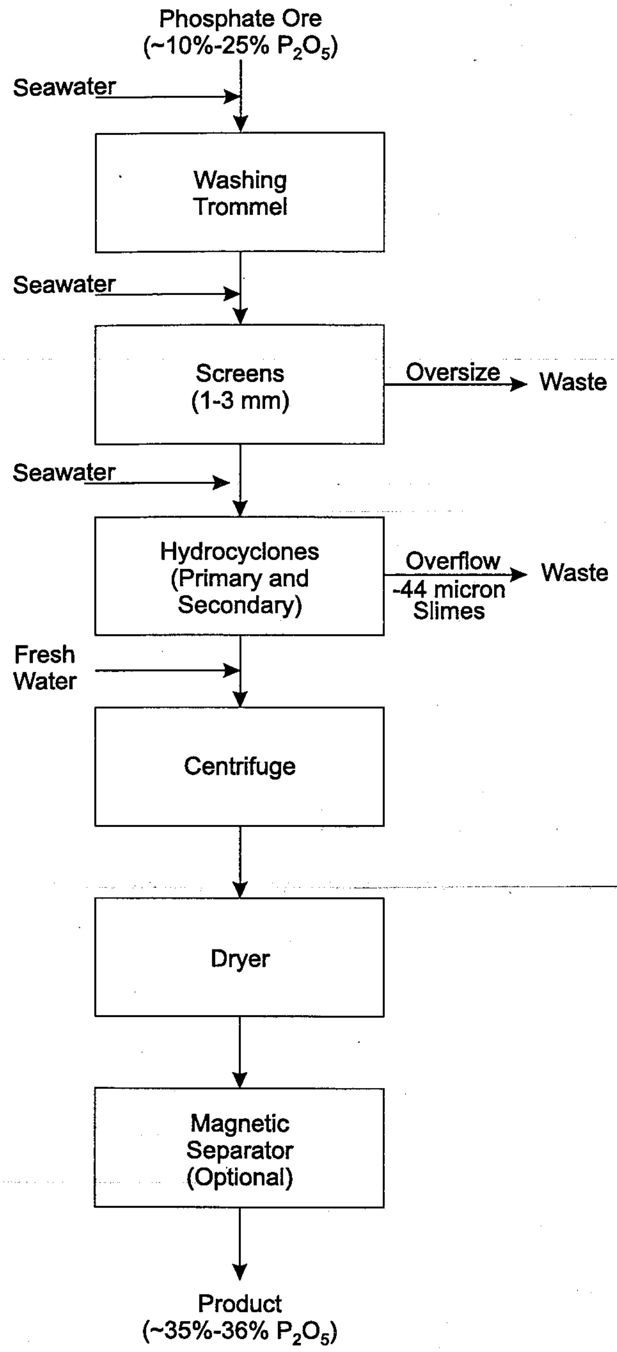


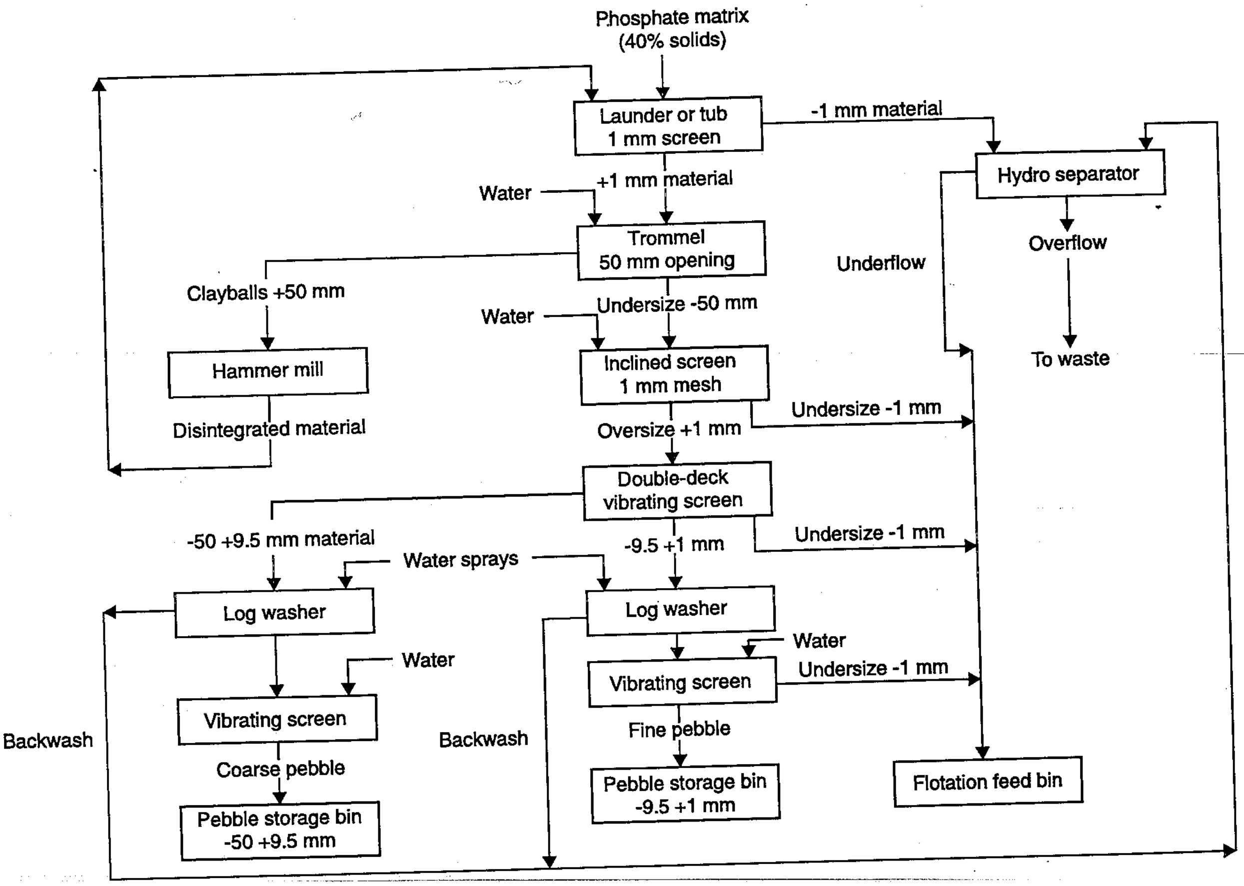
Figure 5.16. Simplified Togo Phosphate Ore Processing Scheme.

In the flotation section, classification units may be used to split the minus 1.0 mm plus 0.1 mm feed into two size fractions for separate treatment. The coarser fraction (minus 1.0 mm to approximately plus 0.4 mm) can be concentrated by gravity (spirals) and froth flotation methods. The finer, minus 0.4 mm plus 0.10 mm, fraction is dewatered to 60%-75% solids. After being conditioned with a pH regulator and a phosphate collector (fatty acids with fuel oil or kerosene as an extender), the pulp goes to the rougher cells. The underflow (silica tailings) is pumped to reclamation areas. The concentrate (froth product) is scrubbed with sulfuric acid to deoil the particle surfaces, washed with water, and then conditioned with an amine for silica flotation. The quartz froth product from the amine flotation is pumped to waste storage areas, and the underflow is the final (double-float) phosphate concentrate, typically assaying 2%-3% silica and 31%-34% P_2O_5 (68%-75% BPL).

The techniques used to beneficiate igneous phosphate ores can be very diverse depending on ore characteristics; two examples illustrate the diversity of igneous ores. Soft and unconsolidated Sukulu phosphate rock ore from Uganda resembles an iron-rich soil. The Sukulu ore is a residual deposit of phosphate and iron minerals that are resistant to weathering or are weathering products. The deposit is developed on an igneous structure called a carbonatite, which was formed deep below the surface of the earth. The precursor carbonatite contains carbonates, magnetite, iron-rich silicates, and apatite. Deep weathering has removed carbonates and increased the relative abundance of iron oxides and apatite in the soil-like residuum formed over the carbonatite. Sukulu ore can be beneficiated by using many of the techniques employed to treat sedimentary ores. Hard igneous phosphate rock from Siilinjarvi in Finland in some ways resembles the unweathered precursor materials from which the soft Sukulu deposit was formed, and it requires different beneficiation techniques.

Prior to the cessation of activities in 1977, the concentrates produced by the Sukulu mine were used to produce SSP. At the Sukulu beneficiation plant, a front end loader fed the loose unconsolidated ore into a hopper with a feeding mechanism, which in turn fed the ore onto a belt conveyor leading to the washer. The ore was slurried, screened, and deslimed with hydrocyclones. The deslimed ore slurry was then pumped to the primary magnetic separators. The partially magnetically separated ore was ground in ball mills and sized down to minus 0.1 mm to liberate apatite and magnetite. This was followed by another step of magnetic separation and slimes removal. The deslimed pulp was then conditioned with a pH regulator and sodium oleate as a flotation agent. Flotation was carried out in stages (one rougher and three cleaner steps) with a scavenger flotation circuit for the tailings of the rougher cell. The phosphate concentrate would typically assay 41.0%-42% P_2O_5 (90% BPL) and less than 1.2% Fe_2O_3.

The low-grade (mill feed is approximately 3.5% to 5.5% P_2O_5) igneous apatite deposit at Siilinjarvi, Finland, on average is composed of about 65% phlogopite mica [$K(Mg,Fe)_3AlSiO_3O_{10}(OH,F)_2$], 19% calcite, 4%

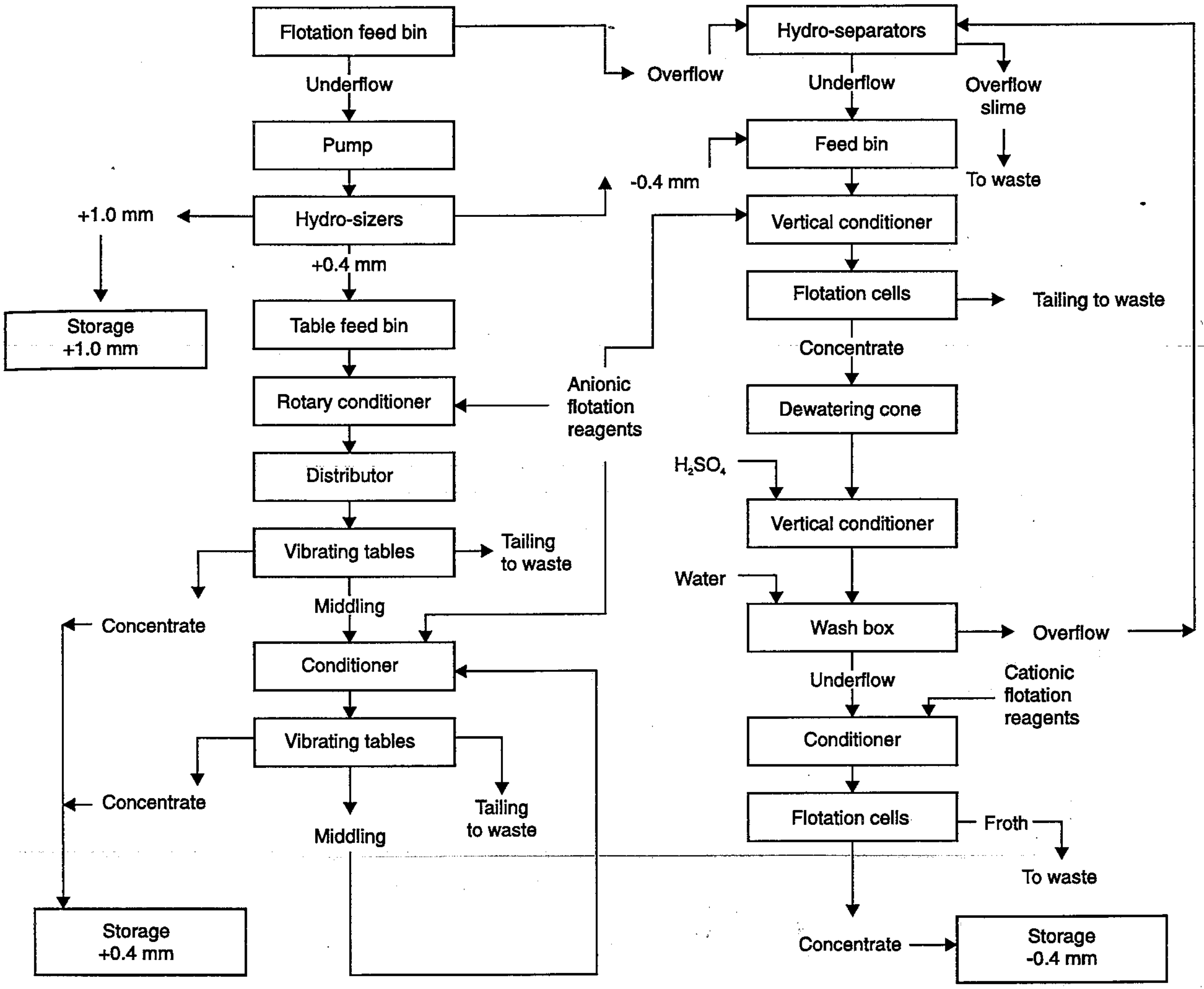


Source: Adapted from Bureau of Mines Information Circular 7814, United States Department of the Interior, 1958.

Figure 5.17a. Florida: Generalized Scheme of Phosphate Rock Beneficiation—Washing.

dolomite, 10% apatite, and 5% other silicates. Mining at Siilinjarvi is controlled by a computer-based open-pit surveying and planning system to reduce the effects of mineralogical variations on further processing. The ore is very hard and must be blasted. The use of blending stockpiles after primary crushing and screening further helps to reduce variations in the ore feed to the beneficiation plant. A flowsheet of the Siilinjarvi plant is shown in Figure 5.18.

Crushing, screening, blending, grinding, and conditioning prepare the Siilinjarvi ore for flotation. All the ore must be treated in this manner. With a hard igneous phosphate ore such as this, there is no option to remove impurities and upgrade the flotation feed by other methods. The ore slurry is fed to the flotation section at 35% by weight minus 74 μm. The slurry is conditioned with an N-substituted sarcosine as a selective phosphate collector. The conditioned pulp is pumped to a distributing box that feeds the rougher flotation cells. Outokumpu double-cell flotation units of 38 m^3 capacity are used. The apatite rougher concentrate advances through a four-stage cleaning process. The final cleaner flotation concentrate flows to a 20-m-diameter center-drive thickener to raise its solid content from 36%-40% to 65% by weight solids in the thickener underflow. The moisture content of the concentrate is then reduced to 6%-8% by using pressure filters. The apatite concentrate averages 85% by weight minus 150 mm and typically assays 35.5% P_2O_5 (77.5% BPL), 6.5% CO_2, 1.95% MgO, 0.03% K_2O, 0.09% Na_2O, 0.5% SiO_2, 0.4% Fe, and 8% moisture. The concentrate is fed directly into a phosphoric acid plant. The beneficiation plant also produces a calcite concentrate, and phlogopite mica is produced as a byproduct.



Source: Adapted from Bureau of Mines Information Circular 7814, United States Department of the Interior, 1958.

Figure 5.17b. Florida: Generalized Scheme of Phosphate Rock Beneficiation—Flotation.

Sedimentary phosphate ores, particularly those that have been subjected to the effects of heat and/or pressure (perhaps deep burial) may become highly consolidated, well cemented, and very indurated. Such phosphate ores are typically of Paleozoic or Precambrian age. The production of well-consolidated and highly indurated sedimentary ores may require mining and beneficiation techniques resembling those typically used for hard igneous phosphate ores. Such phosphate ores are mined and beneficiated in India and China.

5.3.7 Factors Affecting Quality of Phosphate Rock

The wide variety of geologic settings in which phosphate rocks occur results in textures, accessory mineral assemblages, and chemical compositions that range from simple to very complex. Variations in quality from a single phosphate rock source can arise due to the fact that continuous mining removes beds or ore zones that have internal variations, and beneficiation processes may deviate from normal practices for various technical or economic reasons. Impurity contents and compositional differences not only contribute to processing difficulties that have an indirect effect on product quality but also can directly contribute to fertilizer product compositions.

The principal market specification relating to the P_2O_5 content (grade) of phosphate rock is not a reliable indicator of the potential quality of phosphate fertilizer

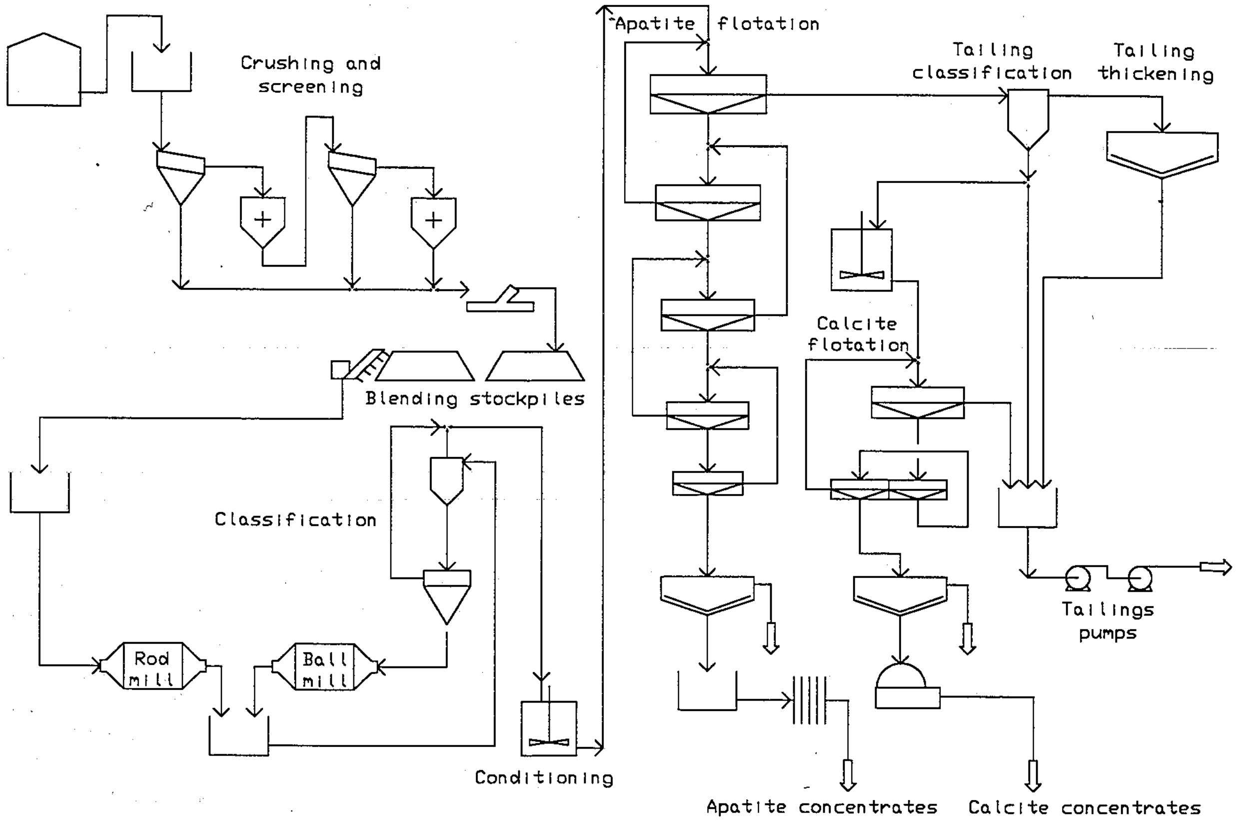


Figure 5.18. Generalized Scheme for Processing Siilinjarvi Phosphate Ore.

produced by a particular process, nor is it an indicator of the similarity of equivalent grade phosphate rocks from different sources. In general, lower P_2O_5 means higher impurity contents. Lower P_2O_5 content results in lower yields, and high impurity contents result in more processing problems and higher costs. Variability in phosphate rock compositions contributes to the physical and chemical quality factors summarized in Table 5.9 [35]. The effects of impurities are not all negative. The presence of some impurities has a positive effect during processing and/or on the physical properties of products [36,37].

5.3.7.1 Physical Factors – Processing of commercial phosphate rock concentrates depends to a large extent upon their texture. In general, a phosphate rock concentrate has the ideal texture for processing when it is disaggregated and contains relatively soft but competent porous sand-sized sedimentary phosphate particles that are easily handled and metered mechanically. Grinding of these phosphates to a particle size range required for phosphate fertilizer manufacture presents no major problems. Concentrates with porous phosphate particles may be suitable for phosphoric acid manufacture with-

Table 5.9. Quality Factors for Commercial Phosphate Rocks

Physical Factors
Texture: hardness, porosity, cementing, or coating phases
Phosphate particle size: coarse to cryptocrystalline
Degree of crystallinity of the apatite
Effect of physical treatments: natural or calcined state

Chemical Factors
P content of phosphate rock (BPL grade)
F content of the apatite
Carbonate content of the apatite
Free carbonate content
CaO/P_2O_5 weight ratio (phosphate and accessory mineral sources)
Fe and Al content (combined R_2O_3)
Mg content (phosphate and accessory mineral sources)
Content of inert mineral gangue (insoluble oxides and silicates)
Na and K (phosphate and accessory mineral sources)
Organic matter (native types + beneficiation reagents)
Chlorides (from evaporite salts, phosphate substitution, process water)
Heavy metals (Cd, Pb, Zn, Hg)
Potentially toxic elements (Se, As, Cr, V)
Radionucleides (U, Th, Ra, Rn) from phosphate minerals

Source: Adapted from Lehr [35].

out grinding. Many of these desired textural properties are common to many sedimentary phosphate concentrates, but not to concentrates produced from igneous or metamorphic phosphate deposits [38].

Sedimentary phosphate rocks with compact, indurated, coarse particles, or concentrates containing coarse apatite crystals such as those of igneous or metamorphic origin are often slowly reactive in acidulation processes. Reaction/retention times may become long, and phosphate losses may become unacceptable due to blinding of phosphate particle surfaces. These types of concentrates may require fine grinding to an acceptable particle size, thereby increasing surface area, to be suitable for acidulation. A common grind for relatively unreactive phosphate rocks is 70% minus 200-mesh (Tyler). Calcined phosphate rocks may have low reactivity because of agglomeration, loss of porosity, and thermally induced crystal growth of the apatite. When francolites are treated with heat, carbonate is expulsed and the apatite recrystallizes, producing apatites similar in composition and reactivity to igneous apatites.

5.3.7.2 Chemical Factors – In spite of the known physical, mineralogical, and chemical differences that exist among various types of phosphate rocks, grade is typically the primary criterion used to differentiate phosphate rocks and is often expressed in terms of tricalcium phosphate [$Ca_3(PO_4)_2$]. The trade name for tricalcium phosphate is "bone phosphate of lime" or BPL. Early workers believed that tricalcium phosphate was the chief constituent of commercial phosphate rock. Later studies have shown that bones and phosphate rock consist of varieties of apatite. Because these commercial terms are widely used, the following conversion factors are included for reference purposes:

$P_2O_5 = 0.4576 \times BPL$

$BPL = 2.1852 \times P_2O_5$

$P = 0.1997 \times BPL$

Commercial phosphate rocks vary in grade from about 80 BPL to about 60 BPL. Most international trade involves the higher grade phosphate rock, and lower grade rock is often used at local processing facilities. The economics of shipping and processing low-grade phosphate rocks are not favorable.

Phosphorus Content – A somewhat loose terminology may be used to indicate processing quality according to grade although no absolute marketing specifications presently exist. Each producer will have its own specifications. Trade organizations have established grade categories for record-keeping purposes. For example, the International Fertilizer Industry Association (IFA), Paris, France, uses five grade categories (65 BPL and under, 66-68 BPL, 69-72 BPL, 73-77 BPL, and 78 BPL and over) at the present time.

Premium-grade phosphate rock concentrates were considered by Lehr [35] to contain at least 31% P_2O_5 (over 68% BPL). Lehr [35] considered phosphate concentrates to be nonpremium grades when the P_2O_5 content was below 31% and the concentrations of accessory mineral impurities were correspondingly higher. Regardless of grade, marginal phosphate rocks were considered by Lehr to be raw materials with high contents of accessory mineral impurities that render them marginal or unsuitable for chemical processing.

Robinson [39] indicated that in Europe phosphate rocks were generally considered high grade if they had P_2O_5 contents in the 33%-39% range (over 72 BPL). Phosphate rocks were considered low grade if their P_2O_5 content was in the 28%-33% range.

Phosphate rocks from both igneous and sedimentary sources are generally lumped together in statistical tabulations by grade. There are very few sedimentary phosphate deposits from which most of the concentrate production is entirely over 33% P_2O_5. There are several major sedimentary deposits where a proportion of the production is over 33% P_2O_5 but most is below 33% P_2O_5. In contrast, concentrates produced from igneous phosphate rocks are almost invariably over 33% P_2O_5 and are usually over 35%-36% P_2O_5 (~78 BPL).

It is not important that phosphate rocks be placed in categories according to grade. It is important to realize that higher P_2O_5 contents translate to lower impurity contents. Increased P_2O_5 contents in concentrates result in increased yields per tonne of material shipped, handled, and processed. Lower impurity contents generally result in increased reaction efficiencies, fewer processing problems, and less waste. In general, higher P_2O_5 concentrates command higher prices. Processing of phosphate rocks containing less P_2O_5 and more impurities results in less product, higher processing costs, and less potential profit. Correspondingly, phosphate rocks with lower P_2O_5 content are priced lower.

Carbonates – Carbonate, to varying degrees, is part of the crystal structure of sedimentary apatite (francolite). It is desirable that the free carbonate contents of phosphate ores and concentrate be as low as possible. The carbonate content of internationally traded phosphate rock is usually minimal and generally confined to the carbonate component. Carbonates cause foaming in the production of phosphoric acid and consume valuable acid in any acid-attack processing scheme. If carbonates are disassociated by calcination, the CaO (and perhaps MgO) remaining must be removed by slaking, or acid consumption will still be high. The dissolution of dolomite (calcium magnesium carbonate) releases magnesium impurities in processing systems. A benefit of the carbonate content of the francolite in phosphate rock is seen in SSP and TSP manufacture by the den process. Phosphate rocks that contain carbonate produce a porous friable den product that is more easily cut and handled.

Iron and Aluminum — High iron and aluminum contents are not desirable in commercial phosphate concentrates. High R_2O_3 ($Al_2O_3 + Fe_2O_3$) contents can lead to poor physical properties in superphosphates, fertilizer intermediates that are difficult to handle, and phosphoric acid-based products that are difficult to dry and that may cake in storage. When concentrations of R_2O_3 exceed about 3%, problems resulting from precipitation of iron and aluminum phosphate compounds can be expected during concentration, cooling, and storage of phosphoric acid. Fertilizers produced from phosphate rocks and phosphoric acid containing high amounts of R_2O_3 also contain less water-soluble P_2O_5 as a percentage of total P_2O_5 due to the formation of water-insoluble iron and aluminum compounds. Furthermore, the presence of high iron and alumina contents can lead to reversion of water-soluble P_2O_5 compounds to insoluble compounds over the passage of time in storage. An acceptable level of the R_2O_3/P_2O_5 weight ratio in phosphate rock feedstocks for processing to fertilizers is about 0.1 or less [36].

Low aluminum contents (<0.1%-0.2%) in phosphate rock concentrates can lead to needle-like gypsum crystal formation in phosphoric acid manufacture, low filtration rates, low wash efficiency, and unacceptable P_2O_5 recovery. Low Al_2O_3 and perhaps low Fe_2O_3 content in phosphoric acid used to produce ammonium phosphates results in products that tend to cake easily. Iron-rich high-aluminum clays (kaolinites) have been added during the granulation of SSP and TSP produced from high-purity phosphate rock and phosphoric acid to promote granulation and assist in the formation of strong granules.

Magnesium – High magnesium contents in concert with high R_2O_3 contents result in similar processing and product problems. High magnesium contents can result in the formation of compounds that increase the viscosity of phosphoric acid upon concentration, even when the R_2O_3 contents are low. The presence of magnesium leads to the precipitation of insoluble phosphate compounds in the manufacture of liquid ammonium phosphate fertilizers.

Fluorine Content – Phosphate concentrates with high fluorine contents and low silica contents yield phosphoric acid that is high in fluorine. In the production of phosphoric acid, excess free fluorine ions result in long, thin, needle-like phosphogypsum crystals, which are difficult to filter and have a low washing efficiency and a high final cake moisture. When a phosphate rock has excess fluorine, the addition of active silica is beneficial to improve the crystal shape [37]. Free aluminum and magnesium may react with fluorine to lower the free fluorine content. High fluorine contents in phosphoric acid have a marked influence on the kinds and amounts of insoluble precipitates that form in the ammoniation products, and the concentration of the residual fluorine in liquid fertilizers is especially critical [40].

Silica and Silicate – Silica present as crystalline quartz is generally unreactive in any acid attack scheme and mainly acts as a diluent. Crystalline quartz increases the erosion rate for beneficiation and fertilizer processing equipment. Fine crystalline quartz can hamper filtration by filling the pores of the cake and plugging the filter cloth. Active silica has a positive effect on the reduction of corrosion, as it complexes with the free fluorine ions and influences the crystallization of phosphogypsum [37]. During phosphoric acid manufacture, blinding of the filter cloth can occur when colloidal silica is formed in the reaction medium.

Sodium and Potassium – The quantity of sodium or potassium in the phosphate rock has an impact on the scaling tendency during phosphoric acid production. If sufficient fluorine and dissolved silica are present in the acid, the formation of Na_2SiF_6 and K_2SiF_6 is expected to increase scaling in the filter circuit. These compounds are water insoluble and act as diluents in monoammonium phosphate (MAP), diammonium phosphate (DAP), and nitrophosphates.

Strontium – Strontium sulfate ($SrSO_4$) has a minimum solubility in 40% phosphoric acid. $SrSO_4$ forms a scale in the heat exchangers of phosphoric acid concentrators. An extremely thin film of this precipitate causes pronounced reductions in the capacities of such units [37].

Organic Matter – Some forms of organic compounds give rise to persistent foams that require the use of antifoaming agents. The presence of organic matter may result in NO_x release in nitrophosphate manufacture. During processing, the presence of organic matter may result in odors that may persist and be objectionable to the population near a fertilizer plant. Organic matter may be a benefit if the phosphate rock is processed by the electric furnace method where the organic matter burns and reduces fuel and energy requirements.

Sulfides – Sulfides can release H_2S, which is a toxic gas, during acidulation. Sulfides produce reducing conditions, increase corrosion rates in phosphoric acid manufacture, and give NO_x release in nitrophosphate manufacture.

Chlorides – The usual sources of chloride ions in phosphate concentrates are the evaporite salts found in some sedimentary ores or from seawater or brackish water that might have been used in beneficiation. Chlorides sharply increase the corrosion rates of steel equipment during acidulation. In general, chloride contents higher than 200-300 ppmw cannot be tolerated because corrosion rates for common stainless steels then become excessive [36]. With special steels, use of plastics, and special concrete construction, higher Cl contents can be tolerated.

Heavy Metals – Heavy metals do not appear to have any adverse effect on fertilizer manufacture but may be potentially hazardous. Some countries have imposed a limit on the $Cd:P_2O_5$ weight ratio.

There is no known process that is capable of removing Cd from phosphate ores at no cost. Limits in fertilizers can only be reached economically by using phosphate rocks with low Cd content or by blending the above-average Cd content phosphate rocks with other ores that contain a minimum amount of Cd. Some phosphate rocks with higher than average Cd content have been excluded from the European market. The bioresponsibility of Cd has not yet been established clearly, and the European Community has committed to studies to clarify this matter. The EC is also giving financial support for studies of processes to remove Cd from phosphoric acid.

Radionucleides – The radioactivity of the commercial phosphate rocks does not interfere with fertilizer manufacture but must be considered because of potential health hazards. Recent interest has been focused on U and Ra, regarding both recovery and potential health hazards in manufacturing and in handling byproducts and final products.

During the digestion of phosphate rock by the dihydrate process, most of the uranium reports to the phosphoric acid solution. Becker [41] estimates that 85%-95% of the uranium in the phosphate rock feed goes into solution. Several processes have been developed for the extraction of uranium from phosphoric acid.

Whereas uranium mainly reports to the phosphoric acid stream during processing, radium-226 preferentially reports to the phosphogypsum byproduct. Radium-226 is a long-lived alpha emitter with a half life of 1,622 years and is a gamma radiation source when accompanied by radon-222 and its progeny. The U.S. Environmental Protection Agency (EPA) has imposed a limit of 10 pCi/g radiation for phosphogypsum, and phosphogypsum produced from Florida phosphate rock must be contained in piles near the processing plant. Phosphogypsum produced from central Florida phosphate rock cannot be sold for any purpose, and its movement is strictly controlled.

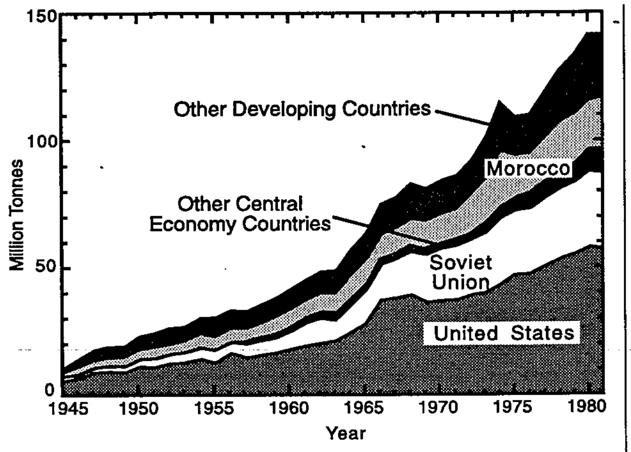
5.3.7.3 Measuring and Estimating the Impact of Phosphate Rock Quality Factors – The quality of phosphate rock influences the design, capital costs, and operating costs of processing facilities. If a phosphate rock source has been used for many years, a wealth of engineering data and expertise has probably been developed concerning its use. However, when new or different sources of phosphate feedstock are to be used, the effects of physical and chemical factors can often be determined only by laboratory and pilot plant-scale testwork. In comparative studies, unknowns are compared with phosphate rocks or intermediates with known processing characteristics and specified processing conditions. The data from such tests can be used in designing or modifying processing plants. It should be stressed that such tests should simulate industrial processes as closely as possible, and be of sufficient scale and duration to provide reliable data for design purposes.

Becker [41] presents a step-by-step approach to make economic comparisons of the use of different phosphate rocks in phosphoric acid production. A case study is presented calculating the equivalent prices for two phosphate rocks differing in grade and impurity contents. In the calculations, consideration is given to processing losses, sulfuric acid consumption, grinding costs, filtration rates, and acid concentration costs. Although some of the losses and sulfuric acid consumption can be based on chemical analyses and realistic assumptions, some of the critical data needed must be obtained by actual testwork. Becker [41] also presents phosphate rock data sheets and guidelines for use which may be helpful in establishing preliminary investment cost estimates for a chosen phosphate rock quality, optimizing plant economics by comparing the economics of a particular rock with other phosphate rocks that might be purchased, and competitive phosphate rock valuation.

5.3.8 World Phosphate Rock Production and Reserves

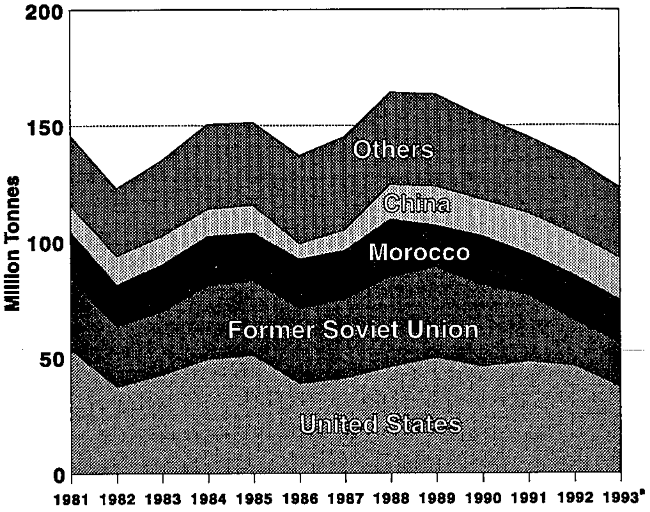
5.3.8.1 World Phosphate Rock Production and Quality – Commercial production of phosphate rock for the production of fertilizers began in the mid-19th century. In 1847, about 500 tonnes of phosphate rock was mined in Suffolk, England [42]. World production increased to 5,000 tonnes in 1850, 10,000 tonnes in 1853, over 100,000 tonnes in 1865, over 1 million tonnes in 1885, over 10 million tonnes in 1928, and over 100 million tonnes in 1974. In the mid-1970s, one estimate indicated that world phosphate rock production would be about 300 million tonnes by the year 2000 [43].

Such estimates proved to be overly optimistic. Figure 5.19 shows world growth in phosphate rock production



Source: [44].

Figure 5.19. World Mine Production of Phosphate Concentrate, 1945-81.



a. Estimated.

Source: Data for 1981-89 compiled from U.S. Bureau of Mines Mineral Commodity Reports, 1983-92, and data for 1990-93 compiled from Mew [46].

Figure 5.20. World Phosphate Rock Production, 1981-93.

between 1945 and 1981 [44]. In 1945 total world concentrate tonnage was just over 10 million tonnes. Growth in phosphate concentrate production seems to have increased linearly to about the mid-1960s, reaching a level of about 50 million tonnes; an abrupt increase in the growth rate then occurred. In the 1980s and into the early 1990s, phosphate rock production growth stagnated (Figure 5.20) and seemed to have leveled off at a world production rate of around 150 million tonnes prior to the breakup of the Soviet Union (1990/91).

World phosphate rock production figures for 1988 are given in Table 5.10. The figures for 1988 were chosen for illustrative purposes because the world phosphate market was relatively stable at this time. Based on 1988 data, four countries – the United States, FSU, Morocco (including Western Sahara), and China – collectively produced about 75% of the world's phosphate rock. The top 12 countries produced about 95% of the world's total phosphate rock.

Trade conflicts in the world phosphate market in 1989 did not prove to deter phosphate rock production, and world production increased slightly to approximately 163 million tonnes, according to the United States Bureau of Mines (USBM) [45]. In 1990 world production fell to about 154 million tonnes. U.S. production decreased about 4 million tonnes. With the advent of significant social changes in the FSU and associated economic disruption, FSU production declined from about 35 million tonnes of phosphate rock in 1990 to about 29 million tonnes in 1991. Overall world production dropped further to approximately 145 million tonnes in 1991 [46]. Due mainly to further decreases in production from the FSU and slightly reduced production in the United States, world phosphate rock production fell to 135 million tonnes in 1992.

Estimates of 1993 world phosphate rock production ranged from 117 million to 131 million tonnes [46, 47, 48]. Although production in the FSU was thought to have stabilized near 19 million tonnes (about half of the pre-1990 levels), production in the United States was down about 9 million tonnes and Morocco decreased production about 1 million tonnes. Final USBM figures for 1993 indicate a total world mine production of 120 million tonnes [47].

Estimates of 1994 world production indicate an approximate increase of 10 million tonnes over 1993 production to 130 million tonnes. For comparison with 1988 data (Table 5.10), one set of world phosphate rock production estimates for 1994 is given in Table 5.11. In this compilation, FSU data have been separated into Russia, Kazakhstan, and other countries, and therefore several producers have changed positions in ranking. While overall world production decreased approximately 32 million tonnes from 1988 to 1994 (about 20%), the top 4 producing countries still produce about

Table 5.10. World Phosphate Rock Production, 1988

	Product (thousand tonnes)	World Total (%
United States	45,389	28.0
Former Soviet Union	34,400	21.2
Morocco and Western Sahara	25,015	15.4
China	16,600	10.2
Subtotal Top Four	**121,404**	**74.8**
Jordan	6,611	4.1
Tunisia	6,103	3.7
Brazil	4,672	2.9
Israel	3,479	2.1
Togo	3,464	2.1
Republic of South Africa	2,850	1.7
Syria	2,342	1.4
Senegal	2,326	1.4
Subtotal Top Twelve	**153,251**	**94.6**
Nauru	1,540	0.8
Algeria	1,332	0.8
Iraq	1,273	0.8
Egypt	1,146	0.7
Mexico	835	0.7
India	739	0.4
Finland	584	0.3
North Korea	500	0.3
Vietnam	330	0.2
Sweden	142	0.1
Zimbabwe	125	0.1
Turkey	74	<0.1
Colombia	35	<0.1
Pakistan	35	<0.1
Sri Lanka	23	<0.1
Tanzania	15	<0.1
Australia	13	<0.1
Peru	13	<0.1
Mali	10	<0.1
Chile	9	<0.1
Thailand	8	<0.1
Philippines	8	<0.1
Indonesia	1	<0.1
Venezuela[a]	-	-
World Total	**162,041**	**100.0**[b]

a. No Venezuela production reported for 1988; 99,000 tonnes reported for 1987; and 237,000 tonnes reported for 1989.

b. Totals may not add to 100% due to rounding.

Source: [49].

Table 5.11. **World Phosphate Rock Production, 1994**[a]

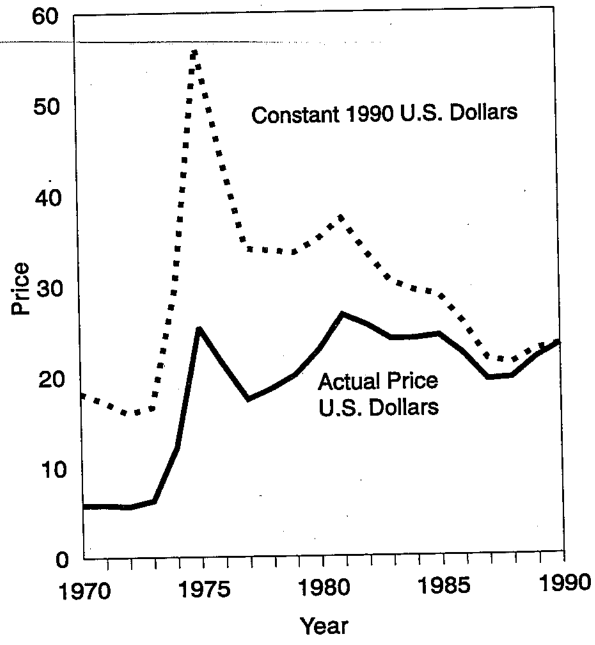
	Product (thousand tonnes)	World Total (%)
United States	41,000	31.7
China	24,000	18.5
Morocco and Western Sahara	19,500	15.1
Russia	8,500	6.6
Subtotal Top Four	**93,000**	**71.9**
Tunisia	6,200	4.8
Jordan	4,500	3.5
Kazakhstan	4,000	3.1
Israel	3,600	2.8
Brazil[b]	3,500	2.7
Republic of South Africa	3,000	2.3
Senegal	2,000	1.5
Togo	2,000	1.5
Subtotal Top Twelve	**121,800**	**94.2**
All Others[c]	7,500	5.8
World Total	**129,300**	**100**

a. Estimated data mainly from USBM [47].
b. Data from Barboza, et al. [50].
c. USBM data corrected using Brazil data.

72% of the world's phosphate rock and the top 12 producing countries account for 94% of total production.

Phosphate rock is a relatively low-cost bulk commodity. The average cost of phosphate rock in the United States was $22.00/tonne in 1994. For comparative purposes, the average cost of rock salt in the United States in the same year was $20/tonne and the average cost of raw peat was $26/tonne [47]. Over the past 15-20 years since the phosphate rock shortage of 1975, the price of U.S. phosphate rock in constant dollars has steadily declined, with only minor recovery in 1980 and 1981 and in the early 1990s (Figure 5.21). In general, world phosphate rock prices have behaved similarly to U.S. phosphate rock prices. In 1993 world phosphate rock prices dropped to 20-year lows [46,52].

World phosphate rock production capacity has been estimated as 195.5 million tpy [49]. At 150 million tpy, world capacity utilization is about 77%. At 130 million tpy, world capacity utilization is about 66%. Perhaps most significant in this scenario are the production capacities of the two primary players in the export market: the United States (55 million tpy) and Morocco and Western Sahara (32 million tpy). Competition, together with the overcapacity of the major players and of the world as a whole, is one of the prime reasons that world phosphate rock prices have not increased over the past 15-20 years.



(Average annual U.S. producer domestic and export price, f.o.b. mine.)

Source: [51].

Figure 5.21. Time-Price Relationships for Phosphate Rock.

It has been widely suggested for many years that, in general, there has been a continuous decrease in world phosphate rock quality as reserves of high-quality rock are being depleted [14,53]. Perhaps it would be more appropriate to say that high-grade concentrates from some sources are becoming depleted (principally Florida) and, in general, the quality of phosphate rock that was utilized on a worldwide basis was lower as demand for phosphate rock grew.

Table 5.12 shows a breakdown of world phosphate rock production by grade as percentages of total production from 1971 to 1993. This is a partial breakdown of world production in that this table and the following tables (Tables 5.13 and 5.14) do not include data from the FSU or other countries with centrally planned economies. During this time period, a vast amount of growth occurred in the world phosphate rock and fertilizer industry, and most of the increased demand was satisfied by increased production of lower grade (-68 BPL) phosphate rock.

Table 5.12. World Production of Phosphate Rock by Grade, 1971 to 1993[a]

Time Period	Grade (BPL) -68	69-72	73-77	78+
	(% of total production)			
1991-93	48.5	29.9	10.3	11.2
1986-90	43.7	33.4	11.4	11.5
1981-85	45.4	31.5	12.8	10.2
1976-80	38.1	36.7	12.6	12.6
1971-75	28.8	24.0	31.9	15.2

a. Does not include data from former Soviet Union or other centrally planned economy countries.

Source: IFDC unpublished data.

Table 5.13. U.S. Production of Phosphate Rock by Grade, 1971 to 1993[a]

Time Period	Grade (BPL) -68	69-72	73-77	78+
	(% of total production)			
1991-93	71.4	22.1	6.4	
1986-90	62.4	28.1	9.4	
1981-85	59.5	28.4	12.1	
1976-80	56.6	32.8	10.6	
1971-75	55.7	23.7	20.5	0.4

a. Does not include data from Former Soviet Union or other centrally planned economy countries.

Source: IFDC unpublished data.

Table 5.14. World Production of Phosphate Rock by Grade, Non-U.S. Producers, 1976 to 1993[a]

Time Period	Grade (BPL) -68	69-72	73-77	78+
	(% of total production)			
1991-93	28.5	36.6	13.7	21.0
1986-90	29.4	37.6	13.0	20.0
1981-85	33.2	34.2	13.4	19.2
1976-80	18.6	40.8	14.7	25.8

a. Does not include data from former Soviet Union or other centrally planned economy countries.

Source: IFDC unpublished data.

These world production data are highly influenced by the data from U.S. producers. Table 5.13 shows U.S. production of phosphate rock by grade as percentages of total production for the period from 1971 to 1993. Increased demand was largely met by increased production of lower grade rock (-68 BPL) which could be mined and processed profitably. As a percentage of total production, the production of the highest grade phosphate rock typically produced in Florida (73-77 BPL) steadily decreased.

When U.S. production is subtracted from world production figures (Table 5.14), a different picture of world production is obtained. Table 5.14 shows that, between the periods of 1976-80 and 1981-85, production of -68 BPL phosphate rock by non-U.S. producers significantly increased (about 78%); however, since 1985, the percentage of -68 BPL phosphate rock has steadily decreased. The relative amount of 69-72 BPL phosphate rock produced dropped significantly between the periods of 1976-80 and 1981-85 and then has increased and perhaps has stabilized at about 37%-38% of total production. Although a drop in percentage of total production for the higher grades (73-77 BPL and 78+BPL) occurred between the time periods of 1976-80 and 1981-85, the production of these grades has slightly increased or is stable.

High-grade phosphate rock is available from many sedimentary and igneous sources (Togo, Senegal, Morocco, and South Africa, to name a few). However, premium rocks from these sources are available at premium prices. Because of the increase in demand and availability of lower cost, lower quality phosphate rock, phosphate fertilizer process engineers have modified their technology and are exploring new technologies to cope with lower grade rocks containing higher levels of impurities.

5.3.8.2 World Phosphate Rock Reserves and Resources – There is no system accepted worldwide for classifying phosphate rock reserves and resources. In the best cases, facts and figures used to compile world phosphate rock reserve and resource estimates are derived from deposit-specific reports and generally available scientific papers. The phosphate industry is a highly competitive industry, and many producers consider the status of their production and phosphate rock reserves a trade secret. Thus, documentation concerning many deposits is simply not available. In many cases, reserve estimates are obtained by word of mouth and only in general terms. The reliability of information obtained in this manner is highly variable. For most phosphate deposits, there is generally a lack of information concerning the extent of exploration and various criteria used to determine the economics of production or the potential for economic development. As a result of these factors, world phosphate reserve and resource estimates developed by various authors are highly variable. Most authors do attempt to distinguish between phosphate reserves and resources.

Reserves are defined as "identified resources of mineral or fuel-bearing rock from which the mineral or fuel can be extracted profitably with existing technology and under present economic conditions" [54]. The use of the term "reserves" usually indicates that enough exploration or development work has been done to define the extent and grade of a deposit with a reasonable degree of accuracy. It also indicates that the deposit could be mined and processed to recover a marketable product at the time of the study or under a specified economic scenario. Reserves may be further classified as proven, probable, or possible and as indicated or inferred, depending upon the degree of exploration activities. Reserves may also be classified as economic, marginal, or subeconomic, depending on the estimated cost of exploitation and current and projected market values. This terminology and this type of highly detailed reserve/resource classification system have been developed by the USBM and the U.S. Geological Survey (USGS) [55,56]. Many international authors may use this terminology; however, adherence to the definitions for certain terms can be highly variable.

Reserve estimates may be stated in terms of the total amount of ore and percentage of P_2O_5, or the estimates may be stated as the amount and grade of recoverable product. Estimates of the amount of product potentially available from a deposit require extensive detailed information. When this detailed information is not available, assumptions must be made concerning the amount of the original P_2O_5 that can be recovered in the product and the eventual grade of the product.

Resources are defined as "reserves plus all other mineral deposits that may eventually become available – either known deposits that are not economically or technologically recoverable at present, or unknown deposits, rich or lean, that may be inferred to exist but have not yet been discovered" [54]. Use of the term "resources" implies that the extent and quality of a phosphate deposit cannot be definitively estimated because of insufficient information. The term "resources" also implies that the deposit cannot be economically exploited under current conditions.

Most reserve/resource estimates are subjective; they depend on the standards assumed by the author or his organization in determining the circumstances that may render a deposit economically useful. For example, one estimate [56] indicates there are several hundred million tonnes of phosphatic limestone (16%-20% P_2O_5) in the United States. The authors do not include these figures in their estimates for the total "identified recoverable resources" of the United States, apparently because these phosphatic limestones cannot be processed using current technology and the United States presently has vast amounts of recoverable rock. Similar deposits in phosphate resource-poor countries might be listed as resources and possibly even as "reserves," depending on the author's perception of the term "reserves."

This section relies heavily on several data sources. Substantial differences in reserve and/or resource estimates and other data may exist between various sources. It is not the purpose of this paper to critique these sources; however, it is prudent to point out that these discrepancies exist and that all such quoted figures should be considered as order of magnitude estimates.

Phosphate deposits are widespread throughout the world, occurring on all continents with the possible exception of Antarctica. Figure 5.22 includes only those deposits that are currently worked, have been worked in the past, or have been shown in detailed studies to be potentially economically viable under certain conditions. The figure includes several very small deposits that are worked for direct-application phosphate rock. The figure does not include every occurrence that might be termed a deposit. By definition, a deposit is "earth material of any type either consolidated or unconsolidated that has accumulated by some natural process or agent" [57]. The term "deposit" does not imply that phosphate exists in a form, quantity, or quality that is technically or economically feasible to produce. The average

Figure 5.22. Economic and Potentially Economic Phosphate Deposits of the World.

abundance of P_2O_5 in the earth's crust is 0.22 weight % [58]; a concentration of 1.0 weight % P_2O_5 is certainly anomalous and therefore can be termed a deposit.

Tables 5.15, 5.16, and 5.17 illustrate three sources of world phosphate reserve and resource data. Estimates are provided by country in Tables 5.15 and 5.16 and by continent and country in Table 5.17. Table 5.18 provides estimates for sites in the United States by cost per tonne.

The source of the data for Table 5.15 is the USBM [47]; the table lists the top 10 producing countries, their reserves, and their reserve base. In this context, reserve base can be considered synonymous with the term resources. No reserve data are listed for Russia, Senegal, Togo, or Tunisia in this compilation. These countries are mining, processing, and/or exporting phosphate concentrates and will do so for many years. Even without the reserve data for these countries, it is evident that 6 of the top 10 producing countries possess about 88% of the world's phosphate reserves. The reserve base data, which include data from all top 10 producing countries, indicate that about 91% of all the phosphate resources of the world are found within these countries.

A slightly different set of figures is given in Table 5.16. Williams and Griffin [59] used the USBM data for 1989 with some revisions. In this compilation, no data on reserves were available for Israel. Under this compilation, approximately 95% of the world's economic reserves were held by the world's present top nine producers in 1990. Williams and Griffin [59] also computed the present life of reserves based on current production rates for these countries. Based on the present extraction rates and economic conditions in 1990, over half of the top 10 phosphate-producing countries will have exceeded the life of their reserves in less than 50 years. Under this scenario, the reserves of both the United States and the former Soviet Union will be depleted in about 30 years (assuming late 1980s' production rates).

Herring and Fantel [61] modeled depletion of world phosphate rock reserves based on demand created by population growth. Using USBM world reserve data and a base year of 1990, they considered various scenarios of unconstrained growth with no future additions to reserves. The results of this study generally indicate that world reserves will be depleted in about 50 years from 1990, the base year, and additional resources (termed a

Table 5.15. World Phosphate Rock Reserves and Reserve Base

Country	Reserves[a]	Reserve Base[b]
	(thousand tonnes)	(thousand tonnes)
United States	1,200,000	4,440,000
China	210,000	210,000
Israel	180,000	180,000
Jordan	90,000	570,000
Morocco and Western Sahara	5,900,000	21,440,000
Senegal	-	160,000
South Africa	2,500,000	2,500,000
Togo	-	60,000
Tunisia	-	270,000
Russia	-	1,000,000
Other countries	1,300,000	3,000,000
World Total	**11,380,000**	**33,830,000**

a. Cost less than $40/tonne. Cost includes capital, operating expenses, taxes, royalties, and a 15% return on investment f.o.b. mine.

b. Criteria for reserve base established by a joint U.S. Bureau of Mines and U.S. Geological Survey working group.

Source: [47].

Table 5.16. World Phosphate Rock Reserves and Resources (thousand tonnes)

Country	Economic Reserves[a]	Life (years)	Resources
United States	1,300,000	27	5,200,000
Former Soviet Union	1,300,000	33	1,300,000
Morocco and Western Sahara	7,000,000	318	22,000,000
China	210,000	12	210,000
Jordan	600,000	100	700,000
Tunisia	267,000	41	533,000
Israel	-	-	190,000
Togo	40,000	12	70,000
South Africa	2,500,000	960	2,500,000
Senegal	160,000	73	160,000
Others[b]	725,000	-	3,725,000
Total	**14,102,000**		**36,588,000**

a. Producible at <$35/tonne, including 15% rate of return on investment.

b. Revised to include centrally planned economies and market economy countries.

Source: [59].

Table 5.17. World Economic Identified Phosphate Concentrate Resources

Continent and Country	Reserves (million tonnes)	Inferred Reserve Base and Reserve Base (million tonnes)
North America		
United States	1,260	22,587
Canada	37	37
Mexico	208	2,416
South America		
Brazil	551	558
Peru	428	1,353
Other	120	211
Africa		
Algeria	250	435
Morocco and Western Sahara	2,100	62,575
Senegal	155	200
South Africa	1,800	6,781
Tunisia	70	1,021
Other	82	1,216
Asia		
China	170	1,000
Iraq	296	296
Israel	70	449
Jordan	530	1,542
Other	241	807
Oceania		
Australia	340	850
Other	51	51
Europe		
Former Soviet Union	6,500	8,000
Finland	-	46
World Total	**15,259**	**112,431**

Source: [60].

Table 5.18. U.S. Phosphate Rock Reserve Base in Terms of Cost[a]

	Cost (1989, $/tonne)						
	<20	20-30	30-40	40-60	60-80	80-100	Total
	(million tonnes)						
Florida	224	263	258	1,101	520	173	2,539
North Carolina		392		339			731
Western United States		73	14	70	762	177	1,096
Tennessee	2	3		8			13
Total	**226**	**731**	**272**	**1,518**	**1,282**	**350**	**4,379**

a. Tonnes available at indicated cost.

Source: [51].

modified reserve base), which may or may not be economically minable, would be depleted in perhaps another 50 years.

The United States and other countries will not, however, simply run out of phosphate rock at some predetermined date in the future. Table 5.18 indicates the amount of phosphate reserves available from various mining areas in the United States in terms of cost per tonne. Most of the current reserve figures assume a maximum cost of $40/tonne for estimates. If the cost of phosphate rock reaches $60/tonne, the U.S. reserve base more than doubles to 2.8 x 10^9 tonnes. These types of detailed data are not available for most other world producers although Fantel, Peterson, and Stowasser [62] have estimated the amounts of potentially recoverable phosphate rock at various production costs from all deposits in market economy countries, the United States, North Africa, and the Middle East. It is reasonable to assume that a similar situation governs the reserve/resource situation in other countries around the world. If phosphate rock prices eventually rise worldwide, a portion of the phosphate rock now classified as resources in many countries will be reclassified as reserves.

Sheldon [60] categorized phosphate concentrate reserves and resources by continents and regions (Table 5.17). According to this scheme, it may appear at first glance that each major continent/region has ample reserves of phosphate rock concentrates with the possible exception of Oceania (391 million tonnes); each of the other categories has over 1 x 10^9 tonnes. However, within a region, the total reserves may be dominated by the reserves of a few countries, or even one country. According to Sheldon [60], the United States holds approximately 84% of the reserves of North America. The former Soviet Union holds all of the reserves of Europe. In this scenario, the phosphate reserves of Finland are probably considered uneconomic by world standards. The phosphate rock mine in Finland is integrated with downstream processing facilities for the production of several marketable products with added value; it would probably not be economically viable to produce phosphate rock concentrates as the only product.

According to Sheldon's figures, Morocco and South Africa possess about 87% of African phosphate reserves. It should be noted that these countries plus Algeria, Senegal, and Tunisia possess over 98% of the African total of concentrate resources. Togo, currently the world's ninth or tenth leading producer, is among the remaining countries holding 2% of the reserves in Africa. Other countries in Africa hold 1.2 x 10^9 tonnes of inferred reserves (resources) or less than 2% of the total African resources. Significantly, with the exception of phosphate producers in West Africa as well as in South Africa and perhaps Zimbabwe, most of the deposits of sub-Saharan Africa are termed resources and are not commercially viable or are considered uneconomic to exploit at the present time.

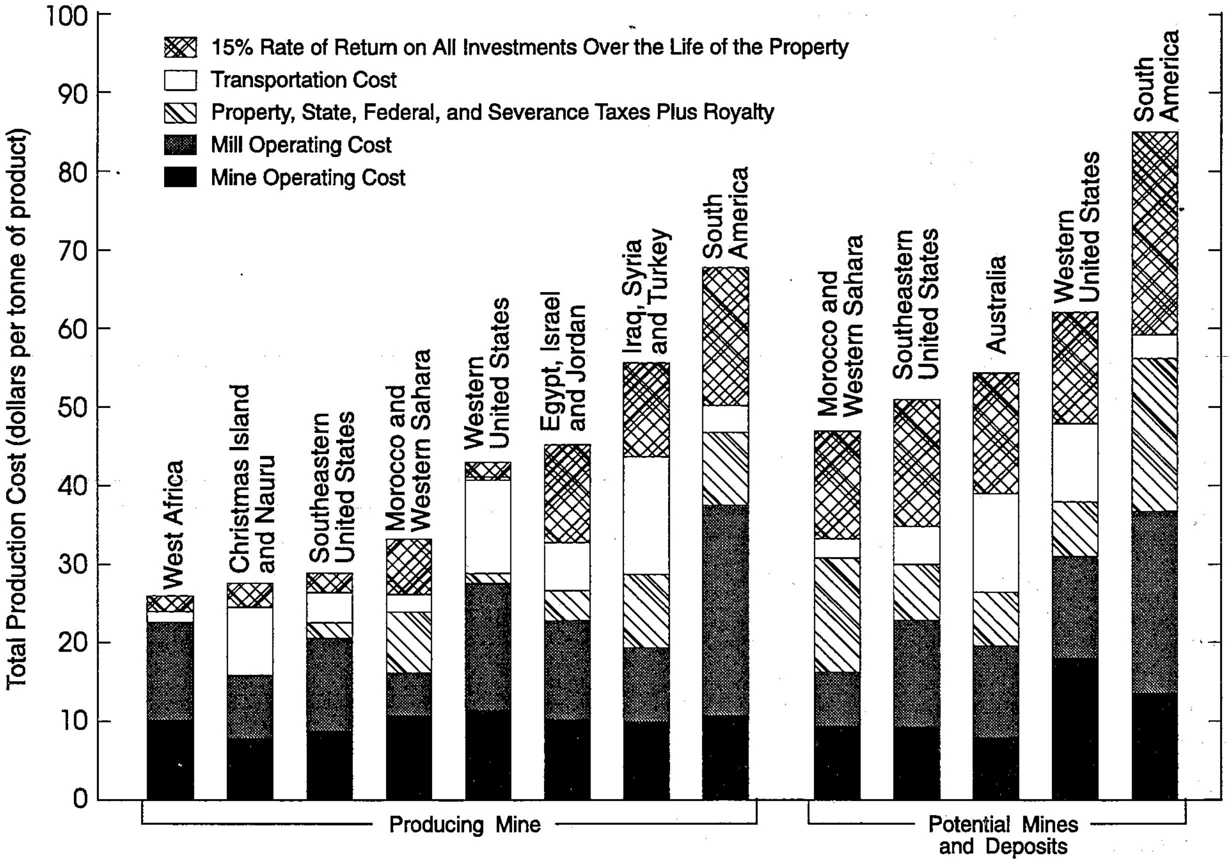
The reserves of South America are dominated by Brazil and Peru. Although total South American resources may seem substantial (1.1 x 10^9 tonnes), other countries hold only about 12.0% of this total. The Peru deposit (Sechura) has not yet been developed commercially. Production costs for the mines in Brazil appear to be very high (Figure 5.23), and production costs from any other new mines in South America are likely to be high.

In Sheldon's scenario, the Asian reserves are distorted by countries that might be more properly termed Middle Eastern countries and that are aligned for all practical purposes with North African producers. Of Asia's total reserves (1.3 x 10^9 tonnes), 68% may be ascribed to Iraq, Israel, and Jordan. The "other" reserves category for Asia may also include other Middle Eastern countries. China is the one distinctly Asian country in this category, and its reserves are rather limited (170 million tonnes).

The Oceania reserve figures are dominated by Australia with approximately 87% of the total reserves (340 million tonnes). The Australian deposits have not been developed commercially. Among the other deposits are Nauru and Christmas Island. These insular deposits have contributed significantly to regional trade in the past and, although both are presently being worked, their economic reserves are very small (perhaps 10-20 million tonnes total).

5.3.8.3 Future Trends in World Phosphate Rock Production – One phosphate rock production forecast for the present top four world producers, formulated prior to the political events in the former Soviet Union and world downturn in phosphate production in 1991, is given in Table 5.19. Under this scenario, the United States, former Soviet Union, and China basically would maintain their production in a market that is assumed to grow at an annual average of 1.8% to the year 2000 [59]. Morocco would increase production and its market share during this period. During this time period, Morocco would become the dominant world exporter in terms of both rock and chemical products (Table 5.20). Jordan would also increase its production during this period. China and the former Soviet Union do not appear in Table 5.20 because they were not foreseen to become significant phosphate exporters.

Prior to the situation of the late 1980s and early 1990s, World Bank estimates indicated that the stagnant phosphate rock market of the 1980s would continue until the end of the century [63]. By the year 2000, European imports may decline by 3-4 million tonnes,



Source: [62].

Figure 5.23. Estimated Production Costs for Selected World Phosphate Surface Mines and Deposits.

Table 5.19. Phosphate Rock Production Forecast for Current Top Four Producing Countries

	1990	1995	2000
	----- (million tonnes) ----		
United States	48	50	48
Former Soviet Union	39	39	41
Morocco	23	34.5	40
China	17	18	19

Source: [59].

whereas Asian imports may increase by 2-3 million tonnes; overall there may be a decrease in total production. One source [64] indicated that the need for capital investment in new mines is expected to keep phosphate rock prices slowly increasing in the early 1990s. If investments in new mines are not forthcoming, depletion of reserves will cause a tight market in the mid-1990s and prices may rise sharply.

Beyond the year 2000, production from the southeastern United States was predicted by Stowasser [51, 65] to fall sharply to about 31.2 million tonnes between the years 2000 and 2005 and to about 24.5 million tonnes by the year 2015 (Table 5.21). A projection to

Table 5.20. Major Phosphate Exporters

Country	1990			1995			2000		
	Rock	Products[a]	Total	Rock	Products[a]	Total	Rock	Products[a]	Total
	(million tonnes equivalent phosphate rock)			(million tonnes equivalent phosphate rock)			(million tonnes equivalent phosphate rock)		
Morocco	14.8	8.2	23.0	14.8	16.2	31.0	15.8	22.2	38.0
United States[b]	8.0	17.7	25.7	7.5	19.5	27.0	7.0	18.0	25.0
Jordan	5.0	0.9	5.9	5.0	2.0	7.0	5.0	3.9	10.0
Tunisia	1.0	3.5	4.5	1.0	3.4	4.4	1.0	3.4	6.0
Togo	3.4	0	3.4	3.4	0	3.4	3.0	0	3.0
Israel	2.4	1.2	3.6	1.0	1.1	3.5	2.4	1.1	3.5
South Africa	1.0	1.3	2.3	1.0	1.3	2.3	1.4	1.3	3.0
Senegal	1.5	0.5	2.0	1.5	0.6	2.1	1.5	1.5	3.5

a. Values refer to amount of rock used for chemically processed products.

b. Domestic use in the United States will be about 22-23 million tonnes in the 1990s.

Source: [59].

the year 2040 indicated that total U.S. phosphate rock production may be as low as 17.4 million tonnes [51]. Several factors probably contributed to these analyses. Only two new phosphate rock mines were in the planning stage at the time of these projections. The Florida rock reserves of higher grade and quality are becoming depleted. Mining in Florida is competing with other land use options; minable lands may be worth more as residential or commercial property. Environmental concerns may also exclude tracts and/or entire mining areas from future consideration. Although additional rock is available from lands peripheral to the traditional central Florida phosphate district (mainly to the south), overburden may be thicker and the ore grades are lower. Phosphate concentrates produced from these lands will generally be of lower grade with higher impurity contents. Because of these factors and ever-increasing and more stringent environmental regulations, the costs of mining and processing in Florida and the rest of the United States will continue to increase, especially if new mines are developed. Based on Stowasser's analyses [51, 65], U.S. production eventually may not be able to meet U.S. agrochemical industry demands.

Not all U.S. producers will be affected similarly by the depleting reserve situation and declines in rock quality, and the effect may not be as dramatic as predicted by Stowasser [51,65]. IMC-Agrico is the largest U.S. producer. IMC-Agrico operates 10 mines in Florida and five phosphate fertilizer facilities in the United States. The total capacity of IMC-Agrico mines is 28.2 million tpy [48] or approximately half of total U.S. production capacity. Prior to and during the last 10 years, as the Florida phosphate rock industry has undergone considerable rationalization, IMC-Agrico (or precursor companies) has acquired mining lands, often through the acquisition of preexisting mining operations. IMC-Agrico has quoted its estimated recoverable reserves as 336 million tonnes of concentrate or about 17 years of production at the 1992 production rate (about 20 million tpy) [48]. The

Table 5.21. Projected U.S. Phosphate Rock Concentrate Production

	1995	2000	2005	2010	2015
	(million tonnes)				
Florida and North Carolina	39.2	48.1	31.2	24.5	24.5
Western United States	6.8	5.8	5.8	5.8	5.8
Total United States	**46.0**	**53.9**	**37.0**	**30.3**	**30.3**

Source: [65].

company has proven probable reserves of 484 million tonnes, of which 262 million tonnes is available under option arrangements. Although IMC-Agrico has substantial reserves for the future, the reserves of most Florida producers are much more severely limited. However, several new mines are currently being opened or are in the permitting process (Cargill – formerly Mobil Mining and Minerals Company, South Fort Mead, 3.2 million tpy; C. F. Industries, South Pasture, 2.7 million tpy), and the lives of these operations are projected to be between 30-40 years.

Potash Corporation of Saskatchewan Phosphates or PCS Phosphates (formerly Texasgulf Inc.) operates the Lee Creek Mine at Aurora, North Carolina. The present capacity of the mine is 5.4 million tpy. The company has plans to double its capacity if and when the market for phosphate rock and phosphate products improves. The company has indicated that it has reserves for the next 200 years at current production rates [48].

Several mines are operating in the western United States with an approximate combined capacity of about 7 million tpy [48]. Several new mines have recently been opened in this area including the Rasmussen Ridge Mine (1993, Rhône Poulenc, capacity 2.3 million tpy), Smoky Canyon Mine (1992, J. R. Simplot, 1.4 million tpy), and the FMC Mine at Dry Valley (1993, 1.36 million tpy). SF Phosphates, a joint venture between J. R. Simplot and Farmland Industries, operates a mine at Vernal, Utah. This mine has a capacity of 1.81 million tpy and an estimated life of 50 years at current production rates (about half capacity). Although these western producers will not affect the world market, they will supply a portion of the U.S. and Canadian phosphate requirement for many years.

The data from individual producers indicate that the analyses of Stowasser [51,65] were perhaps too pessimistic. On the basis of data from IMC-Agrico, the development of new mines by Cargill and C. F. Industries, the capacity of the PCS Phosphates operation, and the contributions of western producers, and assuming these estimates are correct, the United States should be able to maintain a production capacity of 45-50 million tpy for the next 10-15 years or until the time period of 2005 to 2010. If demand is sufficient and/or the price of phosphate rock increases, it is also possible that additional new mines could be developed in Florida and the western United States and/or that PCS Phosphates could increase production. It is also possible that new mining techniques such as borehole mining might be used to produce deposits that presently are not economically recoverable.

Although the grade and quality of Florida concentrates are declining and are foreseen to continue to decline in the future, the Florida phosphate industry has learned to cope with lower grade ores and concentrates. The Florida phosphate rock industry has significant vertical integration, and fertilizer producers are taking advantage of highly developed infrastructure and favorable raw materials and energy costs. At present only about 3 million tpy of total U.S. production (mostly from Florida) is exported as phosphate rock. Fertilizer producers in the United States have learned to use concentrates with grades as low as 60-65 BPL.

China is not foreseen to become a significant factor with respect to phosphate exports in the future. China is presently a net importer of phosphate products. Reserves of phosphate rock in China, although widespread, are very limited according to USBM sources [47]. The quality of the phosphate rock from these deposits is low by world standards. Chinese phosphate rocks may contain high levels of MgO, CO_2, and/or silicate impurities, and the concentrates produced from these deposits are not generally suitable for export. China's status as a net importer is not expected to change.

The future production status of the countries constituting the former Soviet Union is speculative. The grade of ores from the Kola deposits has progressively declined. As near-surface reserves have been depleted, the cost of production has increased [64]. Extensive exploration in the former Soviet Union has resulted in few significant discoveries to support declining output from the Kola deposits. The sedimentary deposits of the former Soviet Union are generally of low grade and quality when compared with concentrates available on the world market.

The Kola deposits, operated by P.O. Apatit, formed the core of FSU phosphate rock and fertilizer production capabilities. In 1989, P.O. Apatit produced about 20 million tonnes of phosphate rock [66]. The P.O. Apatit production estimate for 1993 was about 8.5 million tonnes. Due to the drop in demand and to rationalization and privatization, mines and several processing plants have been closed. The downturn of the Kola industry (and Russian economy) is also intimately intertwined with FSU sedimentary phosphate rock production and the fertilizer industry based on this rock. The production of many fertilizer plants in the FSU used high-quality phosphoric acid feedstock produced from Kola apatite and locally obtained lower grade sedimentary phosphate rock to produce off-grade TSP products.

Prior to the breakup of the Soviet Union, about 3 million tpy of Kola rock was exported, mostly to eastern Europe. Export sales had fallen to about 800,000 tonnes in 1992 and were estimated to be even less in 1993 [66]. Possibly the Kola deposits could be further developed for the world export market. Rationalization of the Russian industry will occur, and it is uncertain at what costs Kola rock can be produced and if it will be competitive on the world market.

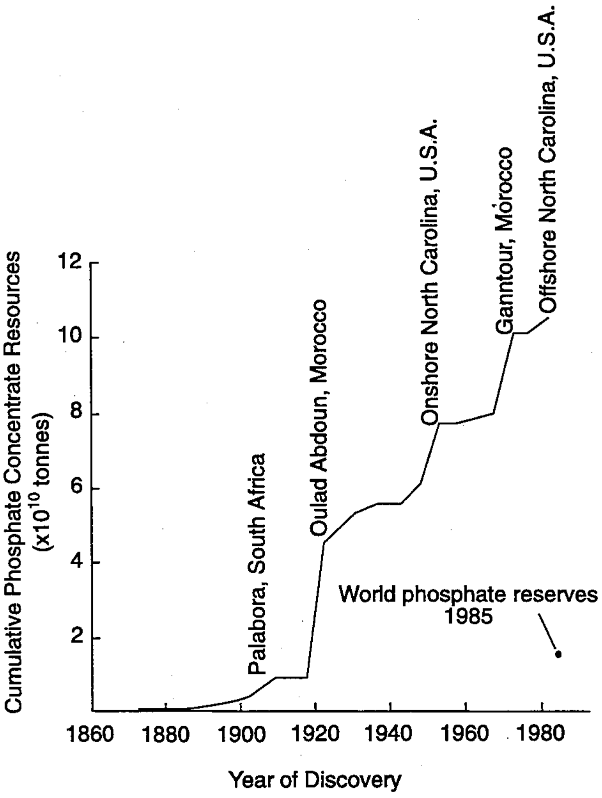
Among the current top four phosphate rock producing countries, Morocco is certainly in the most advantageous position. Depending exactly on which reserve/resource classification is used, Morocco may possess over one-half of the world's phosphate rock reserves. Morocco has invested heavily in the mining and downstream phosphate processing industry and has tremendous potential to expand both mining and processing activities. As in Florida, lower grade phosphate rock concentrates are used for production of added-value products and higher grade phosphate rock is generally destined for the export market. Moroccan processing costs will increase in the future. However, production costs for new mines should eventually be less than production costs of new mines in the southeastern United States (Figure 5.23).

In the future, potential increased production of phosphate rock may also come from Jordan, Iraq, or South Africa. Production from Jordan is expected to reach about 9 million tonnes by the year 2000. Production at current or declining levels is expected from Tunisia, Togo, Algeria, Israel, Senegal, Syria, Brazil, and Nauru. Mine-out on Nauru is expected in the next 5-10 years, depending on the production rate. The Togo deposit will probably be mined out in less than 20 years, depending on the production rate and whether a new mining area (Dagbati) is opened.

Potentially increased phosphate rock production could come from several new mines, including Sechura, Peru; Al-Jalamid, Saudi Arabia; Bofal-Loubboira, Mauritania; Farim, Guinea-Bissau; Sra Ouertane, Tunisia; and Duchess, Australia, to name several. Studies performed on these deposits indicate they are marginally economic or may be economic under certain conditions.

There is also the potential to discover new deposits. Phosphate deposits have been discovered within the past 100 years at a rate far greater than the rate of consumption (Figure 5.24) [60]. It is expected that new deposits will be discovered in the future. However, oil exploration programs have probed most of the coastal sedimentary basins of the world during the past 20-30 years, and any large-scale discoveries of phosphate rock probably would have occurred in conjunction with these activities.

Another source of future phosphate production is offshore deposits. Deposits of this type occur along the southeastern coast of the United States, on the Peru-Chile shelf, offshore Namibia, on the Chatham Rise off New Zealand, offshore Baja California, Mexico, and off the Congo River delta. At the present time, none of these offshore deposits are mined, and they probably will not be mined as long as ample reserves exist onshore.



Source: [60].

Figure 5.24. History of the Discovery of World Phosphate Resources.

Phosphate rock prices will increase when demand approaches the limits of supply. When phosphate rock prices increase, some resources become reserves, marginal mining projects become viable, and production is stimulated. In the future, fuel and fuel-related transportation costs may become even more important components in the world phosphate rock production scenario. Political disruptions, always an unknown factor, can profoundly influence the supply and demand for fertilizer raw materials on a worldwide basis.

5.3.9 Factors That Influence Economic and Commercial Viability of Producing Phosphate Deposits

For every phosphate deposit there is a combination of factors that define whether production is both technically and economically feasible. No one factor is absolute, and phosphate deposits differ so much in their geologic character and processing characteristics that largely parallel conditions rarely, if ever, exist. Mining cannot be considered as a single factor in itself because it is technically and economically linked to beneficiation and transportation. Ultimately the costs of transportation to a site from where the phosphate concentrate can be distributed, or to where fertilizers are produced, may be the most significant factor in determining if mining and producing a phosphate deposit are economically feasible.

Some of the major factors that affect the viability of producing phosphate deposits include the size of the market for product and production level, location, availability of water, costs of transporting both products to market and needed inputs to the mine site, geologic character, ore to waste ratios, mining method or methods, ore grade and quality, ratio of concentration, potential seasonality of operations due to climatic conditions, cost of infrastructure (living facilities, transportation, power), costs of raw materials (fuel, reagents, etc.), availability and cost of labor, stability and effectiveness of raw material supply systems, stability of governments and political issues, environmental issues, and the availability and cost of capital. This list is presented in no particular order and is not intended to be all-inclusive. However, any of these factors, and other factors, can change a phosphate deposit from an economic reserve to an uneconomic resource. Each of these factors can substantially influence the cost of production.

The difference between production costs over the life of the project and the price of phosphate rock determines what profit may be realized by developing a deposit. The selling price of phosphate rock is determined by the characteristics of the product, the price that customers will pay, the profit margin a producer is willing to accept, and other factors associated with a competitive free market. On a worldwide basis, this situation is confused by the fact that many phosphate producers are government owned and/or governments may subsidize and promote the use of phosphate fertilizers. Producers with the lowest costs should be able to offer products at the lowest selling price. Of course, grade and quality factors must be considered in the selling price.

It is very difficult to determine current production costs for phosphate rock mining. Production costs are generally withheld by producers due to the competitive nature of the global phosphate rock industry. There are few data in the generally available literature concerning direct mining costs for specific operations. It is also often very difficult to differentiate the costs associated with the operating costs of the mine and mill, debt servicing, various taxes and royalties, and profits.

In general, surface mining costs are much lower than the costs of mining underground. Limited data in McClellan and Hignett [67] indicate that the cost of underground mining may be about 2-3 times the cost of surface operations.

Figure 5.23 gives an indication of the relative overall costs of production and a comparative ranking among the producers listed. Figure 5.23 was based on data and cost estimates developed prior to 1985. These data and indicated cost levels may still be appropriate in 1996 as most of the same producers are operating under similar conditions. In 1985 phosphate mine operating costs were about $10/tonne for the lowest cost producers to nearly $20/tonne for the highest cost producers. Mine plus mill operating costs ranged from about $15/tonne to over $30/tonne for the highest cost producers. Taxes and royalties, transportation costs, and a significant return on investment over the life of a property further increase production costs.

Limited data indicate that the total production costs for all Florida mines in 1995 was about $17/short ton ($18.74/tonne) of concentrate. During 1995, average prices for all grades of phosphate rock f.o.b. central Florida were $22-$24/short ton ($24.25-$26.45/tonne). In 1995 Florida phosphate rock shipped f.o.b. from Tampa cost $32-$34/short ton ($35.27-$40.78/tonne) for 68-BPL rock and $36-$38/short ton ($39.68-$41.89/tonne) for 72-BPL rock.

In mid-1995 various grades of phosphate rocks were available from North Africa producers at prices from $30 to $37/tonne. Prices of Moroccan phosphate rock are usually quoted FAS (free-along-side), which means customers must pay for loading. Phosphate rock from Jordan sold in the range of $38-$46/tonne, depending on the grade. It can be assumed that, similar to Florida prices, these prices reflect production costs plus a profit.

Quite often it is perceived that small phosphate deposits in developing countries can be mined by small-scale, low-cost, labor-intensive methods to produce low-cost raw material for local fertilizer plants or for use as direct-application phosphate rock products. This may or may not be the case, depending on the situation. Over the course of history, mining and transportation of products have progressively become more mechanized to increase productivity and overcome the limitations imposed by simple manpower. Indeed before the development of steam engines and subsequent advances, draft animals were employed to overcome the strength and endurance limitations imposed by manpower. Phosphate rock is a bulk commodity that is used by the tonne. The mining of a few hundred or thousands of tonnes is a significant undertaking. Phosphate rocks used for direct application typically must be ground in order to enhance their dissolution rates in soils. The grinding of phosphate rock, while one of the most simple processing options available, is the first step in subsequent processing; it requires fabricated equipment, a source of power, and significant amounts of energy. The movement of tonnes of phosphate rock or fertilizer over hundreds or thousands of kilometers and possibly through several handling steps is expensive and energy-intensive.

Many factors may limit the feasibility of developing small phosphate deposits in developing countries. If the apatite of the rock is not a highly reactive variety, it simply may not be agronomically suitable for direct application. A small market for phosphate rock in a country or area limits the potential size of operations and leads to potentially high per unit costs. Often it seems that phosphate deposits are remotely located far from agricultural or industrial areas in developing countries. The costs of transportation to market may be prohibitive. Almost invariably, mining or processing equipment must be imported, and this is costly. In a developing country, a substantial inventory of spare parts and fuel must be maintained. Lack of critical parts can shut down an operation for indefinite periods (sometimes months) until parts are obtained.

If infrastructure (transportation, power, housing, etc.) is lacking, development can be very costly, and it becomes more costly the more remote a location is. Poor roads lead to high maintenance costs for vehicles. If railroads do exist, service may be less than optimal under developing country conditions, and poor service can cripple an operation. Fuel and electrical power costs can be very high in energy-poor countries.

Phosphate rock is only one of the materials needed in the production of phosphate fertilizers. Although the availability of low-cost phosphate rock is certainly advantageous in any phosphate fertilizer production situation, the total costs of providing other needed chemicals (sulfur, sulfuric acid, etc.) and power (electrical, fuels) may more than overshadow the advantage of a low-cost phosphate rock source in a developing country. When all the development costs and production costs are tabulated, the low cost of labor in a developing country may be a minor factor.

Case studies by IFDC of small-scale phosphate rock mining and production in many developing countries have indicated production costs from about US $25/tonne to several hundred dollars per tonne. At the lower costs, almost invariably the mining and production equipment and initial technical expertise were donated. At the higher costs, typically the operations were established and/or subsidized by a host government or aid organization; however, capacity was severely underutilized.

Phosphate rock can often be purchased on the world market from high-volume, low-cost producers and transported to sites in developing countries at lower costs than those incurred for developing a small indigenous deposit. Further, phosphate fertilizers can often be purchased on the world market from high-volume, low-cost producers and transported to developing countries at lower costs per unit of nutrient than can be provided by indigenously produced phosphate rock.

5.4 Sulfur

Sulfur is one of the more common constituents of the earth's crust and can be ranked as the 16th or 17th most abundant element [68]. The mean sulfur content of the rocks forming the crust of the earth is estimated to be about 400 ppmw. Sulfur naturally occurs as elemental sulfur, metal sulfides in coal and mineral ores, sulfates, hydrogen sulfide in natural gas, and complex organic sulfur compounds in crude oil and coal. All of these various forms of sulfur are used as sulfur sources, but the most important sources are elemental sulfur, hydrogen sulfide in natural gas, and iron pyrites.

The uses of sulfur are as varied as its sources, but approximately 80%-85% of the sulfur that is produced is used to manufacture sulfuric acid. Approximately half of this acid is used in fertilizer production, mainly to convert phosphates to water-soluble forms. Sulfur is an important plant nutrient, and elemental or other forms of sulfur are sometimes added or mixed with other fertilizers to correct sulfur deficiencies. Elemental sulfur can also be used in agriculture as a pesticide or fungicide.

5.4.1 Sulfur Sources

Native sulfur or brimstone, sulfur naturally occurring in the elemental form, is found in several geologic environments. During volcanic activity, sulfur may be sublimated directly around volcanic vents. Although sulfur production from volcanic deposits is generally limited, considerable tonnages have been produced in Japan from such deposits.

Native sulfur may be formed from gypsum and anhydrite in evaporite deposits through the movement of saline waters and hydrocarbons and the influence of anaerobic sulfate-reducing bacteria. Major sulfur deposits associated with salt domes such as in the U.S. Gulf Coast and stratified sulfur deposits such as found in Sicily, Poland, and Iraq are thought to have been formed by this process.

Deposits of pyrite (FeS_2) or other iron sulfides are found in many countries. Sulfides are found in a broad spectrum of geologic environments from igneous rocks (both volcanic and intrusive) to sedimentary rocks. Iron sulfide deposits can be extremely important for those countries that do not possess other sulfur sources. The importance of iron sulfides has been diminishing to a certain extent due to high production costs and the move to a global economy. Iron sulfides are mainly used for the direct production of sulfur dioxide and sulfuric acid. The cinder obtained by roasting iron sulfides has been utilized in some cases for iron and steel making [69].

Many of the non-ferrous metals such as copper, lead, zinc, and nickel are obtained from sulfide ores. One of the final stages of the extraction processes for these metals is the separation or removal of sulfur by roasting; sulfur is recovered in the off-gases.

Fossil fuels such as coal, crude oil, and natural gas contain sulfur in low but variable quantities; the amount mainly depends upon the geologic origins of the fuels. In the United States, coals from portions of the eastern, midwestern, and southern states are relatively high in sulfur (2%-4% S), while coals from portions of the eastern states and from the western states may contain less than 1% S. The sulfur content of German lignite is usually 1%-2%. South African coals range in sulfur content from 0.3%-2.8% S [70]. Occasionally, some of the pyrite that occurs in coals can be mechanically separated. However, fine pyrite and the sulfur that is organically bound in the coal are very difficult to remove or cannot be removed. When coal is burned to generate heat, sulfur will escape to the atmosphere as sulfur dioxide if the off-gases are not treated. During the coking of coal, most of the sulfur will be converted to hydrogen sulfide, which has to be removed from the gases. This potential pollutant/byproduct is converted to sulfur dioxide, sulfuric acid, and ammonium sulfate.

Crude oil usually contains between 0.1% and 2.8% sulfur. A few individual crudes contain over 3% S [71]. Sulfur is largely removed during oil processing, resulting in substantial quantities of byproduct hydrogen sulfide and mercaptans.

The composition of natural gas varies widely. Some natural gases may contain almost no sulfur; in others, the hydrogen sulfide content may be extremely high. Gas originating from southwestern France, for instance, contains 15% H_2S, and some of the natural gases from Canada (Alberta and northeast British Colombia) contain about 30% H_2S. Natural gas and crude oils containing substantial amounts of H_2S are termed "sour." In general, sour crude oil and sour natural gas are associated with production from carbonate formations.

Among the naturally occurring sulfate ores, only gypsum has ever been of any importance as a raw material for sulfur production, and only in the direct production of sulfur dioxide for sulfuric acid manufacture. Byproduct calcium sulfate from phosphoric acid production (phosphogypsum) has been used to produce sulfuric acid. Elemental sulfur has never been extracted from sulfates on any significant scale because of high energy costs. Experimental work has been done on both chemical [72] and microbiological [73] methods of reducing gypsum to hydrogen sulfide.

5.4.2 Production Methods

5.4.2.1 Production From Native Sulfur Deposits – Sulfur-containing ores are usually excavated by conventional open-pit or underground mining methods. In the deposits around the Gulf of Mexico that are associated with salt domes, and in one or two other places in the world, elemental sulfur is produced directly from deposits by melting with hot water and pumping the molten sulfur to the surface (Frasch process) [74]. Many processes have been used or proposed for extracting sulfur from sulfur ores [75]. However, only a few processes have gained commercial importance, including flotation, melting out, distillation, and the Frasch process.

Flotation can be used to upgrade sulfur ores [76]. After grinding the ore to the liberation size (the size at which the sulfur particles are free from the associated gangue minerals), sulfur is floated with foaming agents such as pine oil, cresylic acid, or amyl alcohol. When the gangue minerals contain carbonates, certain depressants such as water glass (sodium silicate) are recommended. Flotation results in concentrates containing 70%-90% S. The disadvantages of flotation are that it does not produce pure sulfur, as do most other processes, and that the sulfur concentrate has to be dried.

Producers in Sicily used the melting-out process and had a virtual world monopoly in sulfur production until 1904 [69]. Sulfur melts at 112°-114°C, but becomes highly viscous at temperatures above 158°C. Originally, sulfur was melted out in moundlike ore piles known as "calcarilli." Calcarilli were built up on small hearths equipped with drain holes and simply ignited. Approximately one-third of the sulfur was recovered by this method; the other two-thirds was burned and lost to the atmosphere as sulfur dioxide. A substantial improvement in yield was achieved by covering the ore pile with soil, as practiced in charcoal making; sulfur yields increased from 30% to approximately 60%. The melting process was substantially changed by the introduction of chamber furnaces, which improved the yield of sulfur up to 78%. The Sicilian sulfur monopoly effectively ended with the introduction of the Frasch production method and development of deposits in the Gulf Coast region of the United States.

Distillation of sulfur has been practiced in Japan by the "Yakutori Process" [77]. Sulfur-bearing ore is heated by external firing with coal to above 440°C (the boiling point of sulfur). The process uses small retorts (0.4 m^3) which are made of 13% chromium steel and hold approximately 0.24 tonne of ore. Up to 100 retorts can be coupled to form one furnace. To produce one tonne of recovered sulfur, 0.41 tonne of coal is consumed.

The most effective and economic method of extracting sulfur from native deposits *in situ* under suitable conditions is the Frasch process [74]. The process involves injecting hot water directly into the sulfur deposit and then pumping the molten sulfur to the surface. The sulfur is then pumped to storage areas where it solidifies. In this way, blocks of pure sulfur are obtained. Frasch-produced sulfur can be quite pure (99.7%-99.8%) and light yellow in color. If the sulfur is associated with small amounts of bituminous residues, it is brown or blackish. This so-called dark sulfur may contain up to 1% carbon, mainly present as complex organic sulfur. The United States, Poland, and Iraq practice Frasch sulfur production on a commercial scale, as did Mexico until 1993.

5.4.2.2 Sulfur Recovery From Gases – Recovered sulfur accounts for over 60% of the total world production of elemental sulfur. Most of the recovered sulfur originates from the processing of fossil hydrocarbons, especially natural gas, oil, and coal. In natural gas, sulfur is mainly in the form of hydrogen sulfide, but in oil and coal it is also present as organic compounds such as mercaptans and as sulfides, disulfides, and heterocyclic compounds.

Hydrogen sulfide cannot be tolerated in natural gas, even in low concentrations, because of its great toxicity. Hydrogen sulfide is also corrosive. Therefore, "sour" natural gas containing hydrogen sulfide is usually desulfurized near the wellhead to very high standards of purity.

In the refining of crude oil, sulfur partly comes off as hydrogen sulfide, but mostly tends to accumulate in the heavy fractions. The practice of using high-sulfur heavy oils containing 3%-4% sulfur as industrial fuels is no longer permissible under the pollution control regulations in force in many parts of the world. Therefore, heavy oils are often treated with hydrogen to reduce the organic sulfur to hydrogen sulfide [78].

There are essentially three types of practical processes for removing hydrogen sulfide from gas streams: sorption on a solid; reversible chemical or physical absorption in a liquid medium; and absorption and oxidation in an oxidizing liquid medium (direct conversion). In the direct conversion processes, not only is hydrogen sulfide removed from the sour gas stream, but it is also converted into elemental sulfur in the same liquid medium. There are two methods by which this conversion can be achieved. One is the so-called "Wet Claus" process, in which sulfur dioxide is introduced and reacts with the hydrogen sulfide according to the following equation:

$$2\,H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Processes of this type are most frequently used for processing tail gases from Claus sulfur recovery plants, which are operated to contain the correct stoichiometric proportions of hydrogen sulfide and sulfur dioxide [79]. The other type of direct conversion process uses an alkaline solution (often sodium carbonate) containing one or more mild oxidizing agents that oxidize hydrogen sulfide to sulfur and are then themselves regenerated by oxidation with air [80].

Where coal is used as a fuel for industrial and power station boilers, coal processing for the purpose of removing sulfur is too costly, and very large quantities of coal, including the high- sulfur varieties, are still burned directly. Often high- and low-sulfur coals are blended to stay within specified sulfur-emission limits. In the best of cases, both pyritic and organic sulfur in the coal is burned to sulfur dioxide and discharged with the combustion gases. Where emission standards must be met, some method of removing at least a portion of the sulfur dioxide from the off-gases must be used [69]. However, although the technology exists, it is seldom economically justifiable to recover sulfur or any other useful sulfur product under these conditions.

5.4.2.3 Sulfur Production From Sulfide Ores and Sulfates – Non-ferrous metal ores such as copper, zinc, lead, and cobalt are found mainly in the sulfide form. A typical copper ore concentrate composition is 27% Cu, 28% Fe, and 32% S. In the roasting stage the sulfide components are broken down under the influence of heat to cuprous sulfide and elemental sulfur [81].

Various methods have been used or have been proposed for the production of elemental sulfur from sulfide ores. Methods of treating sulfide ores fall generally into several groups. Thermal decomposition of pyrites occurs at about 600°C; in the absence of air, pyrite decomposes and sulfur gases can be recovered from the off-gases by condensation [82]. Roasting and/or smelting sulfides under reducing conditions with coal, coke, or a reducing gas produces a gas mixture containing hydrogen sulfide and sulfur dioxide. These compounds can be converted to sulfur in a Claus plant [80]. Reacting pyrite with sulfur dioxide can produce elemental sulfur and magnetite:

$$3FeS_2 + 2SO_2 \rightarrow Fe_3O_4 + 8S$$

Sulfide ores can be treated with chlorine or hydrogen chloride. Wet chemical or biological/chemical extraction methods can also be used to produce sulfur from sulfide ores.

Although off-gases from smelting operations are somewhat more concentrated than gases from the burning of coal, the economics are generally not in favor of recovering sulfur from smelting off-gases. Sulfur recovery may help offset costs associated with pollution controls to conform to emission standards.

Sulfates are not currently a significant commercial source of sulfur because of economic factors. Large inputs of energy are required to reduce sulfur from sulfates. Most of the chemical methods proposed involve reduction of a sulfate to a sulfide followed by acidulation of the sulfide to produce hydrogen sulfide, which is then processed to sulfur by the Claus process. Suitable reducing agents include coke, hydrogen, or reducing gases (hydrogen + carbon monoxide produced by partial combustion of a fuel).

5.4.3 World Production, Sulfur Reserves and Resources

Sulfur ore bodies that are worth exploiting on a large scale are restricted to a few regions in the world. However, there are many deposits of local importance. Table 5.22 lists world sulfur reserves and the world sulfur reserve base. Significant sedimentary sulfur deposits are located in several regions. Deposits are found in the Gulf of Mexico Basin in the states of Louisiana and Texas in the United States and also in Mexico. In the Mediterranean Basin, the main deposits are in Sicily, but there are other deposits on the Italian mainland and on the French and Spanish coasts of the Mediterranean. In the Eastern European Basin, sulfur deposits are found along the Volga River and the coast of the Caspian Sea along the Caucasus Mountains. North of the Carpathians in Poland, sulfur deposits are found in the Central European Basin. Sulfur deposits are located in Turkmenistan and Uzbekistan of the former Soviet Union and in Afghanistan.

Table 5.22. World Sulfur Reserves and Reserve Base

	Reserves[a,b]	Reserve Base[a,c]
	(tonnes x 10^3)	
United States	140,000	230,000
Canada	158,000	330,000
China	100,000	250,000
France	10,000	20,000
Iraq	130,000	500,000
Italy	10,000	15,000
Japan	5,000	15,000
Mexico	75,000	120,000
Poland	130,000	300,000
Russia	NA	NA
Saudi Arabia	100,000	130,000
Spain	50,000	300,000
Ukraine	NA	NA
Other Countries	470,000	1,300,000
World Total	**1,400,000**	**3,500,000**

a. All forms as elemental S.
b. Defined as economically producible under current conditions.
c. Resource base from which reserves are estimated. Reserve base may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics.
Source: [83].

Volcanic-related sulfur deposits are found in several areas of the world. In the East Pacific Basin, volcanic sulfur deposits extend along the Philippines, Japan, the Kuril Islands, and the Kamchatka Peninsula. In the West Pacific or Cordillera Basin, deposits extend along the western side of North and South America through Mexico, Peru, Bolivia, and Chile [69].

Large deposits of pyrite are present in several areas of the world including India, Poland, Albania, China, and the former Soviet Union. However, the use of pyrites is not as technically or economically favorable as the use of other sources of sulfur. Pure pyrite contains about 53.5 wt % S, and high-grade ores may contain 46% sulfur. Freight charges for shipping pyrite are high compared to shipping pure sulfur. At approximately 35% S, pyrite combustion in pyrite-burning furnaces may not be self-sustaining, and auxiliary fuel sources may be required. Capital costs are higher for sulfuric acid plants using pyrites than for those plants using elemental sulfur, and operating costs are also higher. Pyrite-burning sulfuric acid plants have more troublesome pollution problems than do sulfur-burning plants due to materials-handling problems and particulate emissions. The disposal of the iron oxide sinter may also present problems in that pyrites may contain several potentially harmful heavy metals, which may be concentrated in the sinter.

It is difficult to make a significant estimate of the total world reserves of sulfur because of the wide variety of forms in which it occurs. Reserves may total 1.4 x 10^9 tonnes [83]. Total resources are probably about 5.0 x 10^{11} tonnes, to 7.5 x 10^{11} tonnes, of which more than 99% is present in coal, oil shales, and gypsum; these are materials that do not make a significant contribution to present world production. World resources of elemental sulfur in evaporite, volcanic deposits, and sulfur associated with natural gas, petroleum, tar sands, and metal sulfides may amount to about 5 x 10^9 tonnes (Table 5.22).

Table 5.23 shows the world production of sulfur from 1992 to 1994 as elemental sulfur and sulfur in all forms,

Table 5.23. Production of Sulfur in All Forms and as Elemental Sulfur, 1992-94

	1992		1993		1994	
	All Forms	Elemental	All Forms	Elemental	All Forms	Elemental
	(thousand tonnes S-equivalent)					
Belgium/Lux	330	150	335	156	341	160
Finland	617	46	612	32	636	40
France	1,232	988	1,326	1,073	1,369	1,084
Germany	2,140	1,350	2,206	1,451	2,131	1,400
Greece	140	130	100	100	80	80
Italy	630	310	639	350	590	345
Netherlands	401	273	441	318	440	323
Norway	229	13	144	16	105	15
Spain	889	159	822	180	798	160
Sweden	183	54	157	55	146	50
United Kingdom	232	165	248	183	219	154
West Europe[a]	**7,114**	**3,715**	**7,119**	**3,991**	**6,946**	**3,889**
Bulgaria	232	10	149	15	155	15
Ex-Czechoslovakia	76	60	78	65	86	70
Poland	3,149	2,952	2,105	1,901	2,360	2,160
Romania	277	30	282	35	287	40
Ex-Yugoslavia	213	10	134	15	139	20
Central Europe[a]	**3,971**	**3,082**	**2,781**	**2,056**	**3,063**	**2,335**
Former USSR	**8,114**	**5,284**	**6,523**	**3,941**	**5,858**	**3,589**
South Africa	575	167	618	171	572	190
Africa[a]	**802**	**170**	**801**	**174**	**765**	**193**
Canada	7,406	6,521	8,474	7,567	8,993	8,048
United States	11,604	9,368	11,779	9,568	12,252	10,101
North America	**19,010**	**15,889**	**20,253**	**17,135**	**21,245**	**18,149**
Brazil	301	77	270	77	287	85
Chile	353	24	372	1	489	-
Mexico	1,893	1,593	1,252	912	1,212	860
Latin America[a]	**2,917**	**1,969**	**2,358**	**1,340**	**2,485**	**1,328**
Iran	763	763	881	881	935	935
Iraq	375	375	375	375	375	375
Kuwait	-	-	246	246	490	490
Saudi Arabia	1,650	1,650	1,650	1,650	1,680	1,680
Turkey	177	78	178	71	220	65
Middle East[a]	**3,200**	**3,101**	**3,689**	**3,582**	**4,262**	**4,107**
China	6,544	312	6,323	262	6,479	197
India	214	45	229	55	250	60
Indonesia	63	3	65	5	67	7
Japan	2,921	1,375	3,114	1,560	3,068	1,667
Philippines	201	-	196	-	184	5
Singapore	160	160	180	180	180	180
South Korea	375	124	508	222	523	239
Taiwan	152	122	150	120	182	150
South and East Asia[a]	**10,852**	**2,183**	**11,028**	**2,497**	**11,280**	**2,688**
Oceania	**351**	**43**	**379**	**57**	**387**	**73**
World Total	**56,332**	**35,436**	**54,940**	**34,782**	**56,291**	**36,351**

a. Including others.

Source: [84].

including sulfur obtained from pyrites, non-ferrous metal ores, and crude oil and natural gas. World production of all forms of sulfur totalled 56.291 million tonnes in 1994 compared to 56.332 million tonnes in 1992 [84]. World elemental sulfur production totalled 36.351 million tonnes in 1994 compared with 35.436 million tonnes in 1992.

In 1993 world sulfur production was curtailed. Total Frasch and mined sulfur production was at 6.1 million tonnes in 1993 compared with 8 million tonnes in 1992 [75]. There was a significant change in the structure of the Frasch industry with low prices forcing a rationalization of production in Mexico and Poland, which also led to production curtailments at some U.S. mines.

In the United States, Freeport McMoRan brought its Main Pass 299 Mine, which is located offshore Louisiana and was commissioned in 1992, up to full production in 1993. The older Caminada Mine was closed at the beginning of 1994. Pennzoil cut sulfur production further in 1993 and began major cost-cutting exercises. Mexico ceased Frasch sulfur production in May 1993 after producing 150,000 tonnes. Low world sulfur prices and high costs resulted in the demise of the industry in Mexico. The sharp decline in prices in 1993 resulted in Poland further reducing its sulfur production. The open-pit mine at Machow permanently closed in 1993. The new mine at Osiek was completed but was not operated at full capacity. The frasch mine at Mishraq in Iraq has been operated at low rates in recent years due to the lack of export opportunities as a result of the United Nations' sanctions. The mine is capable of producing 2 million tonnes per year [75].

Sulfur consumption by region in 1992-94 is shown in Table 5.24. For the short to medium term, sulfur is expected to remain in surplus due to increased byproduct sulfur production. Increasing demand for natural gas and the increased need for pollution control will lead to increasing production of recovered sulfur. Elemental sulfur from evaporites and volcanic rocks will be available for many years. The fertilizer industry should be able to obtain the sulfur it needs over the next decade, but the lowest cost reserves presently being used have a limited life expectancy.

5.5 Potash

Potassium salts produced and used as fertilizers are generally referred to as "potash," a term that originated from the burning of wood in pots or retorts to obtain potassium salts as "pot-ashes." Potash is now commonly used to describe potassium-bearing materials, and the potassium content is generally expressed on a K_2O equivalent basis.

5.5.1 Geology, Mineralogy, and Origin of Potash Deposits

Large, deeply buried potash deposits are mainly associated with marine evaporite sequences and less commonly with non-marine evaporites throughout the world. Potash deposits occur on every inhabited continent and have been identified in most geologic time periods from the Cambrian to the present. The most abundant potash mineral in commercial potash deposits is sylvite (KCl). Sylvite and halite (NaCl) form the common potash ore called sylvinite. In most occurrences, fairly pure sylvinite

Table 5.24. Consumption of Sulfur in All Forms and as Elemental Sulfur, 1992-94

	1992		1993		1994	
	All Forms	Elemental	All Forms	Elemental	All Forms	Elemental
	(thousand tonnes S-equivalent)					
Western Europe	7,172	3,830	6,668	3,540	6,638	3,637
Central Europe	1,794	905	1,540	815	1,643	915
Former U.S.S.R.	8,430	5,600	6,432	3,850	6,069	3,800
Africa	5,548	4,916	5,394	4,767	5,772	5,200
North America	15,222	12,101	14,145	11,027	14,862	11,766
Latin America	3,008	2,060	3,279	2,261	3,682	2,525
Middle East	1,230	1,124	1,155	1,048	1,455	1,300
Asian CPEs	6,775	410	6,610	393	6,846	440
Other South and East Asia	6,579	4,158	6,373	4,013	6,557	4,331
Oceania	564	295	631	355	684	410
World Total	**56,322**	**35,399**	**52,227**	**32,069**	**54,208**	**34,324**

Source: [84].

exists with essentially no soluble sulfate or other salts. In other deposits, fairly pure carnallite (KCl MgCl • $6H_2O$) is also found with halite. In only a limited number of deposits do soluble sulfate salts occur, such as zones of the Zechstein Basin where the occurrence of "hartsalz" [sylvite plus halite with kieserite ($MgSO_4$ • H_2O) and/or anhydrite ($CaSO_4$)] is common. Double salts occur in deposits in Sicily and Ethiopia where kainite (KCl • $MgSO_4$ • $3H_2O$) is predominant. Double salts also occur in the deposits of the Carlsbad, New Mexico area, and the Carpathian region (Ukraine) where langbeinite (K_2SO_4 • $2MgSO_4$) occurs extensively. In many deposits, there are also some occurrences, or occasionally large amounts, of the insoluble mineral polyhalite (K_2SO_4 $MgSO_4$ $2CaSO_4$ • $2H_2O$). In three locations around the world, sylvinite occurs with carnallite and tachyhydrite ($CaCl_2$ $2MgCl_2$ • $12H_2O$).

On a worldwide basis, there appear to be as many as 100 large buried potash deposits that could produce products of commercial quality and about the same number of significant potash brine deposits. The buried deposits are primarily of marine origin. Surprisingly, the exact mode of the formation of these deposits, as well as a smaller number of deposits that are associated with hot springs, is not known and is the subject of considerable speculation.

Sodium and potassium are major components of seawater. With sufficient evaporation, halite, epsomite, and potash double salts will crystallize. At some point in the geologic history of a potash deposit, this mixture of salts is transformed to either kainite-epsomite-halite or more often to carnallite-kieserite-halite, depending upon the extent of evaporation. There are no circumstances that will cause sylvite to be formed directly from seawater. It is generally recognized that, after evaporite formations are flooded with weaker brines, carnallite is converted to sylvinite, and kieserite is dissolved [85]. However, the kieserite dissolution part of this theory is controversial, and there is speculation that all or most of the sulfate content of the seawater may be removed before final evaporation, either by sulfate-reducing bacteria or by the intrusion of calcium chloride-bearing waters. Either reaction mechanism is fairly easy to discredit, and there is no positive proof of any one mechanism. It is also quite certain that extensive diagenetic changes can and often did occur long after burial of potash deposits, which further complicates the subject.

5.5.1.1 Buried Potash Deposits – The potash deposits of the world vary widely in their size (ore resources and reserves), grade (minable % K_2O), and factors that impact economics, such as their location and the cost of mining and processing. Mining costs depend upon capacity, depth to the ore, thickness and uniformity of the potash bed, dip of the beds, strength and integrity of the overlying strata (to form a strong roof), danger of water intrusion (flooding) and the attendant cost of penetrating the aquifer zones with shafts and pumping the water, problems with toxic combustible gasses or "rock bursts," amount of insolubles in the ore, ease of "desliming," the KCl-NaCl liberation size, and amount of impurities present. Location is very important with respect to the deposit's distance from markets, transportation, infrastructure, and the cost of transportation. Government royalties, taxes or fees, and possible special circumstances in selling the product (i.e., protective tariffs, local or controlled markets, reciprocal trade agreements, etc.) have a great impact on economics. Due to the complexity of these factors, those deposits that are the largest and that have the highest grade and potentially lowest production costs in the world may not be fully exploited, nor do they totally dominate the potash market. A condensed review of the currently produced and better known buried potash deposits will be briefly presented in the following section.

Brazil (Sergipe); Congo; Thailand – Although these deposits are widely separated geographically, they are similar in that they contain medium to small sylvite-bearing sylvinite formations with similar unusual mineral assemblages. There are commercial quantities of sylvinite, considerably more carnallite, significant amounts of tachyhydrite, and smaller quantities of bischofite ($MgCl_2$ • $6H_2O$). All three deposits and their salt beds contain essentially no carbonates (calcite or dolomite) or gypsum (or anhydrite), except at the top of the Sergipe and Congo formations. The lower sections of the basins are filled with land-derived sediments, and the halite rests directly on these sediments. Potash occurs at the very edges of the basins, instead of in the more common structure of halite and/or anhydrite and dolomite surrounding the potash and covering a much wider area.

It appears that these deposits are of continental and not marine origin. The potash source could have been a high-Ca geothermal brine similar to the brines emitted from the rift zones of the Red Sea or Salton Sea. The coast lines near the Congo and Brazil deposits would have been closely dovetailed before continental drift, and they are of identical age (Lower Cretaceous, Aptian). Wardlaw and Nicholls [86] have shown that the Congo and Brazil deposits contain very similar concentrations of 10 trace elements, and a number of the concentrations of these elements are quite different from those found in other potash deposits. Only very hot high-Ca brines (such as now occur at Lake Magadi, Kenya, depositing soda ash) could crystallize such massive deposits of extremely hygroscopic tachyhydrite and bischofite. Potash occurs primarily around the edges of carnallite zones in these deposits, having been formed by water intruding into the carnallite, which was then converted to sylvinite.

The depth of the Sergipe deposit in Brazil varies from 500 to 850 m, and the potash beds are uneven and highly variable in thickness [87]. The thickness of the potash zones at Sergipe varies from 2 to 31.3 m and averages about 20.5 m. The sylvinite zones contain some carnallite, have an average grade of 25% K_2O, and are mined in two layers. Each of those layers is up to 11 m thick and separated by 3-6 m of halite. The tachyhydrite in the floor has low mechanical strength and high creep tendencies, and it is very hygroscopic.

The Congo deposit (Holle) contains less sylvinite, about the same amount of carnallite (estimated at 15% of the total salts), and more bischofite than the Sergipe deposit. A "normal" depositional sequence of thin black shales is followed by halite and then carnallite, with some zones converted to sylvinite. In most areas, the uppermost mineralized zones contain tachyhydrite or bischofite. A commercial potash operation was initiated in 1969, but developed many mining problems leading to poor productivity. The sylvinite beds were often thin and not very continuous, irregular in dip and variable in composition, and they occurred within an oddly shaped area (a large U). At Holle, sylvinite was found primarily in the second highest salt (9th evaporite) cycle in four separate beds. Two layers, beds 3 and 7/8, were mined. In the mining area, the upper bed (7/8) occurred at a depth of 288-380 m over an area of 28 km^2 and averaged 18% K_2O. Bed 3, which was 10-20 m below bed 7/8, had an average thickness of 3 m with an ore grade up to 38% K_2O and only 0.1% insolubles. On June 20, 1977, water from an overlying aquifer began to enter the mine. Water flow rapidly increased, and within 36 hours the entire mine was flooded. Most of the equipment was lost, and the mine was abandoned [88]. In recent years, there have been several proposals to reopen the mine as a carnallite mine because of the thickness and uniformity of the carnallite beds.

A much larger basin of this type, also of Cretaceous age, occurs in Thailand and extends into neighboring Laos. The basin is divided by the Phu Phan mountain range into the Khorat Basin to the south and the Sakhon Nakhon Basin in the north. The potential ores of this deposit contain up to 3.7% boracite ($MgClB_7O_{13}$). The deposit is composed largely of carnallite. Sylvinite beds appear to occur primarily on the flanks of salt domes or anticlines [89]. ASEAN Potash Mining Company Ltd., a consortium funded by several countries in the region, has been studying the feasibility of producing and processing carnallite based on a traditional room and pillar mining system in a portion of the deposit at Bamnet Narong in the Khorat Basin. An incline is currently being driven to the potash zone. Total ore resources are approximately 366 million tonnes K_2O. Total minable reserves are approximately 83.4 million tonnes K_2O.

A private company, Asia Pacific Resources Ltd., is developing sylvinite resources in the Sakhon Nakhon Basin near Udon Thani. Thus far, drilling has indicated a reserve base of 250 million tonnes of sylvinite ore, of which 160 million tonnes is deemed minable reserves at 25% K_2O. This ore can be treated using traditional flotation processes.

Canada: New Brunswick – The New Brunswick potash deposits associated with the Windsor Group evaporites are found in three structures at the southern end of the Moncton Basin: Penobsquis (mined by Potash Corporation of Saskatchewan [PCS], formerly operated by Potash Company of America [PCA]); Clover Hill (mined by Potacan); and Millstream (development rights acquired by IMC, Canada). Each deposit lies within gradual-to-steep flanks of synclines formed by salt doming. Even though each deposit is located in a separate structure, the potash beds have the same cycles and general thickness of layers within beds. Some carnallite occurs at Penobsquis, but there is little carnallite at Clover Hill. The sylvinite layer is divided into units called A, B, C, and D. The lower unit, or A zone, is 1-10 m thick, fine grained, and varies from high-grade sylvinite to barren halite. The B (1-15 m thick) and C (0.5-10 m thick) zones comprise the main mining levels. The D zone is more variable and occasionally is extensively folded. The crystal size of the sylvinite ores ranges between 2 and 5 mm. The ores contain 0.5%-5.0% insolubles, and grade averages 28% K_2O at Clover Hill (Potacan) and 26% K_2O at Penobsquis. Ore depth varies from 460 to 1,035 m, and the deposits vary from 10 to 35 km^2 in area [90].

Canada: Saskatchewan – The largest and most minable potash reserves in the world occur in Saskatchewan, Canada, extend slightly into Manitoba, and extend substantially but at considerable depth (1,000 m to over 3,500 m) into Montana and North Dakota in the United States. Sylvinite ore occurs in three members of the Prairie Evaporite Formation (Upper Middle Devonian). The lowest potash member is called the Esterhazy. Above the Esterhazy there is a comparatively minor bed, the White Bear (these two beds do not occur in the northwest area of the Evaporite Basin), followed by the Belle Plaine Member. The Patience Lake Member occurs at the top of the sequence. The Patience Lake Member is divided into two main ore zones (upper and lower). The potash beds dip slightly to the west and more strongly to the south at a rate of 3-9 m/km. Potash is difficult and expensive to mine at depths below about 1,100 m, and the conventional shaft mines lie in the shallowest northwest edge of the Patience Lake Member near Saskatoon, or the northeast edge of the Esterhazy Member near the town of Esterhazy. Solution mines are not so depth-limited, and one mine is located west-northwest of Regina where an appreciable thickening of the Belle Plaine Potash Member occurs. Another solution mine is developed on the flooded PCS Patience Lake Division mine near Saskatoon [91].

The minable zone of the Esterhazy Member is reasonably thick and high in grade, has a low insolubles content, and is overlain by a comparatively strong strata ("roof" rock). An approximately 2.4-m-thick zone of the Esterhazy Member is mined at three locations (IMC K1, IMC K2, and PCS Rocanville). The ore from the Esterhazy Member averages 25% K_2O and 1% insolubles. Some carnallite is present in the ore, varying from less than 1% (normal) to as much as 10%. The sylvite liberation size is unusually large (much of the ore is liberated at plus 3-mesh [Tyler] or plus 6.7 mm).

Other shaft mines in Canada mainly produce from the Patience Lake Member. Most operations mine the top 2.74-3.35 m of the 3.66- to 4.57-m-thick Upper Patience Lake Member. One mine operates on the lower ore zone and recovers nearly all of the 4.57- to 5.79-m-thick potash bed. The ore grade (20%-26% K_2O) recovered in these mines is generally inversely proportional to the thickness mined. The insolubles content typically is 4%-7%, primarily resulting from several thin clay partings located within the potash zone.

Europe: The Zechstein Basin – During the Permian period, the Zechstein Basin was a large gulf that covered much of present-day Germany, parts of the North Sea, the Netherlands, an edge of England, Poland, and the Baltic region. Marine shale, limestone (or dolomite), and gypsum (or anhydrite) were deposited over all of the basin, and halite was deposited over large areas. Potash deposits were formed in more limited areas. All of these potash deposits exhibit some minor-to-major plastic flow, fracturing, and possibly basalt intrusion, and they have been altered by geothermal or other water. These postdepositional alterations have resulted in quite variable strata and mineralization.

The four Zechstein evaporate cycles or series are described by Z numbers. The oldest formation, the Z1 Werra Series, contains two potash beds, the Hessen and Thüringen, and is found only in southern Germany. The Z1 beds vary considerably, but in general, the lower Thüringen bed contains sylvite (15%), kieserite (10%), and carnallite (10%), and is capped by a carnallite breccia. The upper, or Hessen, bed contains much less carnallite and averages 15%-20% in both sylvite and kieserite content. The second evaporite cycle, or Z2 Stassfurt Series, is found predominately in central Germany. The Stassfurt Series contains carnallite or carnallite-kieserite, grading laterally into sylvite-kieserite (hartsalz). The Stassfurt Series is often capped by gypsum and kainite, apparently formed by a conversion of the carnallite-kieserite mixture. In the third evaporite cycle, or Z3 Leine Series, there are two potash beds, the Ronnenberg and Riedel, which are found predominantly in northern Germany. Both the Ronnenberg and Riedel beds are usually found only in small lenses (with a few exceptions, such as at Zielitz), and contain fairly pure sylvinite. The fourth evaporite cycle is the Z4 Aller Series. In England, the Z3 Leine Series and Z4 Aller Series contain only sylvinite or carnallite. Potash from the Zechstein Basin is commercially produced in England and Germany.

England (North Yorkshire Deposit) – A comparatively small but very interesting potash occurrence is commercially mined in England. The Boulby potash bed is assumed to be Z3 (with the Z4 missing in that area) and extends just under the English east coast at a depth of 1,100-1,200 m in the mining area. To the south of the mining area, where the Z4 also occurs, both potash beds occur about 200 m or more deeper. The average potash grade as mined in 1992 was about 40% KCl (24% K_2O), and the ore contained 10%-15% (usually near the higher number) insolubles. It is also one of the world's most unusual sylvinite formations. Talbot et al. (1982) have proposed that the sylvinite reached the present position by flowing into the overlying grey anhydrite shale and salt clay. The sylvinite resembles a metamorphic gneiss, both in terms of crystal fabric and because it contains many rounded fragments of rocks from adjacent beds. According to theory, the fluid mass of sylvinite presumably circulated to form extensive pillow-shaped structures that follow the underlying fault system in the area. The NaCl and KCl crystals of the sylvinite contain significant amounts of gases under high pressure.

Germany – In southern Germany, both Z1 beds (Hessen and Thüringen) are mined and processed at four plants. The ore consists of various types of hartsalz, perhaps formed as a result of the low permeability of the underlying Kupferschiefer shale (copper shale), which prevented the leaching of magnesium sulfate. The beds in the area are comparatively flat-lying and continuous, but within the deposit there are various fold structures, barren zones, faults, basalt intrusions, and sudden thickening and thinning of the ore. The Thüringen bed consists of halite, sylvite, kieserite, and carnallite and averages 3 m in thickness. A carnallite-shale breccia often overlies this potash zone and at places is the dominant formation. There is about 20 m of halite separating the two potash beds, with the upper or Hessen bed ranging from 2.0 to 2.5 m thick and containing 9%-10% K_2O and 5%-10% $MgSO_4$. At the top of the Hessen bed is a mixed carnallite zone up to 3 m thick, and peripheral carnallite zones can be up to 15 m thick. Mining in the Werra-Fulda District can be difficult. Basaltic intrusions and block faulting have greatly altered the potash beds in some locations, and high-pressure carbon dioxide is trapped in halite or sylvite crystals [93]. Pressure release often results in rock bursts in these areas. Several major earthquakes have apparently resulted from injecting plant waste liquors into an overlying fissured dolomite formation.

The Z2 Stassfurt Series forms the most extensive minable potash deposits in central Germany. The Z2 Series is always found on the flanks of diapirs (salt domes) in the former West Germany, and thus occurs as highly contorted and predominately steeply dipping deposits. The Z3 Ronnenberg or Riedel beds are also associated with some of these deposits. The Stassfurt bed exists predominately as a carnallite-kieserite mixture, often with a low potassium content, and the bed may not be economical to produce alone. The Stassfurt bed is underlain by a bituminous, high-organic shale or dolomite, which along with a thick anhydrite layer may have reduced the permeability sufficiently to prevent magnesium sulfate from leaching from the bed. Some of the carnallite has been converted to sylvite in the outer edges of the deposit, and the potash bed is often capped with a kainite mixture, presumably formed by a carnallite-kieserite reaction. In some zones, a schoenite mixture is found on top of this kainite; this is also most likely a reaction product. These minerals appear to have been formed by the intrusion of brines at a much later date.

The Z3 Ronnenberg and Riedel beds consist mainly of sylvinite with sporatic occurrences of carnallite and with no magnesium sulfates. Both beds exist as isolated discontinuous units, and occasionally each is minable alone, for example, the Ronnenberg bed at the Zielitz deposit. Here the Ronnenberg bed slopes steadily from 18° to 25° and is found at depths of 400-1,000 m. The bed is 6-9 m thick and contains about 25% KCl (15% K_2O), with no sulfates and only minor amounts of insolubles. The halite that overlies the Ronnenberg bed at the Zielitz deposit contains some carnallite.

Europe: Tertiary Deposits – Exploitable potash areas of Tertiary age are found in France, Italy, and Spain. These occurrences vary considerably in size, potash content, and potential for future production.

France – The Tertiary Period (Oligocene Epoch) Alsace-Wittelsheim potash deposit in France contains two potash beds separated by about 20 m of halite. The lower bed is found in an area of about 300 km^2 and is 1-5 m thick; the ore contains 12%-20% K_2O. The upper bed covers an area of 115 km^2; it averages 1.5 m in thickness, and the ore contains 20%-27% K_2O. The potash content of the beds diminishes to less than 11% at their edges, where they thin to 1 m or less. The beds are found at depths of 420-1,800 m, and they dip slowly and variably to the north-northeast at 0°-25°. To the east of the Wittelsheim deposit, and separated by the Mulhouse uplift, is the Munchhouse deposit. A small high-grade companion potash deposit (the Büggingen deposit) occurs in Germany a few miles to the east. The Büggingen deposit is found in an area of 1.6 km^2, has a potash bed thickness of 0.5-4.0 m, and occurs at depths of over 800 m. The last mine to operate on the Büggingen deposit closed in the early 1970s. There have been many mines on the Wittelsheim deposit, but only two remained in operation in 1994, with less than 10 years of minable reserves. Both mines are operated by Mines de Potasse d'Alsace. Conditions are adverse in the area. The long-wall mining technique used in the area liberates variable quantities of methane as the shale in the roof falls. There is a high geothermal gradient in the area, and the rock temperature is 47°C at 800 m and 54°C at 1,000 m.

Italy – The potash deposits of Italy are located on the island of Sicily and were formed during the late Miocene when the Mediterranean Sea was a partially or totally isolated gulf. The deposits are composed of isolated ore bodies in two generally parallel troughs 115 km long, 5-10 km wide, and separated by 11-25 km. Kainite is the dominant potash mineral in the deposits. The ore in most of the individual ore bodies occurs as six layers of variable thickness and has a grade of 10%-16% K_2O (pure kainite contains 18.9% K_2O), with very little insoluble content (0.4%-2.0%). There has been considerable tectonic activity in the area, and the deposits are structurally disturbed. Little if any of the limestone associated with the deposits has been converted to dolomite, nor has the gypsum associated with the deposits been converted to anhydrite. This evidence, along with isotopic data, indicates that when the deposits were formed the evaporation of the parent seawater did not usually proceed past the kainite crystallization point. The largest ore body is at Pasquasia, covering a 24-km^2 area at depths of 300-800 m. There are five beds at Pasquasia in highly undulating synclinal and anticlinal forms. The No. 2 bed is the thickest, averaging perhaps a 30-m thickness of 10.5% to 13.5% K_2O ore [94].

Spain – Spain has two exploitable potash areas, occurring at opposite ends of a long (300 km), narrow depositional basin of Upper Eocene age, formed between the Pyrenes, the Iberian ranges, and the Catalonian coastal range. The saline mineral sequences in both deposits are quite similar, with an "old halite" at the base, a sylvinite-producing horizon, and carnallite and halite above the main producing horizon.

The western or Navarra basin covers a 400-km^2 area and contains a sylvinite bed averaging 2 m in thickness. The sylvinite bed is made up of 18 thin layers 4-14 cm thick alternating with layers of halite 2-12 cm thick. On top of the sylvinite bed is a massive halite bed, generally 0.7-1 m thick, but sometimes absent altogether, and above the halite is a 10- to 12-m bed of carnallite. The deposit has a synclinal structure with two major fracture systems dividing it into three blocks. Two of the blocks are uplifted, and the central block is downfaulted as much as 300-600 m.

The second exploitable area, the Castean or Catalonia potash basin, is located 75 km northwest of Barcelona and covers an area of about 2,600 km^2. The Catalonia deposit contains 2 to 4 layers of potash ore. The lower sylvinite bed or A bed is typically 3.0-3.2 m thick and averages 18% K_2O. Above the A bed is a 2.5-m halite layer, followed by 0.7-0.9 m of sylvinite called the B bed, which analyzes about 35% K_2O. Above the B bed are two thin marl layers followed by 6-8 m of alternating carnallite-halite beds.

At the Llobregat mine, the potash beds are nearly horizontal (5° dip), with some folding, and are generally in the form of a large syncline. At Llobregat the beds are found over a 10-km^2 area, and the depth to the beds varies from 300 to 400 m.

At the Cardona mine, the deposit is formed around a diapiric anticline. The potash beds form a horseshoe-shaped deposit 1 km wide and 5 km long around the northern flank of the salt dome. Beds with 20°-80° dips are mined in stopes at depths up to 1,025 m. The potash zone mined varies from 8 to 20 m in thickness and averages 11%-12% K_2O.

At Suria, potash is mined on the southern flank of the Suria anticline. One or two of the four potash beds are recovered (in two mines) from depths between 550 and 880 m. The potash beds dip at angles up to 20° and have generally been thickened; there are a number of barren and folded zones. The lower (A) bed may average 6.5 m thick with ore averaging 20.6% K_2O. The upper bed (B) averages 5.5 m at 27% K_2O. A portion of the overlying carnallite bed has been converted to sylvinite, which is also mined [95].

Former Soviet Union: Belarus (Soligorsk or Starobin) – The second largest potash deposit in the former Soviet Union (FSU), and one of the world's larger potash deposits, is of Upper Devonian age and is found in the Pripyat Depression. The deposit has as many as 30 individual potash beds and four main potash-bearing layers, numbered from the upper bed down. Four mines, Soligorsk 1, 2, 3, and 4, usually mine Bed 2 and the lower section of Bed 3. In the mining area, Bed 2 is at a depth of 350-620 m and is 1.8-4.4 m thick. The sylvinite ore contains an average of 11% K_2O with 5% insolubles over an area of 250 km^2. Bed 2 is nearly horizontal, sloping gently to the east. Bed 3 lies about 160 m below Bed 2. The lower sylvinite zone of Bed 3 (1.5-2.8 m thick) averages 13.4%-16.4% K_2O with 9% insolubles and extends over a 350-km^2 area.

Former Soviet Union: Ukraine (Carpathian Deposit) – High-sulfate potash deposits occur in the Carpathian area of western Ukraine. Up to 15 discontinuous ore bodies contain predominately langbeinite and kainite, with varying but substantial quantities of carnallite, sylvite, and polyhalite. Lesser quantities of kieserite, schoenite, leonite, and glaserite are also found in the ore, as well as large amounts of insolubles. The deposits occur in a 170 km by 15 km area in two zones, which range from lower to middle Miocene in age. The main deposits are centered near Kalush and Stebnik, about 70 km apart. There are often two to five potash beds, typically occurring as 1- to 5-m-thick lenses 0.5-1.0 km long and 200-300 m wide. Most of the ore bodies are moderately to steeply inclined at depths of 0-800 m (an open-pit mine is developed on one ore body). The ores average about 10% K_2O with 10%-18% insolubles and are very difficult to process.

Former Soviet Union: Russia (Upper Kama Basin) – The largest potash occurrence mined in Russia, and second in size only to the Saskatchewan deposits in Canada (although perhaps smaller than the less extensively explored Russian Siberian deposits), is of Permian age and is located in the Pre-Ural Trough adjacent to the Kama River and the Ural Mountains. Six mines and plants (one mine flooded and was abandoned) are centered about the towns of Solikamsk, Berezniki, and Romanovo. The potash deposit underlies about a 3,000-km^2 area and consists of 13 potentially minable beds. The lower sylvinite horizon is 26-30 m thick and contains the major sylvinite beds. The upper sylvinite-carnallite zone is 70-80 m thick. Several of the major beds were mined in 1991: the Red II (also called the KrII or Kp), Red I (or KrI or R), A, B, and V. The Red II is the principal bed worked across the region. The beds that are mined are 1.2-6.1 m thick, and the average interbed thickness of halite is 1.5-2.0 m. The ore averages about 15% K_2O with 3%-5% insolubles. The potash beds generally have very gentle dips of 0°-4°, but there are some gradual uplifts and folds as well as occasional cavities and numerous barren zones. Halite beds with clay partings lie on top of the mined potash, with thicknesses of 0.8-1.2 m, limiting roof spans to 3-16 m. The depth of the deposit varies from 75 to 450 m, and there is a high-pressure aquifer above the deposit.

United States: Carlsbad, New Mexico – The Carlsbad deposit is stratigraphically and mineralogically complex and contains 11 potash beds separated by thick halite and sporatic thin anhydrite or polyhalite layers. The potash ore bodies vary considerably in terms of their area, shape, and location, but they are fairly flat with only moderate undulations, faulting, and folding. The main ore minerals are sylvite and langbeinite. To the east of the commercial potash deposits, there is a massive polyhalite formation. The lowest potash member is known as the first ore zone and consists principally of sylvinite. It has been commercially mined by all Carlsbad operators and has been largely depleted. This ore zone, 3.0 to 4.6 m thick, contains three generally dark red potash beds, each about 0.6-0.9 m thick and containing >20% KCl. The potash beds are separated by 0.1-0.5 m of orange halite. The upper 0.6-0.9 m and bottom 0.3-0.6 m of the first ore zone are low in potash and often contain 5%-10% brown clay. The potash beds that have been commercially exploited are the lst, 4th, 5th, 7th, and 10th beds. Langbeinite has been principally produced from the 1st, 4th, and 5th potash beds [96].

United States: Paradox Basin, Utah and Colorado (Cane Creek) – The Paradox Basin covers an area of 16,000 km^2. Potash has been found in 18 of the basin's 29 evaporite cycles, and 11 of the cycles contain potash beds that may be considered of economic importance. The cycles are numbered from the top down, and cycles five and nine appear to be the most promising. Carnallite and sylvite occur in large quantities, and in some beds the K_2O content exceeds 30%. Some of the beds of individual cycles are quite extensive; the potash beds of cycle 19 can be observed over a distance of 180 km. Within the basin there is a series of parallel northwest-trending anticlines composed of individual diapiric salt structures that have often penetrated the overlying beds. In the anticlines, the thickness of the salt beds may have as much as doubled. The only structure that has been commercially exploited to date is the Cane Creek anticline near Moab, Utah. The fifth potash cycle is produced at a depth of about 1,200 m. The ore zone averaged 3.4 m in thickness over an area of 31 km^2 with 25%-30% K_2O. The mine originally was a shaft mine and room and pillar operation. However, the mine was gassy (contained methane) and hot (up to 35°C), the sylvinite bed was highly irregular in thickness and dip, and there were many faults. All these factors made mining very difficult and costly. In 1970 the mine was intentionally flooded, and the mine now operates as a solution mine.

Undeveloped Major Deposits – There are several potash deposits around the world that may be worthy of commercialization. Several of these deposits will be discussed in the following section.

In southwest Argentina, a deposit containing 300 million tonnes of deep resources has been reported in an area of 300 km^2. The Argentina deposit is located 260 km from an existing railroad and 650-850 km from a port. There are two potash zones: One zone is 2.2-2.5 m thick and analyzes 28%-32% K_2O; the second zone is 10-20 m thick with 20%-27% K_2O ore. A $10 million solution mining pilot plant and a 250,000-tpy KCl production plant were announced in 1992.

In the Amazon Basin of Brazil, sylvinite has been discovered in two evaporite cycles at depths of approximately 1,000 m. Reserves may be substantial. Each potash zone is 2.5-2.7 m thick and contains 28%-33% K_2O as sylvinite.

Perhaps the world's youngest large buried potash deposit is located in Ethiopia. The potash deposits of the Danakil Depression are Pleistocene in age and contain separate beds of both kainite and sylvinite. The lowest potash bed consists of fine-grained kainite (to 74%) with halite and varies from 4 to 14 m in thickness. Above the lower kainite bed are 3-24 m of mixed carnallite salts trending toward more kainite on the bottom, with more sylvite near the top. The upper zone or sylvinite bed is a 0- to12-m interval, with an abundance of sylvite near the top and increasing amounts of carnallite, polyhalite, and kainite near the base. The upper sylvinite bed also contains considerable anhydrite, indicating that a high-Ca spring (which still exists) did influence the waters of the basin in their final evaporative stages to precipitate sulfates.

Sylvinite and carnallite deposits have been discovered in Morocco in at least four locations, in three separate basins. The depth to potash zones varies from 500 to 1,000 m, and the potash bed thickness ranges from 2.5 to 9 m. Following a United Nations-sponsored drilling program, reserves of sylvinite in Morocco were estimated as 40 million tonnes averaging 13% K_2O, and carnallite reserves were estimated as 200 million tonnes averaging 10% K_2O.

In Poland, potash occurs in the Zechstein Z3 and Z4 beds but in generally limited quantity and at low grades (8%-9% K_2O). In one area, carnallite beds up to 25 m thick occur. However, the greatest attention has been given to the Puck Bay area's extensive polyhalite formations.

In addition to the two major and one minor potash-producing areas in the countries of the former Soviet Union, there are at least six occurrences that appear to be major deposits (Gaurdak-Kugitang Basin, Pre-Caspian Depression, Dnieper-Don Basin, Pripyat Basin, Siberian Platform, and the Pre-Ural Trough). The Siberian Platform may contain one of the world's largest potash deposits, with comparatively easily mined, high-grade sylvinite beds. Plans had been formulated to commercially develop several of these deposits, but with the political and economic changes in central and eastern Europe, these plans have been postponed or canceled. Most of the deposits are of medium- to high-grade sylvinite, but in parts of the Carpathian Foredeep, considerable deposits of langbeinite have been discovered. One of the announced mines (Karlyuk in Asia) was planned as a solution mine. Another project (Petrikov, Pripyat Basin) was planned as a joint magnesium metal-potash operation based on carnallite production.

In the Silurian Michigan Basin of the United States, potash-bearing salts may occur over an area of 33,800 km^2. Sylvinite zones with thicknesses up to 27 m and beds containing up to 25% K_2O (but averaging much less over the potash-bearing interval) have been discovered. A 40,000-tpy KCl solution mining pilot plant has operated on a potash zone at a depth of 1,540-2,560 m for several years.

5.5.1.2 Brine or Surface Potash Deposits – In addition to the buried potash deposits, there are brine or surface potash deposits in North America, South America, and Asia/Middle East. This section gives a brief review of these deposits.

Chile: Chilean Nitrate Deposits – The Chilean nitrate deposits are unique, and the formation of these soluble salt mineral deposits is one of the great mysteries of the world. It is beyond the scope of this chapter to discuss the various theories concerning the origin of these deposits. The deposits occur in the Atacama Desert region of northern Chile over a north-south range of approximately 700 km and an east-west distance of 10-150 km as an almost continuous deposit of sodium-potassium nitrate and other soluble salts. The Atacama Desert is one of the driest regions in the world with as much as 20 years between rainshowers. These deposits are the only substantial concentration of potassium and sodium nitrate, iodate, perchlorate, and chromate salts found anywhere in the world. This deposit contains an estimated 10^9 tonnes of sodium nitrate, slightly less sodium chloride, and perhaps twice that amount of sodium sulfate. Potassium nitrate, magnesium sulfate, and boric acid may total about 100 million tonnes each, while the iodine and sodium perchlorate contents are about 5 million tonnes each. Almost no bromine is present. The ore occurs as a "caliche" and is generally most concentrated from 1 to 5 m below the surface. High-grade zones have been commercially extracted since the 1800s.

Chile: Salar de Atacama – The Salar de Atacama in northern Chile is a large (approximately 50 km x 100 km), high-altitude dry lake. It is bounded by the Andes Mountains on the north and east and a fuming volcanic cone to the south. The average surface elevation is 2,300 m. The San Pedro River flows into the northern edge of the basin forming a partially flooded shallow delta. The El Tatio geyser, producing high-lithium geothermal brines, also flows into the basin. The lake floor covers about 3,000 km^2, and over 40% of this area is covered with salt crusts. A complex, saturated brine is found within 0.6 m of the surface over most of the lake's area, and extends to depths of at least 40 m in the areas tested. The potassium concentration in the brine varies from 15 to 44 g/l, indicating the presence of at least 120 million tonnes of KCl and 80 million tonnes of K_2SO_4. The brine also contains considerable lithium and boron, and both lithium and potash are presently commercially recovered.

China: Qarhan Lake, Qaidam Basin – There are a number of saline lakes in China that can be considered potential potash deposits. The largest of these lakes occur in the Qaidam Basin, a 120,000-km^2 area that contains both wet and dry (playa) lakes with a wide variety of mineralization. The Qaidam Basin is located in the north of the Qinghai-Xizang (Tibet) Plateau about 2,800 km west of Peking at an elevation of 2,600-3,200 m. The climate is arid, windy, and very cold in the winters. The largest of the potash-bearing sub-basins are the Qarhan and Dalongtan playas, which contain beds of carnallite as well as potassium-bearing brines. The estimated reserves of Qarhan Lake are 360 million tonnes K_2O ([97]. In 1989 commercial exploitation began, and the Qinghai Potash Fertilizer Factory had an announced initial capacity of 200,000 tpy of KCl. Plans were being formulated in 1994 for developing additional capacity of 800,000 tpy. Solar evaporation of lake brine produces carnallite (as at the Dead Sea operations), and the carnallite is harvested and converted into KCl.

Israel and Jordan: The Dead Sea – The Dead Sea, which lies in both Israel and Jordan, is the lowest point in the long (600 km), narrow (10-20 km) rift valley that extends northward from the Red Sea between Aqaba and beyond the Sea of Galilee. It is the lowest natural lake on earth; the surface is about 396 m below sea level. The Dead Sea is 76 km long and 16 km wide; it has an area of 930 km^2 and a mean depth of 329 m. It contains an estimated 47 x 10^9 tonnes of salts, of which perhaps 1 x 10^9 tonnes is KCl. The brine in the Dead Sea has a high $MgCl_2$ and $CaCl_2$ content, and this composition is quite unusual. The brine is processed by first crystallizing out halite in large solar ponds, and then continuing the evaporation of the brine in a second set of ponds to deposit carnallite and halite. The impure carnallite is harvested and fed to the processing plants to produce KCl and other products. Residual brine is returned to the Dead Sea. All phases of both the Israeli and Jordanian operations are very large, and Israel is probably the world's lowest cost potash producer.

Mexico: Cerro Prieto (Salton Sea Geothermal Brine) – The highest temperature brines of the Salton Sea geothermal system are centered in pools just southeast of the Salton Sea in California, and much further south in the Cerro Prieto area of Mexico. The Salton Sea Basin is an inland trough that is an extension of the Gulf of California rift-fault system. The northern geothermal area in the United States covers an area of about 50 km^2, and the southern area in Mexico is somewhat smaller. In the north, brine temperatures have measured

300°C at a depth of 900 m and 360°C at 2,100 m. At Cerro Prieto, geothermal power-production wells draw brines from depths of 780-1,450 m with temperatures of 250° to 344°C. The northern reservoir contains a concentrated brine with a very complex chemical composition, and is estimated to contain a total of 165 million tonnes of KCl. Plans have been made for further solar evaporation of the Cerro Prieto geothermal power plant exhaust brine to recover the potash. However, the project has not yet become operational.

United States: Great Salt Lake, Utah – The Great Salt Lake is a large, nearly saturated inland saline lake with a brine much like seawater bitterns. The Great Salt Lake is a remnant of a much larger pre-existing lake, Lake Bonneville. The lake extends for 110 km in maximum length and 50 km in width; it had an area of about 2,600 km^2 in 1965. The Great Salt Lake is quite shallow. The deepest part has varied from 8.1 to 14.2 m during recorded history, and volume has changed more than threefold. The Southern Pacific Railroad built a large semiporous rock-filled causeway (with two large culverts) across the lake in 1955, which resulted in the northern one-third of the lake (about 1,000 km^2) receiving less annual water input and becoming more concentrated. Brine is withdrawn from the northern third of the lake and sent to solar ponds to crystallize mixed potash salts (primarily kainite and NaCl), which are harvested and converted to potassium sulfate. The estimated reserves are about 200 million tonnes of potassium sulfate.

United States: Bonneville Salt Flats, Wendover, Utah – The potash operation near Wendover, Utah, processes subsurface brines that are remnants of the waters of ancient Lake Bonneville, just as the brines are in the Great Salt Lake, 200 km to the east. These brines are associated with the salt crust and shallow sediments of the Bonneville Salt Flats, which cover an area of approximately 400 km^2. The brine is gathered from extensive trenches in the surface of the flats and directed to solar evaporation ponds. The brine contains considerably less sulfate than does the brine in the Great Salt Lake, and upon solar evaporation most of the potassium salts crystallize as sylvite with halite. The sylvinite is harvested, and KCl is recovered by flotation.

United States: Searles Lake, California – Searles Valley lies near the eastern slope of the Sierra Nevada Mountains in south-central California; the city of Los Angeles is located approximately 200 km to the south-southwest. Searles Lake is a nearly elliptical desert playa about 16 km long and 10 km wide. Approximately two-thirds of its surface (100 km^2) consists of mud, and one-third (37 km^2) is composed of halite. The water-soluble minerals in the lake sediments are a mixture of many salts with hanksite ($9Na_2SO_4 \bullet 2Na_2CO_3 \bullet KCl$) being one of the major components. The upper and lower salt (younger) beds are porous and contain the brine that has been used for commercial potash production by evaporation and crystallization since early in the twentieth century. The total reserves of potassium chloride equivalent appear to be in excess of 90 million tonnes.

5.5.2 Potash Mining

There are two basic types of potash mining: conventional mining, which encompasses several standard methods, modified as necessary for specific situations, and solution mining.

5.5.2.1 Conventional Mining – Each potash deposit has its own characteristics and mining problems that must be handled on an individual basis. However, many standard methods have become widely accepted within the potash mining industry. For potash beds that are relatively flat and uniform in thickness, or for cutting entries, boring machines with two or four cutting arms have proven to be the most effective and economical mining method. For moderately inclined, undulating and/or thickening-thinning potash seams, continuous miners with cutting "drums" mounted on one or two moveable arms are the most effective. For highly variable ore bodies, or ore with potential rock-bursts or other special needs, drilling and blasting are still required.

Most mine configurations are the conventional room and pillar design, except that "stress relief mining" (multiple entries with outer yield pillars) has proven highly effective for the deeper mines with plastic flow (of the ore) or unstable roof conditions. For thicker or highly inclined potash seams, the open stope (successive horizontal cuts for thick beds) or cut and fill methods allow both a high ore recovery and an easy means of disposing of both waste produced underground and plant tailings.

For those mines without high-pressure aquifers above the potash and with somewhat plastic overlying strata, the long-wall mining method, which allows the roof to descend soon after the ore is cut, can provide very high ore recovery rates and result in high productivity. In the case of long-wall mining, the beds must be fairly uniform and continuous (very minor faulting, etc.) over the width and length of individual mining panels. Although long-wall mining can produce ores at relatively low costs per tonne, equipment and development costs can be high and the method is not as flexible as other methods.

Underground ore transport is now accomplished almost entirely by conveyor belts. Conveyor belts may be suspended from the roof or set on the floor. For the highest capacity mines with continuous (borer or drum) mining machines, flexible belt conveyors attached to or directly fed from the miner and directly feeding a panel belt have produced considerable savings. Some mines employ either shuttle cars to take the ore from the mining machines to the feeder-breaker at the panel belt, or load-haul-dump (LHD) machines that pick up ore from the floor and then haul it to a feed station. Most mines have considerable underground ore storage capacity to even out the flow, as well as feed bins where the ore is loaded into high-speed "skips" (elevator bins) that take the ore to the surface and dump it, with all aspects of the loading-lifting-dumping cycle being done automatically. A few shallower mines bring the ore to the surface with conveyor belts in long inclined tunnels.

The costs of potash mining by conventional methods can vary tremendously. Mining is the major expense of potash production in operations that require more manpower because of low-grade ore or difficult mining conditions. For ore bodies and situations that allow high-capacity operations, mining can be somewhat less expensive than the processing of potash ores at the surface.

5.5.2.2 Solution Mining – In 1994 three potash plants in Canada and the United States utilized solution mining as their method of operation. The mine of Kalium Chemicals, near Moose Jaw, Saskatchewan (Canada), was designed as a conventional 3-pipe (pipes to inject water near the top, withdraw brine from the bottom, and pad the upper surface all in one well) solution mining operation to take advantage of a major thickening of the Belle Plaine Member at about 1,650-m depth. Brine from the well field is evaporated in triple-effect evaporators to crystallize dissolved halite, and the brine is then cooled to crystallize the potash salts. The residual brine is recirculated to the evaporators, although in the winter it is first sent to ponds to be further cooled and to precipitate additional potash salts.

The PCS Patience Lake Division uses solution mining for a former conventional mine that had been extensively operated for 22 years and then was accidentally flooded. Due to the tremendous surface area of the previous workings, the operation selectively dissolves only the KCl. Brine is withdrawn from the mine in the winter and sent to a pond, which was formerly used for tailings before being rebuilt as a holding and cooling reservoir. Potash is crystallized, and then the residual brine is returned to the mine. The potash is harvested by floating dredges and sent to the plant for further processing and drying, screening, and compaction.

A similar intentionally flooded mine is operated at the Moab Cane Creek, Utah (U.S.A.) plant. The potash brine is solar evaporated to crystallize sylvinite. The sylvinite is dry harvested and sent to a processing plant for conventional flotation.

5.5.3 Beneficiation and Processing of Potash Ores and Brines

The beneficiation of raw potash ore into marketable products, similar to potash mining operations, requires a somewhat different scheme and equipment for each processing plant. The ore composition (mineralogy), ore grade (K_2O content), liberation size (amount of maximum particle size required to allow separation of the different minerals), and type and amount of slimes (insolubles such as clay, anhydrite, dolomite, silica, etc.) are different for every deposit, and perhaps may be highly variable within a single deposit. Accordingly, the modern potash processing plant must have an efficient, highly versatile process to accommodate variations in the feed yet still maintain product quality at as low a production cost as possible.

Four basic beneficiation techniques have been applied in the potash industry: flotation, heavy media separation, electrostatic separation, and thermal dissolution-crystallization. Other techniques have also been experimented with. These include ammoniacal leaching and gravity separation using shaking tables. Ammoniacal leaching has proven too costly, and gravity separation can only produce impure concentrates (about 80% KCl). Most potash processing plants practice a combination of beneficiation techniques. Each method will be reviewed separately in the following sections.

5.5.3.1 Crushing and Grinding – The first step in the beneficiation of a solid potash ore is to reduce the ore to a size where the potash is liberated from the other ore constituents and can be separated from them. A prime consideration in crushing and grinding is that a minimum amount of fines be produced. Any fines produced by grinding must be processed by more costly methods. Larger and closely sized product is more valuable, and less energy is spent on grinding. Another prime consideration is that both the capital costs involved in establishing the operation and the production costs be minimized. To accomplish these goals, processing usually begins with various size reduction equipment and coarse (0.6-1.2 cm) screens working in closed circuit (recycling the oversize) because coarse ore crushing and screening are relatively simple and less expensive than other steps. There are a large number of equipment choices, but most modern plants start out with dry screening. The oversize is recycled to an impactor, and the undersize is sent to other types of size classification equipment.

The second and third stages of grinding and classification involve even greater choices of equipment, but are relatively more expensive. For small liberation sizes (usually between 100- and 150-mesh, Tyler), wet ball or rod mills are required. For larger liberation sizes (plus 100-mesh, Tyler), wet or dry impactors or cagemills are used. The oversize closed circuit separators are either screens or, if wet processing is utilized, screens and rake or screw classifiers. Undersize separators (usually to split at 100- to 200-mesh, Tyler) are typically wet cyclones and/or hydroclassifiers.

5.5.3.2 Desliming – Fine particles, both ore minerals and insolubles, are always removed to the greatest extent possible before the potash separation step. In flotation, fine particles with high surface areas tend to adsorb excessive quantities of flotation reagents. Excessive amounts of fines can significantly raise reagent costs and cause contamination of the product. Fine gangue particles may float or become mechanically entrapped in the product. The ore slurry is first "attrition scrubbed" to liberate and disperse the fines. The equipment used varies widely, in that any form of intense agitation is effective in slimes removal. In a few plants, some or all of the slimes are separated by selectively floating the slimes from the sylvinite (Figure 5.25). However, most plants deslime by using one or more stages of cyclones and hydroseparators (Figure 5.26). A liberation size of about 150-mesh has been determined to provide the best cut-off range for flotation of most potash ores. Many plants (especially those employing fine grinding) make a second size classification at 200- to 400-mesh to reduce potash losses. These fine solids are then floated in a fines flotation circuit, and the impure float is usually sent to a hot leach-crystallization plant for further processing. In several plants, the slimes slurry is hot leached to further recover potash (Figure 5.27). Whatever treatment is used, the residual slimes are finally thickened and sent to tailings areas for disposal. If regrinding of coarse flotation tails is practiced, these solids are also deslimed again before being refloated.

5.5.3.3 Flotation – Flotation is a selective beneficiation process that utilizes the differences in surface properties of various minerals. By conditioning ores with specific reagents, selected minerals can be induced to become either hydrophobic (water repellent) or hydrophilic (water attracting) in solutions. If a solution is then agitated and aerated by introducing air bubbles, mineral particles that are hydrophobic will preferentially attach themselves to the air bubbles and float to the surface where they can be removed. The waste (gangue) materials in the pulp at the bottom of the cells are disposed of as tailings. This type of flotation, where the valuable minerals are removed in the froth, is termed direct flotation and is the most common flotation technique employed in the potash industry.

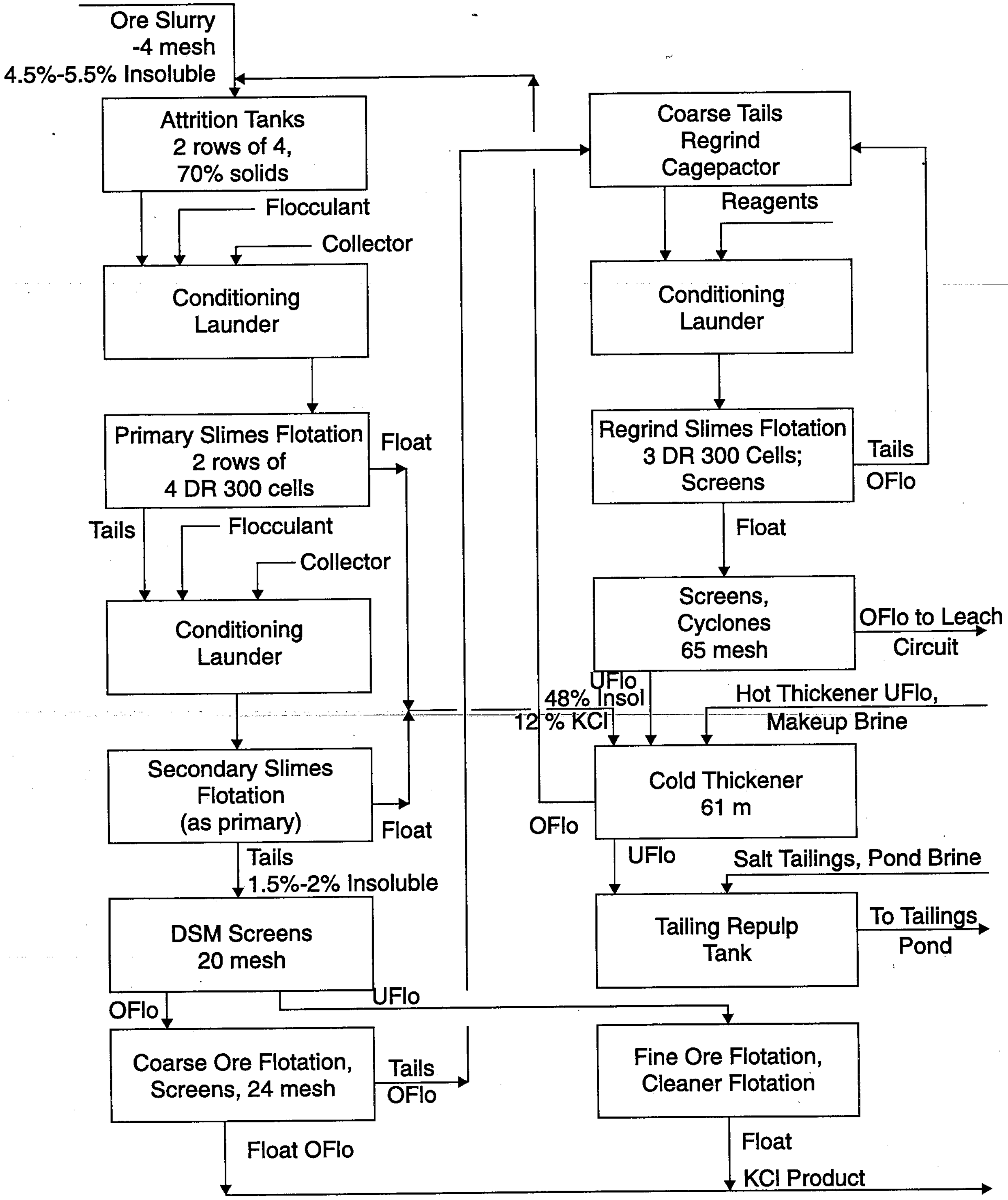
The most important reagents used in flotation are collectors. In the case of flotation to treat sylvinite ores, a cationic collector is added to the closely sized and deslimed ore slurry. These collectors are mostly straight-chain aliphatic primary amines derived from natural fats and oils that are neutralized by acetic or hydrochloric acid before use. The polar end group of the reagent is selectively adsorbed on potash, rendering its surface hydrophobic. The salt (NaCl) and other gangue minerals sink in the pulp and are removed from the bottom of the flotation cell.

Another category of reagents that is commonly used is known as frothers. Frothers are used to aid the formation of, and stabilize, the flotation froth. Generally, these reagents are organic heteropolar compounds. Pine oil, a widely used frother, contains aromatic alcohols. A wide range of synthetic frothers is also available. A conventional frother, MIBC (methylisobutyl carbinol), is used in potash flotation as a modifier to inhibit the formation of excessive amine froth [98].

Modifiers or regulators constitute another class of flotation reagents that are used to control the process. In potash flotation, slimes depressants such as starch, guar gum, dextrine, and synthetic compounds are typically used [99].

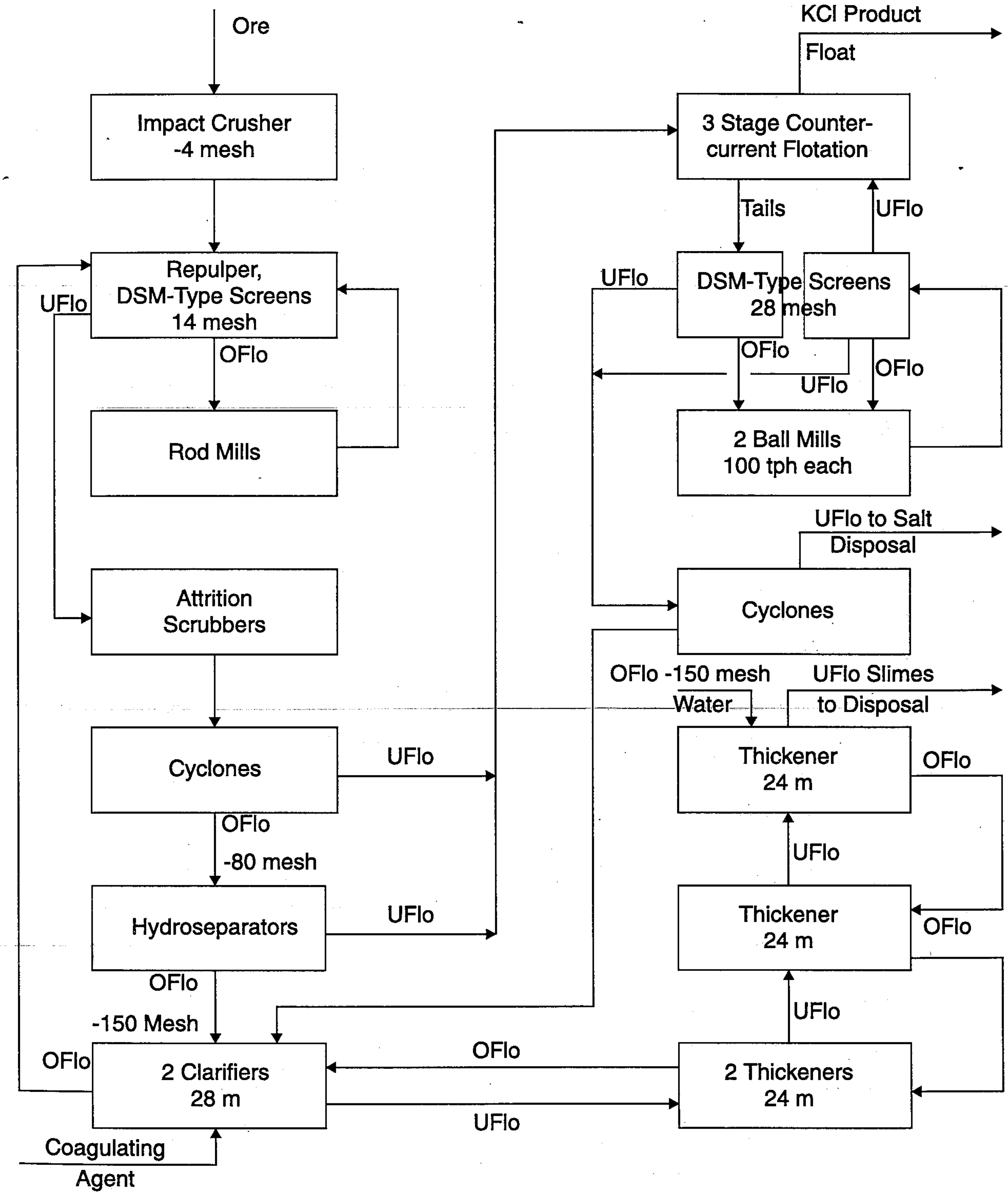
In potash flotation the objective is usually to separate sylvite from halite by using cationic collectors. When the potash ores contain sulfate minerals like kieserite, sulfate salts can be floated by using fatty acids or sulfated fatty acids as collectors. Combined salts such as kainite ($KCl \bullet MgSO_4 \bullet 3H_2O$) can be floated by using coconut amine, as performed in Sicily, Italy. Schoenite ($K_2SO_4 \bullet MgSO_4 \bullet 6H_2O$), processed from Great Salt Lake, U.S.A., brines, can be floated by using coconut fatty acid [100]. Ores containing carnallite may be pretreated to remove magnesium chloride and give simple potassium chloride and halite, which then can be floated with tallow amine [98].

Potash flotation circuits always have both rougher and cleaner cells. In the rougher cells, an attempt is made to float as much potash as possible, while in the cleaner cells the purity of the floated product is the prime consideration. The coarse particles of the rougher tailings and the tailings from the cleaner cells are usually reground to a smaller size range and refloated. In situations where the potash ore is liberated at fairly coarse sizes, the coarse size fraction is conditioned with reagents and floated separately from the fines, thus decreasing reagent consumption and generally improving recovery (Figure 5.28). With very fine ores, some companies (such as MDPA, France) use countercurrent flotation because the use of traditional flotation cells leads to excessive mechanical entrainment of the salt (Figure 5.26). In this case, the tailings from each stage are returned to the previous stage and the float advances to the next stage, both to be repeatedly refloated [101]. If the fine-floated potash product is not quite up to grade, it may be hot or cold leached to dissolve halite and to increase the purity.



Source: [102,103].

Figure 5.25. Cominco, Canada, Slimes Flotation Circuit.



Source: [104].

Figure 5.26. Crushing and Slimes at MDPA Amelie Plant.

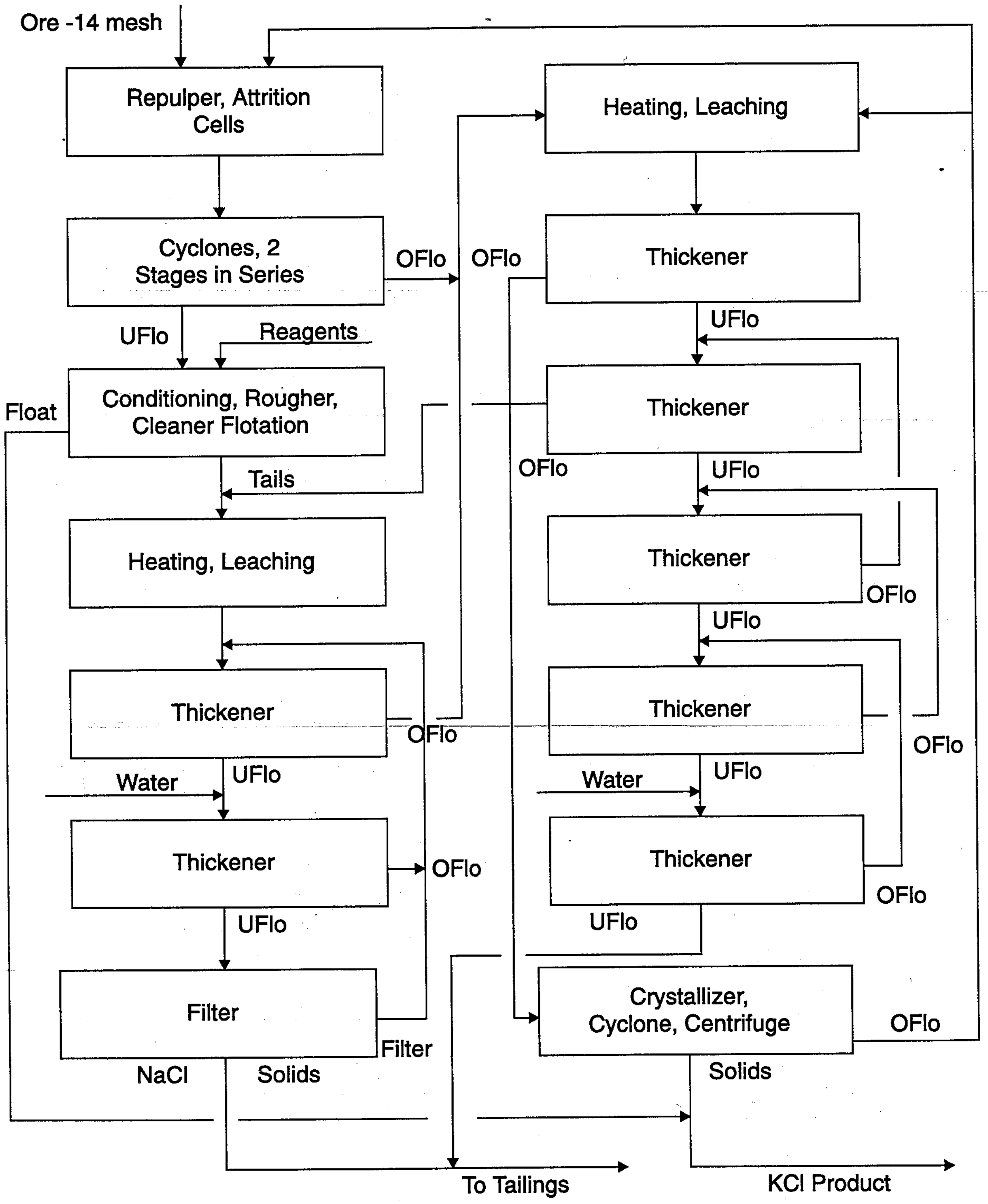
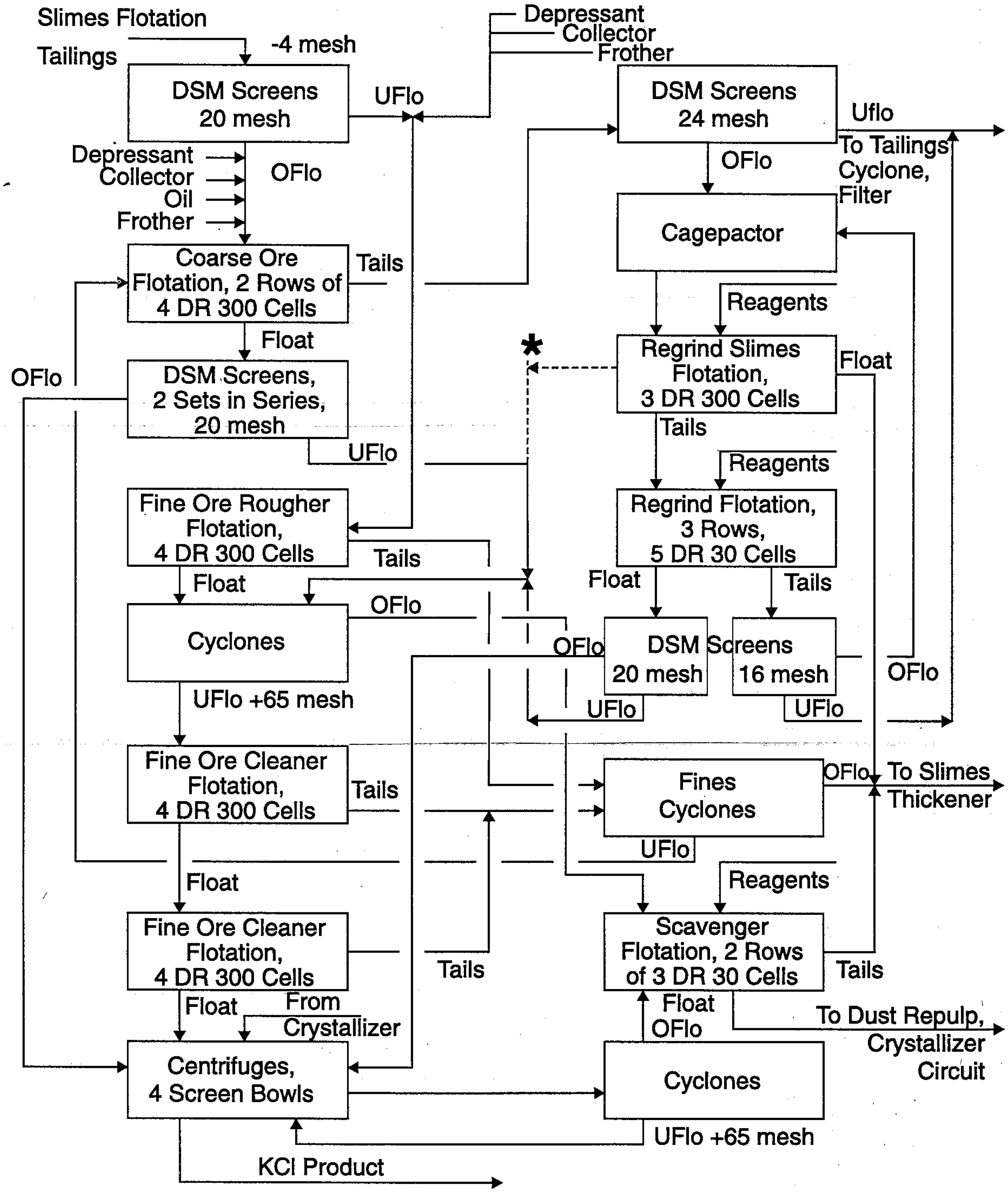


Figure 5.27. Potash Processing at the Mississippi Chemicals Operation, Carlsbad (Former National Potash).



*When 65-mesh float screens were used, the screen OFlo was recycled.

Source: [102,103].

Figure 5.28. Cominco, Canada, Flotation Circuit.

5.5.3.4 Heavy Media Separation – Heavy media separation is a useful beneficiation process as a preliminary scalping operation or in combination with other techniques. The process utilizes the difference in specific gravity of sylvite (KCl) and halite (NaCl). Halite is the more dense mineral (specific gravity 2.13 versus 1.9 for sylvite). In a liquid of intermediate specific gravity, halite will sink and sylvite will float. Commercial heavy media operations use a very finely divided weighting agent, typically ferrosilicon or magnetite of minus 200-mesh, which is slurried to create an artificial heavy medium at the specific gravity required for separation. After separation, the magnetite or ferrosilicon is recovered by magnetic separation and recirculated to the system [105].

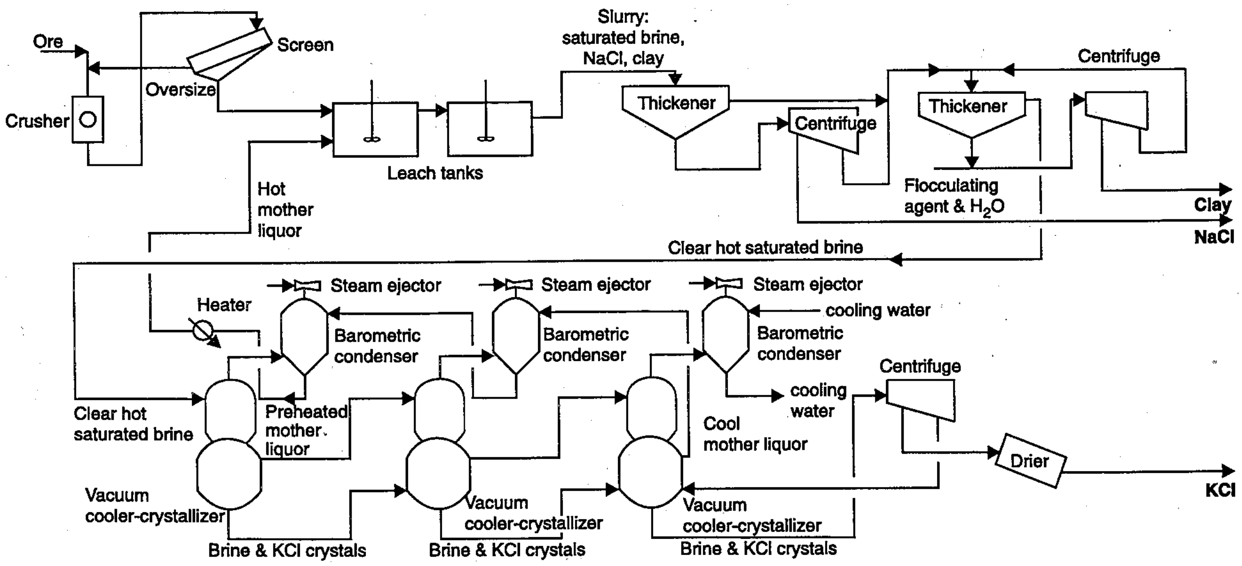
5.5.3.5 Electrostatic Separation – Electrostatic separation is a dry technique in which a mixture of minerals may be differentiated according to their electrical conductivity. For potash minerals, which are not naturally conductive, the separation must be preceded by a conditioning step that induces the minerals to carry electrostatic charges of different magnitudes and, if possible, different polarities. For potash, fractional or triboelectric charging is used; the charges are induced through repeated physical contact between the different minerals.

In Germany, the potash ore is ground to between minus 1 and 2 mm. The ground ore is conditioned with one or more reagents, preferably aromatic and aliphatic monocarboxylic acids. The mixture is then heated in a fluidized bed, and the relative humidity is adjusted to enhance charging of the particles. The ore is then fed into the electrostatic separator, to yield three fractions, i.e., product, residue, and middlings. The middlings, after further grinding, are recycled to the conditioning stage.

Using this process provides two main advantages in terms of costs and environmental impact. By using a dry pre-enrichment step in the mine (underground), hoisting costs are reduced because only valuable preconcentrated ore is moved to the surface. Thus, the process decreases the environmental impact of disposing of salt tailings on the surface or the costs of returning salt tailings to the mine. Using a dry process to improve product grade also eliminates drying costs [106].

5.5.3.6 Thermal Dissolution-Crystallization – Thermal dissolution-crystallization is possible because potassium chloride is much more soluble in hot water than in cold and sodium chloride is only slightly more soluble at 100°C than at 20°C. In saturated solutions containing both salts, sodium chloride is actually less soluble at higher temperatures. When a brine that is saturated with both salts at 20°C is heated to 100°C, it is capable of dissolving substantial amounts of KCl but not NaCl.

A typical dissolution-crystallization flow diagram is illustrated in Figure 5.29 [107]. Sylvinite ore is crushed



Source: [105].

Figure 5.29. Beneficiation of Potash Based on Thermal Dissolution-Crystallization.

to minus 3-mesh and washed with cold, saturated NaCl-KCl solution. Clays are removed from the solution by desliming, and the clarified solution is then heated and used to dissolve the potash in the washed ore. Undissolved NaCl is discarded as tailings. The brine solution is then cooled under vacuum, and the KCl crystallizes out and is separated, washed, and dried. The remaining brine is recycled. When a high-purity KCl for chemical use is required, the crystalline KCl is redissolved and recrystallized to produce a double-refined product containing more than 99.9% KCl.

Commercially, the thermal dissolution-crystallization process is used in France by MDPA at the Marie-Louise and Amélie refineries and in Germany by Kali und Saltz at the Sigmundshall, Neuhof-Elmers, and Friedrichshall refineries. In eastern Europe and the former Soviet Union, this process is used to treat potash ores that contain high levels of clays and magnesium chloride levels that exceed 30% $MgCl_2$. The main disadvantage of this process is the high energy consumption required to heat all the mother liquor. Corrosive hot brines must be handled, which results in higher plant maintenance costs and requires the process equipment to be manufactured of special high-cost materials. Although thermal dissolution-crystallization is used only in solution mining, a wider application would be the extraction of potash from brines.

5.5.3.7 Beneficiation of Carnallite Ores and Brines – Carnallite ores are the source of only a small percentage of the world's potash supply even though there are large deposits of carnallite-containing ores in many regions. One disadvantage of carnallite ores is their low grade. Pure carnallite ($KCl \bullet MgCl \bullet 6H_2O$) contains only 17% K_2O. Carnallite cannot be used as a direct-application potash fertilizer because it is deliquescent. Dissolution and recrystallization methods must be used to process carnallite ores, and these methods are energy intensive and expensive. A large volume of byproduct magnesium chloride solution is produced in carnallite processing, which is likely to pose a disposal problem. In spite of many disadvantages, ores or brines containing carnallite are processed to produce KCl in several countries including Germany, Israel, Jordan, and Spain, and may be utilized in the future in Thailand, Pakistan, and the Congo.

Carnallite has been mined, beneficiated, and processed in Germany for approximately 130 years. These operations were economically sustainable only as long as the German mines supplied a very significant portion of the world potash market. As a result of international competition based on the production of sylvinite ores, carnallite processing plants in Germany that only produced KCl were forced to close and potash production in Germany was concentrated at mines with significant amounts of sylvinite ores.

The conventional mining and beneficiation sequence for potash recovery from carnallite encompasses the operations of mechanically mining the ore, hoisting ore to the surface, beneficiating the ore to a carnallite concentrate, dissolving the carnallite, recrystallizing potassium chloride, disposing of saline solid wastes, and disposing of saline liquid effluents. Carnallite ore processing methods vary widely and depend upon accessory minerals that are associated with the ore.

There are two general methods of carnallite processing: cold leaching and hot leaching. Cold leaching processes are carried out at 20°-25°C. Carnallite ore from Klodawa, Poland, is processed to recover a liquor saturated in magnesium chloride, a coarse sodium chloride solid product, and a fine residue of sylvite and kieserite. Initial grinding of the ore determines the eventual purity of the coarse and fine decomposition products. The temperature used to decompose the carnallite is not critical, but must be below 25°C to prevent sulfate from remaining in the magnesium chloride liquor. Decomposition of the ore is carried out using unsaturated brine recirculated from a later filtration stage. In order to prevent reprecipitation of carnallite, the decomposition liquor is allowed to reach only 90% saturation in magnesium chloride. The fine decomposition product contains sylvite and kieserite and meets the specification for some potash-magnesium fertilizers (46% potassium chloride and 45% magnesium sulfate). However, flotation can be used to separate kieserite from sylvite [98].

Carnallite ores may also be treated by a hot leach at about 100°C to dissolve $MgCl_2$, KCl, and any NaCl that may be present. The hot solution is then clarified to remove solid impurities and then evaporated and cooled. After the KCl and NaCl crystals are recovered, they are separated by one of several beneficiation techniques.

In Germany, at the Hattorf and Wintershall mines, carnallite ore is first ground to minus 4 mm. The ore is then leached at approximately 90°C, and the carnallite decomposes. Saturation in potassium chloride is not reached, and only sodium chloride and kieserite remain as solids. The solids and brine are separated by filtration; the brine is cooled to a temperature of approximately 30°C in vacuum crystallizers, and KCl is precipitated. The 40% K_2O product is upgraded by the addition of a liquor from the potassium sulfate section of the refinery. On centrifuging, a 60% KCl product is recovered [108].

Processing of the Dead Sea brine by the Arab Potash Company (APC) in Jordan traditionally utilizes solar evaporation and the hot leach process to produce potash. However, APC's current expansion involves processing by flotation followed by cold crystallization [109]. The Dead Sea brine typically contains 11.5 g/l KCl.

The concentration of other salts is: $MgCl_2$ 130 g/l, NaCl 87 g/l, $CaCl_2$ 37 g/l, and MgBr 5 g/l. Brine is pumped from the Dead Sea into a 10-km-long gravity canal feeding a series of solar ponds. The solar ponds are divided into three basic sections: the salt ponds, the pre-carnallite ponds; and the carnallite ponds. Sodium chloride is precipitated in the salt ponds. The pre-carnallite ponds are used to regulate the concentration of the brine that is fed to the carnallite ponds as close as possible to the point at which carnallite precipitation begins. Carnallite is recovered with a specially designed floating-track harvesting machine. A screw-type cutterhead harvests the 30- to 50-cm-thick carnallite layer. The carnallite slurry (20%-25% solids) is cycloned to reduce the water content and pumped at 40% solids to the processing plant.

The slurry is first wet screened to separate the large high-grade carnallite crystals, which are fed to cold crystallizers. Undersize slurry from the screens is mixed with brine discharged from the cold crystallizers. Additional carnallite is then crystallized, and the slurry is thickened. The thickener overflow is returned to the evaporation ponds. The underflow is subjected to salt flotation. Floated NaCl slurry is pumped to the tailings area. The carnallite sink fraction is settled in a thickener. Thickener underflow is dewatered in centrifuges. The cake from the thickener underflow is conveyed to the cold crystallizers where carnallite is decomposed by the addition of water and recycle brine. Crystallizer discharge slurry is wet screened to remove large particles. Crystallizer screen undersize slurry is subjected to leaching in agitated pans to dissolve any remaining sodium chloride. The leach tank discharge slurry is transported to a thickener, then to two stages of dewatering centrifuges, and finally to a rotary dryer. The dried potassium chloride product passes through screens to be separated into two fractions, standard and fines, according to the required size specifications. The products are collected and stored. A typical block diagram for the cold crystallization process is shown in Figure 5.30.

5.5.3.8 Disposal of Brines and Tailings – A major problem in all plants that process potash ores is the disposal of excess brine and tailings. Until recently, plants merely stacked their waste salt and slimes and injected the excess brine underground, or dumped both into the nearest river. New plants have been required to eliminate these practices. Cleveland Potash, England, repulps the tailings in seawater and discharges them one mile offshore at the bottom of the turbulent North Sea. Frequent inspections have shown that there is no sediment buildup or impact on marine life in the area. The two potash operations in New Brunswick, Canada, run a much tighter water balance in their plants and evaporate excess brine. This results in a 5%-15% higher yield than in other potash plants. Tailings, containing small amounts of residual $MgCl_2$ brine, are mechanically or hydraulically backfilled into the areas previously mined. The tailings are compacted as equipment is driven over them to make the next cut in inclined potash ore bodies. This process of dewatering and backfilling costs more than surface impoundment or river disposal, but greater potash recovery and other savings help to defray additional costs.

5.5.3.9 Beneficiation of Sulfate Ores – The processes for beneficiating langbeinite, alunite, and complex sulfate ores into marketable products are discussed in this section.

Langbeinite – Langbeinite ($K_2SO_4 \bullet 2MgSO_4$) is separated from sylvite and halite by selective washing, froth flotation, or heavy media separation. Langbeinite may be marketed as fertilizer or animal feed as a source of K, Mg, and S, or it may be converted to other products. Potassium sulfate is produced by reacting one molecule of langbeinite with four molecules of KCl. Potassium magnesium sulfate is produced by refining langbeinite. The reactions to produce potassium sulfate and potassium magnesium sulfate are as follows:

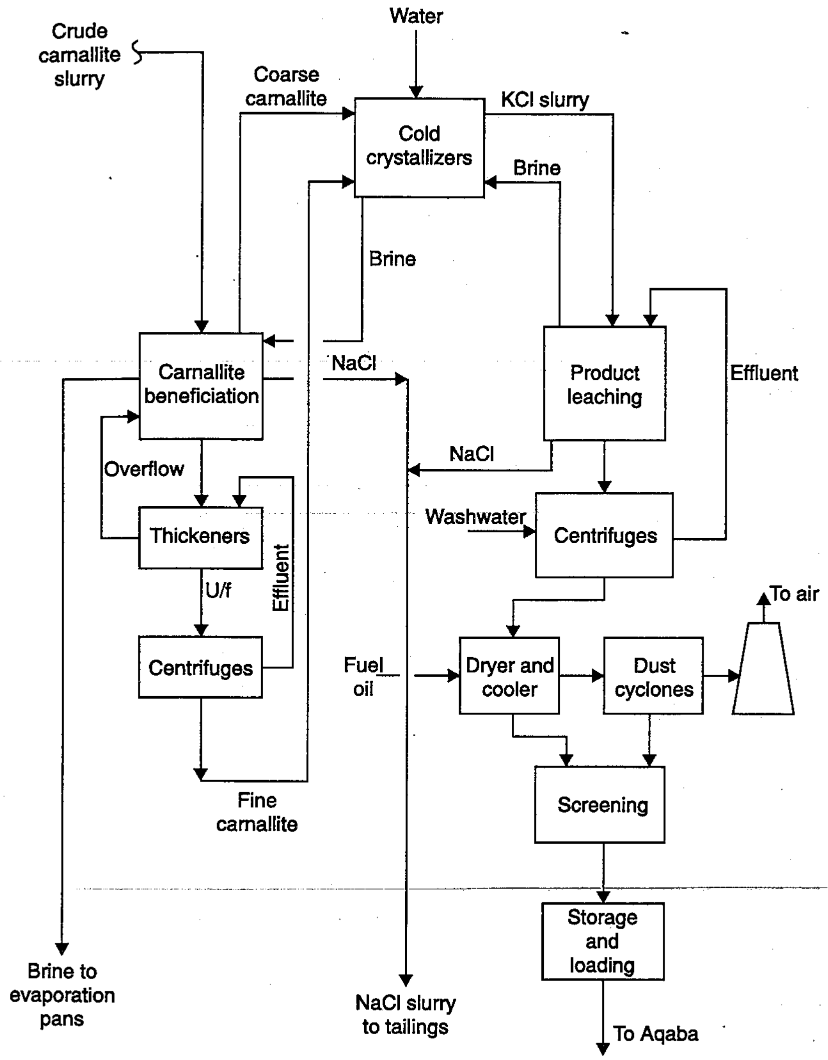
$$\underset{\text{Langbeinite}}{K_2SO_4 \bullet 2MgSO_4} + \underset{\substack{\text{muriate}\\\text{of potash}}}{4KCl} \rightarrow \underset{\substack{\text{potassium}\\\text{sulfate}}}{3K_2SO_4} + 2MgCl_2$$

$$\underset{\text{Langbeinite}}{2(K_2SO_4 \bullet 2MgSO_4)} + \underset{\substack{\text{muriate of}\\\text{potash}}}{2KCl} \rightarrow \underset{\substack{\text{potassium}\\\text{magnesium sulfate}}}{3(K_2SO_4 \bullet MgSO_4)} + MgCl_2$$

A flowchart of the production of potassium sulfate from the Great Salt Lake, U.S.A., is shown in Figure 5.31. Water from the lake is pumped and distributed to shallow ponds covering an area of 19,200 acres. Solar evaporation causes the brine to reach saturation with sodium chloride, and the salt settles on the pond floor. Further evaporation of the brine in subsequent ponds results in the precipitation of kainite, sylvite, and carnallite, which are harvested from the ponds for further processing. Fractional crystallization is used to separate the final potassium sulfate product from the other minerals [110].

Alunite – Alunite [$K_2 \bullet Al_6(OH)_{12} \bullet (SO_4)_4$] is a potential source of potassium sulfate, alumina, and sulfur dioxide byproduct. The economics of production hinge on the value of the alumina. Processing involves ore comminution, roasting, and leaching to recover potassium sulfate solution. Filtered solids can be processed in a Bayer-type process plant for alumina recovery [111].

Production of 1 million tpy of alumina (Al_2O_3) would require about 10 million tonnes of alunite ore and would yield about 500,000 tonnes of potassium sulfate and nearly 800,000 tonnes of sulfuric acid. Energy costs



Source: [109].

Figure 5.30. Cold Crystallization of Carnallite at the Arab Potash Company, Jordan.

and the utilization of the coproducts limit the potential for the production of alumina or potassium sulfate from alunite.

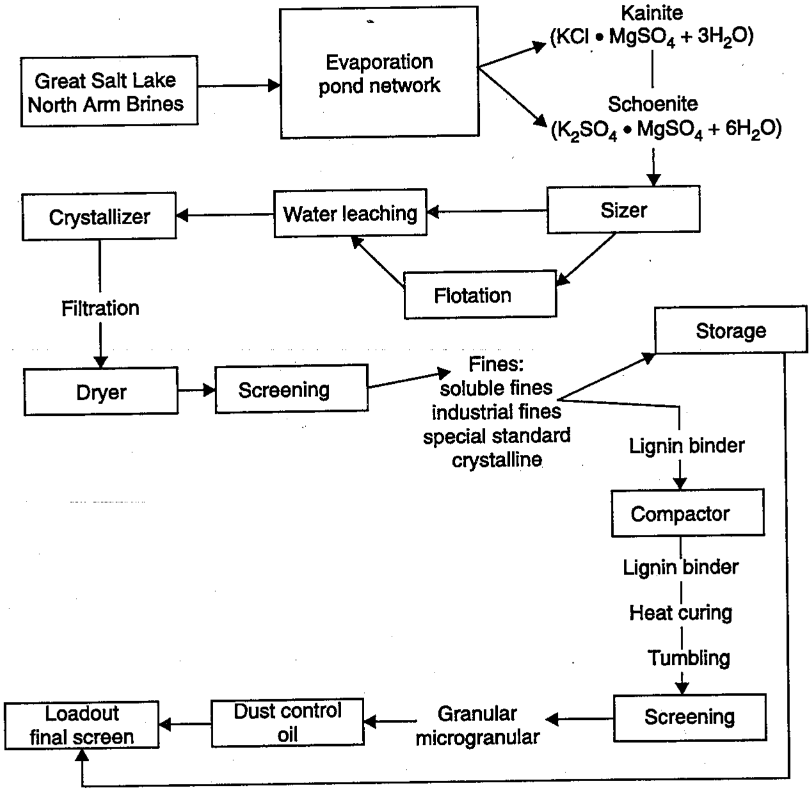
Complex Sulfate Ores – Complex mixtures of potash ores may contain any or all of the following minerals: anhydrite, epsomite, halite, kainite, kieserite, langbeinite, polyhalite, and sylvite along with clays. Extraction of potassium salts from such ores becomes quite complicated because the mineralogical forms of the various components can be unstable. Whenever potassium sulfate is the desired product, free sylvite and kainite must be present in the same molecular proportions. Ideally the reaction is as follows:

$$KCl + \underset{\text{kainite}}{KCl \bullet MgSO_4 \bullet 3H_2O} \rightarrow K_2SO_4 + MgCl_2 + 3H_2O$$

When the ore is deficient in sylvite, schoenite is produced:

$$\underset{\text{kainite}}{2KCl \bullet MgSO_4 \bullet 3H_2O} \rightarrow \underset{\text{schoenite}}{K_2SO_4 \bullet MgSO_4 \bullet 6H_2O} + MgCl_2$$

Potash ores from the Carpathian deposits in the Ukraine contain several minerals, and processing involves grinding and hot leaching with a "synthetic kainite" solution. The leaching process dissolves epsomite, kainite, and sylvite. Langbeinite, halite, and polyhalite are insoluble in this liquor. Clay remains suspended until it is



Source: [110].

Figure 5.31. Production of Potassium Sulfate at Great Salt Lake.

clarified. As the liquor begins to cool, potassium salts begin to crystallize out of solution. Normally, potassium chloride and sodium chloride would precipitate first, but their precipitation is inhibited by the addition of a solution that is saturated with magnesium and potassium sulfate. Under these circumstances, only schoenite will precipitate [111]:

$$2KCl + 2MgSO_4 + 6H_2O \rightarrow K_2SO_4 \bullet MgSO_4 \bullet 6H_2O + MgCl_2$$

The precipitated schoenite is thickened and filtered, and part of it is mixed with water to produce potassium sulfate:

$$K_2SO_4 \bullet MgSO_4 \bullet 6H_2O \rightarrow K_2SO_4 + MgSO_4 + 6H_2O$$

The potassium sulfate is removed as an end product by centrifugation. The hot liquor is recycled to the settling tanks, and the clear solution is recycled to the dissolving tanks.

During the conversion of kainite to schoenite, magnesium chloride is also formed. The concentration of magnesium chloride in solution is controlled by withdrawing a part of the schoenite filtrate, which is evaporated to remove enough potassium and sodium to maintain a constant concentration of these materials in the system. This process permits the use of a complex ore to produce potassium sulfate, schoenite, and sodium sulfate and magnesium chloride liquors.

5.5.4 World Potash Production and Reserves

To the present time, world potash production has been only partially based upon economic merit. In the countries of the former Soviet Union and in East Germany, the potash operations were entirely government owned and controlled. These centrally planned economy countries had constructive, but forced-use internal markets, and capital and operating costs were often not critical factors. Consequently, the potash industry in many of these countries employed excessive numbers of workers per tonne of potash produced. Often mines with low-grade ores or processing plants using relatively expensive methods were kept open for social rather than economic considerations. Much less extreme but similar operating practices are occurring or have been employed in other government-controlled or partially subsidized potash production operations in Brazil, Canada, Chile, China, Congo, France, West Germany, Israel, Italy, Jordan, and Spain. A second distinguishing feature of the potash industry is that, because of generally poor economics in the industry and similarities in mining and processing options, research and development often were not promoted; therefore, cost reductions and efficiency changes have been comparatively infrequent. Finally, increasing maintenance costs and usually much higher mining costs are incurred as potash operations age and face dwindling reserves, declining ore grades, longer distances from mining faces, and often thinner or deeper ore zones.

Production of potash in 1994 was estimated at 21.6 million tonnes K_2O, some 0.7 million tonnes higher than 1993 (Table 5.25). This production level represents an overall capacity utilization of about 60% of the world potash mine capacity (36 million tpy). Output from the former Soviet Union countries was projected to stabilize in 1994; however, production may still be on a downward trend. The production of FSU countries has been mainly limited by the progressive loss of domestic demand, and by lower demand in the traditional markets of central Europe. The longer production remains far below installed capacity, the more increasingly difficult it will be to regain higher capacity utilization. After operating for some 30 years, Soligorsk 1 in Belarus was expected to close in 1995 due to exhaustion of reserves. Capacity reduction and possible closure may take place at other Soligorsk mines, potentially leaving only the Soligorsk 3 mine open. The older mines of the Uralkali and Silvinit combines in the Upper Kama Basin in Russia may also face closure. However, the second phase of Uralkali 4 was scheduled for completion in 1995. Overall, capacity in the countries of the FSU could decline by 1.5 million tpy K_2O or more within the next several years. In 1994 both the Silvinit and Uralkali combines were in the process of being privatized [114]. In 1993, the three FSU producers formed a joint venture company, International Potash Company (IPC), and effective February 1994, IPC became the vehicle for potash exports, replacing Agrochimexport.

Table 5.25. World Potash Production

	1992	1993	1994[a]
	(thousand tonnes K_2O)		
Canada	7,330	6,840	7,600
Germany	3,530	3,250	3,000
Russia	3,450	2,590	2,800
Belarus	3,310	1,940	2,000
U.S.	1,700	1,500	1,425
Israel	1,300	1,340	1,350
France	1,140	1,000	950
Jordan	810	820	820
Spain	590	660	600
U.K.	530	550	560
Brazil	85	170	255
Ukraine	182	160	200
Chile	35	55	55
China	25	25	25
Italy	86	0	0
Total	24,103	20,900	21,640

a. Estimated.

Source: [112,113].

Potash production in Canada increased about 4% in 1994. Over 80% of output was accounted for by Saskatchewan mines and the remainder by the two operations in New Brunswick. Overall, the Canadian industry operated at about 63% of installed capacity. As in previous years, mine closures were used to control inventories, particularly in Saskatchewan. In September 1993, Potash Corporation of Saskatchewan acquired the operations of the Rio Algom subsidiary, Potash Company of America; the Sussex mine in New Brunswick; and the solution mine at Patience Lake, Saskatchewan.

Potash production in the United States was slightly lower in 1994, at 1.4 million tonnes K_2O. Exports declined, while domestic sales were about the same. Imports from offshore remained the same at about 4.4 million tonnes K_2O [115]. In April 1994, Horizon Potash suspended production. The Great Salt Lake Minerals Corporation completed a 34-km brine transportation trench that will enable the company to double its production of potassium sulfate to 380,000 tpy.

Production in Germany declined about 8% in 1994. Capacity continues to be reduced as the country undergoes vast social changes and the industry rationalizes its operations. Production from France continued to decline in 1994. In Italy, the operations of Italkali in Sicily remained closed for the entire period of 1993 and 1994.

In the Middle East, the first phase of expansion at Arab Potash Company of Jordan was completed in July 1994 with a capacity of 1.1 million tpy K_2O. The second phase of expansion will result in a capacity of 1.34 million tpy K_2O by 1998. Dead Sea Works, Israel, planned a capacity increase to 1.5 million tpy K_2O by 1995.

In Asia, ASEAN Potash Mining engaged Jacobs Engineering to review and update its feasibility study for an underground mine, based on carnallite production, at Bamnet Narong in Thailand. Asia Pacific Resources continued development activities on its lease area near Udon Thani and was listed on the Toronto Stock exchange in 1996. The mine near Udon Thani would be based on sylvinite reserves and traditional processing methods.

Unidade Operacional Taquari-Vassouras, a subsidiary of CRUD, Brazil, invested in equipment that would allow the Sergipe mine to attain the design capacity of 300,000 tpy K_2O by 1995. Sociedad Quimica y Minera de Chile (SQM) began construction of the first phase of the Minsal project, and production of 80,000 tpy KCl was scheduled for 1996. Full production capacity would be 300,000 tpy. Construction work at the joint venture project between China and the Dead Sea Works of Israel is proceeding, which will increase the annual capacity at the Golmud plant in Qinghai Province to 1 million tonnes KCl.

The potash industry will continue to face challenges in the coming years. A recent survey predicted that the potash industry will inevitably face significant overcapacity even beyond the turn of this century. The surplus of potential supply over demand currently amounts to about 4 million tonnes K_2O, and excess capacity is predicted to be 2.5 million tonnes K_2O in 1999 [116]. As a result of overcapacity, large producers will have to continue to operate at reduced capacities, primarily in Canada and the countries of the FSU. In the 1970s, Canada and the FSU dramatically expanded potash production capacities on demand projections that proved eventually to be largely incorrect. With tough market conditions, producers are bound to enhance their positions in home markets through cost or logistic advantages, customer service, and quality of product.

It is difficult to estimate the amount of minable potash reserves for the major deposits of the world for a number of reasons. First, most of the deposits have been incompletely explored, and exploration data are not made public. Second, the definition of economically minable ore changes with time, technological development, the price of potash, and the owner's interests. Also few details are published on the fraction of barren zones, areas in mines that must be left because of faults, intrusions, fear of water breakthrough or rock bursts, or very sudden ore body changes. Finally, it is unknown whether solution mining will be considered at the end of conventional mining. Perhaps the most authoritative estimate on world potash reserves has been made by Mayrhofer [117], but his figures are now somewhat old, optimistic for the German deposits, and conservative for the others. Table 5.26 lists these values, along with those from Searls [112,113], which are partly the reported reserves of various governments and, in some cases, estimates by the authors.

5.6 References

1. Anonymous. 1996. *BP Statistical Review of World Energy 1996*, The British Petroleum Company, London, England, 41 p.
2. McConnell, D. 1938. "A Structural Investigation of the Isomorphism of the Apatite Group," *American Mineral*, 54:1379-1391.
3. McClellan, G. H., and J. R. Lehr. 1969. "Crystal Chemical Investigation of Natural Apatites," *American Mineralogist*, 54:1374-1391.
4. McClellan, G. H. 1980. "Mineralogy of Carbonate Fluorapatites," *Journal of the Geological Society of London*, 137:675-681.
5. Van Kauwenbergh, S. J. 1995. "Mineralogy and Characterization of Phosphate Rock," IN *Direct Application of Phosphate Rock and Appropriate Technology Fertilizers in Asia — What Hinders Acceptance and Growth*, pp. 29-47, K. Dahanayake, S. J. Van Kauwenbergh, and D. T. Hellums (Eds.), Institute of Fundamental Studies, Kandy, Sri Lanka.
6. McClellan, G. H., and S. J. Van Kauwenbergh. 1990. "Mineralogy of Sedimentary Apatites," IN *Phosphorite Research and Development*, pp. 23-31, A.J.G. Notholt and I. Jarvis (Eds.), Geological Society Special Publication, No. 52, London, England.
7. McClellan, G. H., and S. J. Van Kauwenbergh. 1990. "Relationship of Mineralogy to Sedimentary Phosphate Rock Reactivity," IN *Proceedings of the Workshop on Phosphate Sources for Acid Soils in the Humid Tropics of Asia*, pp. 1-17, Malaysian Rubber Research Institute and Malaysian Society of Soil Science, Kuala Lumpur, Malaysia.
8. Van Kauwenbergh, S. J., and G. H. McClellan. 1990. "Comparative Geology and Mineralogy of the Southeastern United States and Togo Phosphorites," IN *Phosphorite Research and Development*, pp. 139-155, A.J.G. Notholt and I. Javis (Eds.), Geological Society Special Publication, No. 52, London, England.
9. McClellan, G. H., and S. J. Van Kauwenbergh. 1991. Mineralogic and Chemical Variation of

Table 5.26. Estimates of the World's Potash Reserves

	Mayrhofer, 1983		Searls, 1995[a]	
	Minable	Total	Reserves	Reserve Base
	-----(million tonnes K_2O)-----		----(million tonnes K_2O)----	
A. Underground Deposits				
Canada (total)			***4,400***	***9,700***
Saskatchewan	6,137	507,218	-	-
New Brunswick	70	182	-	-
Russia	2,110	10,822	2,800	2,200
Belarus	100	444	800	1,000
Ukraine	25	129	25	30
Germany (total)			***750***	***900***
East	245	730	-	-
West	218	650	-	-
England	60	240	23	30
U.S.A. (total)	33	800	78	260
Brazil, Sergipe (total)	25	100	50	600
Spain (total)	21	100	24	40
France	20	217	13	35
Sicily	6	30	20	40
Congo	0	0	-	20
B. Brine or Surface Deposits				
China	-	-	320	320
Chile	-	-	10	50
Dead Sea (Israel, Jordan)	-	-	103	1,200
U.S.A. (total)	-	-	200	300
C. Carnallite Deposits				
Congo	-	-	-	100
Thailand, Laos	-	-	-	120
U.S.A., Paradox Basin	-	-	-	800

a. Data mainly from Searls [113], with data from Searls [112], and authors' estimates.

Francolites With Geologic Time, *Journal of the Geological Society*, London 148:809-812.

10. Fransolet, A. M., P. Keller, and F. Fonton. 1986. "The Phosphate Mineral Associations of the Tsaobismund Pegmatite, Namibia," *Contributions to Mineralogy and Petrology*, 92(4):502-517.

11. Deer, W. A., R. A. Howie, and J. Zussman. 1982. *An Introduction to Rock Forming Minerals*, Longman Group Limited, Essex, England, 528 p.

12. Taborszky, F. K. 1972. "Chemismus und Optik der Apatite," *Neus Jahrbuck fur Mineralogic*, 2:79-91.

13. Nriagu, J. O., and P. B. Moore. 1984. *Phosphate Minerals*, Springer-Verlag, New York, NY, U.S.A., 442 p.

14. McClellan, G. H., and L. R. Gremillion. 1980. "Evaluation of Phosphatic Raw Materials," IN *The Role of Phosphorus in Agriculture*, pp. 43-80, American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, WI, U.S.A.

15. Van Kauwenbergh, S. J., J. B. Cathcart, and G. H. McClellan. 1990. "Mineralogy and Alteration of the Phosphate Deposits of Florida," U.S. Geological Survey Bulletin 1914, 46 p.

16. McClellan, G. H., and S. J. Van Kauwenbergh. 1990. "Clay Mineralogy of the Phosphorites of the Southeastern United States," IN *Phosphate Deposits of the World*, Vol. 3, *Neogene to Modern Phosphorites*, pp. 337-348, W. C. Burnett and S. R. Riggs (Eds.), Cambridge University Press, Cambridge, England.

17. Lehr, J. R., and G. H. McClellan. 1972. *A Revised Reactivity Scale for Evaluating Phosphate Rocks for Direct Application*, Bulletin Y-43, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.

18. Van Kauwenbergh, S. J., and G. H. McClellan. 1990. "Mineralogy of Sedimentary Apatites and the Relationship to Phosphate Rock Reactivity," Paper presented at the National Workshop on Fertilizer Efficiency, Cisarua, Indonesia, November 12-13, 1990.

19. Lawendy, T.A.B., and G. H. McClellan. 1993. "Flotation of Dolomitic and Calcareous Phosphate Ores," IN *Beneficiation of Phosphate: Theory and Practice*, pp. 231-243, H. El-Shall, B. M. Moudgil, and R. Wiegel (Eds.), Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, U.S.A.

20. Lawendy, T.A.B., W. R. Clayton, and G. H. McClellan. 1987. "Beneficiation of Some Indigenous Phosphate Ores," Paper presented at 194th American Chemical Society National Meeting, New Orleans, LA, U.S.A.

21. Abu-Eishah, S. I., et al. 1991. "Beneficiation of Calcareous Phosphate Rocks Using Dilute Acetic Acid Solutions," *International Journal of Minerals Processing*, 31:115-126.

22. Doheim, M. A., M. M. Tarshan, and M. M. El-Gendy. 1978. "Calcination of Phosphate Rock in a Fluidized Bed Furnace," *Journal of Applied Chemistry and Biotechnology*, 28(8):531-538.

23. Unkelbach, K. H., and H. D. Wasmuth. 1991. "A High Intensity Drum-Equipped Magnetic Separator With Superconducting Magnet," *Industrial Minerals Supplement*, pp. 48-54.

24. Smani, S. M., P. Blazy, and J. M. Cases. 1975. "Beneficiation of Sedimentary Moroccan Phosphate Ores," *Trans. SME-AIME*, 298(2):176-182.

25. Lowver, J. E., W. O. McClintock, and R. E. Snow. 1983. "Method of Beneficiating Phosphate Ores Containing Dolomite," U.S. Patent 4,372,843.

26. Lehr, J. R., and S. S. Hsieh. 1981. "Beneficiation of High Carbonate Phosphate Ores," U.S. Patent 4,287,053.

27. Rule, A. R., D. E. Larson, and C. B. Dallenbach. 1982. "Application of Carbonate — Silica Flotation Techniques to Western Phosphate Minerals," U.S. Bureau of Mines, Report of Investigations No. 8728.

28. Houot, R., and J. L. Polgaire. 1980. "Inverse Flotation Beneficiation of Phosphate Ores," IN *Proceedings of the 2nd International Congress on Phosphorus Compounds*, pp. 231-246, Institut Mondial du Phosphate (IMPHOS), Paris, France.

29. Hedi, E. 1979. "Flotation of Phosphate Minerals, Part I. Elimination of Siliceous and Calcareous Exogangue," *Industrie Minerale Mineralurgie*, 22:147-149.

30. Snow, R. E. 1979. "Beneficiation of Phosphate Ores," U.S. Patent 4,144,969.

31. International Fertilizer Development Center (IFDC). 1990. "Technical Evaluation of Producing Phosphate Concentrates From Matongo Deposit, Burundi," IFDC Technical Report, pp. 34-41, Muscle Shoals, AL, U.S.A.

32. Russel, A. 1992. "Magnetic Separation: An Ever More Exacting Science," *Industrial Minerals*, 294:39-57.

33. Lawendy, T.A.B., and S. J. Van Kauwenbergh. 1993. "Flotation of High-Iron Phosphate Ores and Phosphatic Iron Ores," IN *Beneficiation of Phosphate: Theory and Practice*, pp. 29-43, H. El-Shall, B. M. Moudgil, and R. Wiegel (Eds.), Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, U.S.A.

34. Qi, G. W., A. Parentich, L. H. Little, and L. J. Waren. 1992. "Selective Flotation of Apatite From Iron Oxides," *International Journal of Minerals Processing*, 134:83-102.

35. Lehr, J. R. 1980. "Phosphate Raw Materials and Fertilizers: Part I – A Look Ahead," Publication No. X491, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.

36. McClellan, G. H., and J. R. Lehr. 1982. "Impurities of Phosphate Rock – Good or Bad," IN *Proceedings of 32nd Annual Meeting of Fertilizer Industry Roundtable*, pp. 238-252, Atlanta, GA, U.S.A.

37. Smith, P. A. 1991. "High Grade Phosphate: Are Impurities a Bonus or a Penalty?" *Fertilizer News*, 36(12):35-41.

38. McClellan, G. H., and L. R. Gremillion. 1980. "Evaluation of Phosphatic Raw Materials," Publication No. X498, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.

39. Robinson, N. 1978. "Fisons Experience on the Effect of Phosphate Rock Impurities on Phosphoric Acid Plant Performance," IN *Proceedings of*

the ISMA Technical/Economic Conference, Orlando, FL, U.S.A., October 23-27, pp. 97-112.

40. Lehr, J. R. 1968. "Purification of Wet-Process Acid in Phosphoric Acid," IN *Phosphoric Acid*, Vol. 1, Part 2, A. V. Slack (Ed.), Marcel Dekker, Inc., New York, NY, U.S.A.

41. Becker, P. 1989. *Phosphate and Phosphoric Acid – Raw Materials, Technology, and the Economics of the Wet Process*, Fertilizer Science and Technology Series, Vol. 6, Marcel Dekker, New York, NY, U.S.A., 740 pp.

42. Gray, A. N. 1930. *Phosphates and Superphosphates*, International Superphosphate Manufacturers Association, Paris, France.

43. Anonymous. 1976. "World Wide Study of the Fertilizer Industry 1975-2000," Draft report prepared by the United Nations Industrial Development Organization (UNIDO) and presented on November 16-18 at a meeting in Vienna, Austria.

44. Krauss, U. H., H. G. Saam, and H. W. Schmidt. 1984. *International Strategic Minerals Inventory Summary Report – Phosphate*, U.S. Geological Survey Circular 930-C, 41 p.

45. U.S. Bureau of Mines. 1991. *Mineral Commodity Summaries, Phosphate Rocks*, pp. 118-119, U.S. Department of the Interior, Washington, D.C., U.S.A.

46. Mew, M. C. 1994. "Phosphate Rock – First Green Shoots of Recovery," *Engineering and Mining Journal*, 195(3):50-53.

47. U.S. Bureau of Mines. 1995. *Mineral Commodity Summaries, Phosphate Rocks*, pp. 124-125, U.S. Department of the Interior, Washington, D.C., U.S.A.

48. Anonymous. 1994. "Rocky Prospects for U.S. Producers," *Phosphorus and Potassium*, 190(March-April):11-15.

49. Stowasser, W. F. 1990. *Phosphate Rock*, Annual Report, Bureau of Mines, U.S. Department of the Interior, Washington, D.C., U.S.A., 18 p.

50. Barboza, F.L.M., W. Chamber, P. Santa, and M. L. Maron. 1995. "Brazil," IN *Mining Annual Review*, pp. 78-82, The Mining Journal Ltd., London, England.

51. Stowasser, W. F. 1991. "Phosphate Rock – Analysis of the Phosphate Rock Situation in the United States: 1990-2040," *Engineering and Mining Journal*, 192(9):16CC-16II.

52. Anonymous. 1994. "Phosphate Rock: No Respite," *Mining Journal*, 322(8272):293-295.

53. Anonymous. 1992. "Phosphate Rock Grade and Quality," *Phosphorus and Potassium*, 178(March-April):28-36.

54. Brobst, D. A., and W. P. Pratt. 1973. *United States Mineral Resources*, U.S. Geological Survey Professional Paper 820, 722 p.

55. U.S. Bureau of Mines and U.S. Geological Survey. 1981. *Principles of a Resource/Reserve Classification for Minerals*, U.S. Geological Survey Circular 831, 5 p.

56. U.S. Geological Survey. 1982. *Sedimentary Phosphate Resource Classification System of the U.S. Bureau of Mines and the U.S. Geological Survey*, U.S. Geological Survey Circular 882, 9 p.

57. Bates, R. L., and J. A. Jackson. 1980. *Glossary of Geology*, 2nd Edition, American Geological Institute, Alexandria, VA, U.S.A., 749 p.

58. Carmichael, R. S. 1982. *Handbook of Physical Properties of Rocks*, Vol. I, CRC Press Inc., Boca Raton, FL, U.S.A., 404 p.

59. Williams, J. M., and A. W. Griffin. 1990. "Overview of Major World Phosphate Mining Operations in the 1990s," Paper presented at the Fifth Annual Regional Phosphate Conference, Lakeland, FL, U.S.A., September 29, 1960.

60. Sheldon, R. P. 1987. "Industrial Minerals – With Emphasis on Phosphate Rock," IN *Resources and World Development*, pp. 347-361, D. J. McLaren and B. J. Skinner (Eds.), John Wiley & Son Limited, New York, NY, U.S.A.

61. Herring, J. R., and R. J. Fantel. 1993. "Phosphate Rock Demand Into the Next Century: Impact on World Food Supply," *Nonrenewable Resources*, 2(3):226-246.

62. Fantel, R. J., G. R. Peterson, and W. F. Stowasser. 1985. "The Worldwide Availability of Phosphate Rock," *Natural Resources Forum*, 9(1):5-24.

63. Constant, K. M., and W. F. Sheldrick. 1990. "Outlook for Fertilizer Demand, Supply and Trade," Asia Technical Department, The World Bank, Washington, D.C., U.S.A.

64. Mew, M. 1990. "Phosphate Rock," IN *Metals and Mineral Annual Review*, pp. 110-112, The Mining Journal, Ltd., London, England.

65. Stowasser, W. F. 1992. Personal Communications.

66. Anonymous. 1993. "Coming to Terms With the New Order," *Phosphorus and Potassium*, 188(Nov.-Dec.):12-14.

67. McClellan, G. H., and T. P. Hignett. 1978. "Some Economic and Technical Factors Affecting Use of Phosphate Raw Materials," IN *Phosphorus in the Environment: Its Chemistry and Biochemistry*, pp. 49-73, Ciba Foundation Symposium 57, Elsevier/Excerpta Medica/North Holland Inc., New York, NY, U.S.A.

68. Carmichael, R. S. 1982. *Handbook of Physical Properties of Rocks*, Volume 1, CRC Press Inc., Boca Raton, FL, U.S.A., 407 p.

69. Fischer, H. 1984. "Sulfur, Sulfur Dioxide, and Sulfuric Acid," The British Sulphur Corporation, Ltd., London, England.

70. Hoddinott, P. J. 1994. "Energy Minerals," IN *Metals and Minerals Annual Review*, pp. 105-115, Mining Journal Ltd., London, England.

71. Hagar, R., G. E. Smith, and R. Vielvoye. 1983. *The Oil and Gas Journal*, 81(11):23-26.

72. Anonymous. 1980. "Elemental Sulphur Production: Recovery From Low-Grade Pyrites and Phosphogypsum," *Sulphur*, No. 147(March-April):36-38.

73. Conghill, D. 1971. "Sulfates Processing," British Patent (number unknown).

74. Anonymous. 1994. "Frasch Mines Restructure to Live Another Day," *Sulphur*, No. 230(Jan.-Feb.):3.

75. Bain, B. 1994. "Sulphur," IN *Metals and Minerals Annual Review,* pp. 97-98, Mining Journal Ltd., London, England.

76. Forbath, T. P. 1953. "Sulphur Recovery From Low-Grade Surface Deposits," *Mining Engineering*, 5:881-885.

77. Griffith, S. V. 1941. "Extraction of Sulfur," *Mining Magazine*, 64:123-130.

78. Anonymous. 1994. "State of the Art Refinery Symbolises New Germany," *Sulphur*, No. 235(Nov.-Dec.):71-73.

79. Lagas, J. A., and J. Borshoom. 1994. "The Super Claus Process in the Light of Future Development," IN *Proceedings of "Sulfur 94" Conference*, pp. 41-46, Tampa, FL, U.S.A.

80. Goar, B. G. 1994. "Improving the Claus Plant Performance by Oxygen Enrichment," IN *Proceedings of "Sulfur 94" Conference*, pp. 127-132, Tampa, FL, U.S.A.

81. Habashi, F. 1978. *Chalcopyrite, Its Chemistry and Metallurgy*, McGraw-Hill, New York, NY, U.S.A.

82. Anonymous. 1956. "Smelting of Sulfide Minerals," *Quarterly Bulletin* No. 13, pp. 10-12, The British Sulphur Corporation, Ltd., London, England.

83. U.S. Bureau of Mines. 1995. *Mineral Commodity Summaries, Sulfur*, pp. 166-167, U.S. Department of the Interior, Washington, D.C., U.S.A.

84. Anonymous. 1995. "Statistical Supplement," *Sulphur*, No. 241(Nov.-Dec.):32-35.

85. Garrett, D. E. 1996. *Potash: Deposits, Processing, Properties and Uses*, Chapman & Hall, New York, NY, U.S.A.

86. Wardlaw, N. C., and G. D. Nicholls. 1972. "Cretaceous Evaporites of Brazil and West Africa and Their Bearing on the Theory of Continent Separation," IN *Proceedings of the 24th International Geological Congress*, pp. 43-55, Montreal, Canada, Sect. 6.

87. DeEston, S. M., and W. J. Hennies. 1991. "Considerations of Environmental Engineering and Mine Safety at the Sergipe Potash Mine," Paper presented at "Kali 91," Second International Potash Technology Conference, Hamburg, Germany, May 26-29, 1991.

88. DeRuiter, P. A. 1979. "The Gabon and Congo Basins' Salt Deposits," *Economic Geology*, 74:419-431.

89. Hite, R. J. 1986. "Potash Deposits of the Khorat Plateau, Thailand," IN *Fertilizer Minerals in Asia and the Pacific*, Vol. 1, pp. 51-73, United Nations Economic and Social Commission for Asia and the Pacific.

90. Roulston, B. V., and D. C. Waugh. 1983. "Stratigraphic Comparison of the Mississippian Potash Deposits of New Brunswick, Canada," IN Sixth International Symposium on Salt, Vol. 1, pp. 115-129, The Salt Institute, Alexandria, VA, U.S.A.

91. Fuzesy, A. 1982. *Potash in Saskatchewan*, Saskatchewan Geological Survey Report 181, 44 p.

92. Talbot, C. J., C. P. Tully, and P. J. Woods. 1982. "The Structural Geology of the Boulby Potash Mine," *Tectonophysics*, 85(3-4):167-204.

93. Messer, E., and H. Roth. 1983. "Geology of the Werra-Fulda Potash Deposit," Monograph Series on Mineral Deposits, Vol. 22, pp. 79-107, Gebruder Boontrager, Stuttgart, Germany.

94. Ramberti, L. 1980. "Potash Salt Deposits of Sicily; Genetic, Stratigraphic and Paleogeographic Characteristics," *Bollettino Della Associazione Mineria Subalpina 17*, (2):327-353.

95. Salas, R. G., et al. 1991. "Geological-Mining Survey of Suria K S.A. in the Catalonian Potash Basin," Paper presented at "Kali 91," Second International Potash Technology Conference, Hamburg, Germany, May 26-29, 1991.

96. Griswold, G. B. 1982. "Geologic Overview of the Carlsbad Mining District," New Mexico Bureau Mines and Mineral Resources, Circular 182, pp. 17-22.

97. Sun, Dapeng, and D. E. Lock. 1990. "Origins of Potash Deposits in the Qaidam Basin, China," *Science in China*, Series B., Vol. 33, No. 2, pp. 198-210.

98. Anonymous. 1986. "Beneficiating Potash to Commercial Product," *Phosphorus and Potassium*, No. 145(Nov.-Dec.):30-36.

99. Foot, D. G., C. E. Jordan, and J. L. Huiatt. 1980. "Direct Flotation of Potash From Carnallite," U.S. Bureau of Mines Report of Investigations 8678.

100. Anonymous. 1992. "Potash Extraction by Flotation," *Phosphorus and Potassium*, No. 182(Nov.-Dec.):20-26.

101. Medemblik, L. 1991. "Treatment of Clay Suspensions in MDPS's Potassium Chloride Flotation Plant," IN *Preprints of the XVII International Mineral Processing Congress*, pp. 104-120, Dresden, Germany.

102. Cormode, G. A. 1992. "Personal Communication," Cominco Fertilizers.

103. Mireau, R. M. 1992. "Personal Communication," Cominco Fertilizers.

104. Medemblik, L. 1992. "Personal Communication," Mines de Potasse d'Alsace.

105. Anonymous. 1983. "Mining and Beneficiating Potash," *Phosphorus and Potassium*, No. 128(Nov.-Dec.):26-31.

106. Larmour, D. 1983. "Electrostatic Separation of Potash-PCS Mining Experience," Paper presented at the First International Potash Technology Conference, Saskatoon, Canada.

107. Breniaux, J., and J. P. Marx. 1991. "Equipment of a Long-Life Panel at MDPA," Paper presented at "Kali 91," Second International Potash Technology Conference, Hamburg, Germany, May 26-29, 1991.

108. Duchrow, G., I. Fitz, and N. Grüshow. 1990. "Solution Mining Provides the Solution to an Economic Problem, Possibilities for Profitable Carnallite Extraction in East Germany," *Phosphorus and Potassium*, No. 167(Sept.-Oct.):20-25.

109. Amira, J., W. Stanley, H. Armstrong, and M. Frimodig. 1992. "From Hot to Cold Crystallization," *Phosphorus and Potassium*, No. 182(Nov.-Dec.):28-32.

110. Anonymous. 1992. "Optimization of Solar Evaporation Systems," *Phosphorus and Potassium*, No. 179(May-June):17-25.

111. Anonymous. 1972. "Technical Advances by the U.S.S.R. Potash Industry," *Phosphorus and Potassium*, No. 53(May-June):52-55.

112. Searls, J. P. 1991. *Potash Annual Report*, Bureau of Mines, U.S. Department of the Interior, Washington, D.C., U.S.A., 15 p.

113. Searls, J. P. 1995. "Potash," IN *Mineral Commodity Summaries 1994*, pp. 128-129, Bureau of Mines, U.S. Department of the Interior, Washington, D.C., U.S.A.

114. Spooner, J. 1994. "Potash," IN *Metals and Minerals Annual Review*, pp. 98-99, Mining Journal Ltd., London, England.

115. Warner, P. 1993. "Potash Overview," Paper presented at the International Training Workshop — Indigenous Resource Development for the Fertilizer Sector, IFDC, Muscle Shoals, AL, U.S.A.

116. Anonymous. 1992. "An Outlook for Potash," *Phosphorus and Potassium*, 180(July, Aug.):20-27.

117. Mayrhofer, H. 1983. "World Reserves of Mineable Potash Salts Based on Structural Analysis," IN *Sixth International Symposium on Salt*, Vol. 1, pp. 141-160, The Salt Institute, Alexandria, VA, U.S.A.

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Chapter 6. Production of Ammonia

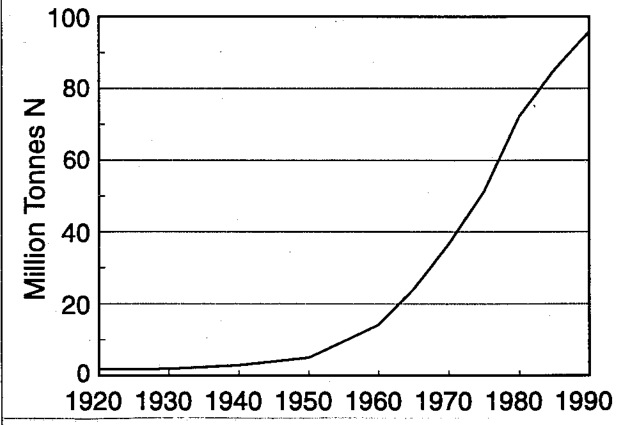
6.1 Ammonia Early Process Development

Synthetic ammonia (NH_3) has become the principal source of all nitrogen fertilizers, particularly since 1945. At present, almost all commercial fertilizer nitrogen is supplied by or derived from synthetic NH_3; only minor percentages are supplied by natural sodium nitrate, byproduct NH_3 from coke-oven gas (usually recovered as ammonium sulfate), calcium cyanamide, and other minor sources. In 1904 the ammonia synthesis process was developed primarily by Fritz Haber, and in 1909 he demonstrated the process on a laboratory scale of 80 g of NH_3 per hour [1]. Carrying out the high-temperature, high-pressure process on a commercial scale presented formidable problems with the technology and materials of construction then available. Carl Bosch, working with Haber, is generally credited with developing the process – first on a pilot scale and then on a commercial scale of 30 tpd. Production started in 1913 at Oppau, Germany. The process was based on the catalytic reaction of hydrogen and nitrogen at high temperature and pressure and in its basic concept is still extensively used today.

Using the Haber-Bosch process and coke-based producer gas and/or coke-oven gas as the source of hydrogen, various countries had constructed ammonia plants by the late 1930s. Thus, the ammonia plants had to be located near steel works. As technology progressed, coal gasification began to be used instead of producer gas as the source of hydrogen. In Europe, coal gasification continued to be the primary source of hydrogen even in the 1950s [2]. In the United States, steam reforming of hydrocarbons replaced the use of coal gasification because of the existence of large amounts of inexpensive natural gas.

Likewise, the use of natural gas enlarged the size of the plants in the United States. In 1953, a plant having a capacity of 165 tpd was put into service for Shell Chemical by the M. W. Kellogg Company [2]. The size of ammonia plants continued to increase. Three hundred tpd plants were being put into service by the late 1950s. By the 1960s, a quickly increasing demand for ammonia led to the commercialization of the large-scale, single-train ammonia plant. The first of these plants was located in Texas City and was built in 1965 by the M. W. Kellogg Company for Amoco [2]. Originally, it was a 600-tpd plant, with three additional 600-tpd units and a 1,000-tpd unit installed during the next few years. Today single-train capacities have reached levels of 1,500-1,800 tpd. The concepts used in the 1960s to construct the first large-scale ammonia plants are still being used today not only in the United States but also globally. From 1960 to 1990, worldwide ammonia capacity increased from 16 million tpy [3] to 138 million tpy. Figure 6.1 illustrates the development of world nitrogen production since the beginning of the century and how it has increased sharply in recent years.

Large single-train natural gas feed plants are also becoming prominent in fertilizer production in the developing countries. Until about 1960, most of the world's ammonia manufacturing capacity was located in developed countries, where plants were relatively small, used a variety of feedstocks, and served local markets. There were very few ammonia plants in developing countries and only a small amount of nitrogen fertilizer was imported by these countries. Beginning in the 1960s, several dramatic changes occurred in the industry. By 1990, the four largest producers and consumers of nitrogenous fertilizers were the U.S.S.R., China, the United States, and India [2]. The ammonia fertilizer market is highly competitive, and today's large-scale plants must be energy efficient and reliable if they are to be economical. Significant improvements have been made in reducing energy consumption of ammonia production. Table 6.1 provides evidence of this over the past 50 years. Over this period, energy consumption was reduced by about 35%-40%. The current efficiency level of about 7 Gcal/tonne of ammonia is approaching the theoretical minimum of about 5 Gcal/tonne, assuming an ideal and reversible thermodynamic process. However, the



Source: [5].

Figure 6.1. World Nitrogen Production.

Table 6.1. Ammonia Plant Energy Consumption [2]

Years	Typical Natural Gas Consumption, LHV, Gcal/t
1943-65	10.5 - 11.1
1965-72	8.9 - 9.4
1972-83	8.6 - 8.9
1983-94	6.9 - 7.2

efficiency of energy consumption can be further improved [2].

6.2 Physical Properties of Ammonia

The following table, Table 6.2, lists many of the important properties of ammonia. Table 6.3 contains the densities of aqueous ammonia at 15° Celsius. Ammonia has flammable limits of 16%-25% by volume in the air and 15%-79% in oxygen [4]. Ammonia-air mixtures are not easily ignited since the ignition temperature is 650° Celsius. The mixture can explode if ignited. Ammonia is readily soluble in water. A large amount of heat, about 2180 kJ (520 kcal), is produced when the dissolution of 1 kg of ammonia gas occurs.

Table 6.2. Physical Properties of Anhydrous Ammonia [4]

Property	Unit	Value
Molecular weight	1	17.03
Boiling point	°C	-33.35
Freezing point	°C	-77.7
Critical temperature	°C	133.0
Critical pressure	MPa	11.425
Specific heat (gas)	J/kg °K	
– at 0°C		2,097.2
– at 100°C		2,226.2
– at 200°C		2,105.6
Heat of formation (gas)	kJ/mol	
– at 0°K		- 39.2
– at 298°K		- 46.2
Solubility in water	%, weight	
– at 0°C		42.8
– at 20°C		33.1
– at 40°C		23.4
– at 60°C		4.1
Specific gravity	g/ml	
– at -40°C		0.690
– at 0°C		0.639
– at 40°C		0.580

Table 6.3. Density of Aqueous Ammonia at 15°C [4]

Ammonia (wt %)	Density (g/cm³)
8	0.970
16	0.947
32	0.889
50	0.832
75	0.733
100	0.618

6.3 Feedstock for Ammonia Production

Before World War II (1939), three million tpy of nitrogen was produced as ammonia; 90% was derived from coal and coke. By 1960, about 16 million tpy of ammonia was produced using cheaply available natural gas in the United States [5]. Naphtha became the most common feedstock in other developed countries because of its low price, and some fuel oil was also used. Naphtha became more popular with the development of the Imperial Chemical Industries (ICI) steam-reforming process for naphtha and led to many new plants around the world. Soon, many of these plants closed as a result of the increase in the price of naphtha because of its increased demand and the 1973 oil crisis. Since 1975, the primary feedstock of most new plants is natural gas, with about 78% of the world ammonia capacity as shown in Figure 6.2.

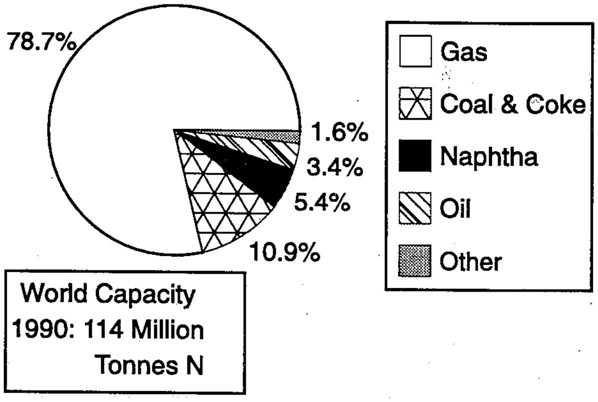


Figure 6.2. Major Feedstock for Ammonia Production.

This percentage is so large because of the low energy needs and investment costs of natural gas. Future predictions show natural gas to remain as the main feedstock due to its reserves and opportunity costs, especially in developing countries [5]. The only exception is China, where coal is the primary feedstock.

Natural Gas – As mentioned previously, natural gas is the principal feedstock for ammonia production. Natural gas is classified as "associated" or "nonassociated." Associated gas occurs with crude oil; it is liberated from the oil when the pressure is released in the oil-gas separator plant. Its composition varies with the pressure at which the separator is operated. Since methane is the most volatile, it can be released at a relatively high pressure. By releasing gas at successively lower pressures, a separation can be made in which methane is released first, and the less volatile gases, ethane, butane, and propane, are collected separately.

The higher hydrocarbons usually have a higher value for petrochemical production or for sale as liquefied petroleum gas (LPG) than methane. Therefore, in most cases, these products are sold separately, and the term "natural gas" usually refers to the fraction that contains mostly methane with only small percentages of ethane and higher hydrocarbons. For use as ammonia feedstock, methane is preferable to the higher hydrocarbons because all carbon in the feedstock is converted to carbon dioxide or monoxide, which must be removed from the ammonia synthesis gas. Therefore, the lower the carbon:hydrogen ratio in the feedstock, the smaller and less expensive the purification units in the synthesis gas preparation section will be.

In ammonia-urea complexes where all of the ammonia is used to make urea, the amount of CO_2 derived from methane feedstock may not be sufficient for the urea plant needs. Urea requires a CO_2:NH_3 ratio of 1:2; whereas, the production of ammonia by reforming pure methane results in a CO_2:NH_3 ratio of 7:16. In this case it would be advantageous if the natural gas contained enough higher hydrocarbons to supply enough CO_2 for urea production. This is often the case as shown by the example of natural gas composition given in Table 6.4.

Both associated and nonassociated natural gases vary widely in composition; the example in Table 6.4 is only an illustration. Gas from some nonassociated deposits may be nearly pure methane. In other deposits gas may contain higher percentages of H_2S, CO_2, or both. Other, usually minor, constituents are N_2 and sometimes He (helium). The CO_2 and H_2S are usually removed by scrubbing before delivery by pipeline to avoid corrosion of the pipeline; the H_2S may be converted to elemental sulfur, which may be a profitable byproduct in some cases.

Table 6.4. Composition of Representative Sample of Natural Gas

	% by Volume	
Constituent	At Well Head	As Delivered by Pipeline
CH_4	75.9	93.3
N_2		2.0
Argon		.4
CO_2	7.3	.01
H_2S	8.9	<5 ppmv
Hydrocarbons		
C_2H_6	3.3	3.3
C_3H_8	1.2	0.9
C_4H_{10}	0.8	0.2
C_5H_{12}	0.5	0.01
$C_6H_{14}^+$	2.3	

Liquefied Petroleum Gas – LPG, which primarily contains butane and propane, has been used as ammonia feedstock in Japan. Liquefied natural gas (LNG) is also used in Japan. These materials are relatively expensive but are often less expensive than naphtha.

Naphtha – In those areas of the world where natural gas is unavailable, naphtha became a favored feedstock for ammonia production by steam reforming, particularly in the period of 1950-74 when naphtha was relatively cheap. In many countries the amount of naphtha produced in oil refining exceeded the demand. Naphtha is the lighter fraction of hydrocarbons; it boils from about 40° to 130°C with an average molecular weight of about 88 and an H:C atomic ratio of about 2.23. Straight-run naphtha is preferred to naphtha produced from higher hydrocarbons by cracking or "hydrocracking" because the latter usually contains sulfur compounds that are difficult to remove. The composition and properties of typical naphtha are given in Table 6.5.

Since 1974 the price of naphtha on the world market has risen more rapidly than that of other feedstocks because of the demand for naphtha for use in the manufacture of motor fuel and petrochemicals (ethylene, propylene, etc.). Therefore, several plants originally designed to use naphtha have switched to other feedstocks such as natural gas. As a result, few new plants are being built to use this feedstock.

The process for steam reforming of naphtha was developed mainly by ICI in England and has been widely used in Europe, Japan, and many developing countries. The main technical problem was to avoid carbon formation on the reforming catalyst without excessive steam

Table 6.5. Composition and Properties of Representative Sample of Naphtha

Constituent or Property	Average Value
Specific gravity at 15.5°C	0.686
Initial boiling point, °C	41
Final boiling point, °C	131
Unsaturates, % (volume)	1
Aromatics, % (volume)	4
Saturates, % (volume)	95
Total sulfur (ppmw)	368
Sulfur as (ppmw):	
H_2S	2
RSH	146
R_2S_2	119
R_2S	80
S	1
Unreactive S	20
C, %	84.4
H, %	15.7
Mol. wt.	88
Heating value, kcal/kg	10,500

consumption. This problem was solved by modifications of the catalyst composition.

Refinery Gases – Petroleum refineries and petrochemical operations produce a variety of byproduct gases that can be used as fuel or feedstock or both. The composition of refinery tail gas varies widely; it usually contains H_2, CH_4, and higher hydrocarbons and can be used as ammonia feedstock by steam reforming. The amount of available tail gas is likely to be insufficient for an economical scale of ammonia production unless the refinery is a very large one. Another drawback is that the volume and composition of the tail gas may vary according to the demand for the various refinery products, and these variations can cause difficulties in the ammonia plant operation. Also, refineries often have a use for the components of the tail gas. For instance, the hydrogen can be separated and used in "hydrocracking" (production of light hydrocarbons by hydrogenating and cracking heavier fractions). Only a few ammonia plants in Europe and Japan use refinery tail gas.

Coke-Oven Gas – Before the 1940s, coke-oven gas was used for a large portion of ammonia production. Coke-oven gas contains about 55% H_2, 25% CH_4, 8% CO, 6% N_2, minor amounts of higher hydrocarbons, CO_2, and various impurities. Presumably, it could be used for ammonia production by steam reforming after purification, but the usual practice is to separate the hydrogen by a cryogenic process involving a liquid nitrogen wash. Many steel-producing plants have an air separation unit to supply oxygen for use in steel production; thus, the liquid nitrogen is available from this source. The cryogenic process produces a nitrogen-hydrogen gas mixture suitable for ammonia synthesis, and the remaining gas mixture of CO, CH_4, and heavier hydrocarbons is used as a fuel. The main drawback is similar to that of refinery tail gas; the amount of coke-oven gas depends on coke production which, in turn, depends on steel production. Only a few plants use coke-oven gas for feedstock.

Heavy Oil – Liquid hydrocarbons heavier than naphtha are used for ammonia feedstock by partial oxidation processes, which will be discussed in a later section of this chapter.

Hydrogen-Rich Off-Gases – Byproduct hydrogen sources have been used for ammonia production in the past. Table 6.6 lists sources of hydrogen-rich gases. In the 1970s, the price of light hydrocarbons began to rise, which led to other feedstocks such as hydrogen-rich off-gases being reconsidered. Some large plants using methanol or other plant purge gases were built [6]. Table 6.7 shows the commercial operations data for three such projects.

Other Feedstocks – Methanol or ethanol can be used as feedstock in steam-reforming processes, but no commercial use has been reported. Other feedstocks such as electrolytic hydrogen, coal, and fuel oil will be discussed separately under applicable process headings.

6.3.1 Feedstock Requirements

In nearly all ammonia plants the same material is used as both feedstock and fuel. The fuel requirements may be 40% of the total or more, depending on the extent to which heat recovery equipment is used. In previous years when fuel was inexpensive, many ammonia plants were built with minimum heat recovery facilities. Buividas et al. give an example of how the fuel requirement (natural gas) was decreased by 34% through more efficient energy use, which primarily included high-pressure steam generation and preheating combustion air to the reformers [7]. The decrease in total fuel plus feedstock requirement was about 15%. The increase in fuel efficiency was obtained at the expense of about 6% increase in plant investment costs. Table 6.8 shows the requirements for fuel plus feedstock that assume efficient heat recovery.

In a natural gas-based plant 20%-30% of the gas is used for fuel and the balance for feedstock. The lower fuel values are for plants equipped with good energy-recovery systems. Fuel requirements do not include electric power generation or steam generation other than that connected with heat recovery. Modern ammonia

Table 6.6. Sources of H_2-Rich Gases [6]

H_2-Rich Gas Stream in %	H_2	CO	CO_2	CH_4	N_2	MeOH	O_2	Cl_2
Methanol purge gas	80.0	2.00	2.60	14.0	1.0	0.4	–	–
Ethylene plant H_2 gas[a]	84.4	0.20	–	15.4	–	–	–	–
CO plant H_2 gas[b]	97.0	1.95	–	0.04	0.09	–	–	–
Caustic soda plant H_2	99.86	–	0.02	–	0.24	–	0.06	15 ppmv
Cyclar and BTX plants	96.6	–	–	4.0	–	–	–	–
Coke-oven gas	60.0	6.5	2.5	22.5	6.5	c	0.5	–

a. Based on ethane feed.
b. CO plant based on cold box for CO separation.
c. Hydrocarbons about 1.5%, after pretreatment.

Table 6.7. Commercial Operations With H_2-Rich Gas [6]

Owner (Location)	Capacity (million tpd)	Feed	Process Schemes	On-Stream Date
Georgia Pacific (U.S.A.)	520	MeOH purge & H_2 from caustic plant	LT shift, CO_2 removal, N_2 wash, conventional syn loop	1977
Ocelot (Canada)	545	MeOH purge	CO_2 removal, N_2 wash, modern syn loop	1986
Kemira Ltd. (U.K.)	750	H_2 from CO plants	N_2 wash, modern syn loop	1988

Table 6.8. Energy Requirements Per Tonne of Ammonia [36]

Feedstock and Fuel	Assumed Heating Value[a]	Quantity	Gcal
Natural gas	8,015 kcal/m^3	873 m^3	7.0
Naphtha	10,556 kcal/kg	0.72 t	7.6
Fuel oil	9,722 kcal/kg	0.87 t	8.5
Coal	6,333 kcal/kg	1.54 t	9.8

a. All values are lower heating values (LHV).

plants are self-sufficient in steam supply, and much of the mechanical power is supplied by steam rather than electricity. However, in developing countries, a captive electric generating plant usually is considered essential for a dependable supply of electricity. Also, if a urea plant is associated with the ammonia plant, additional fuel will be required to supply the steam needed for urea production. Therefore, total fuel requirements may be larger than those mentioned above.

When a high-cost feedstock is used for ammonia production, it may be advantageous to use a lower cost fuel for heating and for producing steam and electricity. Likewise, when the supply of feedstock (such as natural gas) is inadequate for both fuel and feedstock, a different material may be used as fuel. Several plants in the United States that use natural gas feedstock are equipped to use a light fuel oil for heating the reformer. In cases where the fuel oil is more expensive than natural gas, the fuel oil system may be used only when the natural gas supply is limited.

Use of heavy oil or coal for fuel could be considered for plants using expensive or scarce feedstocks. However, these fuels cannot be used to heat reformer furnaces unless some extensive modifications are made. Impurities in heavy oil or coal would adversely affect the reformer tubes by causing corrosion or erosion unless design modifications were made. Deane and Brown have described a naphtha-based flowsheet in which a "non-premium fuel" is used for preheating the feedstock and the air to the secondary reformer [8]. Obviously, there would be no technical problem in using coal for steam and electric power in units designed for that purpose. Direct use of coal for heating the reformer furnace would present serious difficulties, but indirect use such as byproduct gas derived from coal may be technically and economically feasible in some cases.

Energy consumption in the ammonia process depends on the design of the different process units. In practice at least a dozen different combinations of process units are used depending on site-specific conditions. There is no single ammonia process model suitable for all situations. The energy-saving processes usually have higher investment costs, and a detailed study on combinations of the available process units should be carried out. Production costs, for obvious reasons, are not published; therefore, a comprehensive evaluation requires a detailed engineering study. The results of this type of study have been provided by Topsoe [9]. In all cases Topsoe technology has been used, the plants have been considered "stand alone" ammonia plants with no export/import of steam or power with a cooling water temperature of 30°C. Three cases were considered:

Case I – minimum energy consumption

Case II – realistic concept of low-energy plant

Case III – low investment cost

The results are given in Table 6.9.

Obviously the site conditions will influence strongly the thermal efficiency. This is especially valid for the subtropical and high-temperature regions. The case study [9] showed that an increase in the cooling water temperature from 20°C to 35°C would raise the energy consumption by 0.23 Gcal/tonne of ammonia. Supply of the cooling water from open reservoirs instead of a pressurized system would increase the energy consumption by another 0.1 Gcal/tonne of ammonia.

These examples indicate why only detailed case studies may show the real energy consumption of an ammonia plant.

6.4 Production Technology of Ammonia

Production of ammonia may be considered as being composed of two major steps:

Table 6.9. Energy Consumption in Different Process Configurations

Parameters/Case	Case I	Case II	Case III
S/C ratio	2.5	2.8	3.3
Pre-reformer	Yes	No	No
Shift configuration[a]	MT + LT	HT + LT	HT + LT
CO_2 removal	Physical	MDEA	HPC
Final purification	Methanation	Methanation	Methanation
Synthesis	S-250	S-200	S-200
Steam from condensate stripping	MP	MP	HP
Energy consumption, Gcal/t	6.60	6.85	7.00

a. HT = high temperature, LT = low temperature, MT = medium temperature.

- Preparation of the ammonia synthesis gas composed from nitrogen and hydrogen in a molar proportion of 1:3.
- Synthesis and separation of the ammonia.

A simplified flow diagram for the production of ammonia by steam reforming of natural gas or naphtha is shown in Figure 6.3. In the following discussion, each of the steps will be discussed in the sequence in which they occur.

6.4.1 Synthesis Gas Preparation Processes

Synthesis gas for ammonia production consists of hydrogen and nitrogen in about a 3:1 mole ratio, residual methane, argon introduced with the process air, and traces of carbon oxides. There are several processes available for synthesis gas generation, and each is characterized by the specific feedstock used. A typical synthesis gas composition by volume is: hydrogen, 74%; nitrogen, 24%; methane, 0.8%; argon, 0.3%; carbon oxides, 2-10 ppmv; and water vapor, 0.1 ppmv [4].

The source of nitrogen is always air; however, hydrogen can be derived from a variety of raw materials including water, light and heavy hydrocarbons resulting from crude oil refining, coal, natural gas, and sometimes a combination of these raw materials. In all cases, part of the hydrogen produced is derived from water.

Synthesis gas preparation consists of three steps: (1) feedstock conversion, (2) carbon monoxide conversion, and (3) gas purification. Table 6.10 gives the main processes for each of the feedstocks used. In each case, except for water electrolysis, simultaneous to the reactions shown, the water-gas shift reaction occurs.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$\Delta H = -41\ \text{kJ/mol}\ (-9.8\ \text{kcal/mol})$$

Equilibrium is achieved in steam reforming; equilibrium is approached for partial oxidation processes [4]. The reactions are given in Table 6.10.

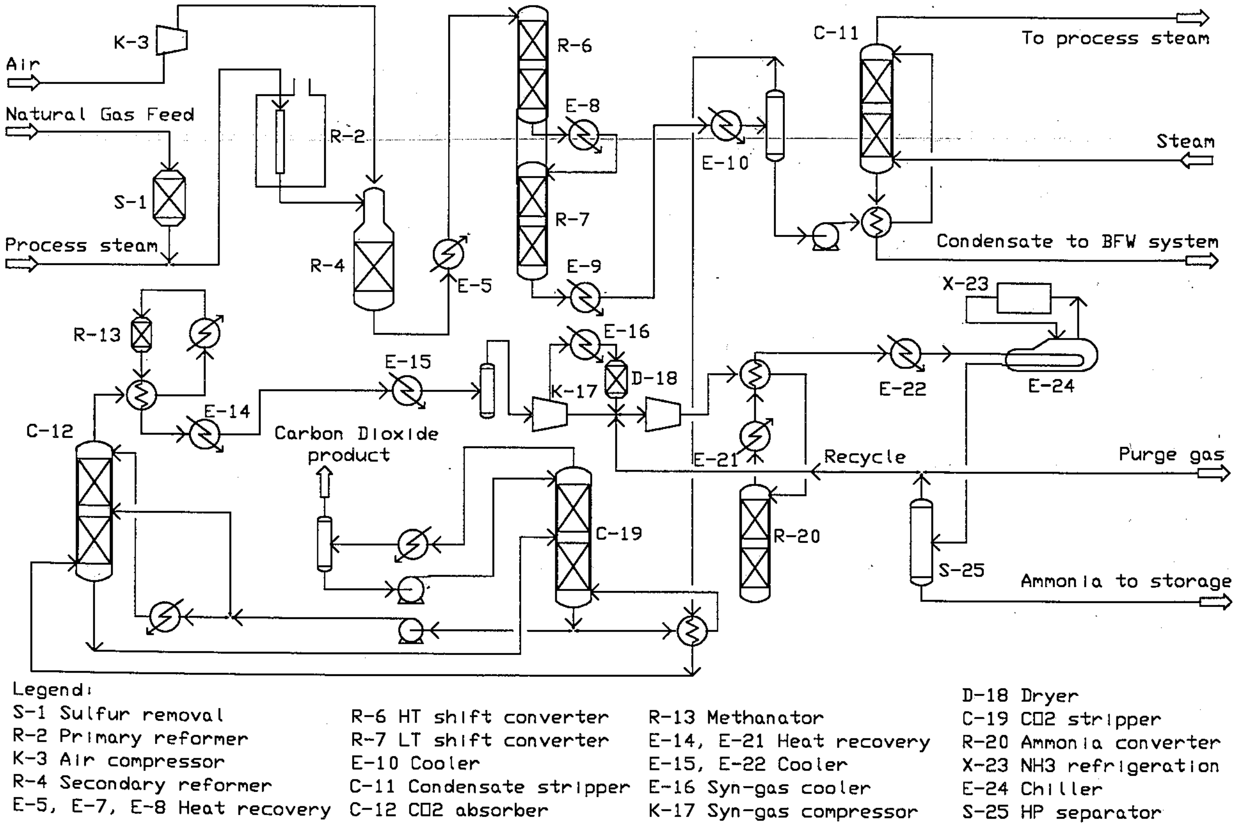


Figure 6.3. Simplified Flowsheet of Ammonia Production.

Table 6.10. Hydrogen Generation Raw Materials and Processes [4]

Raw Material	Process Description	Feedstock Conversion Reaction
Natural gas	Steam reforming[a]	$C_nH_{(2n+2)} + nH_2O \rightarrow nCO + (2n+1)H_2$
Naphtha	Steam reforming[b]	$C_nH_{(2n+2)} + nH_2O \rightarrow nCO + (2n+1)H_2$
Fuel oil	Partial oxidation	$C_nH_{(2n+2)} + n/2O_2 \rightarrow nCO + (n+1)H_2$
Coal	Coal gasification	$C + 1/2O_2 \rightarrow CO$
Water	Electrolysis	$H_2O \rightarrow 1/2O_2 + H_2$

a. Nickel is used as catalyst.
b. Promoted nickel is used as catalyst.

The most economic hydrocarbon feedstock is likely to be the one having the highest hydrogen:carbon ratio. From Table 6.10 it can be seen that, for a given amount of carbon (feed), proportionally more hydrogen is generated by steam reforming than by partial oxidation. Thus, in the manufacture of hydrogen for ammonia synthesis, partial oxidation processes require more feed, which ultimately leads to larger carbon dioxide removal facilities. In addition, the raw synthesis gas generated by partial oxidation is much higher in carbon monoxide content than that coming from a steam-reforming operation. This high CO content requires larger facilities, both in terms of equipment and catalyst, for shift conversion. Because more CO_2 removal and higher shift conversion lead to higher investment and operating costs, partial oxidation processes are normally used only for materials that cannot be handled by steam reforming such as coal or heavy hydrocarbon feeds [4].

6.4.1.1 Steam Reforming

Feedstock Preparation – As mentioned previously, most natural gas requires some purification, particularly the removal of CO_2 and H_2S, which may be done by the natural gas producer if the gas is transmitted by pipeline. If the gas is taken directly from wellheads, the user (ammonia producer) may have to purify the gas. Depending on the source, natural gas may contain entrained dust or droplets of liquid (oil or water), which should be removed by separators, filters, etc.

After the initial purification, natural gas is compressed to reformer pressure, if not already at that pressure, and preheated. Then, any remaining sulfur is removed to avoid poisoning of catalysts. The sulfur may be removed by adsorption on activated carbon at ambient temperature or by absorption by hot zinc oxide (290°-400°C) after the gas has been preheated.

$$ZnO + H_2S \leftrightarrow ZnS + H_2O$$

In some cases both treatments may be used. Some natural gas may contain significant amounts of chlorides, which can poison catalysts, particularly the low-temperature shift catalyst. Catalysts or absorbents are available to remove chlorides. If the feedstock contains nonreactive sulfur, hydrotreating is required. The preheated gas or vaporized naphtha is mixed with a small amount of hydrogen (recycled synthesis gas) and passed through a "hydrotreater" containing a cobalt-molybdenum catalyst, which converts sulfur compounds to H_2S; the gas then goes to a sulfur-removal catalyst (zinc oxide).

$$RSH + 1/2H_2 \leftrightarrow H_2S + RH$$

Since naphtha usually contains unreactive sulfur, hydrotreating or hydrodesulfurization is commonly used in naphtha-based plants. The catalysts (absorbents) used in the guard beds are expensive and cannot be regenerated. Therefore, if the feedstock contains much sulfur or chloride, some means for removing most of these impurities as a pretreatment should be considered. In the case of natural gas, absorption in an alkaline solvent such as monoethanolamine or potassium carbonate, which can be regenerated, is commonly used for removing most of the sulfur.

Sulfur and chlorides (and other catalyst poisons) can enter the ammonia plant in the steam or in the air to the secondary reformer; thus, precautions should be taken to eliminate such impurities insofar as is practical. In addition, a layer of guard absorbent may be placed on top of the catalyst, particularly in the case of the low-temperature shift catalyst.

Primary Reforming – The purpose of the primary reforming step is to convert the bulk of the hydrocarbon feed to H_2 and CO by reaction with steam.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$\Delta H = 206 \text{ kJ/mol}(49.2 \text{ kcal/mole}) \quad [10]$$

Nickel catalyst is used for this reaction. The shift conversion reaction also occurs to some extent:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$\Delta H = -41$ kJ/mole [11]

The overall reaction is endothermic and requires a large amount of heat to be applied to the reactants.

The primary reformer is a furnace with a large number of catalyst-packed vertical tubes. The fuel is burned in the furnace, whereby the required heat is provided for the reaction occurring inside the tubes at 750°-850°C. The preheated feedstock and high-pressure steam at 3-4 MPa pressure are mixed and enter at the top of the furnace.

Centrifugally cast reformer tubes made of alloy A 698 HK 40 have been widely used for steam reforming. In the last decade, newer alloys such as A 297 HP and Manaurite 36X were developed. See Table 6.11 for the composition of these alloys.

Manaurite 36X has a much higher nickel content than HK 40 and a little more chromium, and it is stabilized with niobium [12,13]. Its creep rupture behavior is superior to HK 40 and A 297 HP, which never found broad acceptance [14]. By using superior alloy, the reformer can be designed for higher pressure, up to 4.3 MPa at the reformer outlet. The higher pressure is compensated by higher temperature for achieving the same methane conversion in the primary reformer. The reformer tubes range from 7.5 cm to 20 cm in diameter with a wall thickness of 0.6 cm to 2.5 cm and a length ranging from 3 m to 14 m [15]. The tubes are packed with catalyst containing nickel on a calcium aluminate base, usually in the shape of a ring about 16 mm in diameter by 16 mm long. The nickel content typically is 14%-16%. Promoters such as potassium may be added, and the composition of the base may be varied to increase its strength, durability, and porosity. The temperature of the gas leaving the reformer tubes may be 750°-850°C, and the temperature of the tube wall may be 900°-950°C or more. This high temperature and the high pressure constitute severe conditions that require expensive materials of construction at the reformer outlet and careful design and operation. The heat in the combustion gas leaving the reformer is used successively to produce steam, to preheat the incoming feedstock-steam mixture, and, where fuel economy is important, to preheat combustion air.

There are many designs of reformer furnaces; all of these designs aim at efficient heat transfer by radiation, convection, and even heat distribution to prevent overheating or underheating any of the tubes or portions of the tube. The fuel burners may be placed at the top, sides, or bottom of the furnace. Various means are used to cope with the difficult problem of connecting the tubes to the inlet and outlet gas connections so that thermal stress will not cause failure of the tubes or their connections. Some designs permit the isolation of a tube or tubes that have failed. This arrangement permits the plant to continue operation even after some of the tubes have failed. During scheduled shutdowns, tubes that have failed or that are in poor condition can be replaced.

Secondary Reforming – The gas leaving the primary reformer usually contains 5%-15% methane (dry basis). The object of the secondary reforming step is to complete the conversion of methane to H_2, CO, and CO_2 and to supply the required proportion of N_2 for NH_3 synthesis. This is done by adding air in the amount required to give an N:H atomic ratio of 1:3 in the synthesis gas after the shift conversion step. This means that the mole ratio of $N_2:(H_2 + CO)$ should be 1:3 in the gas leaving the reformer unless more N_2 or H_2 can be added in some subsequent step of the process. The oxygen accompanying the nitrogen in the air burns part of

Table 6.11. Chemical Composition of Reformer Tube Alloys (wt %) [14]

Grade	Ni	Cr	Mn	Si	Nb	Mo	C	P	S
A 698 HK 40	19	23		0.5	–		0.35		
(min)			1.5			0.5		0.04	0.04
(max)	22	27		2.0			0.45		
A 297 HP	33	24			–		0.35		
(min)			2.0	2.5		0.5		0.04	0.04
(max)	37	28					0.75		
Manaurite 36X	32	23					0.35		
(min)			1.5	1.5	1.5			0.03	0.03
(max)	35	27					0.45		

the combustibles (H_2, CO, and CH_4) in the partially reformed gas, thereby raising the temperature high enough for rapid completion of the reforming.

Although most processes involve the use of air alone, in some cases oxygen-enriched air is used to supply more heat and, thereby, take some of the load from the primary reforming step. In fact, it is possible to add enough oxygen so that the reforming process becomes "autothermal" and the primary reforming step can be omitted entirely. On the other hand, less air can be used than required for nitrogen supply, and part of the nitrogen can be added separately, preferably at a later step in the process. This arrangement places more load on the primary reformer but decreases the amount of feedstock required. This can be an advantage when the feedstock is expensive (or in short supply) and a less expensive fuel is used in the primary reformer.

In the usual case when air to the secondary reformer is the sole source of nitrogen, the heat input is limited to that generated by combustion reactions plus the sensible heat in the preheated air and in the gas from the primary reformer.

A typical secondary reformer is a cylindrical, refractory-lined, insulated vessel. The upper part is empty and serves as a combustion chamber in which the gas from the primary reformer is partially oxidized by preheated air. The lower part is filled with a catalyst similar to that in the primary reformer. The air should be free from dust that might clog the catalyst bed and from catalyst poisons (S, Cl, and As). The air is filtered, compressed to reformer pressure, and mixed with the gas in a burner at the top of the vessel. The combustion causes the temperature to rise to about 1200°C in the combustion chamber. As the hot gas descends through the catalyst bed, it is cooled by the endothermic reforming reactions and leaves the reformer at a temperature of about 950°-1000°C. The gas at this point contains, on a dry basis, about 56% H_2, 12% CO, 8% CO_2, 23% N_2, plus argon, and usually less than 0.5% CH_4. It also contains excess steam ranging from one-third to one-half of the total gas volume.

6.4.1.2 Gas Processing Into Pure Hydrogen

Carbon Monoxide Conversion – Gas from the secondary reformer is cooled (generating steam) to about 375°C, which is the usual temperature for the shift conversion reaction:

$$CO + H_2O \rightarrow H_2 + CO_2$$

$$\Delta H = -41 \text{ kJ/mole}$$

The reaction is exothermic; therefore, it is usually carried out in two steps with heat removal between steps. The rate of reaction is more rapid at high temperatures, but equilibrium is more favorable at low temperatures. Thus, it is common practice to operate the first step at a higher temperature than the second so that most of the CO is converted in the first step (from 12% to 3% content in the gas), and in the second step the CO is reduced to less than 1% (often as low as 0.2%).

Prior to 1960, the same type of catalyst was used in both steps. This catalyst is mainly iron and chromium oxides, about 55% Fe, and 6% Cr. It is active only at relatively high temperatures (350°-430°C) and is known as a high-temperature shift (HTS) catalyst. About 1960 a new copper-based catalyst came into use, which is active at lower temperatures (200°-260°C) and is known as low-temperature shift (LTS) catalyst. Most LTS catalysts contain zinc and alumina in addition to copper and are poisoned by sulfur and chlorine compounds.

It is possible to use a guard bed ahead of the LTS catalyst bed. Formally, it used to be a ZnO bed. Nowadays a sacrificial LTS catalyst volume is provided on top of the LTS bed.

Carbon Dioxide Removal – After leaving the shift conversion step, the gas may contain 18% CO_2 or more depending on the feedstock composition. It is then cooled, if necessary, to a temperature range that depends on the requirements of the absorbent used in the CO_2 removal step. Absorption in water was commonly used in pre-1940 plants. Its disadvantages were high energy consumption and loss of H_2 and N_2, which are appreciably soluble in water at the high pressure used. Recovering CO_2 that had adequate purity for urea production was difficult. Between 1940 and 1960, a 20% solution of monoethanolamine (MEA) was favored. After 1960, most new plants used potassium carbonate solution with various additives to promote absorption and inhibit corrosion. The main advantage of potassium carbonate solution is lower heat requirements for stripping the CO_2 from the solvent. However, there are several other solvents in use, mainly organic liquids, some of which have a proprietary composition.

The potassium carbonate system operates mainly isothermal-CO_2 absorption at high pressure and CO_2 release at low pressure. In the absorption step the pressure is typically about 3.0 MPa (reformer pressure minus pressure losses), and the temperature may be 100°C. The CO_2 is absorbed chemically by the conversion of potassium carbonate to bicarbonate. When the solution pressure is reduced to about atmospheric pressure, part of the CO_2 and water vapor escape. CO_2 release is assisted by steam stripping. The steam is raised in the regenerator reboiler heated by the gas from the LTS shift converter; thus, some or most of the heat required by the CO_2 removal process is derived from the heat in the incoming gas. The regenerated solution is returned to the absorber.

In contrast MEA absorption-regeneration operates on a temperature differential with absorption at a relatively low temperature, 27°-60°C, and regeneration at 100°-140°C. Thus, it is necessary to cool the incoming gas to the absorber and to heat the MEA solution in the regenerator with steam. The MEA process has been improved by the addition of promoters and corrosion inhibitors, thereby lowering heat requirements.

Much attention has been given in recent years to methods for removal of acid gases (mainly CO_2 and H_2S), not only from ammonia synthesis gas but also from natural gas, synthesis gas for products other than ammonia, and fuel gas produced by coal gasification. Numerous processes have been developed, and the choice of process for an ammonia plant may depend on a balance between energy cost, capital costs, and other factors. Since partial oxidation of heavy oil or coal yields gases containing H_2S and CO_2, the acid gas removal process for this use must be capable of removing and separating these impurities. Some partial oxidation processes produce gas containing small percentages of hydrogen cyanide, which must be removed and converted to nontoxic compounds.

A complete discussion of CO_2 removal processes is beyond the possibility of this manual; however, Table 6.12 briefly summarizes the characteristics of the main processes. The energy consumption is related to the existing installations. This is an update of a summary provided by Quartulli [16].

Methanation – The gas leaving the CO_2 absorption step still contains about 0.3% CO and 0.1% or less CO_2. These oxides must be removed prior to the ammonia synthesis step because they would decrease the activity of the ammonia synthesis catalyst and cause deposition of ammonium carbamate in the synthesis loop. The methanation reactions are [4]:

$$CO+3H_2 \rightarrow CH_4+H_2O, \quad \Delta H_{25C} = -206.1 \text{ kJ/mol}$$

$$CO_2+4H_2 \rightarrow CH_4+2H_2O, \quad \Delta H_{25C} = -164.9 \text{ kJ/mol}$$

These reactions are the reverse of the reformer reactions, and a similar nickel-based catalyst is used. It will be noted that each molecule of CO and CO_2 consumes three or four molecules of H_2, respectively. Therefore, it is necessary to efficiently remove CO and CO_2 to the minimum practical level.

The methanation step is usually carried out with a gas inlet temperature of 300°-350°C; therefore, the gas must be preheated to that temperature. Since the reactions are exothermic, the temperature may rise to 320°-400°C at the gas outlet, depending on the CO + CO_2 content of the gas. A heat exchanger is commonly used to preheat the incoming gas and cool the exit gas.

Compression – The synthesis gas leaving the methanation step typically contains about 74% H_2, 24% N_2, 0.8% CH_4, and 0.3% Ar, dry basis. The gas must be compressed to the pressure required by the synthesis step. Before centrifugal compressors came into general use, reciprocating compressors were used. These reciprocating compressors often involved as many as five stages of compression with the various gas purification steps at intermediate pressures. Synthesis pressures varied widely from 10 to 80 MPa depending on the process. Reciprocating compressors are still used for small plants (less than 500 tpd), but centrifugal compressors are now used in most new plants that have capacities of 600-1,800 tpd. Synthesis pressures in these new plants usually are in the range of 15-25 MPa although some of the larger plants may operate at 30-35 MPa. Centrifugal compressors are driven by steam turbines using high-pressure steam generated mainly from hot process gas leaving the secondary reformer. The steam is exhausted at a lower pressure and used in the reforming process and other process steps.

Because reciprocating compressors are driven by electric motors, they are more efficient than centrifugal compressors. Typical efficiencies are reported to be 87% for reciprocating compressors as compared with 70% for the centrifugal type. However, reciprocating compressors are more expensive, especially for large plants. Their maintenance costs are also higher.

Centrifugal compressors are usually built with two or three casings and often with interstage cooling. Compressor design is highly specialized, and the details of design, arrangement, and operation are complex. Cooling and compressing the gas condenses nearly all of the water vapor remaining in it. The compressed gas enters the synthesis loop at various points depending on the process design.

Drying of Synthesis Gas – No water is allowed to enter the synthesis converter because of its adverse effect on the catalyst. The older plants used to remove the residual water by mixing the makeup synthesis gas with the converted gas ahead of the ammonia condensation and separation. However, it required more compression power since converter effluent undergoes recycle compression before product condensation. It also diluted the ammonia concentration of the converted gas and resulted in a lesser amount of ammonia condensed and higher recycle flow rates. Most modern plants use molecular sieve dryers to remove water in the synthesis gas to less than 1 ppmv. The sieves are usually located at the interstage of the synthesis gas compressor [4]. The dried makeup gas can then be combined with the recycle and sent directly to the ammonia converter.

Excess Nitrogen Rejection – Some processes use excess air in the secondary reformer to reduce the

Table 6.12. Processes for Removal of CO_2

System	Solvent	Corrosion Inhibitor	Acid Gas Content in Treated Gas	Heat Required	General Comments
Chemical Type Systems					
Amine-Based					
MEA	15%-20% monoethanol amine	None	Less than 50 ppmv	High	High utility consumption. Requires extensive use of alloy materials to combat corrosion.
Inhibited MEA	25%-35% MEA plus UCAR amine guard	Yes	Less than 50 ppmv	Medium	Inhibitor allows higher CO_2 loading, reducing solution circulation and utilities consumption [15].
TEA/MEA	Triethanol amine and monoethanol amine	None	Less than 50 ppmv	Low	Used in several NH_3 installations. Separate absorption and stripping system is required for each solvent.
AMDEA	40%-50% MDEA plus additive	None	100-1,000 ppmv	Low	Two-stage configuration normally used in ammonia plants [53,54].
Potassium-Carbonate Based					
Benfield	25%-30% K_2CO_3 plus additives	Yes	500-1,000 ppmv	Low	Used extensively for ammonia. Low operating costs. Used both as single-stage and two-stage systems [55,56].
Catacarb	25-30% K_2CO_3 plus additives	Yes	500-1,000 ppmv	Low	Has been used in ammonia plants up to 1,540 tpd capacity [16].
Carsol	K_2CO_3 plus additives	Yes	500-1,000 ppmv	Low	Used as a single-stage or two-stage system. Used in NH_3 plants up to 1,360 tpd capacity.
Flexsorb HP	K_2CO_3 plus sterically hindered amine	Yes	500-1,000 ppmv	Low	Commercialized recently in a 1,640-tpd and a 472-tpd ammonia plant previously using conventional K_2CO_3 processes [57].
Lurgi	25%-30% K_2CO_3 plus additives	Yes	500-1,000 ppmv	Low	Used in several installations in Germany and other areas [16].
Vetrocoke	K_2CO_3 plus As_2O_3	Arsenic inhibits	500-1,000 ppmv	Low	Use of arsenic presents disposal and pollution problems. Considerable experience.
Vetrocoke	K_2CO_3 plus glycine and secondary amine	Yes	250-1,000 ppmv	Low	Low-energy flowsheet uses two-pressure-level regeneration, reducing regeneration heat by 50% compared to traditional process [58].

(Continued)

Table 6.12. Processes for Removal of CO_2 (Continued)

System	Solvent	Corrosion Inhibitor	Acid Gas Content in Treated Gas	Heat Required	General Comments
Sulfinol	Sulfolane, di-isopropanol-amine solution	None	Less than 100 ppmv	Low	Process can be used for CO_2 and H_2S removal applications in synthesis gas and natural gas services. Chemicals cost relatively high.
Physical Absorption Systems					
Purisol (NMP)	N-methyl-2-pyrrolidone	None	Less than 50 ppmv	Low	Used in high-pressure processes such as partial oxidation-based plants. Excellent acid gas cleanup. Solvent is non-corrosive.
Rectisol	Methanol	None	Less than 10 ppmv	Low	System circulates refrigerated methanol. Several columns required. Can be used for CO_2, H_2S, and COS removal in partial oxidation and coal gasification processes. High investment.
Fluor solvent	Propylene carbonate	None	Dependent on pressure	Low	Has high degree of solubility for CO_2. Acid gas desorbed by release of pressure without application of heat. Requires intermediate flash operation. Process works to best advantage at high pressure [59].
Selexol	Propylene glycol dimethyl ether	None	Dependent on pressure	Low	Suitable for high pressure absorption services.Can operate at low pressure but increased residual gas content. Can also be employed for natural gas treatment. Part of CO_2 is lost during flash [60].

primary reformer duty and make its operating conditions less severe. The excess nitrogen in the synthesis gas must be removed before it is sent for ammonia synthesis. The Braun Purifier process is a well-known process using the concept of excess air in the secondary reformer. In this process excess nitrogen is removed cryogenically as shown in Figure 6.4.

The dry synthesis gas is cooled and expanded in a turbine to liquefy a portion of the gas. After further cooling, the vapor from the partially liquefied stream is scrubbed in the purifier column to remove all but about 0.2% argon and almost all the methane [4]. The vapor from the top of the column contains the desired H_2:N_2 ratio. The excess nitrogen stream, containing methane and other impurities such as argon and a small amount of carbon monoxide from the purifier column, is used as a regeneration gas for molecular sieve beds and eventually as fuel after recovering refrigeration in the heat exchangers. There are other processes that use Pressure

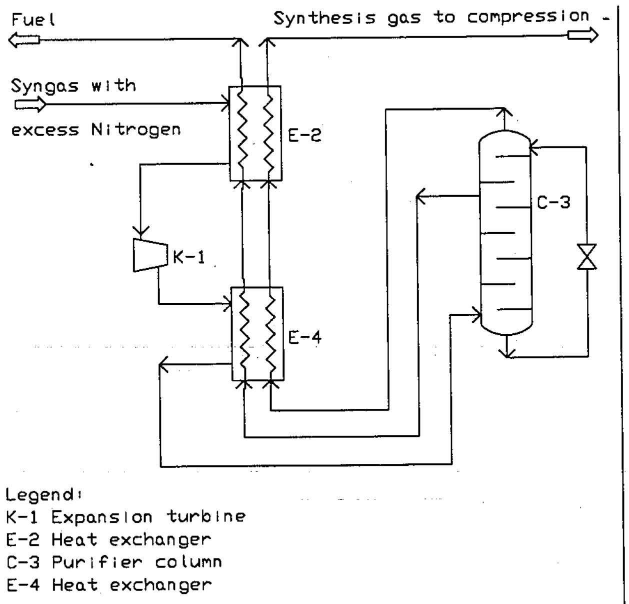


Figure 6.4. Braun Purifier.

Table 6.13. Equilibrium Content of Ammonia for a Gas Containing a Hydrogen: Nitrogen Ratio of 3:1 [22]

Equilibrium in % of Ammonia

	Pressure, kPa			
Temperature in °K	10,133	20,265	30,398	40,350
Using 0% Inerts				
633	35.10	49.62	58.91	65.72
713	17.92	29.46	38.18	45.26
793	8.32	16.13	22.48	28.14
873	4.53	8.80	12.84	16.72
Using 10% Inerts				
633	28.63	40.53	48.14	53.70
713	14.60	24.06	31.21	37.02
793	7.18	13.16	18.38	23.04
873	3.69	7.17	10.49	13.68

Swing Adsorption (PSA) for excess nitrogen rejection. These processes are discussed later in this chapter.

6.4.2 Ammonia Synthesis

6.4.2.1 Thermodynamics and Kinetics [4]

The synthesis of ammonia is composed of the following reversible reaction of hydrogen and nitrogen.

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

This reaction is exothermic; the net heat of reaction is about 11,000 cal/g mole at 18° Celsius (647 kcal/kg of NH_3), assuming NH_3 is in the gaseous state. The net heat released by the reaction increases with rising temperature and may be 15% - 20% higher at the usual operating conditions of 400° - 500°C. The following is a mathematical equation of this:

$$\Delta H = [2.2523 \times 10^{-2} + 34.7236/T + 1.89905 \times 10^{7}/T^{3}]p - 22.3792T - 1.057 \times 10^{-3}T^{2} + 7.08048 \times 10^{-6}T^{3} - 38327.0 \quad [17]$$

The amount of ammonia present in an equilibrium mixture at different temperatures and pressures was experimentally developed for pressures ranging from 1,000 to 101,000 kPa (10-1,000 atm) [18,19,20]. This led to the calculation of the reaction equilibrium constant [21], which is dependent on temperature, pressure, and the ratio of hydrogen and nitrogen present. Table 6.13 lists ammonia equilibrium concentrations for a feed using a 3:1 hydrogen to nitrogen ratio and either 0% or 10% inerts [22].

A catalytic surface, often based on metallic iron, is always used to form ammonia from an industrial-scale reaction of hydrogen and nitrogen. The metallic iron catalyst is primarily made from magnetite, Fe_3O_4, that has been promoted using alkali in the form of potash and metals, such as aluminum, calcium, or magnesium. Caution must be taken because the catalyst could undergo thermal degradation. It could also be permanently poisoned by sulfur, arsenic, phosphorus, chlorine, and heavy hydrocarbons; oxygen-bearing compounds will cause temporary poisoning, which may be reversed if the exposure was only for a short while [4].

Synthesis pressure, synthesis temperature, space velocity, inlet gas composition, and catalyst particle size all affect ammonia synthesis. LeChatelier's principle helps explain how synthesis pressure affects the synthesis of ammonia. As the ammonia reaction takes place, there is a decrease in volume. Thus, raising the pressure increases the equilibrium percentage of ammonia and accelerates the reaction rate. The ammonia synthesis reaction is exothermic; therefore, higher temperatures increase reaction rates and thermal degradation of the catalyst. But the equilibrium amount of ammonia decreases with an increase in temperature. Space velocity, the ratio of the volumetric rate of gas at standard conditions to the volume of the catalyst, decreases the percentage of ammonia in the gas as it increases. Yet, if the space velocity is increased while the volume of the catalyst remains constant, more ammonia may be produced [4]. This can be seen in Figure 6.5 [22]. Commercial operations usually have space velocities between 8,000 and 60,000 h^{-1}.

The inerts level as seen in Table 6.13, ammonia concentration, and hydrogen-to-nitrogen ratio all determine the effect of inlet gas composition on ammonia synthesis. The reaction rate changes with ammonia in the incoming gas. Though the optimum hydrogen-to-nitrogen ratio may be a little less than 3:1 [22], most commercial facilities operate at a hydrogen-to-nitrogen ratio of 3:1. To increase catalyst activity, the catalyst particle must be made smaller, thus the ratio of the catalyst surface area to its volume is increased. Small catalyst particles also have a lower resistance to mass transfer within the catalyst pore structure. Radial and horizontal ammonia converter designs use the smaller catalysts, ranging from 1.5 to 3.0 mm, for higher activity. Axial flow converters, on the other hand, primarily use 6-10 mm catalysts [4].

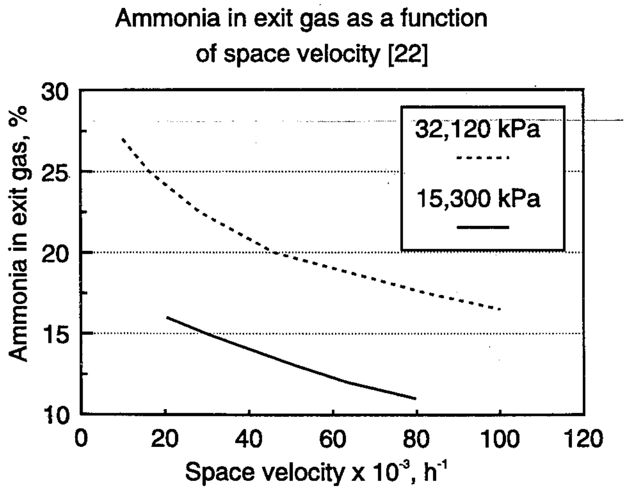


Figure 6.5. Ammonia Content in Exit Gas.

6.4.2.2 Technology of Ammonia Synthesis

As mentioned previously, ammonia synthesis is commonly carried out at 400°-450°C, using an iron catalyst promoted with potassium and alumina. The gas entering the converter consists mainly of gas circulated in the loop with a relatively small amount of fresh synthesis gas called "makeup" gas. The gas entering the converter contains N_2 and H_2 in a 1:3 ratio plus 10%-14% "inerts" and about 2% NH_3. The "inerts" consist mainly of methane, argon, and sometimes helium if the natural gas feedstock contains the element. (Methane is not, strictly speaking, an inert gas, but the term is used in ammonia synthesis context since it does not participate in the reaction.) Since the inert gas concentration tends to increase as the N_2 and H_2 are removed, it is necessary to vent a side stream of "purge gas" to keep the inert gas concentration at a tolerable level.

Ammonia synthesis converters differ in the type of flow: axial, radial, or crossflow. The reactor is designed for good gas distribution throughout the catalytic bed at minimum pressure drop. The converters also differ in the way temperature control of the reactants is achieved (quench or indirect cooling) and how reaction heat recovery is done. The quench converter was popular for some time because of its simple design. In the quench converter, only a part of the recycle enters the first catalyst bed at about 400°C and leaves the bed at about 500°C. The gas temperature is quenched by mixing with cooler (150°-200°C) recycle gas before entering the next catalyst bed.

In an indirect-cooled converter, heat exchangers are used to cool the gas out of each bed. The heat is used to preheat the inlet gas to the converter or to raise steam.

The catalyst efficiency improves by increasing the catalyst surface area per unit volume with a small particle size of 1.5-3 mm instead of 6-10 mm. The small particles increase the reaction rate but increase the pressure drop unless the gas velocity through the catalyst bed is reduced. Radial flow converters provide larger gas flow area compared with an axial flow converter. All modern, low-energy designs use radial or crossflow designs with indirect temperature control [4].

The gas leaving the converter will contain 12%-18% NH_3, depending mainly on the pressure; conversion per pass increases with pressure. The gas is cooled first by heat exchange with the incoming gas, then by air or water, and finally by refrigeration to condense most of the ammonia as a liquid. The degree of cooling required depends on the pressure. At high pressures much of the ammonia can be condensed at temperatures obtainable by water cooling. At lower pressures (15-20 MPa) increased reliance must be placed on refrigeration. If the ammonia is to be delivered to atmospheric pressure storage, it must be further cooled to -33°C (Chapter 7). The gas remaining after ammonia condensation is recycled to the converter by means of a compressor.

Ammonia Converter Design – Today all low-energy designs use indirectly cooled converters. The design and layout offered by various ammonia plant designers differ considerably. Kellogg's Horizontal Converter and Topsoe's Series 200 Converter use two catalyst layers with an intermediate heat exchanger for the feed, all in one vessel for a plant size of at least 1,800 tpd.

The Topsoe Series 200 Converter is a radial flow converter as shown in Figure 6.6. It has two catalyst beds having annular cross sections. The gas flows radially inwards. A single heat exchanger is installed at the outlet of the first bed. The converter inlet gas enters at the bottom and flows through an annular space between the shell and catalyst bed. The annular flow of gas keeps the converter shell at a low temperature and protects it from hydrogen attack [15]. The gas is heated in the interchanger before it enters the first bed. The effluent from the first bed is cooled in the interchanger and flows through the second bed. A large number of old converters have a dead zone of catalyst at the top of each bed. The Ammonia Casale axial-radial converter design is shown in Figure 6.7. The annular top bed is left open at the top to permit a part of the gas to flow axially through the catalyst. The remainder of the gas flows radially through the catalyst bed [15]. Its design is flexible and can be fitted well into existing converter shells. A large number of old converters have been retrofitted to Casale axial-radial flow design; thus, synthesis loop efficiency has been improved.

Uhde uses three catalyst beds. The first two beds and an interchanger are in one vessel. A waste heat boiler generating HP steam cools the gas before it enters a second vessel containing the third catalyst bed. The effluent of the third bed goes through a second HP steam boiler.

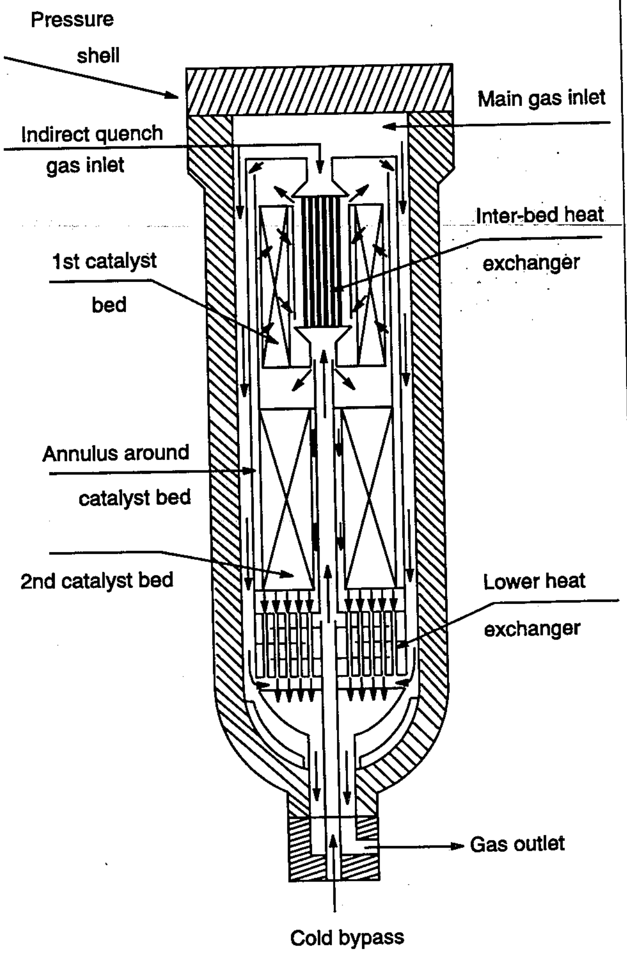


Figure 6.6.Topsoe Series 200 Converter.

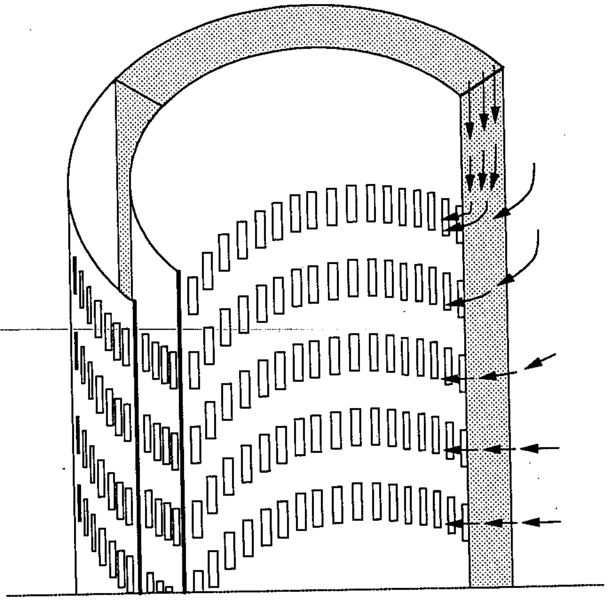


Figure 6.7. Ammonia Casale Converter.

Kellogg uses a horizontal cylindrical converter in which catalyst beds are arranged side by side, as shown in Figure 6.8.

The gas flows vertically through rectangular beds with minimum depth. The catalyst beds and an interchanger are installed on a cartridge that can be inserted into the vessel by a trolley system, rolling on tracks [15].

The Brown & Root Braun Adiabatic Converter is a variation of the concept in which the effluent from the first bed is cooled in a heat exchanger directly coupled to the converter. There are two adiabatic converters in

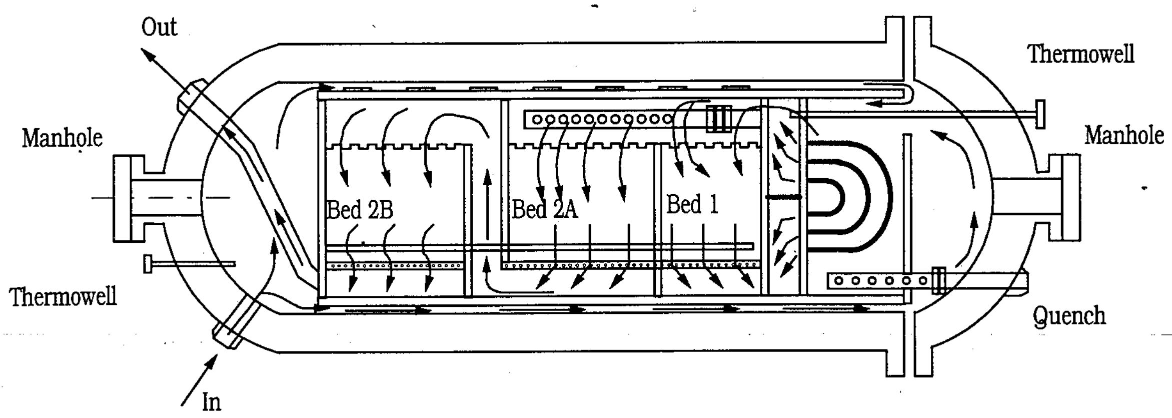


Figure 6.8. Kellogg Horizontal Converter.

series; each contains a single catalyst bed held in a simple cylindrical vessel. The reactor wall comes in direct contact with 400°C gas [15].

Purge Gas Recovery – To control the concentration of inerts in the recycle gas, it is necessary to draw a purge stream from the synthesis loop. In the older plant, this gas was used as fuel in the reformer. The purge gas has a typical composition of 61% hydrogen, 20% nitrogen, 13% methane, 4% argon, and 2% ammonia [23]. Recovering and recycling hydrogen from the purge gas can reduce the quantity of hydrogen to be produced by steam reforming. Cryogenics, membrane, and PSA processes have all been commercially applied in ammonia plants for the recovery of hydrogen and nitrogen from the purge gas.

The **cryogenic process** for purge gas recovery operates at a high pressure, typically 7 MPa. Currently, the process is limited to operation below 9 MPa due to the pressure limitation on the brazed aluminum fin heat exchangers [23]. A hydrogen recovery of 90%-98% can be achieved; in addition, about 30% of the nitrogen can be recovered. The hydrogen-rich stream is returned to the second stage of the ammonia synthesis gas compressor. The cryogenic process requires pretreatment of the purge gas to remove ammonia and water. Ammonia in the purge stream is removed by water wash, and the moisture is removed in a molecular sieve dryer.

Membrane separators are widely accepted for recovering hydrogen from the ammonia plant purge gas [24]. In a two-stage membrane, the first stage accepts feed at 13 MPa and delivers the hydrogen-rich permeate stream at about 7 MPa for recycle to the second stage of the synthesis gas compressor. The non-permeate from the first-stage membrane is fed to the second-stage membrane and delivers permeate at 2.5 MPa to the suction of the synthesis gas compressor. About 65% of the hydrogen is recovered in the first stage, and 35% is recovered in the second stage. Typically, total hydrogen recovery of 85%-90% is achieved at a hydrogen purity of 87% to 90% [23]. The membrane units are modular in nature, and the number of modules is directly proportional to the throughput of the unit.

Pressure Swing Adsorption (PSA) has been used to produce ultra-high-purity hydrogen from ammonia plant purge gas. There are some PSA applications for the production of an H_2 and N_2 mixture from the purge gas. The PSA experience is limited to less than 5 MPa feed pressure. The recovered hydrogen stream is available at a pressure slightly lower than the feed pressure. The argon-rich stream is available at a low pressure of 0.3 to 4 kPa. Hydrogen recovery of 70%-85% in PSA is somewhat lower than the membrane and cryogenic processes. The PSA requires no pretreatment of the purge stream; ammonia and water in the purge stream are removed by PSA in addition to argon and methane.

6.4.3 Advances in Ammonia Technology

6.4.3.1 Advances in Gas Preparation Technology

Steam reforming has remained the prevalent (or prevailing) process for ammonia production. However, the primary reformer, the heart of the steam-reforming process, is the single most expensive piece of equipment in an ammonia plant, is somewhat complicated, and requires close attention to operate. The regular primary reformer operates at less than 50% efficiency; the remainder is recovered as steam produced from waste heat.

The excess steam is normally exported for off-site utilities or for an adjoining urea plant.

Some new concepts have been developed to improve the reforming section heat efficiency.

Introduction of the Pre-Reforming Process

Adiabatic pre-reforming may be used for steam reforming of hydrocarbon feedstock ranging from natural gas to heavy naphtha with a final boiling point above 200°C and an aromatics content up to 30%. The process is carried out in a fixed-bed adiabatic reactor loaded with a highly active reforming catalyst located upstream from the primary reformer (Figure 6.9).

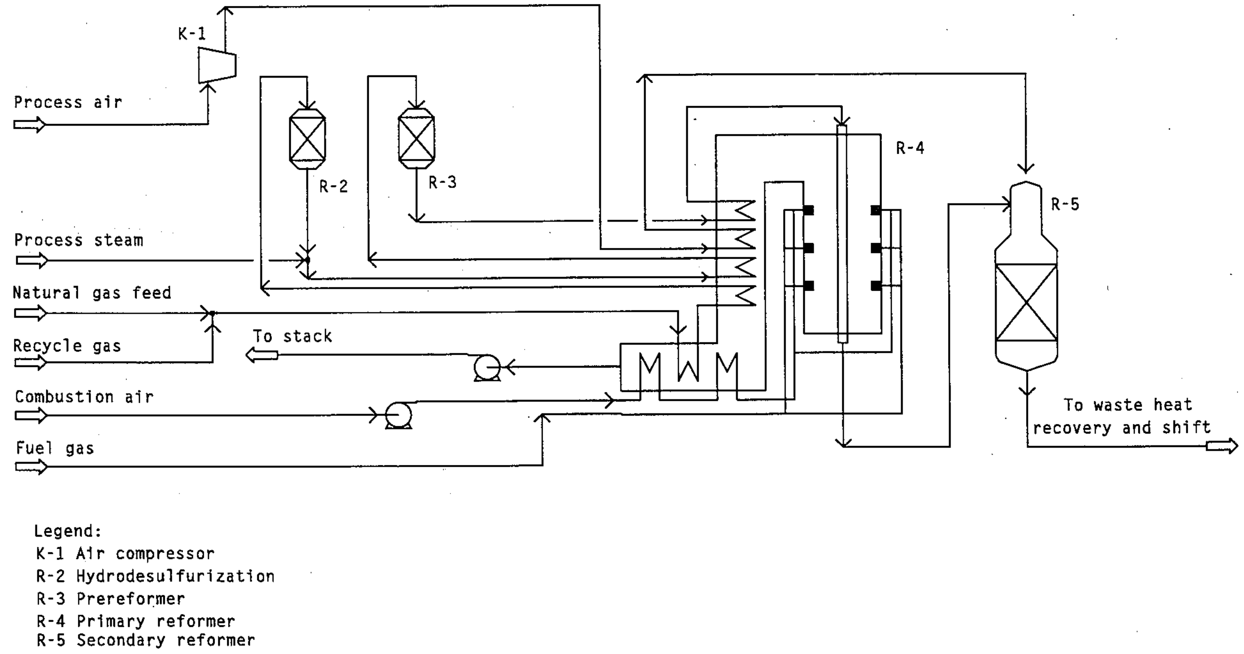
In the pre-reformer, hydrocarbons are converted into a mixture of carbon oxides, hydrogen, and methane. This endothermic reaction is followed by exothermic methanation and shift reaction, which adjusts the equilibrium between the carbon oxides, methane, hydrogen and water. This concept has been proposed by Topsoe [25].

Substitution of the Primary Reformer by Heat Exchanger Reformer

The reforming exchanger offers an alternative to the conventional fired primary reformer. The reforming is done in a tubular exchanger with catalyst-filled tubes. The reforming exchanger concept totally eliminates the furnace and uses a hot secondary reformer outlet as its heat source. Surplus air over the stoichiometric demand or oxygen-enriched air in the secondary reformer is required to balance the heat demand for the primary reforming reaction. Chiyoda proposed this concept in 1984 [26,27]; however, ICI was the first one to commercialize a reformer exchanger called the Gas Heat Reformer (GHR) as part of their Leading Concept Ammonia (LCA) process. The GHR is discussed further under the LCA process section.

Uhde has developed its Combined Autothermic Reformer (CAR) and has successfully operated a demonstration unit, which produces 13,000 m^3/h of process gas at 1.7 MPa [28]. CAR is a combination of reforming exchanger and air partial oxidation in a single vessel. The mixture of natural gas and steam is passed through the tubes filled with catalyst. These tubes are heated externally by hot reformed gas from the partial oxidation section. No commercial CAR unit has been installed as of late 1994.

Similarly, Topsoe has developed a reforming exchanger, which is in commercial operation for hydrogen production. The heat source is external to the process; as of 1994, Topsoe has not implemented the reformer exchanger unit in commercial ammonia production.



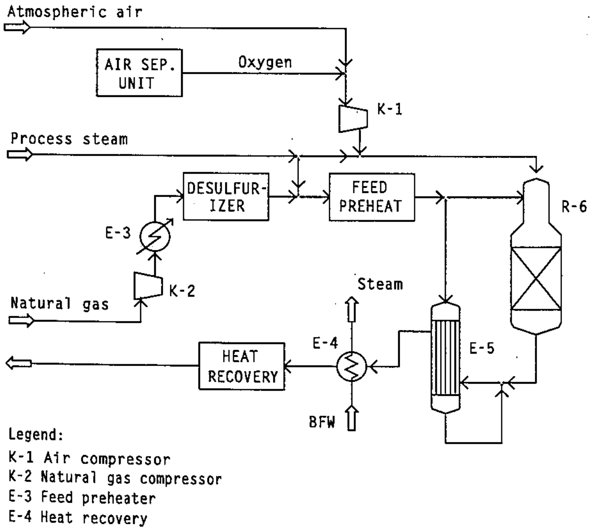
Source: [9].

Figure 6.9. The Concept of the Pre-Reforming Unit.

M. W. Kellogg developed and commercialized their first Kellogg Reforming Exchanger System (KRES) in 1994. Figure 6.10 illustrates Kellogg's concept [29].

Desulfurized natural gas feedstock is mixed with process steam, preheated, and divided into two streams that pass in parallel to the reforming exchanger and the adiabatic reformer (or secondary reformer). Air or oxygen-enriched air is added to the part entering the adiabatic reformer. The effluent from the adiabatic reformer passes directly to the shell side of the reforming exchanger. The mixed feed to the reforming exchanger flows downward through the catalyst-filled tubes, and reformed gas leaving the tubes is mixed with adiabatic reformer effluent. The combined gas then flows upward on the shell side of the reforming exchanger and provides the necessary heat to the catalyst tubes. The reformed gas leaving the shell of the reforming exchanger is sent for further heat recovery and other traditional processing steps such as shift converter, CO_2 removal, etc.

The M. W. Kellogg Co. commissioned its first commercial reforming exchanger in 1994 at Ocelot Ammonia Company plant in British Columbia, Canada. The reforming exchanger supplements the existing feed from the methanol plant purge gas and expands the existing plant capacity from 544 tpd by 40%. Kellogg claims lower capital cost due to reduced equipment and construction costs and a smaller plot; potential of reduced energy consumption; and reduced emission of NO_X and CO_2 by as much as 75% [29]. The capital cost savings or energy savings estimates are not yet available.



Source: [29].

Figure 6.10. Kellogg Reforming Exchanger System (KRES).

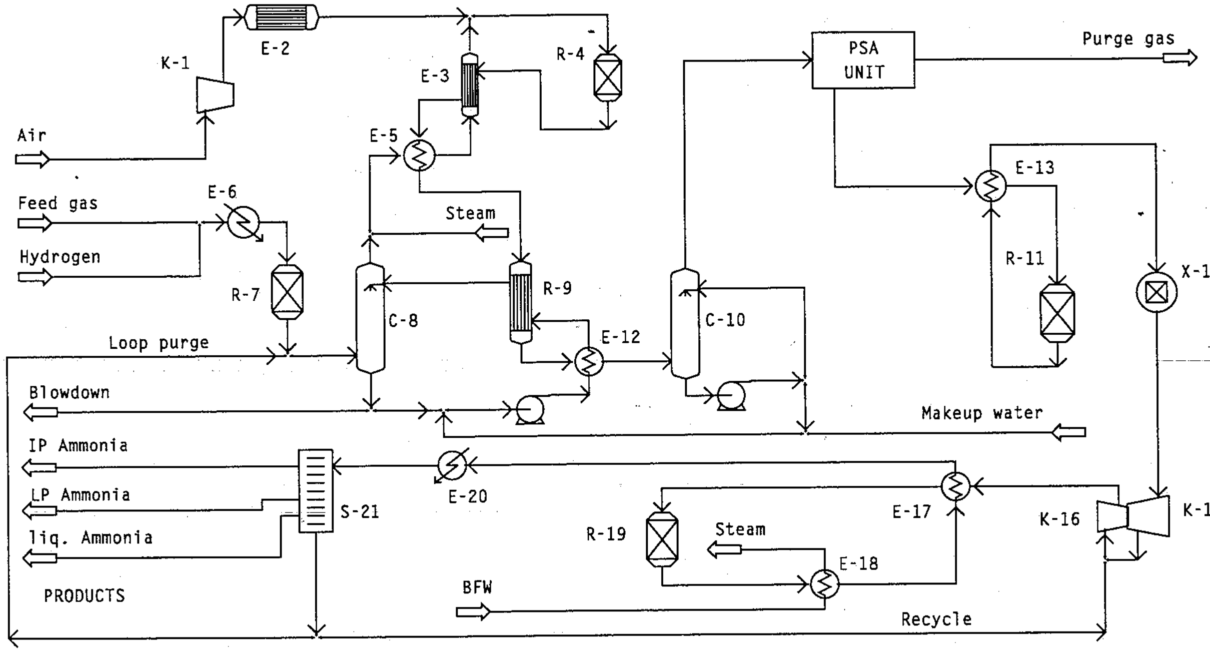
ICI Leading Concept Ammonia (LCA) Process

ICI brought on stream in 1988 two identical 450-tpd ammonia plants based on the LCA process at ICI's own plant at Severnside, U.K. The LCA concept is radically different from the traditional, highly integrated steam-reforming process. The need to raise high-pressure steam, a common feature in a conventional ammonia plant, is eliminated [30]. The LCA concept has a "core" unit consisting of key process operations and a separate utility area containing the power and steam system, refrigeration, CO_2 recovery, and other utilities. Figures 6.11 and 6.12 show a flow diagram for a core unit and how the core unit connects with the common utility section.

The core plant uses a gas heat reactor (GHR) in which the primary reformer is heated directly by the process gas exiting the secondary reformer. The CO shift is performed in a single-stage isothermal shift reactor at 250°C, using a special copper-based catalyst. With this shift catalyst and the low temperature level, there is no danger of a Fischer-Tropsch reaction, allowing the lower steam:carbon ratio of only 2.5 at the reformer [31]. A PSA system removes CO_2 and excess nitrogen in the synthesis gas.

Natural gas is desulfurized and passed through a feed gas saturator where it is contacted with circulating hot process condensate. The saturator provides in excess of 90% of the requirement of steam for reforming. It is mixed with a further quantity of steam to give a steam:carbon ratio of about 2.5, and it is preheated by the reformed gas stream. The reactants enter the GHR, which operates with an exit temperature of 700°-750°C and at a pressure of 3.0-4.5 MPa. The gas mixture is then fed to a secondary reformer for further reforming with an excess of process air. The reformed gas is cooled by providing heat for the GHR and preheating the reactants. The cooled, reformed gas is shifted in an isothermal water-cooled shift converter at 250°C. After shift conversion, the gas is cooled by direct contact with circulating process condensate and then fed to a PSA unit to remove excess nitrogen, CO_2, and part of the inerts. Part of the CO_2 is recovered from the PSA tail gas using an aqueous tertiary amine. The gas leaving the PSA unit is methanated, cooled, and dried [30].

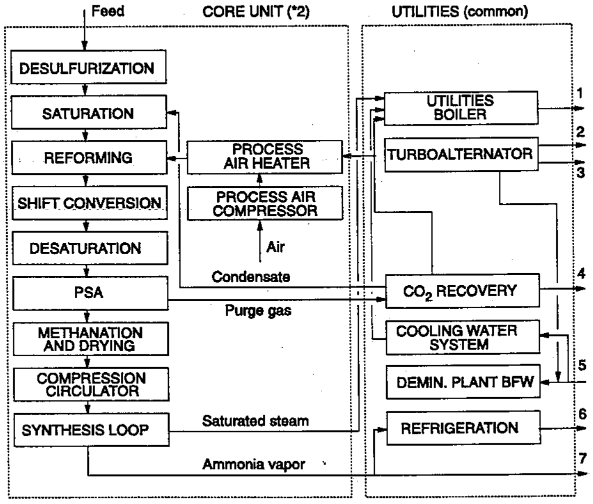
The ammonia synthesis reactor operates at a pressure of 8.0 MPa using ICI's cobalt-promoted catalyst. The gas enters at 225°C and leaves at 380°C [31]. The low-pressure synthesis loop ensures that high machine efficiency is sustained for the two-stage centrifugal compressor, despite the small size of the plant. Electric drives



Legend:

K-1 Air compressor	C-8 Saturator	K-15 Make-gas compressor
E-2 Preheater	R-9 Isothermal shift	K-16 Circulator
E-3 GHR	C-10 Desaturator	E-17 Heat recovery
R-4 Secondary reformer	R-11 Methanator	E-18 Utility boiler
E-5 Heat recovery	E-12 Heat recovery	R-19 Converter
E-6 Heater	E-13 Heat recovery	E-20 Cooler
R-7 Hydrodesulfurizer	X-14 Syngas dryer	S-21 2-stage ammonia separator

Figure 6.11. LCA Process (Core Unit).



Legend:
1 - IP steam export
2 - Electricity
3 - LP steam
4 - CO_2
5 - Makeup water
6 - Liquid ammonia
7 - Ammonia vapor

Figure 6.12. Arrangement of LCA Core Units and Utilities Section.

are used for the synthesis gas compressor and air compressor. Table 6.14 gives typical data for the LCA process.

There are no data available to compare the cost of LCA process with other conventional processes. To date there are only the two above-mentioned plants based on this technology.

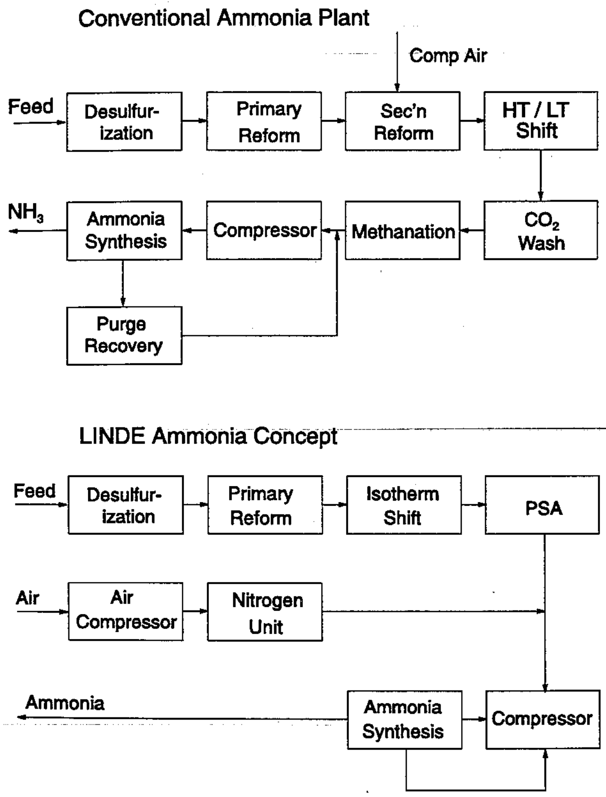
Linde Ammonia Concept (LAC) – LAC is a combination of a hydrogen plant, a nitrogen plant, and an ammonia synthesis loop. The hydrogen plant uses a primary reformer, shift converters, and a PSA unit to get ultra-pure hydrogen. The pure hydrogen is mixed with pure nitrogen from an air separation unit to give inerts-free ammonia synthesis gas. This concept is expected to be implemented in a 1,350-tpd ammonia plant at GSFC, Baroda, India (Figure 6.13).

The following features differentiate this process from the conventional steam-reforming process:

1. It eliminates secondary reforming. The reforming section produces hydrogen, which is later mixed with nitrogen from an air separation plant to make ammonia synthesis gas.

Table 6.14. Representative Data of the LCA Process [31]

Natural gas (feed + fuel)	6.5	Gcal/t NH_3
Import power (5.4 MW at 2,640 kcal/kWh)	0.74	Gcal/t NH_3
Total energy consumption	7.22	Gcal/t NH_3
Liquid ammonia product (14 bar, 30°C)	457	tpd
CO_2 (purity > 99%)	617	tpd



Source: [32].

Figure 6.13. Linde Ammonia Concept.

2. It uses an isothermal shift reactor for CO shift conversion as shown in Figure 6.13 [32].
3. It uses a PSA unit to remove CO_2, CH_4, and a small residual amount of CO from the hydrogen stream, producing 99.999 mole % pure hydrogen.

The following advantages are claimed by the process developer for the LAC process:

- The isothermal shift reactor allows conversion to 0.7% CO (dry basis) in a single step;
- The catalyst bed is kept at a constant temperature of about 250°C by a spiral wound cooling coil;
- Inside the coil tube, process condensate is evaporated and the steam raised is used in the primary reformer.

This isothermal reactor technology has been in commercial use in 10 plants worldwide [32].

The PSA unit is able to supply pure hydrogen even in case of a disturbance upstream in the reformer. This is in sharp contrast to the conventional plant where disturbances in the CO shift or CO_2 removal areas cause a shutdown due to high temperature in the methanator.

PARC Ammonia Process of Kinetics Technology India, Ltd. (KTI) – The PARC process combines air separation (to produce nitrogen) with steam reforming, HT shift, and PSA to make synthesis gas. In the proprietary PSA unit, nitrogen purge is used to enhance hydrogen recovery and introduce the stoichiometric nitrogen requirement. A Rankin cycle is used to generate electric power from the heat of the HT shift converter. This process eliminates the need for secondary reforming, LT shift, CO_2 scrubbing, and methanation. If CO_2 is required for urea manufacture, a CO_2 scrubbing unit is added in front of the PSA. Overall energy efficiency ranges from 7.0 to 7.6 Gcal/tonne NH_3, depending on plant specifics. The CO_2 recovery unit adds another 0.2 Gcal/tonne of ammonia [31].

Topsoe Economic Process – Topsoe continuously improves the energy efficiency of its design by optimizing all units of the ammonia process rather than using radically new schemes. The newly started installations in Indonesia and Bangladesh confirmed energy consumption during the test run at about 7 Gcal/tonne of ammonia [33].

Further improvement is expected from a pre-reformer positioned upstream of the primary reformer to allow reformer feed to be heated to a higher temperature at a low steam:carbon ratio without deposition of carbon. In addition, Topsoe has developed a shift conversion catalyst based entirely on copper, which does not promote a Fisher-Tropsch reaction at a low steam:dry gas ratio.

6.4.3.2 Advances in Ammonia Synthesis

New developments are related to two elements of ammonia synthesis:

- Construction of the reactor.
- Development of a new catalyst.

Regarding the latter, iron catalyst for ammonia synthesis normally has a process life of 10 years or more.

The favorable properties of ruthenium as an ammonia synthesis catalyst have been known for many years. Previously its high price prevented its use; however, ruthenium is now much less expensive, and economics of operation using ruthenium catalyst must be reconsidered. The major differences between the catalysts are much lower volume of the ruthenium catalyst, lower pressure of operation, higher temperature, lower mole % of hydrogen and nitrogen, and high partial pressure of ammonia allowed in the process. The expected immediate energy savings are about 0.2-0.3 Gcal/tonne of ammonia. The stability of ruthenium catalyst must be proven before it will begin to replace iron catalyst. Tests have shown that ruthenium is stable as a catalyst: it does not sinter, and its poisoning susceptibility is similar to the classic catalyst. However, longevity of the catalyst depends also on the carrier. Until now two carriers have been disclosed: special graphite by Kellogg and ceramic support by Topsoe.

Kellogg Advanced Ammonia Process (KAAP) [34] – KAAP is based on a precious-metal-based ammonia synthesis catalyst. This is the first commercially proven process that does not use the traditional iron catalyst. The new catalyst was jointly developed by M. W. Kellogg and British Petroleum (BP). Kellogg and BP demonstrated in a process demonstration unit that the new catalyst using ruthenium supported on a proprietary graphite structure with various co-promoters provided 10-20 times the activity of an iron-based catalyst currently available, while operating at a low synthesis loop pressure of 7-9 MPa, at high ammonia conversion (18%-22%), and over a wide range of hydrogen-to-nitrogen ratios. KAAP technology was commercialized in 1992 at Ocelot Ammonia Co., Kitimat, Canada. The basic sequence of process operations is similar to low-energy ammonia plants based on natural gas steam reforming. The synthesis loop for the KAAP is shown in Figure 6.14.

The KAAP ammonia plant design has the following technical features:

- Single-Case Synthesis Gas Compressor
- Radial Flow, Intercooled Converter Design
- Low-Pressure Synthesis Loop
- High-Activity Ammonia Synthesis Catalyst

The KAAP reactor is a four-bed intercooled radial flow, hot wall vessel. The first bed uses a charge of conventional magnetite catalyst to take full advantage of high ammonia reaction rate at low ammonia concentration. The other three beds are charged with KAAP catalyst. A series of intercoolers and external steam generators are provided for heat integration as shown in Figure 6.15.

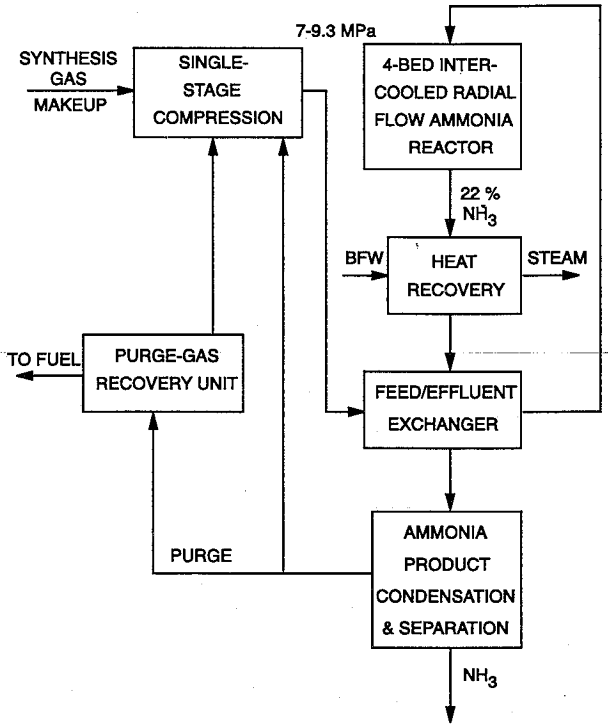


Figure 6.14. The Kellogg Advanced Ammonia Process (KAAP) Synthesis Loop.

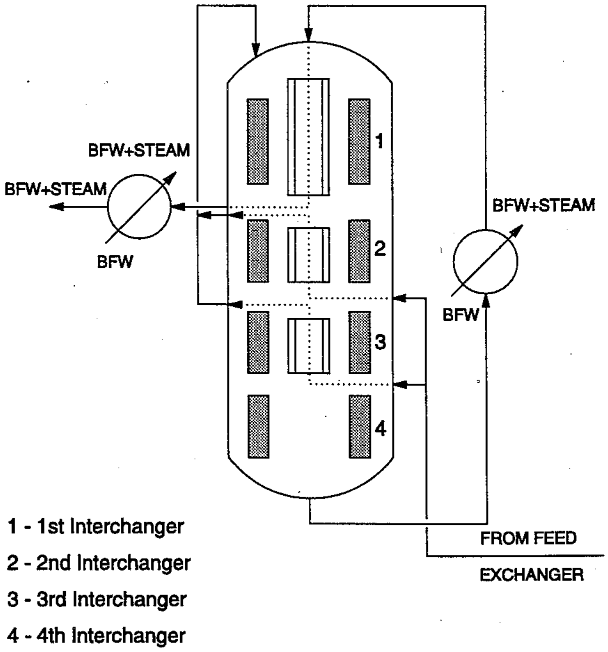


Figure 6.15. KAAP Reactor.

The KAAP reactor at Ocelot is a full flow converter installed in such a manner that it operates in series with the existing magnetite converter. The reactor is a two-bed radial flow, hot wall design with external insulation. An interchanger is provided to exchange the heat between the feed and effluent of the first bed. The feed to the KAAP reactor contains 15% ammonia. The ammonia concentration is increased to more than 21% at the exit of the KAAP reactor. The addition of a KAAP reactor and a new waste heat boiler to produce MP steam by KAAP reactor effluent has the potential of increasing the capacity of the synloop by 40%.

The KAAP technology for a grass root installation relative to current low-energy technology can provide the following benefits: the synloop energy consumption is reduced by 40%; that translates to overall plant energy reduction by about 1.0 GJ/tonne. The overall plant capital cost is reduced by about 5%.

Topsoe Ammonia Reactor Development

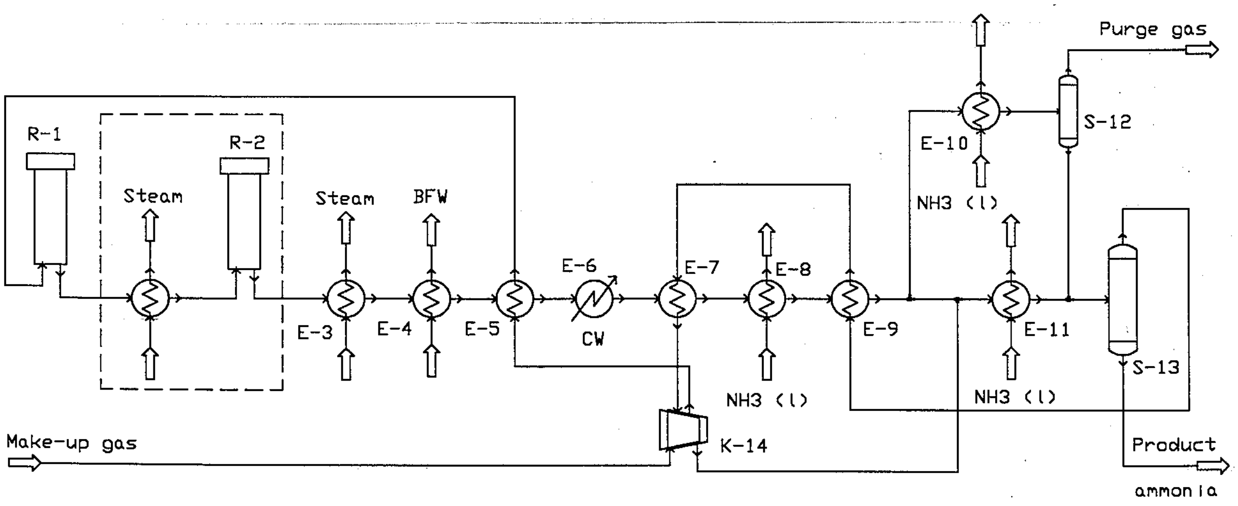
The Topsoe S-250 converter system also uses two radial flow converters in series with waste-heat boilers between the converters and after the last converter. The principle of operation of the S-250 system is shown in Figure 6.16.

This system provides an energy saving of 0.11 Gcal/tonne of ammonia compared to the S-200 loop [35]. Topsoe has developed a new S-300 converter, which is a three-bed radial flow converter with two internal heat exchangers. The Topsoe S-300 converter is shown in Figure 6.17. The S-300 is cheaper than the S-250 configuration, and the energy saving can be up to that of the S-250 system level.

The temperature versus conversion profiles in all three Topsoe reactors are given in Figure 6.18. The S-300 converter retains all features of the S-200 radial converter:

- Low pressure due to the radial flow.
- Use of small catalyst particle size.
- High conversion per pass due to indirect cooling.
- Good operability and easy temperature control.

It is claimed that S-300 compared with S-200 offers either the same performance with smaller catalyst volume or higher conversion by full use of the third bed. The comparison of loop configurations is given in Table 6.15.



Legend:
R-1 S-200 or S-300 converter
R-2 S-50 converter
E-3 - E-11 Heat recovery
S-12 Purge gas separator
S-13 Ammonia separator
K-14 Compressor unit

Source: [9].

Figure 6.16. Topsoe Layout of Synthesis Loop Using S-250 System.

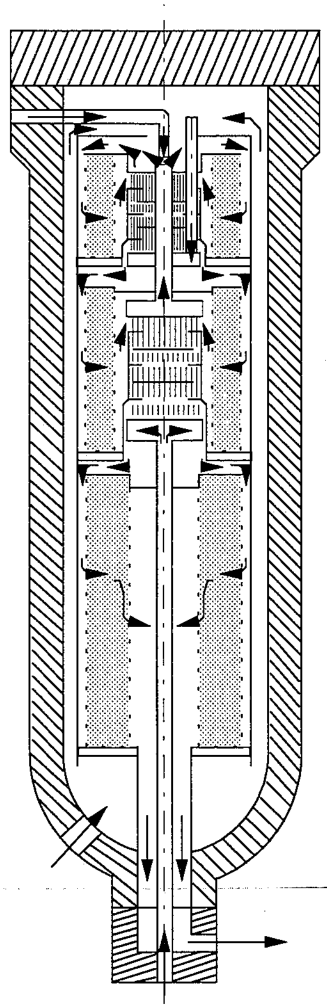


Figure 6.17. Topsoe S-300 Converter.

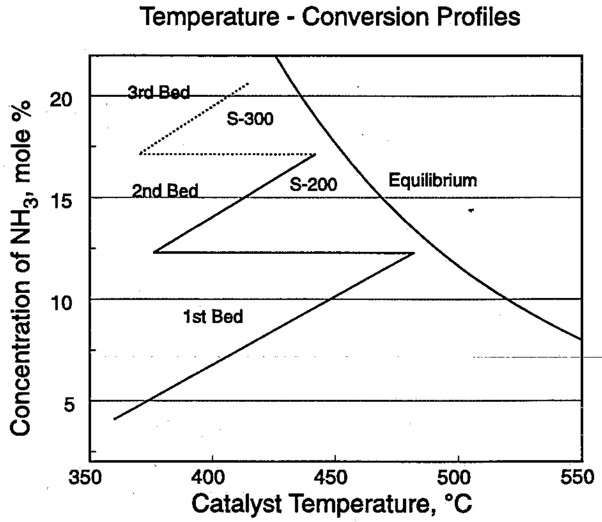


Figure 6.18. Temperature-Conversion Profiles in Topsoe Converters.

6.5 Partial Oxidation Process of Heavy Hydrocarbons

Hydrocarbons heavier than naphtha can be used as feedstocks for ammonia production by partial oxidation processes. Natural gas and naphtha also can be used, but since the plant cost for the partial oxidation process is considerably higher than that for steam reforming, the lighter feedstocks are seldom used. However, the partial oxidation process does offer the advantage of wider choice of feedstock with greater tolerance for impurities.

Crude petroleum can be used as feedstock, but the most common feedstock is heavy residual oil from petroleum refining processes, which has had the more

Table 6.15. Comparison of Topsoe Loop Configurations

Parameters/Converter Type	Units	S-200	S-300	S-250
Operating pressure	MPa	14	14	14
NH_3 concentration IN/OUT	vol. %	4.2/17.1	4.2/20.7	4.2/20.7
Relative feed flow	–	1.0	0.75	0.75
Relative catalyst volume	–	1.0	1.8	1.8
Heat recovered	%	62	50	72
Saving of compression power	kWh/t	0	-29.1	-29.1
Saving of heat	MMcal/t	0	-31	-31
Net energy saving	GJ/t	0	-0.46	-0.46

valuable lighter fractions removed. Such oil may contain high amounts of sulfur, depending on the sulfur content of the crude oil and the refining process. Using such oil for fuel or power generation would involve expensive equipment for pollution abatement in most countries; therefore, it is often available at a relatively low cost.

The feedstock requirement typically is about 0.76 tonnes of heavy oil per tonne of ammonia [36]. In addition, about 0.14 tonnes of oil or the equivalent in other fuel is required for generation of steam and electricity, or 530 kWh of electricity may be imported. In contrast with the steam-reforming process where most of the fuel is used in the reforming furnace, which requires a premium grade of fuel, the auxiliary fuel for a partial oxidation process is used in a separate unit, which can use coal, for example.

The principal partial oxidation processes are known as the Texaco, Shell, and Koppers-Totzek processes. The Koppers-Totzek process is also used for coal and will be described under that heading. The Shell and Texaco processes are generally similar. The Shell gasifier operates at 3.5-6 MPa, and the Texaco gasifier operates up to 9 MPa. Figure 6.19 is a flow diagram of the partial oxidation process.

The gasification pressure in partial oxidation processes has been gradually increased to a range of 60-90 atm, which helps save energy for compression. Texaco's commercial gasifiers for ammonia plants operate at 8.5-9 MPa [37].

Two main problems limit the operating pressure of the gasification process. Conventional HT shift catalyst (Fe/Cr oxide) loses its mechanical strength at approximately 6.0 MPa because under these conditions it cannot withstand the high steam partial pressure. The new catalyst, originally developed by BASF, uses Co/Mo sulfides. The new catalyst requires sulfur in the feed gas, and it can be installed immediately downstream of the gasifier [38].

The other problem for the high-pressure process was the compression of the oxygen required for the

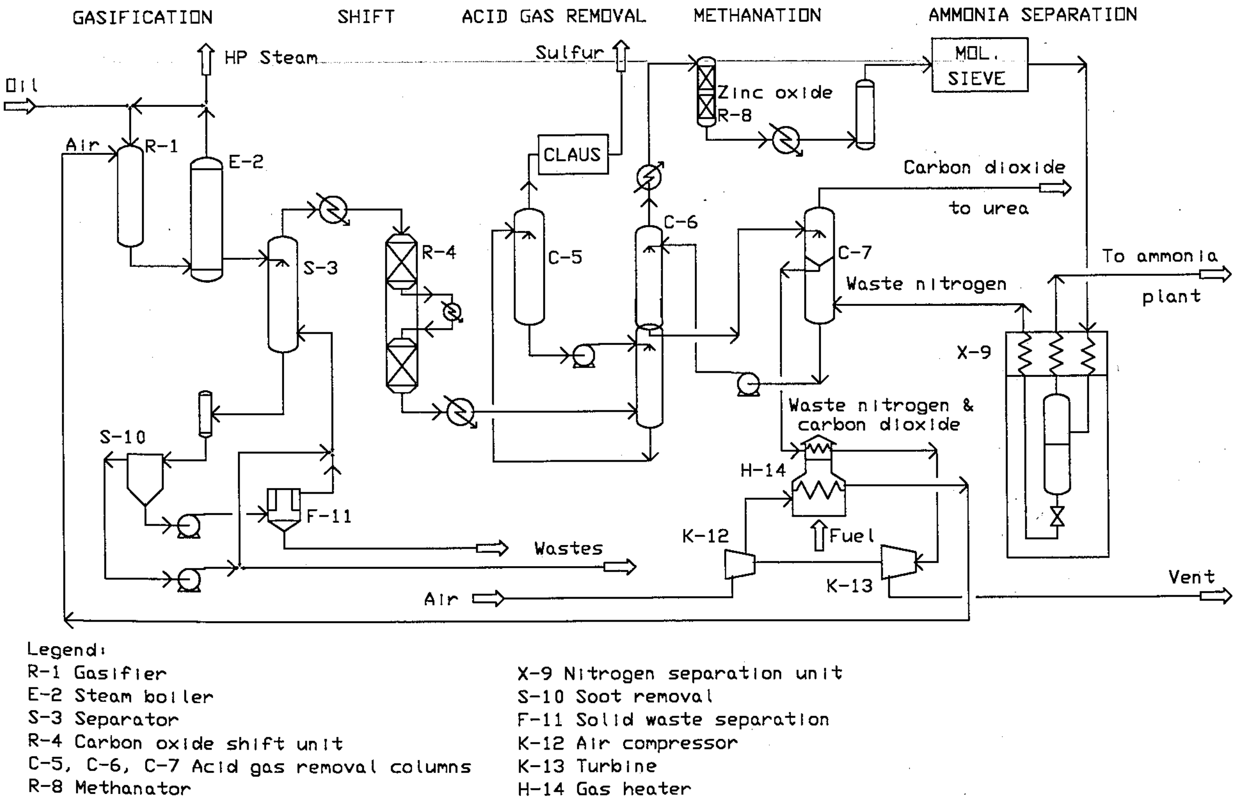


Figure 6.19. Flow Diagram of Partial Oxidation Process.

gasification. Safety is a great concern when compressing oxygen because oxygen reactibility increases with pressure. The maximum pressure attained by turbocompressors is about 7.5 MPa. Reciprocating compressors are not acceptable for modern plants [38]. Linde A.G. developed a liquid oxygen pump to pump the liquid up to 10 MPa. The high-pressure liquid oxygen is vaporized in the cold box to get high-pressure oxygen gas.

Heavy fuel oil is preheated and pumped into the gasifier along with high-pressure steam and preheated oxygen from an air separation unit. The reaction occurs at a high temperature (1200°-1500°C), and no catalyst is required. The chemical reactions involved are complex but can be described by reactions shown in Table 6.16.

Table 6.16. Principal Gasification Reactions [37]

Partial combustion	$C_mH_nS_r+.5mO_2 \rightarrow mCO+(.5n-r)H_2+rH_2S$
Side Reactions	
Hydrocracking	$C_mH_nS_r+(r-.5n+2)H_2 \rightarrow CH_4+(m-1)C+rH_2S$
Steam gasification	$H_2O+C \rightarrow H_2+CO$
Reforming	$H_2O+CH_4 \rightarrow 3H_2+CO$
Water gas shift	$H_2O+CO \rightarrow H_2+CO_2$

A typical composition of the resulting gas is 46% H_2, 47% CO, and 4% CO_2 dry basis with small percentages of H_2S and N_2. A considerable amount of soot (carbon) remains suspended in the gas.

The hot gas is quenched with process water to the inlet temperature of the shift conversion step (about 300°C), and most of the soot is removed in the water, which goes to a soot recovery unit. The soot is eventually recycled in the oil feedstock or used as fuel for steam generation, and the water from which the soot was recovered is recycled to the quench step. The quenching step also vaporizes some of the water into the gas stream, which supplies water vapor needed for the shift reaction.

The shift reaction is carried out by commercially available sulfur-tolerant catalyst; thus, the CO content of the gas is reduced to about 1%. The next step is removal of CO_2 and H_2S by a scrubbing process such as Rectisol or Selexol. The H_2S is recovered separately and sent to a Claus process unit for conversion to elemental sulfur. The CO_2 is of adequate purity for urea production.

The final purification step is a liquid nitrogen wash process, which uses liquid nitrogen from the air separation plant. This process removes CO and also lowers the CH_4 and argon content to a very low level. These impurities leave the process in a gas stream that is useful as fuel in steam generation.

Prior to the nitrogen wash, residual CO_2 and water are removed by molecular sieve to prevent freezing of these gases in the nitrogen wash column.

After purification, nitrogen is added to adjust the N_2:H_2 ratio to the stoichiometric 1:3 ratio, and the gas is compressed for ammonia synthesis. This step is similar to that described under steam-reforming processes. However, it is claimed that because of the efficiency of the nitrogen wash step in removing impurities and inerts, the synthesis step can be operated without gas purge and, consequently, with higher efficiency. Also the gas purity contributes to the long life of the synthesis catalyst.

There are 48 ammonia plants based on Texaco partial oxidation technology. The most recent ones are a 1,350-tpd plant for GNFC, India, which was started in 1981; three 1,000-tpd plants of CNTIC, China, which were started in 1983, 84, and 85; three 1,000-tpd units for CNTIC, China, scheduled for startup in 1995/96; and also a 1,350-tpd plant for GSFC, India, scheduled for startup in 1996. The GSFC plant will use natural gas and naphtha as feedstock, while the other plants are based on residual oil.

Ammonia production using air for partial oxidation or gasification instead of oxygen has been commercialized by Texaco. The air gasification concept can be applied to the complete range of feed materials extending from natural gas and refinery gas, through liquid hydrocarbons, to coal and coke [37]. No oxygen plant is needed in this case. The product from the air gasifier contains about 50% nitrogen. The excess nitrogen is removed from the ammonia synthesis gas by a cryogenic condenser. This cryogenic unit can be designed to remove the inerts (CH_4 + Ar) from the synthesis gas. The synthesis gas out of the cryogenic unit is dry and can be introduced into the ammonia loop at a point downstream of the product ammonia condenser. The waste nitrogen leaves the cryogenic unit at 0.5-1.0 MPa and is heated and expanded to atmospheric pressure; thus, part of the power needed for the air compressor is provided [37].

6.6 Ammonia From Coal

About 10% of the world's ammonia production is based on coal, coke, or lignite. About half of the coal-based capacity is in the People's Republic of China where there are over 1,000 small plants with capacities ranging from 3,000 to 10,000 tpy [39]. It was reported that 1,100 small coal-based ammonia plants were built between 1966 and 1974 and 100 more per year were being added in 1975 [40]. The technology of one of these plants has been described [41]. The feedstock was lump anthracite or semi-anthracite although it was reported that briquetted coal or lower grade coal was used in some plants. In general, the process is similar to the original Haber process, which was described previously. The coal was gasified in a semi-water gas producer blown alternately with air and steam. Gas purification sequence was water scrub, H_2S removal, shift conversion, CO_2 removal by water scrubbing, and copper liquor scrubbing for CO removal. The gas was compressed in six stages by reciprocating compressors with purification steps between various stages. The product from the small plants is often used to make dilute ammonia solution (16%-20%) or ammonium bicarbonate for local use although some of the larger plants make ammonium nitrate.

Staege lists 13 plants built since 1950 for direct use of coal in India, Greece, Turkey, South Africa, Pakistan, Thailand, India, and Zambia [42]. Most of them are small (40 to 340 tpd capacity), and some of them have been converted to other feedstock. However, the list included three large plants (900-1,000 tpd) of which two are in India, specifically Talcher and Ramagundam. The third one is in South Africa; its operation has been described by Waitzman [43]. TVA built and operated a demonstration-scale plant (135 tpd of ammonia) in 1982. It used a Texaco gasifier and operated with a variety of U.S. coals [44].

Coal gasification processes for ammonia production can be classified according to the method of gasification as fixed-bed (Lurgi), fluidized bed (Winkler), or entrained bed (Koppers-Totzek and Texaco). The so-called fixed bed gasification is more accurately called a moving bed. Lump coal (5-30 mm) is charged at the top and descends countercurrently to the gas stream. As it descends, it is first dried and preheated, then carbonized, and finally gasified by the oxygen and steam entering the bottom. The coal ash is discharged from the bottom through a grate, or in one modification, as a slag. Because the countercurrent method of operation results in good heat exchange and very high thermal efficiency, this method requires less heat and, hence, less oxygen than the other methods [45]. Also, the expense of drying and fine grinding of the coal is avoided.

The Lurgi moving bed gasifier usually is operated at 3 MPa (Figure 6.20). It requires the least amount of oxygen –

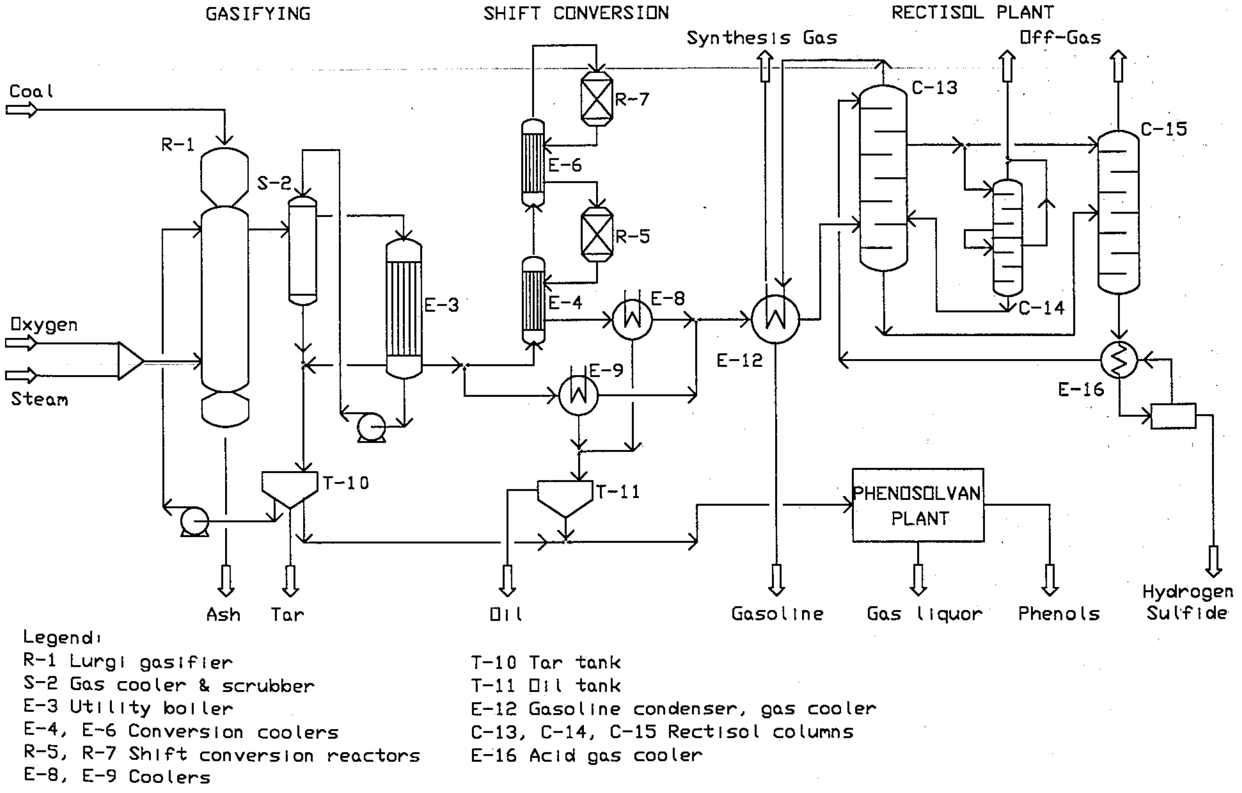


Figure 6.20. Lurgi Coal Gasification Process.

one-third to one-half as much as entrained coal gasifiers. It is not necessary that the oxygen be of high purity; 90% is satisfactory. The gas leaves the top of the gasifier at about 450°C and is cooled and washed to remove tar, liquid hydrocarbons, dust, etc. The washed gas contains CO, H_2, CO_2, CH_4, and other hydrocarbons. It is treated by a series of steps including steam reforming, CO shift conversion, CO_2 and H_2S removal, liquid nitrogen wash, steam reforming of the methane that is separated by the nitrogen wash, nitrogen addition, and compression to produce ammonia synthesis gas [46].

Some limitations of the fixed or moving bed gasification process are that the coal must be in the form of lumps (5-30 mm), the coal must be of the noncaking variety or pretreated to prevent caking, and various byproducts are formed (tar, phenolic compounds, light oils, etc.) that must be collected and used or disposed of. In preparing the sized coal feed, fines are formed that can be burned in an auxiliary plant to generate the steam and electricity requirements of the process. Tar can also be burned or injected into the gasifier at a point where the temperature is high enough to gasify it. Sasol, South Africa, has 13 Lurgi gasifiers of an older type and 3 Lurgi gasifiers of a new type that were installed in 1978 [45].

In the fluidized bed gasification process, of which the Winkler process is the main example (Figure 6.21), coal or lignite is ground to less than 15-mm particle size and introduced into the fluidized bed through feed screws near the bottom. Steam and oxygen are injected near the bottom of the fluidized bed. In contrast to the gradual increase in temperature of the coal in the moving bed process, the fluidized bed is essentially isothermal (1000°C). Consequently, there is neither tar nor other liquid byproducts, and the gas contains mainly H_2 and CO with less than 1% CH_4. A substantial amount of ash is entrained in the gas stream. The hot gas is cooled by waste-heat boilers and scrubbed to remove ash and then purified in a sequence of steps similar to other processes. The process produces a char containing 6%-12% of the carbon in the feed. About 90% of this char is removed from the bottom of the gasifier in a dry state; the remainder is recovered by wet scrubbing of the gas. This char can be burned in an auxiliary boiler to supply steam and electricity.

The Winkler gasifier is widely used to make producer gas for industrial and domestic use, but few have been

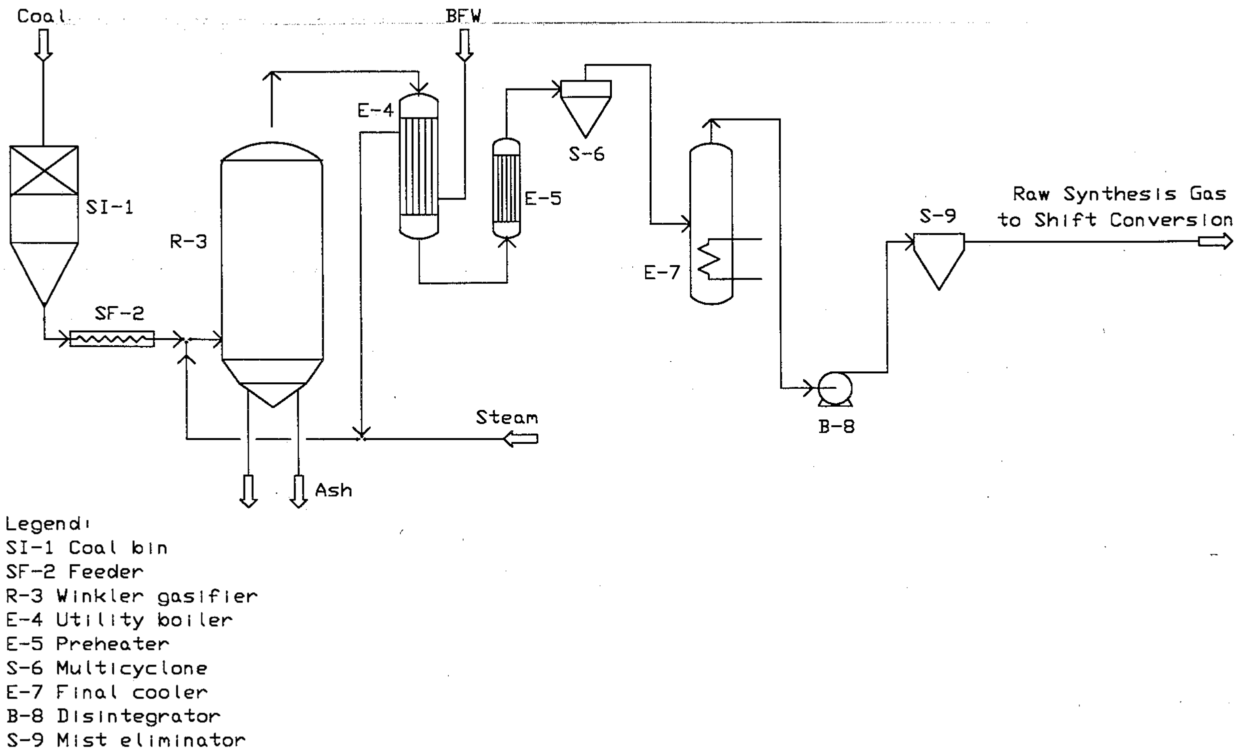


Figure 6.21. The Winkler Coal Gasification Process.

used for ammonia production. A 300-tpd ammonia plant at Neyveli, India, is based on a low-pressure (114 kPa) gasifier. It was put into operation in 1964 [47]. Two smaller plants are in Turkey and Yugoslavia. The advantages of the Winkler gasifer are that it will work with almost any grade of coal or lignite and that it is adaptable to high-capacity units. Disadvantages for ammonia production are low pressure (1-3 atm), which increases compression costs, and the ash content of the gas, which requires an electrostatic precipitator for final cleanup.

Entrained coal gasifiers are typified by the Koppers-Totzek (KT) and Texaco processes. Most of the present coal-based ammonia plants (except in China) use the KT process. The process is essentially a partial oxidation process as are most coal gasification processes. At least two KT ammonia plants have been built to use either coal or heavy oil although only one (in Finland) is known to have used both feedstocks [48]. However, any entrained gasification units presumably could be readily adapted to heavy oil or lighter hydrocarbons including natural gas.

In the KT process coal is dried and finely ground to about 75% through 200-mesh (Tyler). The powdered coal is picked up by streams of oxygen and blown into the gasification chamber through two burners facing each other. More recently, four-burner units have been used. Steam enters through annular openings around the burners. The gasification is complete in about one-tenth of a second at temperatures in the range of 1000°-1200°C. Part of the ash is fused and removed from the bottom of the gasifier, and part is entrained in the gas. The gas typically contains 56% CO, 31% H_2, 11% CO_2, and less than 0.1% CH_4. After being cooled in waste-heat boilers, the ash is removed by wet scrubbing and electrostatic precipitation. The remainder of the ammonia synthesis gas preparation is similar to that described under partial oxidation of fuel oil.

Disadvantages of the process are the need for fine grinding of coal, operation at low pressures (1-3 atm), and higher oxygen consumption than other coal gasification processes.

The Texaco process differs from the KT process in that the finely ground coal is mixed with water to form a thick slurry containing about 35%-40% water. The slurry is preheated and fed, together with oxygen, into a gasifier that can operate at pressures as high as 80 atm (Figure 6.22). The process as applied to ammonia production has been described by Netzer and Moe [49]. In this case the gasifier is operated at 58 atm and about 1300°C. Fused ash is quenched with water in a chamber at the bottom of the gasifier and removed as a slurry. The hot gas is quenched to 1000°C by water, passes through a waste-heat boiler, and is cleaned to remove soot and fly ash in a venturi scrubber. In another configuration of the Texaco process, the gas is further quenched to 215°C before exiting the gasifier; this provides the higher steam:gas ratio that is needed for shift conversion. A utility boiler is not used, and the gas goes directly from the gasifier to a venturi scrubber.

The sequence of the remaining steps of synthesis gas preparation is CO shift conversion, removal of H_2S and CO_2 by Rectisol wash (cold methanol), and liquid nitrogen wash. As in other partial oxidation processes, the H_2S is converted to elemental sulfur. Ube Industries, Japan, commissioned a 1,500-tpd ammonia plant in 1984 using the Texaco coal gasification process. An energy consumption of 10.9 Gcal/tonne of ammonia is stated; this is lower than the normal quoted figure of 11.6 Gcal/tonne of NH_3 for coal-based processes [31]. Another 1,000 tpd coal-based ammonia plant is scheduled for startup at Wehei, China, in 1996.

6.7 Ammonia From Electrolytic Hydrogen

Several ammonia plants have been built to produce ammonia from hydrogen that results from the electrolysis of water. These plants have been located where low-cost hydroelectric power is available in Norway, India (Nangal), Egypt (Aswan), Zimbabwe (Kwa-Kwe), Peru (Cuzco), Iceland, and Canada (Trail, British Columbia). The India (Nangal) plant has already been converted to hydrocarbon feedstock due to the shortage of power in the region. The technology of the electrolytic process has been described by Mrochek and Grundt [50,51]. Purified water is the feedstock; potassium hydroxide is added to increase the conductivity, but it does not participate in the reaction. Commercial cells vary somewhat in efficiency, but a typical power consumption is 4.3 kWh/m^3 of H_2, which corresponds to about 8,600 kWh/tonne of ammonia [51]. Additional energy is required for an air separation plant to produce the nitrogen required for ammonia production. Energy also is required for compression of the hydrogen and nitrogen and recirculation of the gas mixture through the synthesis loop. The total energy requirement is about 10,200 kWh/tonne of ammonia. This energy is equivalent to about 8.8 million kcal/tonne of ammonia, which is higher than that for natural gas-based ammonia plants. Also, if fuel were used to generate electricity, nearly three times as much thermal energy would be required since the efficiency of conversion of thermal energy to electrical energy is seldom more than 38%.

The process generates one volume of oxygen per two volumes of hydrogen or about 0.7 tonne of O_2/tonne of NH_3; thus, a credit for byproduct oxygen can be taken if there is a use for it. For example, the oxygen can be used in an iron and steel industry. A small additional amount of oxygen would be available from the air separation unit. Another potential byproduct is heavy water

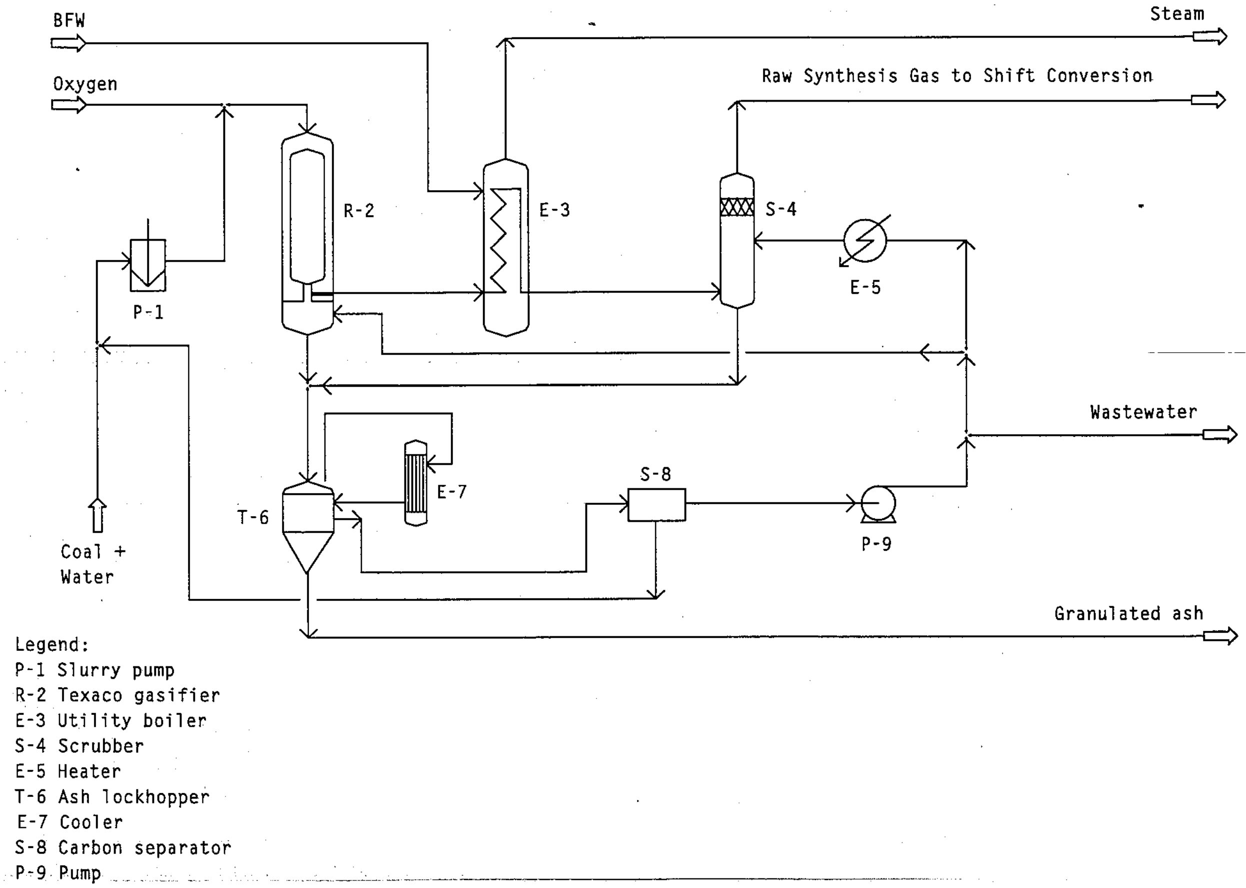


Figure 6.22. Texaco Coal Gasification Process.

(deuterium oxide, D_2O). Pure water contains about 0.0135% D_2O. The hydrogen is electrolyzed more rapidly than its isotope, deuterium; thus, the concentration of D_2O in the electrolyte builds up and can be recovered at a rate of 70 g/tonne of NH_3 [51]. Heavy water is used in some types of nuclear reactors.

Since the electrolytic process does not produce CO_2, ammonia cannot be used to make urea unless CO_2 is available from another source. It can be used to make ammonium salts (sulfates, phosphates, or nitrates), or ammonia can be applied to the soil directly either in the anhydrous form or in aqueous solution.

The cost of ammonia production by the electrolytic process is not greatly dependent on plant size, but, of course, it is strongly dependent on the cost of electricity. Thus, if low-cost electricity is available, the electrolytic plant would be competitive with plants using other processes, particularly for small plants.

A particular advantage in developing countries would be the fact that ammonia production from electrolytic hydrogen is a much simpler process than those using other feedstocks.

Hydrogen is also a byproduct of electrolytic production of chlorine from caustic soda, and several small ammonia plants have used this hydrogen to make ammonia either as the only feedstock or as a supplementary source. The amount of hydrogen available from chlorine-caustic plants is too small to supply a significant portion of the ammonia needs in most situations.

6.8 Economics of Ammonia Production

6.8.1 Investment Costs

Since ammonia production is highly capital intensive, it is especially important that the estimated or assumed capital costs be as accurate and realistic as possible. When the process, feedstock, and location have been selected, an accurate estimate of the capital requirements can be made. The World Bank has considered the following four different scenarios for investment costs.

1. **Existing Site – Developed Location**

   A plant on an existing site in a developed location, where all infrastructure exists. When an additional plant is built on an existing site, a significant saving may be realized not only in infrastructure but also in offsites. It is assumed that the cost of a plant on an existing site would be about 20% lower than a plant on a new site in a developed location.

2. **New Site – Developed Location**

   It is assumed that supporting facilities such as roads, a port, railroad, etc., and social structure exist. People will be available to work in the plant. Equipment can often be provided from local sources and maintained using local facilities.

3. **New Site – Developing Location**

   Some infrastructure is established but not as much as for the scenario described in item number 2. It is necessary to expand port or rail facilities to meet the needs of the project. Local specialized engineering facilities will not be available.

4. **Developing Site – Remote Location**

   There is no supporting infrastructure available. All roads, ports, railroads, etc., and social amenities must be provided as part of the project cost. All equipment has to be imported. Most of the labor to build and operate the plant will have to be brought in from outside. There is no supporting technical infrastructure available before the project. Costs for establishing the required infrastructure will be very high.

Investment costs vary greatly depending on the basis for estimation, often on the bidding location, and on the relative strengths of international currencies. It will also depend on the market situation for the construction of chemical plants [5].

In the past 25 years, process designs have been developed and gradually improved for ammonia production by steam reforming of natural gas, naphtha, and other light hydrocarbons in plants using centrifugal compressors. Standard designs have evolved for four capacities: 900 tpd, 1,040 tpd, 1,360 tpd, and 1,500 tpd. The great majority of new plants built in the past decade have been designed for one of these capacities even though the capability exists for design of larger plants.

The majority of new plants built or ordered in the past decade have been in the 1,000- to 1,500-tpd capacity range. The larger size is sometimes used in locations where site development costs are high; the total project cost may be lower per annual tonne of capacity. However, in some cases where site development costs are high, it may be preferable to locate two or more plants at the same site as has been done in Indonesia and South Korea, for example.

The investment cost data of the World Bank summarized in Table 6.17 represent typical figures based on the investment costs of numerous ammonia projects surveyed.

Relatively fewer plants have been built to produce ammonia by partial oxidation of heavy oil or coal. Most of the plants built in China have capacities of 1,000 tpd, and those in India, 1,000-1,350 tpd. For feedstocks other than natural gas, the capital costs will be estimated by applying the factors listed in Table 6.18.

These factors are a compromise between estimated costs from several sources and are similar to relative costs given by Nichols and Blouin [52]. The factor for naphtha-based plants presumably can be applied with some degree of confidence to standardized plant sizes that are lower and higher than the base case. For other feedstocks there is insufficient data to indicate how the plant cost would vary with capacity. Comparisons of the estimated production costs as affected by factors other than the scale of operation will be based on 1,500-tpd capacity.

6.8.2 Elements of Production Costs

The cost estimates and economic evaluation of ammonia installations are given in Chapter 21. Table 6.19 gives the basic elements of the costs of production of ammonia using four different raw materials.

Table 6.17. Investment Costs for a 1,500-tpd Ammonia Plant [5] (US $ millions)

	Existing Site Developed Location	New Site Developed Location	New Site Developing Location	New Site Remote Location
Ammonia Project @ 1,500 tpd NH_3				
Battery limits including offsites	170	210	230	250
Infrastructure			50	100
Total Project Cost	**170**	**210**	**280**	**350**

Table 6.18. Capital Costs Using Different Feedstocks

Feedstock	Plant Cost Factor	Assumed for Base Case ($ Million[a])
Natural gas	1.00	170.0
Naphtha	1.15	195.5
Heavy oil	1.60	272.0
Coal	2.00	340.0

a. Total plant cost, battery limits x 1.5.

6.8.3 Small-Scale Ammonia Plants

In practice, installations from 100 to 600 tpy of ammonia capacity are considered small-scale plants. All downstream processing operations (urea, nitric acid, etc.) in this size range are also considered to be small-scale plants.

As a result, all fertilizer plants established before 1960 are considered small-scale plants because only after this date were high-pressure turbocompressors introduced to enable the building of high-capacity ammonia units.

UNIDO has organized a program to investigate the possibility of providing small-capacity ammonia plants and has discussed the problem at numerous seminars [33]. Such a concept is needed because in many countries consumption of fertilizers collectively is much smaller than the capacity of a large-scale plant producing 300,000 tpy of nitrogen. This may supply at a medium application rate (40 kg/ha of N) 7.5 million ha of land, and many countries do not have this much agricultural land. Construction of regional plants of normal large capacity is not possible in most cases because of logistic, economic, and political constraints, which include the following:

- For many landlocked countries, which are located at a long distance from seaports, the cost of freight doubles or even triples the price of fertilizers for farmers and, thus, limits consumption.
- In some cases, small natural gas fields or a small source of hydrogen are sufficient to supply a small-scale plant with raw material for many years.

Development of this small-scale alternative requires the establishment of the following infractructure:

- Small-scale ammonia and urea plants at the sources of raw materials.
- If ammonium phosphates are desired, supplies of imported phosphoric acid or of phosphoric acid produced in local plants at the phosphate rock source.
- Affiliated complex fertilizer granulation/compounding plants.

Table 6.19. Cost Components of Ammonia Production (1,500 tpd)

Process	Raw Material	Capital Cost (US $ million)
Steam reforming	Natural gas	170
Steam reforming	Naphtha	195
Partial oxidation	Heavy oil	270
Coal gasification	Coal	320

			Raw Material		
Cost Elements	Unit/t	Natural Gas	Naphtha	Heavy Oil	Coal
Raw materials	Gcal	7.0	0.72[a]	0.76[a]	1.4[a]
Utilities					
Electrical energy	kWh	-	-	530	624
Process water	m^3	1.1	1.1	0.6	0.6
Cooling water	m^3	210	280	216	216
Labor	workhours	0.3	0.3	0.4	0.7

a. Tonne.

With small plants, logistic problems are of limited importance. Local plants play the role of an extension service for farmers and are flexible enough to adapt the production program to the local crop pattern.

Basic parameters that will influence the technical and economic outcome are as follows:

- Local natural gas and phosphate rock cost/price.
- Logistics of fertilizer distribution to the farmer from the small-scale plant (own distribution network, use/extension of existing network, etc.), compared with logistics costs for imported fertilizers.
- Availability of investment capital and equity structure of the project (shareholders: public/private, distributors, etc.).
- Marketing network and sales conditions.

The main technical differences between small- and large-scale ammonia units are summarized in Table 6.20.

In the developing countries small-scale production of fertilizers has been practiced for many years. The number of ammonia plants of 100- to 500-tpd capacity by regions was as follows (1977):

Latin America	9
China	21
Indian Subcontinent	18
South East Asia	8
Middle East	8
Africa	5

The following countries have acquired valuable experience in the construction and operation of small-scale fertilizer plants:

China, India, Pakistan, Indonesia, Turkey, Peru, Mexico, Egypt, Syria and Zambia.

Basic economic and technical data collected during the UNIDO workshop on "Minifertilizer Plant Establishment" held in Lahore, Pakistan, in 1983 showed alternative ways to develop the fertilizer industry and allowed preliminary technical assessment of such a concept. The comparison of several cost components is shown in Table 6.21.

Finally, progress in the heat-exchanger reforming (LCA) process and new developments in electrically driven compressors may make small-scale (300 tpd-400 tpd) installations economically feasible.

In addition, the skid-mounted "serial" installations concept (sometimes called modular) was practically applied. The installations are constructed on a platform or barge at the builder's site and transported in nearly completed form to the operating site. This avoids the problem of a small-scale plant being constructed in a remote place without the necessary industrial infrastructure. Standardized plants using skid-mounting will have a positive impact on:

– shorter construction time.

– lower engineering costs.

– ease of training.

– quicker startups.

– more precise prediction of construction costs.

6.9 Future Development of Ammonia Technology

Even though ammonia technology is a mature technology, there is room for improvements in efficiency and reliability. Recent years have shown that new concepts in mature processes may substantially improve the overall production economics. The projection of future technical changes is obviously not possible. However, present research and development stage process improvements allow a listing of potentially available improvements for existing and new ammonia installations such as the following:

- Pre-reforming and adiabatic reforming process optimization, especially if results obtained by different licensers could be combined and optimized; this would open the possibility to further energy savings.

Table 6.20. Process Features of Large and Small Ammonia Plants

Process Unit	Large Scale	Small Scale
a. Reforming and gas processing	Synthesis gas and high-pressure steam, closed loop	Synthesis gas production and steam as byproduct
b. Gas compression	Turbocompressors	Electrically driven compressors
c. Purge gas process	Usually included	Purge gas used as fuel

Table 6.21. Comparison of the Cost Elements of Different Scale Ammonia Installations

Parameters	Unit/t	Capacity (Consumption Per Tonne of Ammonia)			
		150[a]	300[b]	500[c]	1,000
		(tpd)			
Raw Materials					
Natural gas	Gcal	9.47	8.5	7.8	7.0
Utilities					
Electricity	kWh	540	320	(own production)	
Cooling water	m^3	280	230	230	210
Process water	m^3	1.7	1.6	2.3	2.3
Labor (including maintenance)	workhours	1.95	1.0	0.6	0.3
Depreciation	US $	76	58	44	34

a. Ammonia Casale, Switzerland.
b. Snamprogetti, Italy.
c. KTI, Netherlands.

- New developments in electrically driven compressors (e.g., three-dimensional impellers) would permit more flexibility in steam production. This may influence the minimum economic capacity of ammonia production in small-scale plants.
- Better design of furnace elements, such as burner nozzles, new materials for insulation, and better design of heat exchangers, may increase the saving of energy and improve the operability of the installations.
- Improvement of the steam-generation efficiency. The overall energy consumption can be improved by producing high-pressure steam (over 11 MPa) instead of medium-pressure steam (5 MPa).
- Integration of gas turbine drives with steam turbines and with the heat-recovery system of the ammonia plant.
- More efficient process condensate stripping to produce medium-pressure steam.
- Further development and optimization of the ruthenium catalyst and its alternatives, aiming at high conversion and lower pressure to minimize the investment cost of ammonia reactors.

As a result, the amount of available waste heat will be reduced. This will reduce the amount of export steam. The heat lost in the primary reformer will be minimized by improved reformer designs or by eliminating the direct fired primary reformer. The reforming pressures may rise and the ammonia synthesis pressure may decrease, thus the synthesis gas compressor may potentially be eliminated. Emphasis on capital cost reduction will continue. Safety awareness will continue to rise.

Stringent environmental regulations will be implemented to reduce emissions. Future environmental regulations will require reduced CO_2 and NO_x emissions. Nitrogen oxides are combustion products of the direct-fired reformer furnace. Improved burner designs will decrease the amount of nitrogen oxides produced. There will also be tighter regulations concerning disposal of the process condensate.

In the area of automation, dynamic control systems should become easier to justify economically. These controls will assist the operators in running the plant as close to optimum as possible and will also enhance the plant safety system. The level of automation will increase to improve the efficiency and reliability of the plant.

More integrated ammonia and methanol plants may be built and, thus, provide flexibility to change products depending on market demand.

6.10 References

1. Appl, Max. 1976. "A Brief History of Ammonia Production from the Early Days to the Present," *Nitrogen*, 100:47-58.
2. LeBlanc, J. R. 1992. "Assessment of Fertilizer Technology," Asian Natural Gas IV, Kuala Lumpur, Malaysia.

3. Bumb, Balu L. 1989. *Global Fertilizer Perspective, 1960-95*, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
4. Kirk-Othmer. 1992. *Encyclopedia of Chemical Technology*, 4th ed., Vol. 2, pp. 638-691.
5. Constant, Kurt Michael, and William F. Sheldrick. 1992. *World Nitrogen Survey*, pp. 68-69, 80-88, The World Bank, Washington, D.C., U.S.A.
6. Czuppon, T. A., and J. M. Lee. 1987. "Hydrogen-Rich Offgases Can Reduce Ammonia Production Costs," *Oil and Gas Journal*, 87(36):42-46.
7. Buividas, L. J., J. A. Finneran, and O. J. Quartulli. 1974. "Alternate Ammonia Feedstocks," *Chemical Engineering Progress*, 70(10):21-35.
8. Brown, F. C., and A. A. Deane. 1977. "Ammonia Plants - Efficiency, Reliability or Both," FAI/IFDC 1977 Seminar, New Delhi, India.
9. "New Developments of the Topsoe Ammonia Process." 1994. Haldor Topsoe A/S, Private Communication.
10. Benner, G. S., and co-workers. 1986. U.S. Pat. 4,568,530, M. W. Kellogg Corporation, Houston, TX, U.S.A.
11. Imperial Chemical Industries, Ltd. 1989. *Catalyst Handbook*, M. V. Twigg (Ed.), Wolfe Publishing, Frome, England.
12. Pons, F., and A. Spolidor. 1990. "Latest Developments of High-Grade Alloys," AIChE Ammonia Safety Symposium, San Diego, CA, U.S.A.
13. Mohri, T., T. Shibasaki, and K. Takamura. 1992. "Application of Advanced Material for Catalyst Tubes for Steam Reformers," AIChE Safety in Ammonia Plants Symposium, San Antonio, TX, U.S.A.
14. Appl, Max. 1992. "Modern Ammonia Technology, Where Have We Got to, Where Are We Going?" *Nitrogen*, 199:46-75.
15. "Ammonia." 1985. *Ullmann Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A2.
16. Quartulli, O. J. "Developments in Ammonia Production Technology," Undated publication of the M. W. Kellogg Co., Houston, TX, U.S.A.
17. Kazarnovskii, Ya. S. 1945. *Zh. Fiz. Khim.*, 19:392.
18. Haber, F., S. Tamaru, and C. Ponnaz. 1915. *Z. Elektrochem.*, 21:89.
19. Larson, A. T. 1924. *J. Am. Chem. Soc.*, 46:367-372.
20. Dodge, R. L., and A. T. Larson. 1923. *J. Am. Chem. Soc.*, 45:2918-2930.
21. Beattie, J. A., and L. J. Gillespie. 1930. *Phys. Rev.*, 36:743-753..
22. Nielsen, A. 1968. "An Investigation on Promoted Iron Catalyst for the Synthesis of Ammonia;" *Jul. Gjellerups Forlag.*, 3rd ed., 16-17, 56-57, 64.
23. Krishnamurthy, Krish R. 1993. "Evaluation of Competing Technologies for Hydrogen and Argon Recovery from Ammonia Plant Purge Gas," IN *Cryogenic Processes and Machinery*, Leonard A. Wenzel (Ed.), AIChE Symposium Series, Vol. 89, No. 294, pp. 109-114.
24. Ashton, G. J., and W. H. Isalski. 1985. "Rare Gases and the Ammonia Producers," Fourth Fertiliser Nitrogen Proc., British Sulphur Corp., International Conference of Fertiliser Tech., p. 126.
25. Aziz, Zahid. 1994. Fertilizer Technology Series N1 Ammonia Synthesis, UNIDO Communication, p. 2.
26. Miyasugi, T., et al. 1984. "A Heat Exchanger Type Steam Reformer for Ammonia Production," *Chemical Engineering Progress*, 80:64.
27. Miyasugi, T., et al. 1984. "Energy-Saving Ammonia Process with Heat Exchanger Reformer," Ammonia Safety Symposium.
28. Marsh, H. D., et al. 1992. "CAR-Demonstration Unit on Stream," Ammonia Safety Symposium.
29. *KRES-Kellogg Reforming Exchanger System.* Undated brochure, M. W. Kellogg Co., Houston, TX, U.S.A.
30. Halstead, J. M., A. M. Haslett, and A. Pinto. 1988. "Design and Experience of ICI LCA Ammonia Process," FAI Seminar, New Delhi, India.
31. Appl, Max. 1993. "Modern Ammonia Technology: Where Have We Got to, Where are We Going?" *Nitrogen*, 202:44-53.
32. Stead, Phillips. 1993. "The Linde Ammonia Concept (LAC)," *Fertiliser News*, 38(12):15-20.
33. "Minifertilizer Plant Concept." 1983. Proceedings of the Lahore UNIDO Seminar, Lahore, Pakistan.
34. Czuppon, T. A., et. al. 1993."The Kellogg Advanced Ammonia Process First Commerical Application at Ocelot Ammonia Company," Ammonia Safety Symposium.
35. "Energy Consumption in Ammonia Production-Influence of External Conditions and Key Parameter," Undated Haldor Topsoe brochure.

36. Linde AG - Process Engineering and Contracting Division brochure. 1992.

37. Quintana, Manuel E., and G. F. Skinner. 1990. "Development in Partial Oxidation - Ammonia from Low-Grade Oil Residue," FAI Seminar, New Delhi, India.

38. Hollriegelskrueth, H. J. 1985. "Synthesis Gas from Refinery Residues," *Linde Reports on Science and Technology*, No. 40.

39. Wang, K. P. 1975. *The People's Republic of China*, U.S. Bureau of Mines, Washington, D.C., U.S.A.

40. "American Rural Small-Scale Industry Delegation." 1977. *Rural Small-Scale Industry in the People's Republic of China*, Chapter VI, University of California Press, Berkeley and Los Angeles, CA, U.S.A.

41. Appl, Max. 1992. "Modern Ammonia Technology, Where Have We Got to, Where are We Going?" *Nitrogen*, 200:27-38.

42. Staege, H. 1977. "Gasification of Coal by the Koppers-Totzek Process for the Production of Ammonia," *Chemical Age of India*, 28(11A):903-910.

43. Waitzman, D. A. 1977. "Recent Technological Developments in Nitrogenous Fertiliser Production-Ammonia From Coal Projects," FAI/IFDC Fertilizer Seminar, New Delhi, India.

44. Waitzman, D. A. 1985. "TVA Ammonia from Coal Projects," Ammonia Production via Coal Gasification, Muscle Shoals, AL, U.S.A.

45. Becker, P. D. 1979. "Lurgi Pressure Gasification and its Application for Ammonia Manufacture," TVA Symposium Ammonia from Coal, Muscle Shoals, AL, U.S.A.

46. Sharma, N. C. 1977. "The Modern Route for Ammonia Plants Based on Coal," *Chemical Age of India*, 28(11A):918-923.

47. Bailey, E. E., and T. K. Subramanium. 1979. "Winkler Coal Gasification Process and its Application in Ammonia Synthesis Plants," TVA Symposium Ammonia from Coal, Muscle Shoals, AL, U.S.A.

48. Beck, Bruno. 1979. "The Koppers-Totzek Coal Gasification Process and its Role in Today's Coal-Based Nitrogenous Fertilizer Production," TVA Symposium Ammonia from Coal, Muscle Shoals, AL, U.S.A.

49. Netzer, D., and J. Moe. 1977. "Ammonia from Coal," *Chemical Engineering*, 84(23):129-132.

50. James, G. R., and A. V. Slack (Eds.). 1973. *Ammonia*, Part I, pp. 369-401, Marcel Dekker, New York, NY, U.S.A.

51. Grundt, T. 1977. "Water Electrolysis and Its Possibilities as Basis for Fertilizer Production," Seminar on Development of Small Scale Hydroelectric Power and Fertilizer, Pokhara, Nepal.

52. Blouin, G. M., and D. E. Nichols. 1977. "Economic Considerations of Chemical Nitrogen Fixation," American Chemical Society Meeting, Chicago, IL, U.S.A.

53. Nobles, J. E., L. N. Shay, and J. C. Stover. 1988. "BASF's Activated MDEA Process for CO_2 Removal in Ammonia Plants," *Nitrogen*, 88:243-252.

54. Hefner, W., Y. Ide, and D. W. Stanbridge. 1984. "Recent Developments in the BASF Activated MDEA Process," American Institute of Chemical Engineers National Meeting.

55. Grover, B. S. 1987. "Process for the Removal of Acid Gases from Mixtures," (to Union Carbide), U.S. Patent 4,702,898.

56. Bartoo, R. K., T. M. Gemborys, and C. W. Wolf. 1991. "Recent Improvements to the Benfield Process Extend its Use," *Nitrogen* '91, pp. 127-139, British Sulphur Corporation Ltd., London, England.

57. Song, Cook C., et al. 1992. "Conversion of CO_2 Removal Process for Flexsorb HP Solvent," Ammonia Safety Symposium.

58. Tomasi, L. 1992. "Energy-Efficient CO_2 Removal Process, GV Low-Energy Process," *Fertiliser News*.

59. Lewis, J. L., M. B. Pascoo, and H. D. Truby. 1979. "Fluor Solvent," *Hydrocarbon Processing*, 58(4):112.

60. Huurdeman, T. L., and Vinod A. Shah. 1989. "Synthesis Gas Treating with Physical Solvent Process using Selexol Process Technology," Ammonia Plant Safety AIChE Symposium.

Chapter 7. Transportation and Storage of Ammonia

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Chapter 7. Transportation and Storage of Ammonia

7.1 Introduction

Much of the world's ammonia production is shipped from the plants where it is produced to other locations for further processing into finished fertilizers, for direct use as fertilizer, or for use as a raw material for nonfertilizer products. The total world ammonia trade in 1991 was about 11.5 million tonnes of nitrogen, which was approximately 12.4% of the total world ammonia production. Of this total, about 9.4 million tonnes was transported by sea [1]. About 1.2 million tonnes of nitrogen was exported from Canada to the United States [1]. Over 5.4 million tonnes of ammonia is transported within the United States annually. Ammonia is transported by ships, barges, rail, trucks, and pipeline.

The ships carrying anhydrous ammonia also carry other liquefied gases, especially liquefied petroleum gases (LPG). In general, equipment that is suitable for transporting LPG is also suitable for transporting anhydrous ammonia. Such facilities (trucks, rail tankers, barges, and ships) often are used interchangeably for transport of the two materials. The ammonia shipping and LPG shipping compete for the available shipping capacity.

Ammonia is almost invariably transported in the liquid state; therefore, it must either be compressed or refrigerated or some combination of the two. Ammonia storage tanks may be classified as fully refrigerated, semi-refrigerated, or pressurized, and a similar classification can be applied to transport equipment. Fully refrigerated storage tanks are equipped to maintain a temperature of about -33°C, at which the vapor pressure of ammonia is atmospheric (see Chapter 6). In semi-refrigerated storage tanks, the ammonia is kept at a moderately low temperature, such as 0° to 5°C, at which the gauge pressure is only 400-500 kPa. This permits the use of tanks made of much lighter steel than would be required if the temperature were uncontrolled. Unrefrigerated pressure storage tanks usually are designed for pressures up to about 1.8 MPa, which should be adequate for any ambient temperature normally encountered in most climates.

The metallurgy of the steel used for storage tanks, transport vessels, and pipelines is important but rather too complex for detailed explanation here. However, two points should be noted. Each type of steel has a transition temperature below which it is subject to brittle fracture. The brittle fracture is initiated at a notch or crack, usually near a weld where a stress occurs. Once initiated, a fracture may spread rapidly. Therefore, it is important that a vessel or pipeline not be operated at a temperature below its transition temperature unless it has been thermally stress relieved. Stress relieving is expensive and sometimes impractical. For this reason, pressure vessels and pipelines should not receive refrigerated ammonia; the ammonia should be warmed to a temperature above the transition temperature of the steel used in the vessel.

Another problem is stress corrosion cracking (SCC) of pressure vessels, which may occur over a wide range of temperatures and pressures. SCC in ammonia storage tanks has been reported in various papers over the years. This subject has been frequently discussed in Ammonia Safety Symposiums. The Ammonia Safety Committee of the A.I.Ch.E. conducted a survey of ammonia storage tanks in 1988. With only one exception, previous reports had indicated that SCC was not unusual in pressure storage bullets and semi-refrigerated storage tank spheres, but there were no reports of SCC in the fully refrigerated tanks at temperatures of -33°C or below [2]. The 1988 survey, however, found that, of 37 refrigerated storage tanks inspected, 4 showed surface cracks but 3 were shallow enough to be ground out [2].

Cracks are mainly formed in welds and the heat-affected zones (HAZ) around the welds. In a series of experimental investigations, it has been shown that the susceptibility for SCC can be reduced by complete post-weld heat treatment, by excluding oxygen, and by adding at least 0.2 wt % water. Most of the experiments were done with pressurized ammonia at ambient temperature [3]. Complete exclusion of oxygen when handling ammonia is difficult. Although adding water to ammonia is possible, it is known to cause SCC in the vapor phase of the tank in the presence of oxygen because, in the vapor phase, equilibrium concentration of oxygen is 650 times higher and water concentration 500 times lower than in the liquid phase [3]. Thus the vapor phase will be rich in oxygen with practically no water present. The stress relieving by post-weld heat treatment of the HAZ seems to be the only reliable method to avoid SCC in ammonia tanks. BASF found no sign of SCC in their new stress-relieved 200-m^3 sphere in Ludwigshaften, when it was inspected after 2 years of operation, whereas they found SCC in an older tank that was not stress relieved [3].

Storage and transport of ammonia at the retail level will be described in Chapter 6. The present chapter is concerned mainly with large-scale transport and storage.

7.2 Ammonia Storage

Even when all of the ammonia is used at the plant site where it is produced, it is common practice to have facilities for storage of 3 to 15 days' production so that interruptions in operation of downstream facilities will not require interruption of the ammonia plant operation. In an ammonia-urea complex, for example, when the urea plant must be shut down for repairs, the ammonia plant can continue to operate with the ammonia going to storage.

Following are two preferred methods for storing liquid ammonia. One is the pressure storage at ambient temperature in spherical or cylindrical vessels up to a capacity of about 1,500 tonnes. The other method is atmospheric pressure storage at -33°C in insulated cylindrical tanks up to about 50,000-tonne capacity. Additionally, reduced pressure storage at about 0°C in an insulated, usually spherical vessel for a capacity up to about 2,500 tonnes per vessel is also used [4]. The suitability of storage depends on the required temperature and flow quantity of ammonia into and out of the storage.

The pressurized tanks are suitable for storing small quantities of ammonia from pipeline systems, tank cars, and barges carrying pressurized ammonia. Usually, cylindrical vessels are designed for 2-5 MPa. The larger spherical vessels are designed only for 1.6 MPa to avoid wall thickness above 30 mm [4]. The cylindrical vessels are used for a capacity up to 150 tonnes and the spherical vessels for a capacity up to 1,500 tonnes. A pressure control is required for the bleeding of inert gases flashed off the liquid ammonia.

The low-temperature storage tanks are best suited for the storage of ammonia from the synthesis loop at a low temperature and for the shipping terminals handling a large capacity. The tanks operate at atmospheric pressure, and they are well insulated to minimize the heat leak into the storage tank. The boil-off vapor from the tank is re-liquified by compression and water cooling. The inerts in the boil-off vapors are purged from the compressor loop. Refrigerated ammonia storage tanks are of two types. One type is of double-wall construction; the annular space between the walls is filled with loose perlite insulation and kept slightly above atmospheric pressure with dry air, nitrogen, or inert gas (Figure 7.1). The other type of tank is of single-wall construction, insulated on the outside with foam glass, styrofoam, polyisocyanate foam, or polyurethane foam. Although the investment cost is greater for the double-wall tank than for single-wall construction, maintenance costs usually are lower. The double-wall tank provides a secondary containment feature for added safety. Semi-refrigerated storage tanks are also well insulated; the

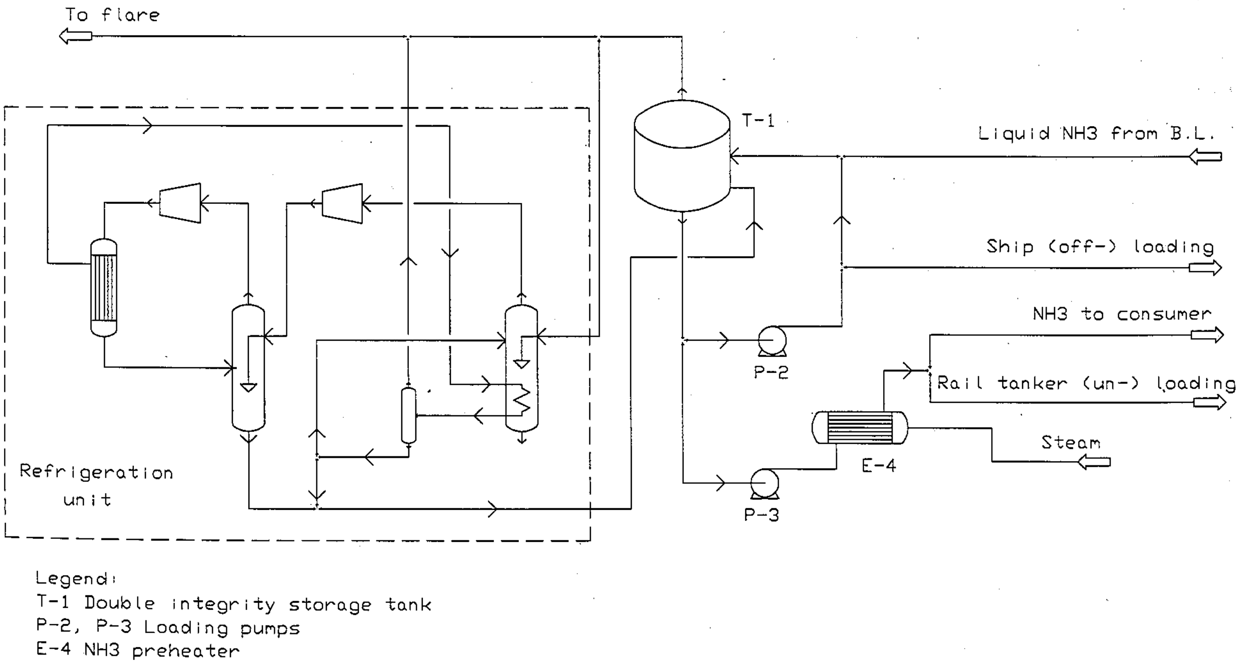

Figure 7.1. Ammonia Storage Installation.

ammonia is held at the desired temperature, usually 0°-5°C, by allowing it to evaporate at a controlled pressure. The vapor is compressed and liquefied by water cooling, and the liquid is returned to the tank. Thus, the system is similar in principle to fully refrigerated storage, but the refrigeration system is much less sophisticated and relatively inexpensive.

A comparison of various types of ammonia storage tanks is provided in Table 7.1. Based on the 1988 survey, a summary of refrigerated ammonia storage in the United States and Canada is given in Table 7.2. Terminals for shipping or receiving liquid ammonia are similar in principle to the in-plant storage facility although there may be important differences. Obviously, a terminal to receive or discharge shipments to ocean-going vessels or barges must be at a location that is accessible to such vessels. Harbors suitable for receiving large ships are not plentiful, and terminal sites adjacent to such harbors may be scarce and expensive. In some locations, considerable expense may be involved in harbor improvement, construction of a pier, and preparation of a terminal site. To minimize port time, ships must be loaded or unloaded rapidly with minimum vaporization of refrigerated ammonia. Thus, high-capacity pumps and large, well-insulated pipelines are needed. Assuming that the ammonia plant is not adjacent to the port, considerable expense may be involved in transport of ammonia to the port.

A summary of fill and load-out rates for refrigerated ammonia storage terminals is given in Table 7.3.

Estimated capital costs for refrigerated storage facilities are shown in Figure 7.2. The cost of in-plant storage includes only the storage tank, its foundation, and refrigeration equipment required for normal in-plant storage and use. Maritime terminals or land-based terminals for receiving and distributing ammonia are likely to cost roughly 50% more than in-plant storage, especially if they are remote from any manufacturing facility. The operating cost of a storage facility consists mainly of fixed charges. Assuming that a maritime terminal of 27,230-tonne (30,000-short ton) capacity costs $10 million, the annual operating cost can be estimated roughly as follows:

Annual Operating Cost, US $

Depreciation, 10% (10 years)	1,000,000
Maintenance, 33% of depreciation	330,000
Taxes and insurance, 20% of depreciation	200,000
Utility	100,000
Labor and overhead	100,000
Total annual cost	1,730,000
Cost/tonne of capacity	$63.53 ($57.67 per short ton)

If such a facility were to receive 100,000 tpy, the cost per tonne of throughput would be $17.30. Similar calculations indicate that, for terminals of 9,080-tonne (10,000-short ton) and 19,160-tonne (20,000-short ton) capacity, the annual operating cost per tonne of capacity would be about $110.16 and $80.96, respectively.

The size of a marine terminal depends mainly on the capacity of ships that are expected to serve it and should be 25%-50% larger than the ship's capacity to allow for

Table 7.1. A Comparison of Ammonia Storage Tanks

Type Storage	Refrigerated Storage Tanks	Spheres	Pressure Storage (Bullets)[b]
Storage Class	Fully refrigerated	Semi-refrigerated	Unrefrigerated
Temperature, °C	-33° to -38°C[a]	0° to 5°C	25° to 50°C
Pressure, kPa	103 to 115	400 to 500	1800 to 2600
Capacity range, tonnes	3,600 to 54,500	450 to 3,000	45 to 270
Typical tonnes of ammonia to 1 tonne of tank steel	41 to 45	10	2.75

a. Ammonia boiling temperature varies from -33°C sea level to -38°C at 1,100 m.
b. These pressure tanks are not included in the survey of Table 7.2.

Table 7.2. Overall Capacity for Ammonia Storage (U.S.A. and Canada)[a]

Number of tanks	335
Number of owners	75
Number of locations	219
Total storage capacity, tonnes	6,063,850 (6,679,720)
Average capacity, tonnes	18,156 (20,000)
Range in tank sizes	
Spheres (tonnes)	454 to 2,996 (500 to 3,300)
Tanks (tonnes)	3,630 to 45,390 (4,000 to 50,000)

a. Short tons in parentheses.

Source: [2].

delays in scheduling shipments and delays due to storms, strikes, etc.

The terminal cost for any given annual throughput decreases as the size of the terminal decreases. However, a smaller terminal capacity requires a larger number of shipments in smaller ships, which may increase freight costs. Therefore, determination of the minimum cost of importing ammonia involves a balance between freight costs and terminal costs.

7.3 Transportation of Ammonia

7.3.1 Ocean Transportation of Ammonia

For overseas or coastal shipment of ammonia, the ships that are commonly used are equipped with well-insulated tanks to contain liquid ammonia at slightly above

Table 7.3. Refrigerated Ammonia Storage Terminals: Fill and Load-Out Rates

Fill Rate in Tonnes Per Hour:

	1983 Survey			1988 Survey		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Storage at plants	12	103	40	5	113	44
Remote Terminals:[a]						
Pipeline	3	77	23	14	53	28
Rail unloading	3	36	15	6	75	31
Truck unloading	3	94	19	94	113	101
Barge unloading	91	908	322	94	454	263
Ship unloading	379	1,816	826	379	1,816	890

Load-Out Rate in Tonnes Per Hour:

	1983 Survey			1988 Survey		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Fertilizer Plant	4	151	44	9	75	31
Remote Terminals:[b]						
Pipeline	4	265	66	15	109	46
Rail loading	18	118	55	9	272	61
Truck loading	9	302	104	7.5	272	115
Barge loading	82	454	245	152	477	284
Ship loading	91	681	387	363	908	529

a. Source of supply.
b. Destination from terminal.

Source: [2].

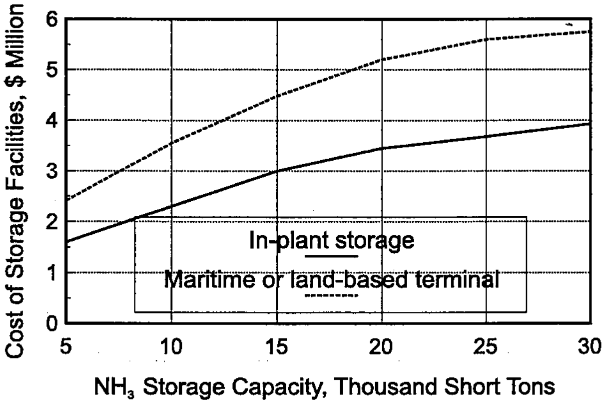

Figure 7.2. Refrigerated Ammonia Storage Capital Cost.

atmospheric pressure and at a corresponding temperature of about -33°C. The ships are equipped with refrigeration facilities that, in principle, are similar to those of a storage facility. The ships are also equipped with pumps of sufficient capacity to discharge the cargo at a rapid rate.

The cost of ocean transport depends on a large number of factors: the cost of the ships or the cost of chartering the ship, distance, ship speed, fuel cost, crew cost, port charges and time in port, number of destination ports, and the supply and demand for shipping space. The last factor is important in that it causes freight costs to fluctuate widely.

Ammonia competes with LPG in the shipping sector. However, there is a dedicated ammonia fleet of 40-65 vessels. Since the start of 1990, the shipment of ammonia has consistently required a total of 65 vessels with an aggregate capacity of 1.7 million m^3 [1]. The total available capacity to carry either LPG or ammonia was estimated at about 8.6 million m^3 in 1992. Generally, the size of the vessel determines whether LPG or ammonia is shipped. Table 7.4 provides the general guidelines. Ships larger than 60,000 m^3 are mostly used for LPG, except for two Russian vessels used exclusively for ammonia.

The C.I.S. countries dominate the anhydrous ammonia export market, currently having 30% of the market with a wide range of customers. Eastern Europe and Western Europe, as well as the United States, import large quantities of ammonia from the region. Other large importers are Morocco, Tunisia, and Jordan. The Arab Gulf states are also large exporters, mainly to India, Turkey, and countries in the Far East [5].

The freight rates for ocean shipping depend not only on the distance the cargo has to travel, but also on the size of the cargo and the availability of the ships in that size range. Some representative freight rates for shipping ammonia for the period of September 1992 to August 1993 are shown in Table 7.5.

The seasonality of the LPG market has a direct bearing on ammonia freight. Demand for both is quieter in the summer months than in the winter, when the colder weather causes demand for LPG to rise sharply. The freight rates fluctuate for every shipment.

It should be emphasized that the total cost of shipping and receiving ammonia includes not only the freight but also the cost of operating loading, receiving, and storage terminals, as discussed previously. Also the total cost may include transport to the terminal. For example, the C.I.S. terminals at Ventspils and Odessa are supplied by pipeline from ammonia plants located several hundred kilometers inland.

7.3.2 Shipment of Ammonia by Barge

Barge shipment of anhydrous ammonia is economical for countries or regions that have inland or coastal waterways and is extensively used in Europe and the United States. Self-propelled barges are commonly used in Europe where inland waterways are often narrow or shallow. Their capacities may range from 500 to 3,000 tonnes. Most of the larger barges are fully refrigerated, and smaller ones are semi-refrigerated. For most of the inland rivers and canals, barges of about 1,000-tonne capacity are suitable; larger self-propelled barges may be useful for coastal shipping.

In the United States, barges play an important role in ammonia transportation. Between 2 and 2.2 million tonnes of anhydrous ammonia moves by barge each year. About one million tonnes of the ammonia transported is used for agricultural business; farmers apply 45% directly on the field, and 55% is converted to other fertilizers such as UAN, DAP, and MAP. The balance of anhydrous ammonia is used for industrial production of chemicals such as nitric acid, adipic acid, acrylonitrile, and aniline [6].

In the United States, towed barges are commonly used, and several barges are lashed together and propelled by a single tugboat. A tow may be formed by two barges or more depending on the width of the waterway. Barges for transport of anhydrous ammonia usually are fully refrigerated, and their capacities may be in the range of 1,500 to 2,500 tonnes; smaller ones are used mainly where the depth or width of the waterway is insufficient for larger ones.

There are currently 39 barges in use for transporting ammonia in the United States. They are typically 90 m

Table 7.4. Ships for Ammonia and LPG

Size of Vessel (m^3)	Number of Ships	Aggregate Capacity (million m^3)	Use
30,000 to 59,999	42	1.8	Most important size in ammonia trade. Higher LPG freight rates attract this size into LPG trade.
20,000 to 29,999	26	0.7	More heavily involved in ammonia trade than LPG trade. This size provides greater flexibility at loading and unloading ports.
10,000 to 19,999	48	0.6	Mostly used for inter-regional and coastal transportation of ammonia.
Under 10,000	400	1.0	Used for short haul transportation of both LPG and ammonia.

Note: 1 m^3 = 0.68 tonne of ammonia at -33°C.

Source: [1].

Table 7.5. Representative Freight Rates (Sept. 1992 - August 1993)

Route	Cargo Size (tonnes)	Typical Freight Rate ($/tonne)
Yuzhnny to US Gulf	35,000	Mid-Upper 20s
Yuzhnny to Gabes, Tunisia	15-18,000	13-Low 20s
Arab Gulf to India	10-15,000	23-24 (West Coast) Mid 20s (East Coast)
Arab Gulf to Taiwan	12-15,000	Mid 20s-Mid 30s
Arab Gulf to S. Korea	30-35,000	Low 20s-32
Yuzhnny to West Coast, India	22-26,000	Low 40s
Yuzhnny to North Africa	35,000	20

Source: [1,10,11].

long and 15 m wide, and can carry up to 2,500 tonnes of ammonia. A typical river tow consists of two barges of 5,000 tonnes in total [1,6]. All the barges in use today were built between 1964 and 1968, when new ammonia plants were being established in Louisiana and along the Gulf Coast. A 13,600-km network of waterways, called The Western Inland River System, efficiently connects the producing plants with many industries that use ammonia and with the corn belt.

The Western Inland River System consists of the Mississippi River, the Gulf Intercoastal Waterways (GIWW), and their tributaries. About half of the U.S. population and more than two-thirds of the agricultural land are in states served by these waterways. The principal rivers include the upper Mississippi between Cairo, Illinois and Minneapolis/St. Paul, Minnesota; the lower Mississippi between Cairo, Illinois and New Orleans, Louisiana; the Missouri to Sioux City, Iowa; the Ohio to Pittsburg, Pennsylvania; the Arkansas to Tulsa, Oklahoma; the Tennessee Tombigbee Waterway; and the GIWW between Brownsville, Texas and St. Marles, Florida [6]. At least 35 ammonia terminals are located on rivers in the United States. Several of these terminals can deliver ammonia from a barge to the Gulf Central Pipeline System.

The market for barging ammonia is experiencing slight growth on the industrial side, but is declining on the agricultural side. Nitrogen solutions are displacing direct-application ammonia. The amount of nitrogen solution used increased from 6.0 million tonnes in 1980 to 7.9 million tonnes in 1993. In the same period, the amount of anhydrous ammonia used as fertilizer dropped from 5.0 million tonnes to 4.0 million tonnes [7]. A further reduction in the barge market is likely as the ammonia-producing industry consolidates, the pipeline network is extended, and plants to produce ammonia derivatives are built next to ammonia plants. Currently there is an oversupply of barges, and barge freight rates are depressed. In the late 1970s, the fair market charter rate for a barge exceeded $1,200 per day. Today, the rate would be less than one-half of that amount. Some typical barge freight rates follow in Table 7.6.

The rates depend on both the difficulty of access and the distance. Small barges must be used on shallow rivers, and the rate is higher for such locations.

Table 7.6. Barge Freight Rates in the United States

From	To	Distance (km)	Rate ($/tonne)
New Orleans	Texas City	640	10-11
New Orleans	Cincinnati	2,080	25

7.3.3 Transportation of Ammonia by Pipeline

Transportation of anhydrous ammonia by pipeline is economically attractive in some cases. Examples of long distance ammonia transport by pipeline are found in Mexico, the former Soviet Union, and the United States. Pipelines may be used to transport ammonia from manufacturing plants to maritime terminals for shipment to factories that produce finished fertilizers or to market areas for direct application. A pipeline may serve some combination of these purposes.

Relatively short pipelines, up to 50 km, have been used for 30 years or more for ammonia transportation. For example, in Sterlington, Louisiana, a pipeline 6.4 km long and 7.6 cm in diameter was in use in the 1950s to transport ammonia from an ammonia plant to an ammonium nitrate plant. Likewise, in Portugal a pipeline 10 cm in diameter and 17 km long was in operation in 1960 to connect an ammonia plant with a fertilizer plant. A 50-km pipeline is used to transport ammonia from an ammonia plant in Carling, France to a urea plant in Besch, Germany; a parallel pipeline supplies carbon dioxide. In Mexico a pipeline which is about 240 km long crosses the country from the Gulf of Mexico to the Pacific. One of the first European pipelines was built in Czechoslovakia between Most and Lovosice.

Pipeline transportation is well developed in the United States. For the purpose of outlining the facilities available in the United States, the four main systems have been broken down as follows:

Gulf Central Pipeline System and Gulf Central
  Storage and Terminal Company
Mid-America Pipeline Company
Tampa Bay Pipe Line Company

Table 7.7 indicates the length of the pipelines.

The following sections include key facts for each of these four company facilities. Maps are included for the Gulf Central Pipeline Company and the Mid-America Pipeline Company.

Gulf Central Pipeline Company System (Santa Fe Southern Pacific Corp.) – The longest pipeline system now operating in the United States extends across seven states with a length of 3,060 km [8]. The seven states are Louisiana, Arkansas, Missouri, Iowa, Nebraska, Illinois, and Indiana.

Ammonia plants primarily in Louisiana supply the ammonia to the pipeline. Gulf Central Pipeline Company has booster pumping stations along the route to

Table 7.7. Ammonia Pipelines (Overall Length)

Pipeline	Miles	Kilometers
Gulf Central Pipeline (Santa Fe)	1,900	3,057
Mid-America Pipeline (MAPCO)	1,090	1,754
Tampa Bay Pipe Line	83	134
Total	**3,073**	**4,945**

Source: [8].

offset pressure drop and changes in elevation as the ammonia leaves the Gulf Coast and moves inland to higher elevations [8].

The main line of the Gulf Central Pipeline originates at anhydrous ammonia production plants near New Orleans, Louisiana. This main line parallels the Mississippi River north to Iowa. The main line then turns west across the state of Iowa and terminates in Aurora, Nebraska.

A major branch from the main Gulf Central Pipeline extends east across the Mississippi River just north of St. Louis, Missouri. This branch then crosses Illinois and Indiana, terminating near Huntington, Indiana (southeast of Chicago) [8]. Table 7.8 summarizes the design basis for this installation.

Gulf Central Storage and Terminal Company – To supplement the Gulf Central Pipeline, the Gulf Central Storage and Terminal Company provides complete operating ammonia terminals for public storage of anhydrous ammonia. Eleven cryogenic storage terminals are located along the pipeline in strategic locations. Each terminal provides full storage and terminal delivery service [8].

Mid-America Pipeline Company (MAPCO) – The MAPCO ammonia pipeline (Figure 7.3) was the first interstate system in operation. The initial charging of the line with ammonia in 1968 came from an ammonia manufacturing plant in Borger, Texas. The MAPCO line now extends about 1,750 km northeast from north Texas across Oklahoma, Kansas, Nebraska, and Iowa, ending in Minnesota. The main line and branches provide connections from three major ammonia plants to 13 distribution centers in four of these six states [8]. Table 7.9 summarizes the design basis for this ammonia pipeline.

Tampa Bay Pipe Line (Florida) – The newest of the U.S. anhydrous ammonia pipeline operations was commissioned in 1978 at a length of 100 km. About 3 years ago, the length was extended to 132 km [8].

The ammonia liquid arrives at the Tampa Bay Port by ship and is unloaded into either the Royster refrigerated ammonia storage terminal or a newer International Mineral Company terminal on the Florida west shore. The Tampa Bay office and pumping station is located about 5 km east of the two terminals.

Refrigerated ammonia from these terminals is first reheated to about 10°C and then transferred to the pipeline pumping station upon request. Table 7.10 summarizes the pipeline design basis.

These pipeline systems are common carriers and are subject to regulation by the U.S. Government (Interstate Commerce Commission), which requires (among other things) that the rates be published.

The common contract rates used by the pipeline are based on 12-month minimum tonnage. Table 7.11 shows rates published by MAPCO Ammonia Pipeline [9]. Note that the rates are not dependent on the distance of the shipment.

The spot market rates depend on the place of origin and the destination. However there is not a large

Table 7.8. Gulf Central Pipeline Design Basis

Control Center	Tulsa, OK
Capacity	1,816,000 tpy (2,000,000 short tons per year). Approximately 5.7 m^3/minute (1,500 gal per minute).
Main Pipe Line	25.4 cm (10") Alexandria, LA to Hermann, MO 20.3 cm (8") to Spencer, IA 15.2 cm (6") from Spencer, IA to Aurora, NE
Branch	20.3 cm (8") from Hermann, MO to Terre Haute, IN
	15.2 cm (6") to Huntington, IN
Maximum Pressure	9,917 kPa (1,424 psig)
Minimum Pressure	2,169 kPa (300 psig)
Overall Length	3,057 km (1,900 miles)

Source: [8].

Figure 7.3. MAPCO Ammonia Pipeline.

Table 7.9. MAPCO Pipeline

Control Center:	Tulsa, OK.
Capacity:	831,000 tpy (915,000 short tons per year). Approximately 2.63 m^3 per minute; 2,270 tpd (700 gal per minute; 2,500 short tons per day).
Main Pipeline:	A. 15.2 and 20.3 cm (6" and 8") from Borger, TX to Hutchinson, KS. B. 15.2 and 20.3 cm (6" and 8") from Tulsa, OK (Verdrigris) to Hutchinson, KS. C. 15.2 and 20.3 cm (6" and 8") from Hutchinson, KS to Mankato, MN.
Overall Length:	1,754 km.

Source: [8].

Table 7.10. Tampa Bay Pipe Line

Control Center:	Tampa, FL.
Capacity:	4.1 m^3/minute, 3,630 tpd (1,075 gpm, 4,000 short tons per day).
Pressure:	
Discharge	6,305 kPa (900 psig).
Inlet	2,169 kPa (300 psig).
Main Line:	15.2 cm (6").
Branch Lines:	10.2 cm (4").
Overall Length:	132 km.

Source: [8].

Table 7.11. MAPCO Ammonia Pipeline: Annual Volume Rates[a]

Twelve Consecutive Month Tonnage, Minimum	$ Per Tonne, Tariff Rate
13,620 (15,000)	14.65 (13.30)
90,780 (100,000)	14.30 (12.98)
181,560 (200,000)	13,87 (12.59)
363,200 (400,000)	11.68 (10.60)
454,000 (500,000)	10.46 (9.50)

a. Short ton values in parentheses.

Source: [9].

variation in the rates between any two locations. MAPCO's published rates (issued March 2, 1992, but still current in 1994) show a variation from $12.83 to $15.25. Some examples of the rates are shown in Table 7.12.

The rates shown are for transportation only. If the ammonia is loaded directly from the pipeline into trucks, there is a truck loading charge of $1.43/tonne if the loading is done by the pipeline company, except at Mocane, Oklahoma where the charges will be $2.45/tonne. When the ammonia is stored in the pipeline company's storage terminal facilities, there is an additional charge for storage space, which may vary from $15 to $38 per tonne. But most of the storage facilities are owned by the shipper or consignee.

7.3.4 Transportation of Ammonia by Rail

Ammonia is transported by rail in the United States mainly in cars having capacities of about 70-78 tonnes.

Table 7.12. Spot Prices for MAPCO's Ammonia Pipeline Transportation, US $/tonne

	From:		
	Cominco, Berger	Farmland, Enid	Terra, Mocane
To:			
Farmland, Farnsworth	12.83	13.70	12.83
Farmland, Mankato	15.25	14.78	14.89
Conway Terminal	13.59	13.52	13.24

Source: [9].

In general, rail transport is used for shorter distances than pipeline or barge transportation, but not always, because rail transport can be more economical for supplying some points than a combination of barge or pipeline and rail or truck. In some areas that are far from a river or pipeline, shipping by rail may be the only option. For instance, for shipping ammonia from Western Canada to the Midwest United States, railroad and truck are the main options. One use for rail transport is from pipeline or large terminal to another storage terminal.

For transport by rail, the ammonia, if taken from refrigerated storage, must be warmed to at least 5°C because the rail cars are not designed for handling -33°C ammonia.

Though the railroads in the United States and Canada are regulated and there is a ceiling on tariff that the railroad can charge, most of the large transporters are able to negotiate contracts to ship ammonia at a rate lower than the regulated tariff rate. Representative freight costs for transportation of ammonia by rail in cars of 78-tonne capacity are shown in Table 7.13. The rates are based on the supposition that the cars are supplied by the shipper. The railroads have few, if any, cars suitable for ammonia transportation.

Table 7.13. Representative Rail Freight Rates for Anhydrous Ammonia

From:	To:	Distance (km)	Single Car Rate ($/tonne)
Savannah, GA	Augusta, GA	240	14.66
Donaldsonville, LA	Macon, GA	925	46.00
Donaldsonville, LA	Enid, OK	1,650	68.00
British Columbia, Canada	Des Moines, IA		110.00

Source: [12].

7.3.5 Transportation of Anhydrous Ammonia by Truck

Truck transportation is the most expensive method of moving anhydrous ammonia and hence is used mainly for short distance. The trucks used in the United States consist of a tractor and a detachable trailer. Truck capacity is in the range of 16-18 tonnes. The trailers are also used to transport LPG. Some examples of truck transport costs are shown in Table 7.14. In the United States, about 4.0 million tonnes of anhydrous ammonia is used for direct application each year. Probably as much

Table 7.14. Cost of Transportation of Anhydrous Ammonia by Trucks

Distance, km	$/Tonne[a]
150	2.48 (2.25)
300	4.63 (4.20)
500	6.33 (5.75)
650	7.71 (7.00)

a. Short ton rates in parentheses.

as 75%-80% of this amount is used in the spring. In any given area, most of it is used within one month. This means that most of the ammonia for direct application must be stored near the users – part of it in local retail storage facilities and part in large terminals served by pipelines, barges, and rails. Because the annual throughput of the storage terminals is no more than twice their capacity, terminal storage costs are high. A typical total cost for storage and transport of ammonia produced in Louisiana or Texas to a retail center in Iowa has been estimated in Table 7.15. This total cost does not include retailer storage cost or transport to farms.

Table 7.15. Combined Costs of Ammonia Transportation

Cost Component	US $/tonne
Pipeline transportation from plant to terminal	14.00
Terminal storage charges	25.00
Truck transport from terminal to retailer	5.00
Total	**44.00**

7.4 References

1. "Transporting Ammonia." 1992. *Nitrogen*, No. 199.
2. Hale, C. C., and W. H. Lichtenberg. 1990. "Survey of Refrigerated Storage in the U.S. and Canada," Ammonia Safety Symposium, Vol. 30.
3. Appl, Max , et al. 1990. "New Cases of Stress Corrosion Cracking in Large Atmospheric Ammonia Storage Tanks," Ammonia Safety Symposium, Vol. 30.
4. "Ammonia." 1985. *Ullman Encyclopedia of Industrial Chemistry,* 5th edition, Vol. A2,222.
5. World Bank. 1994. "World and Regional Supply and Demand Balances for Nitrogen, Phosphate, and Potash, 1992/93-1998/99," Technical Paper No. N252, World Bank, Washington, D.C., U.S.A.
6. Voth, R. A. 1994. "The U.S. Ammonia Barge Industry in 1994," *FINDS*, Vol. IX, Number 1, First Quarter.
7. Data from Fertiliser Institute, Washington, D.C., Private Communication.
8. Hale, C. C., and W. H. Lichtenberg. 1988. "U.S. Anhydrous Ammonia Distribution System in Transition," Ammonia Safety Symposium, Vol. 28.
9. MAPCO Ammonia Pipeline Tariff, I.C.C. MAPO No. 1, issued March 2, 1992.
10. "Representative Freight Rates." 1993. *Nitrogen*, No. 202.
11. "Representative Freight Rates." 1993. *Nitrogen*, No. 204.
12. Quotations of the ammonia transporting companies, Private communication.

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Chapter 8. Nitric Acid, Nitrates, and Ammonium Salts

8.1 Introduction

The purpose of this chapter is to describe the technology and economics of production of nitric acid and nitrates (except potassium nitrate, which is covered in Chapter 15) and the production of ammonium salts for fertilizer use (other than ammonium phosphates, which are covered in Chapter 12). The chapter also includes nitric acid and nitrate technologies developed in Russia and other countries of Eastern and Central Europe. The Commonwealth of Independent States (CIS) was the largest producer of nitric acid, nitrates, and other fertilizers in that area [1,2,3], and all original technologies in the CIS were developed solely by the State Institute of Nitrogen Industry (GIAP).

The sodium nitrate and kalium nitrates mined commercially in Chile beginning about 1830 were the first available inorganic nitrogen fertilizers. Ammonium nitrate was developed as the first synthetic nitrogen fertilizer followed by urea in the mid-1930s, anhydrous ammonia fertilization in the 1940s, and ammonium phosphates in the 1960s. Historical data on nitrogen fertilizer production are given in Table 8.1.

The proportionate decline in the consumption of ammonium nitrate has resulted from massive development of urea production in developing countries and the introduction of complex fertilizers based on ammonium phosphates. However, considering the higher nitrogen use efficiency of ammonium nitrate compared with urea, ammonium nitrate may be the more economical nitrogen source in many situations.

8.2 Nitric Acid

8.2.1 Introduction

Nitric acid is one of the oldest known chemicals. Three methods of production of nitric acid have been developed:

- Acidulation of natural sodium nitrate with sulfuric acid;
- Direct synthesis from nitrogen and oxygen;
- Oxidation of ammonia.

The acidulation of sodium nitrate was conducted commercially in Chile for about 30 years, ending in the early 1920s. Direct oxidation of nitrogen by electric arc was carried out commercially beginning in 1902 in Norway using electrical energy from hydrosources. A commercial plant was also constructed in Poland using the Moscicki process of direct oxidation in an electric arc. That plant operated until the early 1950s.

The first patent on ammonia oxidation was issued to Khulman in 1839; in this case platinum was used as a catalyst to oxidize ammonia with air. The ammonia-oxidation method using a platinum catalyst on a commercial scale, developed by Oswald and Brauer and first operated in Germany about 1908, is at present the principal industrial method of nitric acid production. The main use for nitric acid is in fertilizer production, mainly for ammonium nitrate as such or in compound fertilizers, nitrogen solutions, or mixed salts. About 75% of total nitric acid production is consumed for nitrate fertilizers, mainly as 50%-65% concentration acid. Smaller fertilizer uses are for calcium and potassium nitrates. A primary use is in acidulation of phosphate rock for production of nitrophosphates. Plant capacities for weak nitric acid used for fertilizer production are in the range of 35 to 1,380 tpd although capacities of 2,000 tpd have been designed.

Nitric acid also has many industrial uses for production of nitro-aromatics and nitro-alkanes, of which explosives manufacture is the largest. Another application of nitric acid is for adipic acid production (an intermediate product in Nylon production). In this case the concentrated acid is used. A summary of applications of nitric acid is given in Figure 8.1.

Table 8.1. Historical Data on Ammonium Nitrate Fertilizer Production

	Unit	1950	1960	1970	1980	1990
Ammonium nitrate production	Mln.t/year	1.9	4.6	10.1	14.7	14.0
Ratio in overall nitrogen supply	%	47	43	33	23	18

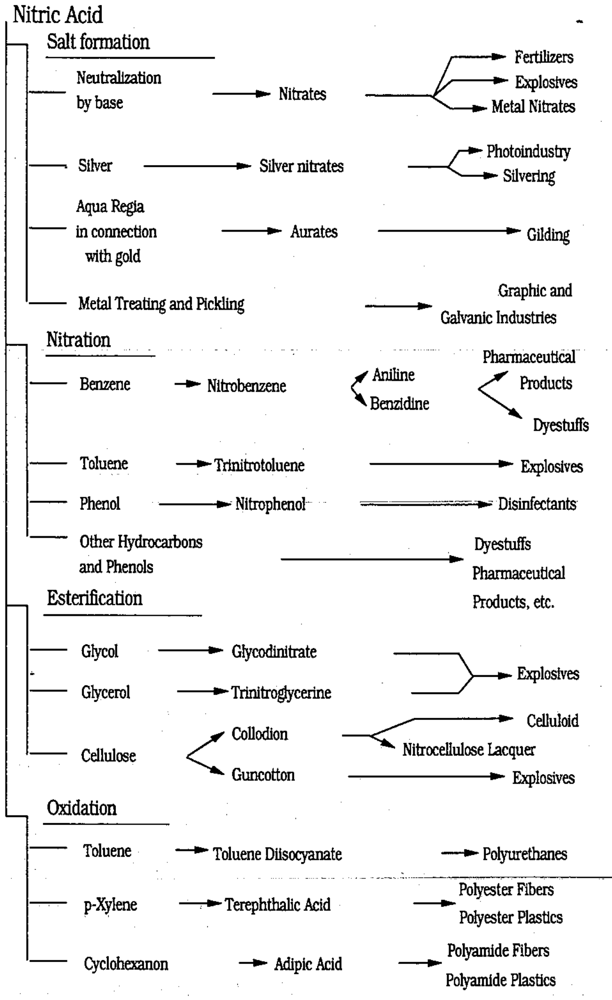


Figure 8.1. Nitric Acid Applications.

8.2.2 Product Quality and Properties

Nitric acid is a strong acid and a powerful oxidizing agent. The concentration of commercial nitric acid destined for fertilizer production depends on the method of production and is usually in the range of 42% to 65%. Such acid is known as weak acid, unlike concentrated acid (96.0%-98.5%) that is used for other industrial purposes. Weak nitric acid is usually directed for captive use. Anhydrous HNO_3 does not normally exist in liquid form. When strong solutions are distilled under special conditions, one obtains almost pure nitric acid having a concentration of 99.7%. When concentrated nitric acid is heated at atmospheric pressure, it boils at 78.2°C but begins to decompose and eventually yields a 68% HNO_3 solution with a maximum boiling point of 120.5°C. When dilute solutions of nitric acid are concentrated under atmospheric pressure, a maximum boiling-point solution again corresponding to 68% HNO_3 results. The more important properties of nitric acid are summarized in Table 8.2.

More particular physical properties of nitric acid are given in handbooks [4,5]. Typical impurities in HNO_3 originate from ammonia or the process. The standard limits are the content of Cl_2 – less than 5 ppmw, and HNO_2 – less than 5 ppmw.

8.2.3 Raw Materials

The anhydrous ammonia and process air used must be free from catalyst poisons, dust, and oil. Platinum catalysts can be poisoned by such elements as As, Bi, P, Pb, S, Si, and Sn. Fortunately, synthetic ammonia is normally of high purity unless it is accidentally contaminated. However, since air can be contaminated by dust or many other pollutants, thorough air cleaning is necessary. Location of the air intake in an area relatively free from contaminants will help. If poisoning by impure ammonia or air should arise, deep penetration may occur, leading to the formation of inactive compounds in the catalyst wires and, perhaps, to the extent of ruining the catalyst. In other instances, contamination by traces of Cr, Fe, or Ni may temporarily reduce conversion efficiency, but this can often be restored by treatment with hydrochloric acid or certain salts.

The physical properties of ammonia are given in Chapter 6. Specifications for ammonia to be used in nitric acid processes basically limit water, oil (from lubrication), and heavy metals. The limits change from licenser to licenser and obviously influence the process yields. At the plants located in the former Soviet Union, established limits for impurities in the feed ammonia are given in Table 8.3 [5]. Limits on air impurities are given in Table 8.4.

8.2.4 Process Chemistry

The oxides of nitrogen that are of interest in nitric acid production are:

Nitrous oxide (dinitrogen monoxide)	N_2O
Nitric oxide (nitrogen monoxide)	NO
Nitrogen dioxide	NO_2
Dinitrogen tetroxide	N_2O_4

Of these, NO and NO_2 are of primary importance. N_2O_4 exists in equilibrium with NO_2 and is not present in significant proportions at temperatures above about 100°C. It acts as a transitory intermediate in low-temperature absorption of NO_2 in nitric acid. N_2O is seldom present in significant amounts. A mixture of nitrogen oxides, usually NO and NO_2, is commonly referred to as NO_x.

The production of weak nitric acid consists of three principal chemical steps:

- Catalytic ammonia oxidation to nitric oxide;
- Oxidation of nitric oxide to nitrogen dioxide;
- Acidic absorption of nitrogen dioxide in water.

Table 8.2. Properties of Nitric Acid

Formula	HNO_3
Molecular weight	63.013
Color	
In liquid state	Transparent to yellow
As gaseous oxides	Transparent to yellow or brown (color darkens on prolonged exposure to light)
Odor	Sweet to pungent
Hazards	
In liquid state	Rapidly attacks flesh and most organic matter
As gaseous oxides	Anesthetic to dangerously toxic
Melting point	41.6°C
Boiling point	82.6°C
Refractive index at 16.4°C	1.397
Density at 0°C	1,549.2 kg/m^3
Solubility in water	Totally soluble at all concentrations
Acidity	A strong acid, having pronounced oxidizing characteristics. Will passivate some metals, such as iron and aluminum
Heat of vaporization at 20°C	626.3 J/g

Table 8.3. Liquid Ammonia Commercial Standard

Component	Unit	Value
Water	%	<0.4
Oil	mg/l	<8
Fe	mg/l	<2

Table 8.4. Impurity Limits in Oxidizing Air for Nitric Acid Production

Component	Unit	Value
Sulfur compounds (S)	mg/m^3	<2.3
Phosphorus	mg/m^3	<0.3
Fluorine	mg/m^3	<0.1
Chlorine	mg/m^3	<0.1

The overall reaction (without taking into consideration side reactions) can be presented as follows:

$NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l) + 437$ kJ/gmol

Oxidation of ammonia without a catalyst results in the formation of only elemental nitrogen.

On a catalyst surface several reactions may occur:

1. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) + 227$ kJ/gmol
2. $2NH_3(g) + 2O_2(g) \rightarrow N_2O(g) + 3H_2O(g) + 276$ kJ/gmol
3. $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g) + 317$ kJ/gmol

Simultaneously some other reactions can take place, including:

4. $4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g) + 451$ kJ/gmol

Various alloys and metallic oxides have been tried as catalysts, but platinum containing between 2% and 10% rhodium is usually preferred [6]. Nitric oxide produced in the ammonia converter must be oxidized further to nitrogen dioxide by the excess air present in the reaction mixture:

5. $2NO(g) + O_2(g) \rightarrow 2NO_2(g) + 57$ kJ/gmol

from which the tetroxide may be formed before absorption in water:

6. $2NO_2(g) \rightarrow N_2O_4(g) + 29$ kJ/gmol

When the temperature is lowered, the equilibrium of reactions 5 and 6 shifts to the right. At low temperatures and in sufficient time to reach equilibrium and in the presence of excess oxygen, one can anticipate transformation of all oxides of nitrogen into dinitrogen tetroxide (N_2O_4). During absorption HNO_2 is formed along with HNO_3:

7. $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$

HNO_2 decomposes and emits NO gas, which must again be oxidized to NO_2.

8. $HNO_2 \rightarrow NO + H_2O$

giving the summary reactions:

9. $3N_2O_4(g) + 2H_2O(l) \rightarrow 4HNO_3(aq) + 2NO(g) + 16$ kJ/gmol
10. $2N_2O_4(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3\ (aq) + 59$ kJ/gmol
11. $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g) + 59$ kJ/gmol
12. $4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq) + 87$ kJ/gmol

Oxidation of NO (reaction 5) is the limiting stage of HNO_3 formation. With decreasing concentrations of nitric oxide and oxygen, the speed of oxidation decreases sharply. Absorber performance, therefore, is improved by higher pressure, lower temperature, and higher oxygen content in the gas phase. In the ammonia converter, however, oxidation of ammonia is favored by lower pressure.

The overall reaction of nitric acid production is strongly exothermic. Of the total heat released, more than half is released in the ammonia oxidation step at a high temperature, and economical recovery as steam or for other purposes is permitted. Also, part of the heat released by the subsequent oxidation of nitric oxide can be recovered at a useful temperature level. The remainder of the heat is released at a temperature too low for useful recovery and requires a net consumption of energy for circulation of cooling water, acid and process gas and, in some processes, for refrigeration.

8.2.5 Nitric Acid Production Technology

Numerous proprietary processes for nitric acid manufacture are now available. They differ primarily in design details or selected operating conditions to suit the plant sizes, cost of raw materials, energy cost, cost of installation, and so forth, not in fundamental principles. The production process usually is composed of the following process units:

1. Vaporization, superheating, and filtration of anhydrous ammonia;
2. Preheating, filtration, and compression of process air;
3. Catalytic oxidation of ammonia;
4. Cooling of nitric oxide by heat exchange with various media, e.g., process air, boiler water, tail gas, etc.;
5. Oxidation of nitric oxide to higher oxides;
6. Absorption of nitrogen oxides in water to form nitric acid;
7. Bleaching of acid by additional air or other means;
8. Treatment of tail gas to reduce air pollution (and to improve total plant efficiency);
9. Recovery of energy in heated and compressed process gases;
10. Recovery of catalysts for resale.

8.2.5.1 Ammonia Preparation – The anhydrous ammonia used must be free from catalyst poisons, and the oil content must be limited to a few parts per million to avoid fouling the vaporizer and catalyst screens. Liquid ammonia is vaporized, filtered, and superheated to eliminate any possibility of liquid droplets entering the catalyst chamber and burning holes in the screens. Liquid ammonia filters remove solid contaminants. All particles larger than 3 mm should be eliminated. Vaporization of the ammonia is often used to provide refrigeration for chilling the absorber. The superheated vapor, after additional filtration, is thoroughly mixed with process air in various ways according to the type of process. Filtration of ammonia gas should remove 99.9% of oil and all solid particles larger than 0.5 mm.

8.2.5.2 Process Air Preparation – Process air must also be free from catalyst poisons, dust, and oil. It is common to incorporate two-stage air filtration on the compressor air intake using a high air filtration efficiency, i.e., approximately 99.9% of all particles larger than 0.5 mm should be removed. For medium- and high-pressure oxidation, rotary compressors of the lobe, vane, centrifugal, or axial-flow design can be used, with an increasing preference for the last two types since these units can be combined with various turbine drives and expanders in the form of one large single-shaft installation.

8.2.5.3 Catalytic Ammonia Oxidation – The ratio of ammonia to air and the flow rate of each component must be carefully controlled to ensure maximum conversion efficiency, prevention of explosion, and maximum plant output. Use of static mixers is common. The percentage of excess air usually results in 8.5%-12.5% of NH_3 by volume in the air-ammonia mixture. The lower explosion limit is about 14.5% of ammonia in the mixture.

The ammonia conversion efficiency, expressed as a percentage of the ammonia that is converted to NO, is mainly a function of the catalyst selectivity and activity, temperature, pressure, thoroughness of mixing of the incoming air and ammonia, and velocity of gas flow through catalyst [7].

- **Catalyst**

The customary choice of catalyst is a platinum-rhodium gauze because this alloy promotes reaction and also meets other operating criteria, such as severe conditions of service. The usual rhodium content is 4%-10%. Because higher percentages tend to give slightly greater conversions and longer life, a 10% rhodium content has become standard in many processes [6]. In high-pressure plants (0.8-1.1 MPa) the usual alloy is 90% platinum and 10% rhodium. In medium-pressure plants platinum alloyed with 5%-7% rhodium is often used.

The need to minimize and control contact time to suppress unwanted reactions and to minimize catalyst requirements led to the early adoption of fine woven screens as a suitable catalyst form. These are usually circular in shape and are stacked in multiple array, because the use of several (5 to 45) screens permits the residence time and contact time to be easily varied to obtain the maximum yield of nitric oxide. Usually a platinum-rhodium catalyst is used in the form of a fine mesh (standardized at 1,024 mesh/cm^2), either of the fishbone or line cloth pattern. In an attempt to achieve higher efficiencies and smaller platinum losses [6], knitted gauzes were introduced not long ago. Chrome-nickel alloy grids are used to support these fine screens.

When first installed, a new gauze exhibits a relatively low activity, but after several days of operation under proper conditions, catalytic efficiency rises to a satisfactory level and remains nearly constant during the useful life of the screen, which should be several weeks or even months for high- and low-pressure burners, respectively. During operation, the crystalline structure of the platinum alloy is modified by the severity of service, and distortion takes place. Erosion also occurs if vibration is present, especially at high temperatures and pressures, which also results in diminished activity. Eventually, the screen wears out and must be replaced.

Most plants, particularly those with high-pressure burners, have some kind of filter that recovers part of the platinum, which is lost from the catalyst. Reported net consumption of platinum catalysts is in the range of 100-200 mg/tonne of HNO_3 for medium- and high-pressure units. In the republics of the CIS more complicated platinum alloys are used (Table 8.5). For instance, in the dual-pressure GIAP process the medium-pressure burner (0.4 MPa) contains seven screens of alloy No. 5 (alloy No. 1 is recommended for startup). Contrary to Western practice, wires that are 0.09 mm (instead of 0.076 mm) in diameter are used. A reported screen-life prior to regeneration of about 90 days of continuous operation is obtained. Total lifetime, prior to change, is 200 days. An overview on the development of nitric acid catalysts in Russia is presented in the article of Chernyshov and Kisil [2].

Table 8.5. Alternative Catalyst Alloys Used in the CIS

	Pt	Pd	Rh	Ru
	(wt %)			
Alloy No. 1	92.5	4.0	3.5	- -
Alloy No. 5	81.0	15.0	3.5	0.5

Ammonia oxidation reactors (burners) for atmospheric and low-to-medium pressures are often 3-4 m in diameter and may incorporate up to seven or more catalyst screens. High-pressure burners usually are smaller in diameter, perhaps 1.2-1.8 m, and may contain 12-45 gauzes. High-pressure units of this size can produce 350 tonnes of HNO_3, or even more, per 24-hour day. Larger size plants are now common; more than 1,000 tpd can be produced with a single burner with either high- or medium-pressure burners although two burners may be preferable for the lower range of medium-pressure processes. However, recent designs of some high-pressure burners in which diameters are increased to reduce gas velocities are said to approach efficiencies formerly attainable only in low-pressure units. Most low-pressure burners operate at approximately 800°-820°C and high-pressure units at about 900°-940°C. The higher temperatures, pressures, and gas velocities associated with high-pressure burners cause greater catalyst losses. Table 8.6 gives an indication of the effect of operating pressure on ammonia conversion efficiency, catalyst losses, and operating time.

Platinum catalysts can be poisoned by such elements as As, Bi, P, Pb, S, Si, and Sn. Contact with these elements leads to the formation of inactive compounds in the wires and decreases catalyst activity. In other

Table 8.6. Ammonia Conversion Efficiency and Catalyst Losses

Pressure (MPa)	NH_3 Efficiency (%)	Catalyst Losses (g/t HNO_3)	Operating Time (months)
0.1	97.5	0.06	6-8
0.5-0.6	95.5	0.14	5-6
0.9-1.0	93.5	0.30	1.5-2

instances contamination by traces of Cr, Ni, or Fe may temporarily reduce conversion efficiency, but this can often be restored by treatment with hydrochloric acid or certain salts. In some factories the gauzes are dismantled occasionally and accumulated solids are removed by gently brushing the gauzes. However, catalyst gauzes should receive minimal handling because they become brittle during service.

- **Temperature and Pressure of Reaction**

As the pressure increases, higher temperatures are needed to preserve high conversion efficiency. The temperature is controlled by preheating the air and ammonia and by the amount of excess air. However, the theoretical temperature limit is about 1000°C, above which the decomposition of ammonia to nitrogen starts to predominate. Ammonia conversion efficiency as a function of temperature and pressure is given in Table 8.7.

Table 8.7. Ammonia Conversion Efficiency

Pressure (MPa)	Temperature (°C)	Conversion Efficiency (%)
0.1	790-850	97-98
0.35	870	96-97
0.8	920	95-96
1.05	940	94-95

- **Contact Time**

An important variable in ammonia conversion is the rate of gas crossing the catalyst. Increased flow rates lead to quicker oxygen transport rates on the catalyst surface and the removal from the catalyst surface of intermediate products. High gas velocities and a short contact time, which is usually approximately 0.001 seconds, minimize undesirable side reactions. Increased flow rates and provision of several layers of catalyst help to minimize the undesirable reaction products. The optimal velocity increases with reaction temperature. The ammonia loading rate, which expresses the flow rate, is considered optimal at the range of 3.6-4.3 kg of ammonia per gram of catalyst per day. Gas velocities are much greater in high-pressure burners, and efficiencies are usually lower. However, the high flow rates increase catalyst losses.

8.2.5.4 Alternative Catalysts for Ammonia Oxidation – The high cost of the metals of the platinum group fosters the continual search for new nonplatinum catalysts for ammonia oxidation. At optimal temperatures (800°-900°C) and atmospheric pressure, catalytic activity of individual oxides of metals to the reaction of ammonia oxidation decreases in the line: $Co_3O_4 > Co_2O_4 > Cr_2O_3 > Fe_2O_3 > Mn_2O_3 > Bi_2O_5 > CuO, Ag_2O > CeO_2 > PbO > NiO > La_2O_3 > Si_2O_3 > V_2O_3 > V_2O_5 > ZnO > Al_2O_3 > WO_3 > MoO_3 < SiO_2$. In most cases the same sequence is observed concerning selectivity for NO formation. Thus, most of the prospective nonplatinum catalysts are based on oxides of the three metals: Co, Fe, or Cr [5].

Because oxidation of ammonia on a nonplatinum catalyst differs substantially from the process on a platinum catalyst, the use of nonplatinum catalysts is restricted. In the republics of the CIS two-step catalysts are widely used. One or several platinum gauzes are used as the first step, and a bed of nonplatinum oxide catalyst is used as the second step. The platinum step offsets the drawbacks of the nonplatinum step. A significant share of the ammonia burners in the CIS operate with the two-step catalysts. Reportedly, this allows the platinum input to be reduced by 40%-50% and platinum losses to be reduced by 15%-30% under equal conditions. The ammonia conversion efficiency is considered to be approximately the same as with conventional catalysts [8,9].

8.2.5.5 Cooling of the Reaction Products – To increase the formation of nitrogen dioxide and to recover heat for use elsewhere in the plant, hot gases leaving the burner are cooled, and the energy efficiency of the process is increased. In most medium- and high-pressure plants, different sequences are used; the gases may pass subsequently through a wasteheat boiler, a tail-gas heater, a cooler-condenser, a compressor (in dual-pressure plants), and a second cooler-condenser. In some cases the gases also may pass through a steam superheater and a combustion air preheater. A platinum-recovery filter usually precedes the cooler-condenser. In one process all major heat exchangers are mounted end-to-end to simplify plant design and to reduce capital costs. In several European processes, some of the heat exchangers are built as an integral part of other equipment, for example, the burner or the wasteheat boilers. Heat recovery of approximately 82%-85% is attained in some plants; higher figures are limited by dew point and corrosion considerations. In certain cases, about 1.1 tonnes of steam per tonne of 100% HNO_3 can be produced. Most of this is normally used for power purposes within the nitric acid plant, but as much as 0.4 tonne may be available for export.

8.2.5.6 Nitric Oxide Oxidation – Nitric oxide produced in the ammonia burner is oxidized in two reactions that occur sequentially:

- Reaction of nitric oxide with oxygen to form nitrogen dioxide;
- A dimerization reaction to produce nitrogen tetroxide.

Both reactions are homogenous, moderately exothermic and noncatalytic reactions. The oxidation reaction is a very slow process with a negative temperature coefficient. The oxidation rate varies with the third power of absolute pressure. The dimerization reaction is instantaneous, is assumed to be always in equilibrium, and is a direct function of pressure and inverse function of temperature.

In atmospheric and some low- to medium-pressure processes, one or more separate oxidation-cooling units are often included prior to gas absorption. These units are built in the form of vertical towers, which are cooled with external water curtains, shell-and-tube units, and also drum and cascade coolers. Excess air in the gas promotes initial oxidation, and some of the water vapor also present condenses to form weak nitric acid, which is later concentrated in the absorption section. Additional air for oxidation usually is injected at some point in the process, often in the absorption tower. In some plants, the gas is rapidly cooled to condense the water vapor without forming much weak acid, thereby helping to increase final acid concentration. A special condenser-cyclone separator unit designed for this purpose is described by Graham et al. [10].

Some high-pressure processes seek to maximize the extent of oxidation of NO to NO_2 in the heat recovery train so that heat generated by this reaction can be recovered at a relatively high temperature level. This can be accomplished by inserting extra chambers in the train to increase retention time, for instance, between the waste heat boiler and the tail-gas heater. Up to 80% of the NO can be oxidized to NO_2 before it enters the cooler-condenser by this means. In some other high-pressure processes, gas cooling and NO oxidation may be undertaken in a combined oxidation absorption column. However, the additional flexibility provided by a separate oxidation-cooling unit and the ability to minimize the amount of weak acid formed prior to absorption is considered advantageous by many producers.

8.2.5.7 Nitrogen Dioxide Absorption – The absorption of nitrogen dioxide comprises two processes:

- Cooling down the gaseous mixture below the dew point to remove excess water and thus to increase the partial pressure of nitrogen oxides.
- Absorption of nitrogen oxides in water.

As already shown, during the absorption reaction additional NO is formed, further oxidized, and absorbed.

Absorber performance is controlled by temperature and pressure. At reduced temperatures the gas-phase equilibrium moves toward the formation of dinitrogen tetroxide and an increased solubility in HNO_3. Therefore, lower temperatures improve the absorption rate and increase the acid concentration. At higher pressures the NO oxidation reaction is quicker, and equilibrium moves toward nitrogen dioxide. In addition, with higher pressure more concentrated nitric acid is produced.

At near atmospheric pressures, oxidation and absorption rates are slow, and earlier atmospheric and low-pressure plants used between five and ten very large towers. Maximum strengths attainable were in the range of 42% to 52% HNO_3. To reduce capital investment and to obtain increased operating efficiencies, absorption under pressure was developed, using various types of equipment, e.g., cascade coolers, packed columns, spray towers, and columns incorporating bubble plates, sieves, and such special devices as the Kuhlman tray.

Because acid concentrations are favored by low-temperature absorption, several different cooling methods have also been developed, e.g., by external units of the plate, drum, or cascade type; by water curtains outside the tower; and also by cooling coils strategically located inside the absorption column. In some plants using low-pressure ammonia oxidation, vaporization of the ammonia is used to prechill the absorber feedwater and cooling water.

Modern pressure-absorption systems permit absorption efficiencies of more than 99% and acid concentrations in the range of 55% to 65% to be obtained. In some processes, concentrations of up to 70% HNO_3 are achieved by using high pressures and cooled water in conjunction with specially designed absorption columns. In some plants, excess air may be injected into either the cooler or absorption column to speed the oxidation reaction. Process water for absorption systems must be very pure to reduce corrosion effects in the nitric acid plant and also in applications involving subsequent use of the acid. In particular, the chloride content must be very low. Hence, water from condensate sources or ion-exchange purification units is often used.

8.2.5.8 Acid Bleaching – Acid produced in most absorber units is invariably yellow or brown in color because of dissolved nitrogen dioxide. This is not acceptable for the handling of nitric acid and for most applications. The nitrogen dioxide is removed either in a separate small bleaching tower or in an additional, lower section of the main absorber column by means of compressed air injection. The gases are recycled to the oxidation tower.

8.2.5.9 Tail-Gas Treatment – Except for atmospheric units, exit gas from the absorber is normally preheated and expanded in a turbine to recover an appreciable amount of the energy used for compression purposes. This gas contains primarily nitrogen, some water vapor, oxygen, and mixed nitric oxides.

In the 1960s typical concentrations of NO_x in the tail-gas ranged from 1,500 to 3,000 ppmv. In recent years concern about pollution control has led to laws and regulations to reduce permissible levels of NO_x in tail-gas from nitric acid plants. For example, the maximum concentration in the United States is equivalent to 200 ppmv of NO_2 for new plants or 500 ppmv for existing plants. (The level is stated in kg of NO_2 equivalent per tonne of HNO_3.) In Russia the regulations are even stricter.

To meet the requirements that authorities in various countries have established, a variety of methods have been used. The principal methods employed to control the level of NO_x in tail-gas are:

- Extended absorption;
- Nonselective catalytic reduction (NSCR) with fuel such as methane or ammonia plant purge gas;
- Selective catalytic reduction (SCR) with ammonia.

Other methods such as absorption by silica gel or molecular sieves or scrubbing with alkalies or urea solutions are also used by some companies but to a smaller extent. Detailed descriptions of tail-gas treatment processes are given in Chapter 19 [11,12].

8.2.5.10 Energy Recovery – Except in older plants operating at atmospheric pressure throughout and in very small medium- and high-pressure installations, most or all of the energy needed to drive the air compressor, or both air compressor and nitrous gas compressor, can be recovered either in the form of mechanical energy (by tail-gas expansion turbine) or in the form of steam. In some instances, surplus steam for export or to produce electricity is generated. The air compressor, steam turbine, and tail-gas expander are usually built in the form of a single, in-line unit. In dual-pressure plants this system is also included. Tail-gas turbines usually supply 35%-85% of the compression energy. The tail-gas turbine is a multistage design usually equipped with partial load valves or adjustable guide vanes to control the plant pressure. It should be mentioned that efficient operation of the plants largely depends on efficient and reliable operation of the machines. For medium- and high-pressure oxidation, rotary compressors of the lobe, vane, centrifugal or axial-flow design are used; the latter two types are preferred because they can be combined with turbine drives and expanders as a single-shaft installation. The heat for air preheating can be provided to some extent by the heat of compression.

8.2.5.11 Platinum Recovery – During operation the surface of the catalyst is damaged by abrasion and vaporization. Vaporization loss dominates at the beginning of operation, but vaporization weakens the metal structure and leads to abrasion and erosion.

The possible range of platinum losses is given in Figure 8.2. Platinum from the catalyst passes into the gas stream in the form of very fine particles, and its loss can substantially increase the production cost. Therefore, several methods of platinum recovery were developed and installed in many plants. Two types of recovery systems – catchment gauzes and mechanical filters – are usually offered.

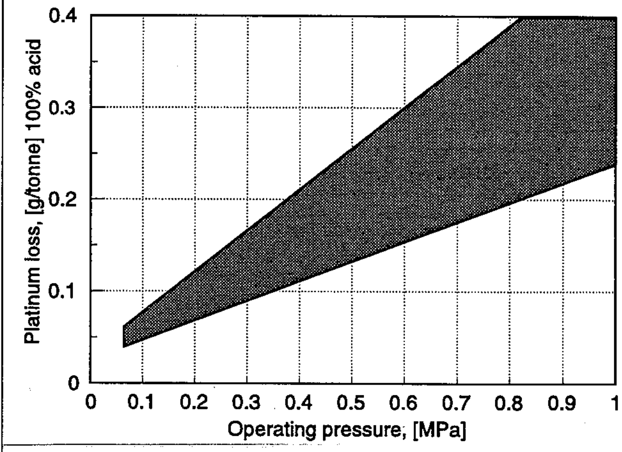


Figure 8.2. Relationship Between Platinum Losses and Operating Pressure.

The principle of catchment gauzes is to collect platinum at a temperature as high as possible while the main portion of the platinum loss is still in vapor form. At these temperatures, platinum atoms strike the metal surface and form an alloy with the catchment metal for subsequent recovery. The system can recover up to 80% of the primary platinum losses [6,13]. The catchment gauzes, which are installed at the bottom of the burner, are composed of a mesh screen and two or more metal gauzes. Catchment gauzes are returned together with the catalyst gauzes to the precious metal refining plant.

The mechanical filters, which are composed of glass wool or silica fibers, are commonly installed downstream of the catalyst where the gas temperature is below 300°C. Recovery rates of 50% have been reported [14].

8.2.6 Construction Materials

The corrosive behavior of nitric acid toward metals requires the proper selection of construction material.

The principal material wherever nitric acid or wet nitric oxides are present is chromium-nickel austenitic steel. The carbon content in this steel must be kept as low as possible because chromium forms carbides that are not acid resistant. The stainless steel used in nitric acid plants to resist nitrous gases and nitric acid is standard austenitic steel of type AISI 304L, 321, 347 (U.S.A.) or W n 1.4306, W n 1.4541, W n 1.4550 (Germany). For equipment in contact with hot, higher concentration nitric acid, special alternative alloys are used (AISI 304 L-nitric grade, AISI 310 L). Alloyed steels are also used for welded parts of pumps, impellers, and rotating elements of compressors. For equipment that handles ammonia, air, and hot, dry gases, normal carbon steel can be used. However, for safety in operation, especially during startup and shutdown operations, nitric acid plants are often equipped with practically all stainless steel equipment. Because they are resistant to nitric acid, various fluorocarbon plastic materials are used for flanges, gaskets, and seals.

8.2.7 Industrial Processes

Industrial plants are classified according to the pressure used:

- Monopressure plants. These plants operate at the same pressure in the ammonia oxidation and absorption sections of the plant. Monopressure plants are classified as low pressure (0.3-0.5 MPa) and high pressure (0.8-1.3 MPa).
- Dual-pressure plants. These plants operate under lower pressure in the ammonia oxidation section than in the absorption section.

In general, high-pressure operation permits smaller plant units to be used for a given output and helps to reduce capital costs. High pressures also favor NO_2 absorption; however, high-pressure ammonia oxidation induces greater catalyst losses and also increases power requirements unless additional equipment is installed for power recovery. Because of recent emphasis on pollution control, the ability of high-pressure processes to attain acceptably low NO_x levels in the tail-gas has favored their adoption. Therefore, most new plants use either mono-high-pressure or dual-pressure (medium-pressure combustion, high-pressure absorption) processes although some mono-medium-pressure processes are used.

According to Honti [15] the high-pressure processes generally will have the lowest capital cost and highest operating cost because of higher platinum losses, less efficient NH_3 conversion, and lower steam recovery. Medium-pressure processes have the highest capital cost and lowest operating cost (assuming the NO_x content of the tail-gas is acceptable). The dual-pressure process represents a compromise. The choice may be influenced by local conditions.

The first nitric acid plants used near-atmospheric pressure throughout. However, practically all modern plants use elevated pressures. A comparison of the different pressure processes is given in Table 8.8. These values are intended to be illustrative only. The choice of the process always depends on local conditions; however, a general principle may be that lower capacity plants favor the high monopressure alternative. The dual-pressure choice seems to be a compromise between the higher investment costs of mono-medium pressure and higher operating costs of mono-high pressure alternative. Table 8.9 gives overall capital costs and typical process requirements for a small dual-pressure plant.

Table 8.8. Typical Parameters of Nitric Acid Processes [17]

Parameter	Units	Mono-Medium Pressure	Mono-High Pressure	Dual-Pressure
Pressure	MPa	0.5/0.5	1.0/1.0	0.5/1.0
NH_3 consumption	kg/t	283	288	282
NO_x abatement (NH_3)	kg/t	0.5	-	-
Pt losses[a]	mg/t	60	130	60
Energy consumption	kWh	8.5	8.0	9.0
Steam credit	t/t	0.6	0.4	0.3
Cooling water	m^3/t	120	140	130
NO_x in tail-gas[b]	ppmv	400	<200	<200
Relative capital cost	%	120	100	110

a. With Pt recovery system.
b. With abatement system.

Table 8.9. Nitric Acid Plant (Dual-Pressure) Process Requirements

Product: Nitric acid (54%)
Capacity: 350 tpd
Capacity utilization: 90%
Annual production: 107,100 tpy

Process: Dual pressure
Investment cost:
– Battery limits US $15.2 million
– Working capital US$ 0.45 million

Cost Components	Unit	Unit/t
Raw materials		
Ammonia	t	0.282
Catalyst	US $	0.93
Utilities:		
Electrical energy	kWh	9.0
Process water	m^3	1.5
Cooling water	m^3	130
Steam (credit)	t	(0.3)
Labor	workhours	0.22

Before particular industrial processes are described, it should be noted that each process is based on information supplied by a different engineering and construction organization. Each of the organizations offers several processes to meet various client needs. In addition, several other companies offer nitric acid processes, and there is no intention to imply that processes offered by the four companies mentioned by name are necessarily superior to those offered by other companies. This does not imply any kind of endorsement by UNIDO or IFDC.

Plant capacities in the following discussion are expressed in terms of 100% HNO_3 although the actual acid concentration produced is usually 55%-68%.

8.2.7.1 Uhde Medium-Pressure Process – In the Uhde medium-pressure process (Figure 8.3) the air required to burn the ammonia is supplied by an uncooled air compressor. The operating pressure is governed by the maximum final pressure obtainable in an uncooled compressor, i.e., 0.4-0.5 MPa in the case of radial compressors (for a plant capacity of up to 200 tpd HNO_3), and 0.5-0.6 MPa with axial flow compressors (for a plant capacity above 250 tpd HNO_3). Hence, plant capacities of 1,000 tpd HNO_3 can be realized by employing only one ammonia combustion element and two absorption towers. The air compressor is normally driven by a steam turbine and by a tail-gas expansion turbine; the steam is generated within the plant. Alternatively, the compressor may be driven electrically, in which case all the steam generated is available for export.

The energy requirements of the plant can be adapted to prevailing conditions. For instance, if the credit for steam is high, the reaction heat may be used extensively to generate steam. Conversely, it may be used to heat the tail-gas for power recovery in the tail-gas turbine.

It is possible with this type of plant to produce acid with a concentration of up to 68% HNO_3, while the NO_x content in the tail-gas leaving acid absorption will be about 500 ppmv. Ammonia refrigeration cooling is used, depending on final pressure, to the maximum extent in connection with the cooling water temperature to optimize absorption conditions according to acid strength and/or tail-gas requirements. The NO_x concentration may be further lowered to less than 200 ppmv by selective catalytic reduction (SCR) using a non-noble-metal catalyst and ammonia as the reducing agent according to the BASF NO_x abatement process. Overall nitrogen yield is 96.2% or 95.8% in conjunction with the BASF process. Uhde also offers a high-pressure process (0.8-1.0 MPa) and a dual-pressure process (ammonia oxidation at 0.5 MPa and absorption at 1.0-1.4 MPa).

8.2.7.2 The Grand Paroisse Dual-Pressure Process – The Grand Paroisse dual-pressure extended absorption process (Figure 8.4) operates at a pressure of 0.35-0.6 MPa for ammonia oxidation and 1.0-1.5 MPa for the absorption step. The absorption is carried out in a single tower, but to improve the recovery in an existing plant that has a shorter tower, a second tower may be added. Chilled water from the ammonia vaporizer is used to cool the upper part of the absorption tower. The NO_x content of the tail-gas is 200 ppmv or less. The nitric acid concentration is up to 68%. At least three plants employing this process were recently constructed: two 902-tpd units for CNTIC in Lucheng,

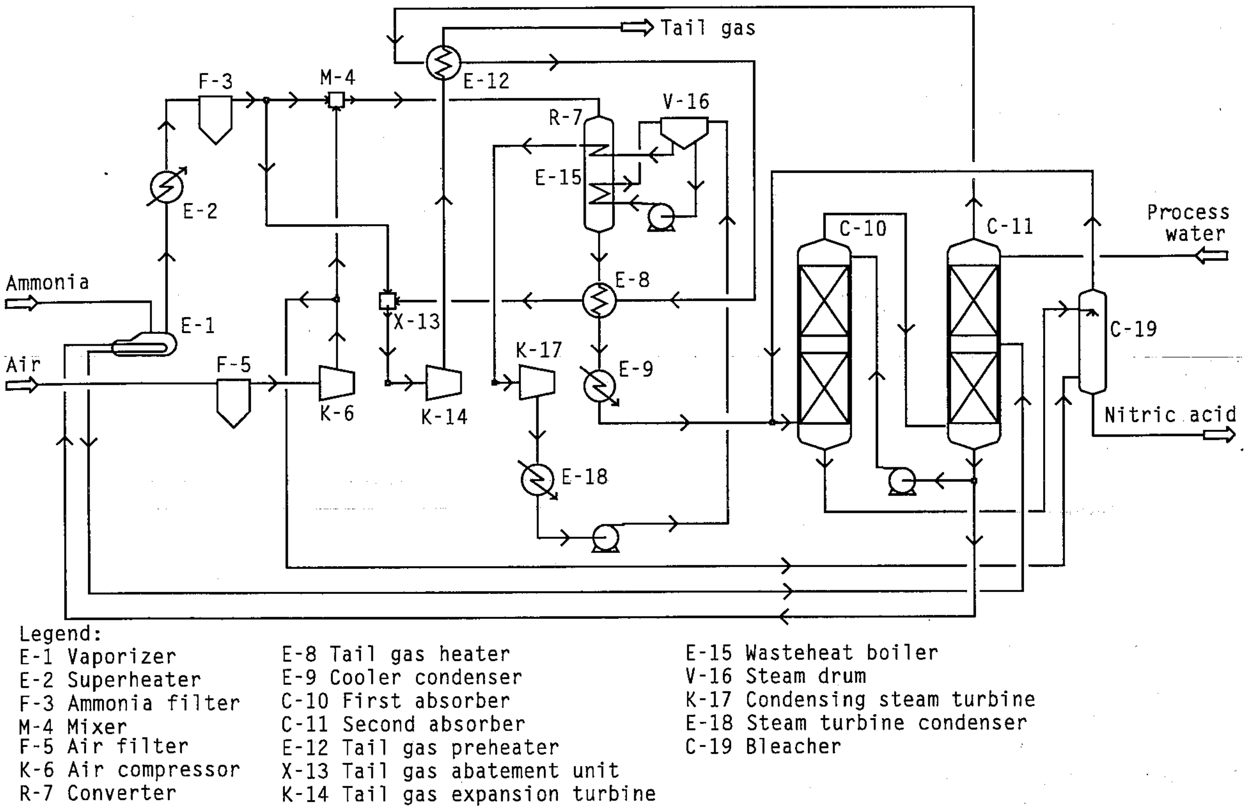


Figure 8.3. Uhde Medium-Pressure Process.

China (1987); 750 tpd for Enfersa in Sagunto, Spain (1988); and 1,200 tpd for Tagas in Mersin, Turkey (1990). The company also offers a monopressure process (0.5-1.0 MPa).

8.2.7.3 GIAP High-Pressure Process – The GIAP (Russia) high-pressure process (Figure 8.5) typically operates at an approximate pressure of 0.7 MPa [5]. The absorption is conducted in a single tall tower (44 m). The main feature of this process is that the air compressor is driven by a high-temperature gas turbine. The process incorporates a nonselective catalytic reduction (NSCR) unit for reduction of NO_x. The tail-gas discharged from the NSCR unit at a temperature about 700°C is used to drive the gas turbine. The high efficiency of energy recovery at such high temperature allows supply of all process energy requirements and for supply of about 1.5 tonnes of export steam per tonne of acid. Alternatively the steam may be converted to electricity. Such a process is especially useful for sites with a large steam consumption because it can decrease investments for steam boilers. The nitric acid concentration is about 60%. The NO_x content in tail-gas may be 50 ppmv or less. More than 100 plants that employ this process are operative in the republics of the CIS and other countries.

The company also offers a dual-pressure process with NSCR or SCR NO_x abatement system.

8.2.7.4 The Weatherly High-Pressure Process – The Weatherly high-pressure process (Figure 8.6) typically operates at about 1.0 MPa pressure for both the ammonia oxidation and absorption steps [16]. The various heat exchangers located from the ammonia oxidizer to the platinum filter are butted against each other to form a compact train and minimize construction costs. Spool pieces are inserted in the train to increase retention time and thereby increase the percentage of NO oxidized to NO_2 at a temperature high enough for economical recovery of the heat of reaction. In the extended recovery option, the upper part of the absorption tower is cooled to about 4°C by using refrigerated potassium carbonate brine as the coolant. The brine may be refrigerated in a low-pressure ammonia vaporizer with the ammonia vapor going to ammonium nitrate production. Alternatively, mechanical refrigeration can be used. With the extended absorption system, the NO_x concentration can be lowered to less than 200 ppmv. The company also offers the alternative of reduction of tail-gas by combustion with fuel gas. The usual nitric acid concentration is 58%-60%.

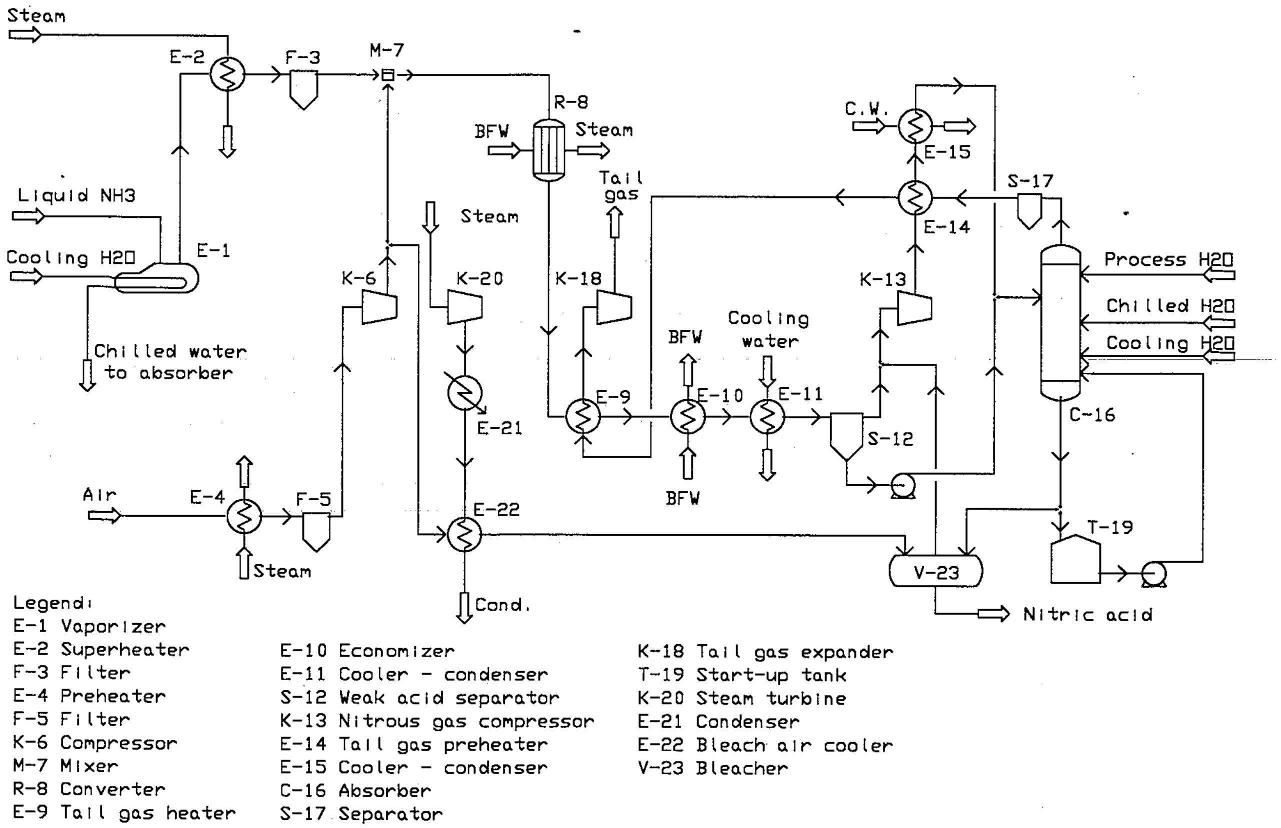


Figure 8.4. The Grand-Paroisse Dual-Pressure Process.

8.2.8 Present Trends and Expected Technology Development

There is little opportunity to improve further the Oswald nitric acid process. The overall efficiency of ammonia conversion into acid is in the range of 94%-96%. The process is self-sufficient in energy supply and can even export steam. Up to 80% of platinum catalyst losses can now be recovered. Capital investments were significantly reduced by the development of high-pressure absorption and with the design of efficient and reliable compressors and expanders. Economies of scale improve little for single-train units with capacities above 1,000 tpd.

The present trends in nitric acid production are as follows:

1. A tendency from low- to medium- or high-pressure processes;
2. Capacities should continue to increase with single-train plants; these plants should produce up to 2,000 tonne of nitric acid per day;
3. Advanced energy recovery and a more efficient use of raw material by using improved methods of calculation are likely to lead to reduced investment costs and thus lower overall production costs [17].

A pattern of incremental improvements in the technology may be expected to continue, but there is little expectation of a significant breakthrough in capital investment and production costs.

Recently, investigations on direct synthesis of nitric oxide in low-temperature plasma were carried out [5]. Two methods were investigated:

- Under high temperatures (2000°-2700°C) in equilibrium plasma [18,19];
- In nonequilibrium plasma at relatively low temperatures.

It was proved that the new process can be realized on a commercial scale. Unfortunately, the consumption of electricity is quite high, and the new process cannot compete with the Oswald process under present prevailing prices of raw materials and utilities.

8.3 Ammonium Nitrate

8.3.1 Introduction

Ammonium nitrate is the most popular form of nitrogen fertilizer in most European countries. In the United States and Canada ammonium nitrate is being slowly

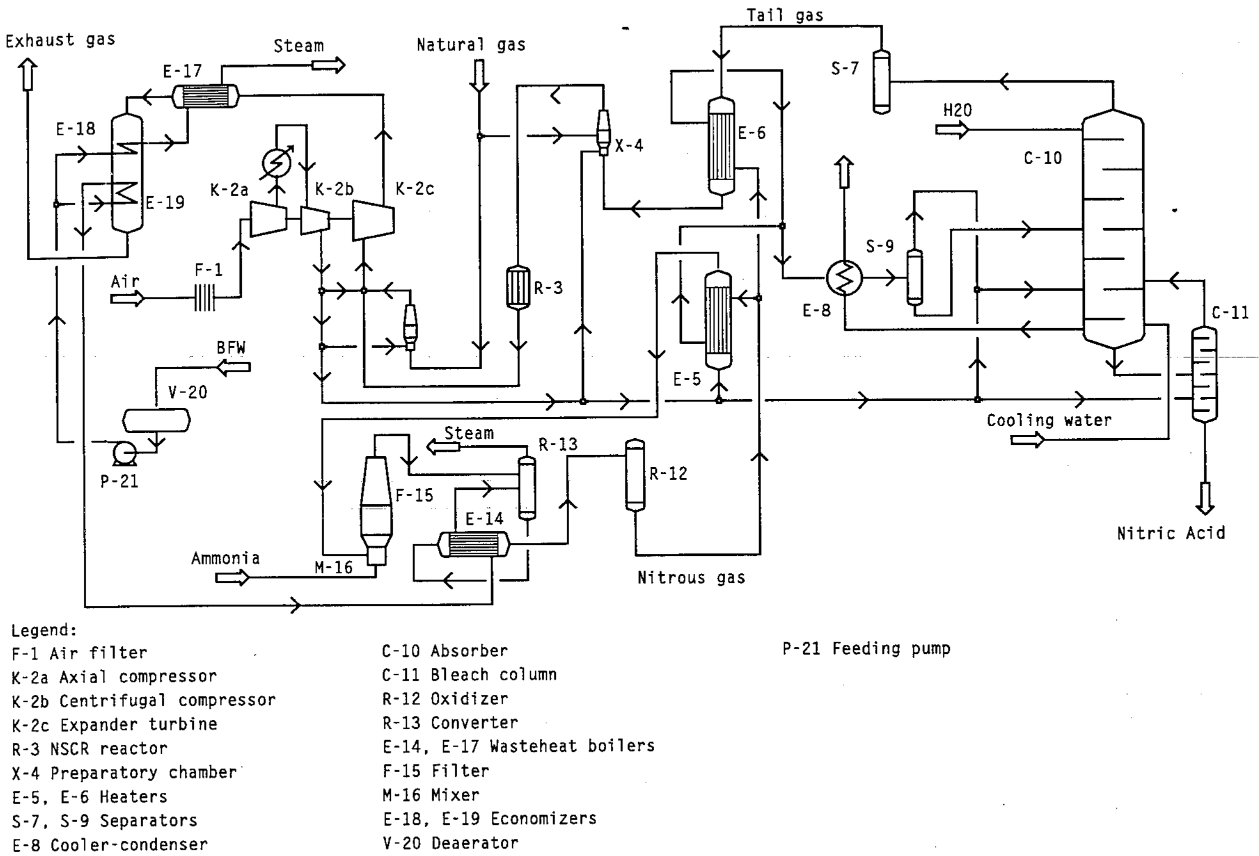


Figure 8.5. GIAP High-Pressure Process.

replaced by anhydrous ammonia and liquid fertilizers. It is rare in the developing countries, where urea dominates the market. It is applied as a straight material or in combination with calcium carbonate, limestone, or dolomite. The combination is called calcium ammonium nitrate (CAN) or ammonium nitrate-limestone (ANL) or various trade names and in compound fertilizers including nitrophosphates. It is also a principal ingredient of most liquid nitrogen fertilizers. The nitrogen in ammonium nitrate is more rapidly available to some crops than urea or ammonium sulfate; most crops take up nitrogen mainly in the nitrate form; thus, ammoniacal nitrogen must be converted to nitrate in the soil before it becomes effective. Many crops respond well to a mixture of ammonium and nitrate nitrogen. Even though the nitrification process is rapid in warm soil, it is slower in cool soil (10°C and below). Urea may cause seedling damage due to volatilization of ammonia, and ammonium sulfate is strongly acid forming. For these and other reasons ammonium nitrate and CAN are effective fertilizers in zones with medium and low temperatures during the cropping period, especially in those with a short vegetation period.

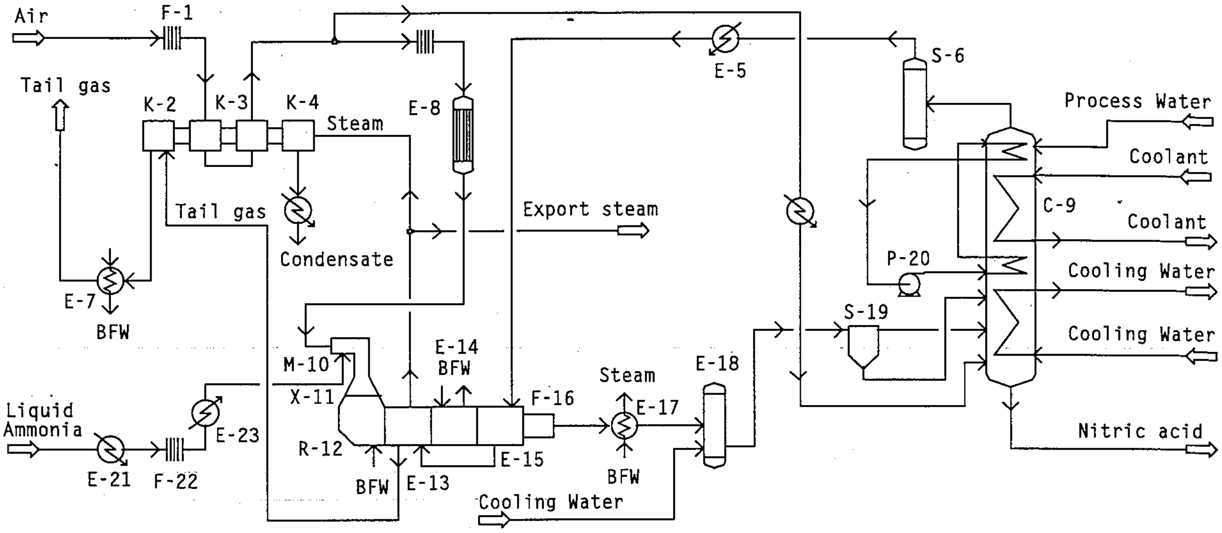
The main disadvantages of ammonium nitrate are as follows:

- It is quite hygroscopic;
- There is some risk of fire or even explosions unless suitable precautions are taken;
- It is less effective for flooded rice than urea or ammoniacal nitrogen fertilizers;
- It is more prone to leaching immediately after application than ammoniacal products.

Although ammonium nitrate is principally used as fertilizer, it also has some industrial uses, notably for production of explosives. Plant capacities for ammonium nitrate or CAN fertilizer production range from 400 to 3,000 tpd.

8.3.2 Ammonium Nitrate Properties

Ammonium nitrate is a white crystalline substance with a nitrogen content of 35% and a density of about 1.725 kg/m^3. The melting points depend on the content of the water, and it is practically impossible to obtain dry



Legend:
F-1 Air filter
K-2 Expander turbine
K-3 Axial centrifugal compressor
K-4 Steam turbine
E-5 Tail gas preheater
S-6 Entrainment separator
E-7 Economizer
E-8 Air heater
C-9 Absorber
M-10 Mixer
X-11 Gauze
R-12 Converter
E-13 Expander gas heater
E-14 Wasteheat boiler
E-15 Gas heater
F-16 Pt/Rh filter
E-17 Wasteheat exchanger
E-18 Cooler-condenser
S-19 Acid separator
P-20 Interchanger pump
E-21 Vaporizer
F-22 Filter
E-23 Superheater

Figure 8.6. The Weatherly High-Pressure Process.

product in the industrial conditions (Table 8.10). The solubility of ammonium nitrate and boiling points of solutions [20] are given in Table 8.11.

In production and storage of ammonium nitrate, transformations of the crystal states that may affect the quality of the product occur. Crystalline states are given in Table 8.12 [21,22]. Critical relative humidities [23] at increasing temperatures are given in Table 8.13.

Some additives such as $Mg(NO_3)_2$, $(NH_4)_2SO_4$, and some others can slightly change the critical relative humidities.

Table 8.10. Melting Points of Ammonium Nitrate

Water Content, % Weight	Melting Point, °C
0	169.6
0.1	167.8
0.2	166.6
0.5	163.2

8.3.3 Commercial Forms of Ammonium Nitrate

A large share of ammonium nitrate is supplied to the domestic and international markets as prilled product although granulated material is preferred in many industrialized countries. The main difference is in the size and strength of the particles. The granules are usually coarser and harder than prills and are more suitable for bulk blending. For industrial use some quantities of crystalline product are produced.

Both primary materials (prilled and granulated) usually incorporate additives (stabilizers) that improve the quality of the product. Prills and granules may be coated with anticaking products. In a number of countries prills or granules are coated with surface-active materials such as amines and others; this process is sometimes called "wet coating." For severe climatic conditions and long-time storage, a "dry coating" by inert material such as kaolin or talcum, in addition to "wet coating," may be used.

When ammonium nitrate is used as straight material, the nitrogen content ranges from 30% to 34.5%. If it is mixed with milled limestone of calcitic or dolomitic type to make CAN, the nitrogen content is usually in the

Table 8.11. Solubility in Water and Boiling Points [20] of Ammonium Nitrate Solutions

Temperature (°C)	Solubility (g/100 g H_2O)	Concentration (%)
Of saturated solution:		
0	119	54.3
20	190	65.5
40	286	74.1
60	421	80.8
80	630	86.3
100	1,024	91.1
150	5,782	98.3
169.6	pure	100.0
At boiling point:		
110	-	51.9
120	-	71.3
130	-	81.4
140	-	87.0
150	-	90.75
160	-	93.4
180	-	95.9
200	-	97.55
220[a]	-	98.9[a]
230[a]	-	100[a]

a. Extrapolated data.

Table 8.12. Crystalline States of Ammonium Nitrate

System	Temperature (°C)	State	Vol. Change (%)
–	>169.6	liquid	-
I	169.6 - 125.2	cubic	+2.1
II	125.2 - 84.2	tetragonal	-1.3
III	84.2 - 32.3	α-rhombic	+3.6
IV	32.3 - (-16.8)	ß-rhombic	-2.9
V	<(-16.8)	tetragonal	-

range of 25%-28%. The most common grades for CAN are 26% N (75% AN) or 27.5% (76.5% AN).

8.3.3.1 Hazards of Ammonium Nitrate and Relevant Regulations – Ammonium nitrate is a strong oxidizer. Under certain conditions (closed volume and elevated pressure, contamination) it can explode. Ammonium nitrate is generally regarded in most countries as posing no unacceptable hazard when specification of the material is fulfilled. Fertilizer-grade ammonium nitrate cannot be exploded by impact, by heat, or by fire alone.

Table 8.13. Critical Relative Humidities (CRH) of Ammonium Nitrate

Temperature (°C)	Vapor Pressure (mm Hg)	CRH
0	3.8	78.0
20	11.0	65.0
30	18.0	58.5
40	29.0	52.5
50	44.0	46.5
60	62.0	41.0

However, explosivity of ammonium nitrate depends on what the material is mixed with, how much carbonaceous material is present, etc. Therefore, some countries prohibit production and application of straight ammonium nitrate. In a majority of countries the detailed specification is regulated by law and the safe handling, transportation, and application of ammonium nitrate are ensured. In Europe the qualities of ammonium nitrate are defined by the regulations of the European Committee No. L-250/7 (23.9.1980) and its complements No. L-38/1 (2.7.1987) and No. L-63/12 (9.3.1988). Table 8.14 gives the European Union's regulations compared with the specifications of The Fertilizer Institute (TFI) in the United States.

In Russia (and probably in other republics of the CIS) the specifications of commercial ammonium nitrate are standardized by the State All-Union Standard GOST 2-85, which is still active. According to this standard two grades of ammonium nitrate are produced: grade A is destined for industrial use and grade B for use as fertilizer. A high-density prilling process is used to produce ammonium nitrate of both grades. The product specifications are shown in Table 8.15.

Compound fertilizers containing ammonium nitrate may be subject to propagated decomposition called "cigar burning," when ignited. Once ignited the decomposition propagates through the mass of material at the rate of 5 cm-50 cm per hour with a temperature in the decomposition zone of 300°-500°C, producing red-brown hazardous fumes. Compound fertilizers with ammonium nitrate, having a content of 4% or more of KCl, are susceptible to this phenomenon. The reaction is inhibited by ammonium phosphate; therefore, NPK grades containing ammonium nitrate and ammonium phosphate are free from this hazard. In addition, hazards

Table 8.14. Specifications of Fertilizer-Grade Ammonium Nitrate

Parameter	European Union	US TFI
Oil retention (five thermocycles 25°-50°C)	<4 weight %	–
Organic matter:		
– product 28.0%-31.5% N	<0.4 weight %	–
– product >31.5% N	<0.2 weight %	<0.2 weight %
pH value of 10% solution	>4.5	>4.0
Fines in product:		
– passing 1-mm screen	<5.0 weight %	–
– passing 0.5-mm screen	<3.0 weight %	
Chlorine	<0.02 weight %	0.15 weight %
Heavy metals	Cu <10 mg/kg	Maximum release of 4.6 ml of H_2 from 50-g sample
Sulfur	–	0.01 weight %

Table 8.15. Ammonium Nitrate Specification in Russia

	Ammonium Nitrate	
Parameters	Grade A	Grade B
Appearance	Prilled product without foreign admixtures	
Nitrogen content		
Calculated as NH_4NO_3, not less than	98%	no limits
Calculated as N, not less than	no limits	34.4
Water content (method of drying), not more than	0.2%-0.3% depending on additives	0.2%-0.3% depending on additives
Content of additives:		
Calcium nitrate and magnesium		
Nitrate calculated as CaO	0.2%-0.5%	0.2%-0.5%
Phosphates calculated as P_2O_5	0.2%-1.2%	0.2%-1.2%
Ammonium sulfate	0.3%-0.7%	0.3%-0.7%
Ammonium sulfate plus phosphate	0.4%-0.6%	0.4%-0.6%
Ability to spill (to disintegrate into prills), not less than	100%	100%
Content of prills 1-4 mm, not less than	no limits	95%
2-3 mm, not less than	no limits	50%

of explosion of ammonium nitrate-containing fertilizers have been acknowledged, and some governments have issued specific regulations (e.g., in the Netherlands). Limits on ammonium nitrate content are given in Table 8.16.

Special requirements may be established for the strength of prills. The strength of ammonium nitrate prills depends very much on the stabilizing additive that is used. The results of tests with three kinds of additives are given in Table 8.17.

8.3.3.2 Product Handling – Ammonium nitrate may be stored in bulk although in most climates this requires air-conditioned facilities. Storage facilities should have adequate ventilation to allow quick dispersion of heat and toxic gases in the event of fire [20,24,25,26, 27,28]. The storage area must be equipped with a high-efficiency sprinkler system. Ammonium nitrate has its own oxygen for burning, and only large amounts of water can extinguish a fire. In most countries the commercial product is bagged in bags that should be "moisture proof"; at least one ply should be impermeable to moisture. If they are properly designed, plastic-film bags or bags with plastic liners are suitable. Bulk shipment is common in some countries using covered, hopper-bottom cars. Before loading, the inside of the vehicle

Table 8.16. Limits of Ammonium Nitrate Content in Compounds

Material Mixed With AN	Maximum Allowable Content of AN in % Weight
Chalk	80
Ammonium sulfate	40-45
DAP	65-70
Calcium phosphate	70
Potassium chloride	70
Potassium sulfate	70

Table 8.17. Static Strength of High-Density Prills [33]

Additives	Static Strength N/Prill (kg/prill)
Sulfate	10 (1.0)
Magnesium	8 (0.8)
Boron/magnesium	12.5 (1.25)

should be thoroughly cleaned. It is important to prevent contamination of ammonium nitrate with organic materials such as grease or other hydrocarbons, chlorates, nitrates, and metal salts (Zn, Cu), which when ignited may support fire. In some countries, modes of transportation are regulated by law; for example, in Russia transportation is regulated by GOST 2-85, whereby only three methods of transportation are allowed: in bags (commonly 50 kg); in large soft containers; and in bulk, closed carriers [5].

8.3.4 Process Chemistry

The process chemistry is simple, and the only reaction observed is the reaction between anhydrous ammonia and nitric acid:

$$NH_3(g) + HNO_3\,(aq) \rightarrow NH_4NO_3 + 145\ \text{kJ/gmol}$$

The production is highly exothermic and proceeds with high speed. The concentration of the nitric acid used in the process may vary from 45% to 60%, depending on the process. The concentration of the resulting solution depends on the concentration of the nitric acid and temperature of the process. Except for the United States, where a large amount of ammonium nitrate is used in liquid form, most ammonium nitrate solution is concentrated and processed into prills or granules.

Prilling and granulation from melt must take into consideration changes in the crystal phase and specific volume. This is shown in Figure 8.7.

According to research results [29] harder prills or granules can be produced when, during ammonium nitrate cooling, the changes in crystal phase occur with minimal volume and structural changes, e.g., when crystals of system II are transformed directly into crystals of system IV. This type of transformation is possible when the moisture content of the melt is less than 0.1% or special inorganic salts that prevent formation of phase III are added.

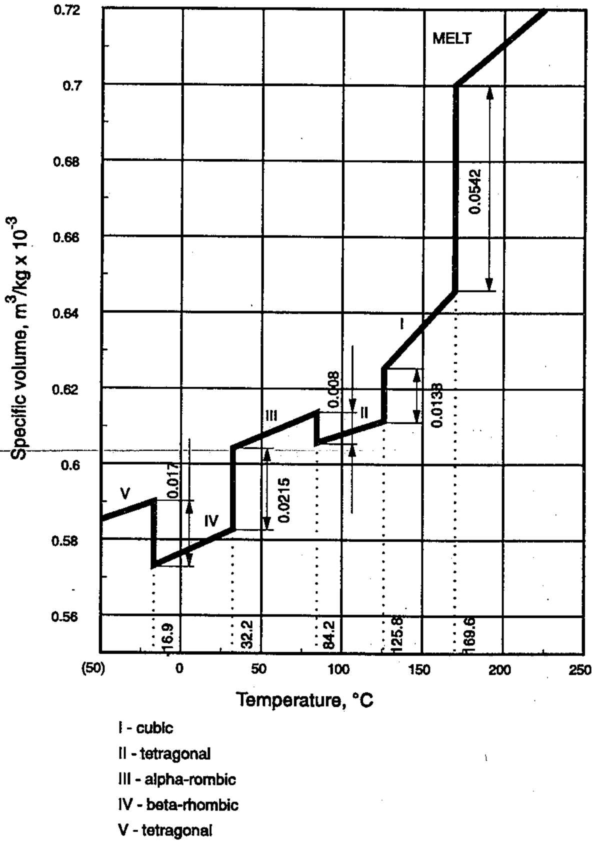


Figure 8.7. Specific Volume Changes of Crystalline Ammonium Nitrate.

Changes in crystal specific volume may cause the granules to degrade during storage or handling. This is especially important in subtropical countries where the phase-change temperature of 32.2°C can be passed through often with a specific volume change of 0.0215 m³/tonne, leading to disintegration of the prills or granules.

Ammonium nitrate is a strong oxidizer that can support combustion. Dry ammonium nitrate should not be heated; the following reactions occur when it is heated:

Between the melting point (170°C) and about 250°C, the following exothermic reaction predominates [29].

$$NH_4NO_3 \rightarrow NO_2 + 2H_2O + 37 \text{ kJ/gmol}$$

Above 250°C, nitric acid and ammonia may be formed:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 - 174 \text{ kJ/gmol}$$

Since this reaction is endothermic, the decomposition temperature can be self-limiting if the NO_2 formed in the previous reaction escapes freely. If not, another, highly exothermic reaction can occur:

$$NH_4NO_3 + 2NO_2 \rightarrow N_2 + 2HNO_3 + H_2O + 232 \text{ kJ/gmol}$$

Therefore, even at low temperature when small amounts of nitric dioxide are present, the reaction can proceed.

The explosive decomposition of ammonium nitrate can be described by the following reaction:

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O + 118 \text{ kJ/gmol}$$

8.3.5 Production Technology

Solid ammonium nitrate is produced in the form of prills, granules, or crystals. Large tonnages of ammonium nitrate are made in the form of highly concentrated (80%-90%) hot solutions that are used for the production of urea-ammonium nitrate solutions (Chapter 10) or are further concentrated for granulation or prilling.

Ammonium nitrate production is composed of the following process sections:

- Neutralization.
- Concentration.
- Finishing.
- Process condensate treatment.
- Vapor treatment with heat recovery.

8.3.5.1 Neutralization – When sufficient steam to operate the plant is readily available from byproduct or other low-cost sources, the use of an atmospheric type of neutralizer may be preferable since such units are relatively low in capital costs and simple to operate. Alternatively, most or all of the steam needed to preheat the feeds and to concentrate the ammonium nitrate solution can be generated by neutralizing acids containing more than 50% HNO_3 in a unit of the pressure type. (By using a 64% acid, about 1 tonne of steam can be produced for each tonne of ammonia neutralized.) In some plants, especially those designed to make a crystalline product, neutralizations are performed under vacuum in equipment similar to that used for ammonium sulfate manufacture.

In pressure-neutralized processes, the neutralizer usually operates at 4-5 atm and 175°-180°C. Nitric acid is fed to the neutralizer at a usual concentration range of 50%-60%. In some cases it may be preheated with byproduct steam. Ammonia is fed to the neutralizer in gaseous form. If it is available in liquid form, it is vaporized in a heat exchanger by steam or air. If air is used the cooled air may be used to cool the prilled or granulated ammonium nitrate product. The neutralizer may be operated at a low pH (3-4) to avoid ammonia loss, and more ammonia may be added later to adjust the pH to 7. The concentration of the solution from the neutralizer is usually in the range of 80%-87% ammonium nitrate. It is evaporated further by using steam from the neutralizer to a concentration of 94%-98%. In many plants, a final evaporator-concentrator is used to increase the solution concentration to 99.5%-99.8%.

In the case of atmospheric pressure neutralization, the temperature in the neutralizer is lower (about 145°C), and the steam generated is at a lower temperature and pressure. The waste steam can be used to vaporize ammonia or to evaporate the ammonium nitrate solution in a vacuum evaporator. Depending on the efficiency of utilization, the heat of reaction, the nitric acid concentration, and other factors, the net steam requirement may range from 0.0 to 0.5 tonne/tonne of AN; in some cases a small surplus of steam may be available for export [30,31].

8.3.5.2 Concentration, Vapor Treatment, and Stabilizing Agents – Practically all types of evaporators and separators are used. Examples are as follows:

- Natural circulation system.
- Falling film (under vacuum or air-swept).
- Forced circulation.

In vapor treatment the tendency is toward well-designed scrubbing columns, either packed columns for the recovery of ammonium nitrate and ammonia, or low pressure-drop trays for the recovery of ammonium nitrate and nitric acid [32,33,34,35]. For process condensate treatment, the ion-exchange process [36] is also considered to be an effective and economical method.

Most fertilizer-grade ammonium nitrate is treated with inorganic stabilizers to retard the 32°C crystal transition and improve storage properties. The most popular salt used to prevent disintegration from the crystal phase change is magnesium nitrate. It is added as a solution to the hot ammonium nitrate solution prior to final concentration or in the form of the dry oxide (MgO) to the melt just before prilling. Final concentrations in the ammonium nitrate product are up to about 1.5% magnesium nitrate or 0.4% as MgO.

Stabilization against thermal disintegration does not prevent caking but does reduce dust formation. The product remains hygroscopic, and caking is best prevented by protecting the product from direct contact with ambient air. For this aim the prills and granules are also coated with very small amounts of anticaking materials such as oil/amine mixtures. Some other materials are used as well.

Magnesium nitrate works only when "melt granulation" or high-density prilling is done; i.e., the melt concentration is about 99.5% weight or higher as for:

- High-density prilling.
- ICI-Nitram process [37].
- NH-pan granulation [38].
- Hydro Agri Fluid Bed granulation [39].

In fluid bed granulation the feed melt concentration is 97%, but the product leaving the granulator has only 0.25% moisture. The water content of the solidifying melt must be significantly lower than the possible water of hydration of the added magnesium nitrate ($Mg(NO_3)_2 \bullet 6 - 7\ H_2O$). The additive thus serves as an internal desiccant agent and shifts the 32°C crystal transition point to about 45°C.

Salts used for other finishing processes including "solution granulation," where the concentration ranges from 93% to 97%, are aluminum and iron sulfates [40,41]. The addition of ammonium sulfate alone increases the hardness. In some countries mixtures of either calcium nitrate and magnesium nitrate or ammonium sulfate and ammonium phosphate are commonly used. An effective but more expensive stabilizing agent is the mixture of boric acid, diammonium phosphate, and ammonium sulfate called "Permalene-34." This additive eliminates the transition point of 84°C and shifts the 32°C one to 43°C [42,43]. According to Olevsky [44,45] the static strength of high-density prills depends considerably on the chemical composition of the stabilizing agents.

8.3.5.3 Finishing Processes – Several finishing processes have been used including graining, flaking, granulation, crystallization, and prilling. In low-density prilling the ammonium nitrate solution is fed to the prill tower at about 95% concentration, and the resulting prills are dried and cooled. The prills are somewhat porous and may have an apparent specific gravity as low as 1.29 compared with 1.65 for high-density prills. Low-density prilling is used to produce ammonium nitrate for use as a blasting agent. A porous prill that will absorb oil is preferred for this use. GIAP has improved this process using special additives that promote the formation of pores in the prills.

The high-density prilling process, using 99+% solution concentration, is used in many plants making straight ammonium nitrate for fertilizer use. High-density prilling requires expensive fume abatement equipment and has low flexibility for production of different N-content products. In addition, the product size is limited and the product is less hard. Capital costs and process requirements for a high-density prilling plant are given in Table 8.18.

Table 8.18. Ammonium Nitrate Prilling Process Requirements

Product: Ammonium nitrate
Capacity: 1,400 tpd
Capacity utilization: 90%

Annual production: 415,800 tpy

Process: High-density prilling
Investment cost:
– battery limits, US $28 million
– storage, US $7 million
Working capital, US $3.6 million

Cost Components	Unit	Unit/t
Raw materials		
Ammonia	t	0.208
Nitric acid (as 100%)	t	0.774
Stabilizer	US $	1.2
Utilities:		
Electrical energy	kWh	26.2
Process water	m^3	0.1
Cooling water	m^3	1.1
Steam	t	0.35
Labor	workhours	0.15

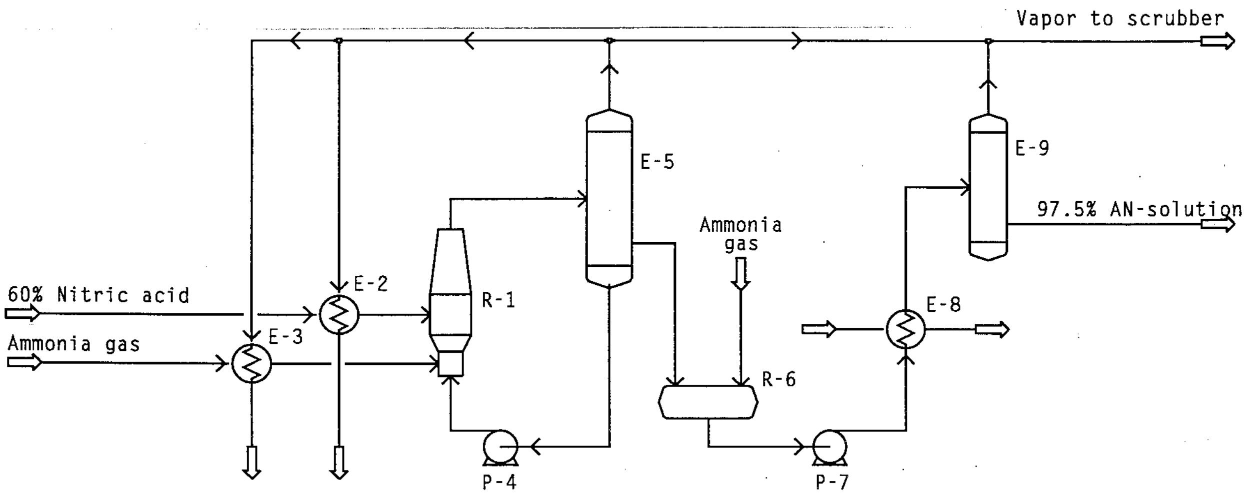
Granulation processes have an advantage over prilling regarding the choice of particle size range of the product. The most widely used granulation methods include rotary pan, rotary drum, and fluid-bed processes.

8.3.6 Industrial Neutralization Processes

8.3.6.1 Uhde Neutralization Under Vacuum or Atmospheric Pressure – This system has the lowest investment cost. The process is shown in Figure 8.8. The reactor is slightly pressurized to prevent ammonium nitrate solution from boiling since this impedes the absorption of ammonia. After it is heated by the reaction, the circulated ammonium nitrate solution is fed via a restriction orifice to the flash evaporator where part of the water is evaporated and the solution is cooled down. By using feed acid at an adequate concentration and preheating the feedstock, the ammonium nitrate solution may reach a concentration of about 95%. The neutralization pressure ranges between 0.03 MPa and 0.12 MPa and the reaction temperature, 130° to 145°C; thus, all of the equipment will be of normal stainless steel (304L). However, the concentration of the ammonium nitrate is slightly low for going directly to the finishing process, and a small final evaporator is needed. The process parameters are given in Table 8.19.

8.3.6.2 Uhde Neutralization Under 0.2-0.25 MPa Pressure – This process was developed to balance the heat requirements but still operate in normal stainless steel equipment. The heat of neutralization is used in a heat exchanger to concentrate ammonium nitrate solution recycled from the flash evaporator. The heat exchanger after flashing can act as a condenser or reboiler. In the latter case, a steam of pressure of 0.4 MPa is produced. The steam from the flash evaporator is condensed, and the AN solution is heated. The process is carried out at 0.2-0.25 MPa pressure and is shown in Figure 8.9. The process parameters are given in Table 8.20.

8.3.6.3 Hydro Agri Neutralization Under 0.4-0.5 MPa Pressure – Neutralization is carried out at 0.4-0.5 MPa, but the operating temperatures (175°-185°C) require highly resistant materials (special low carbon 304L and titanium). The process flowsheet is shown in Figure 8.10. The heat of reaction is used for concentrating the AN solution to 95% and production of steam for export.



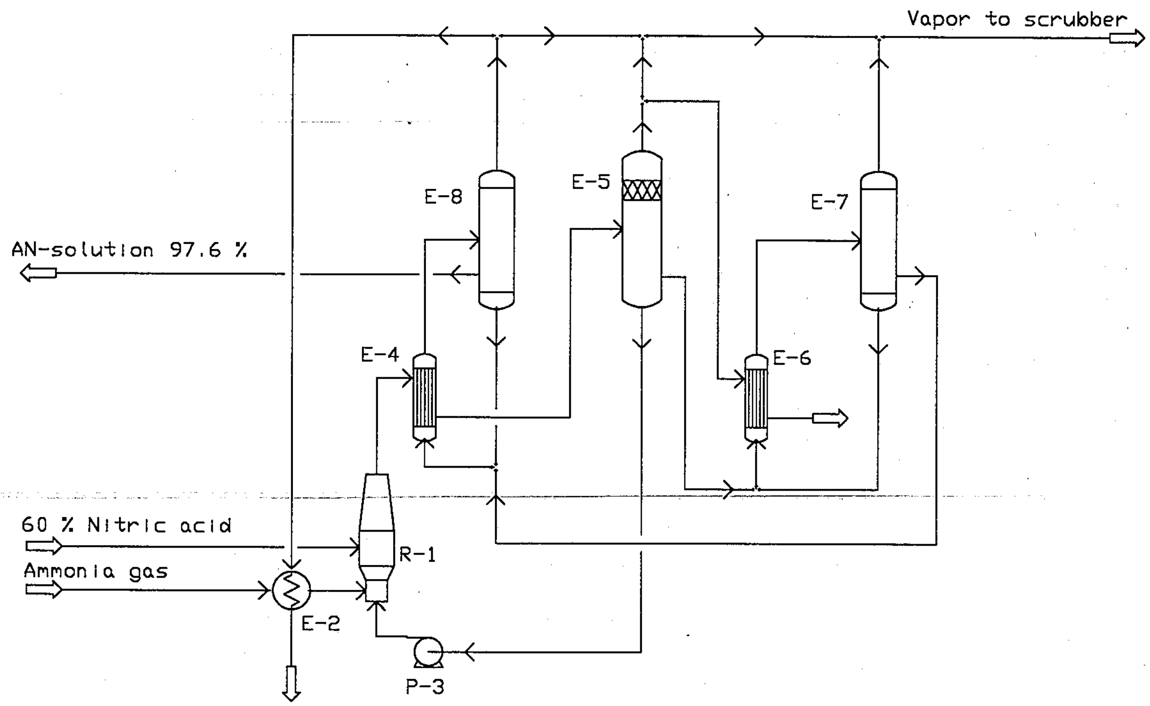
Legend:
R-1 Reactor
E-2 Nitric acid Preheater
E-3 Ammonia Preheater
P-4 Circulating pump
E-5 Flash evaporator
R-6 Neutralizer
P-7 AN-pump
E-8 Reboiler
E-9 Flash evaporator

Figure 8.8. Uhde Neutralization Process Under Vacuum or Atmospheric Pressure.

Table 8.19. Uhde Neutralization Process Parameters

Flashing Pressure (MPa)	NH$_3$ (kg/t AN)	HNO$_3$ 100 % (kg/t AN)	Concentration After Neutralization (%)	Final Concentration (%)	Steam Consumption 1 MPa (kg/t AN)	Cooling Water Consumption (m^3/t AN)	Electric Power Consumption (kWh/t AN)
0.05	213	789	92.5	97	80	28.5	3.5
0.1	213	789	90.0	97	90	5[a]	3.5

a. Without scrubbing.

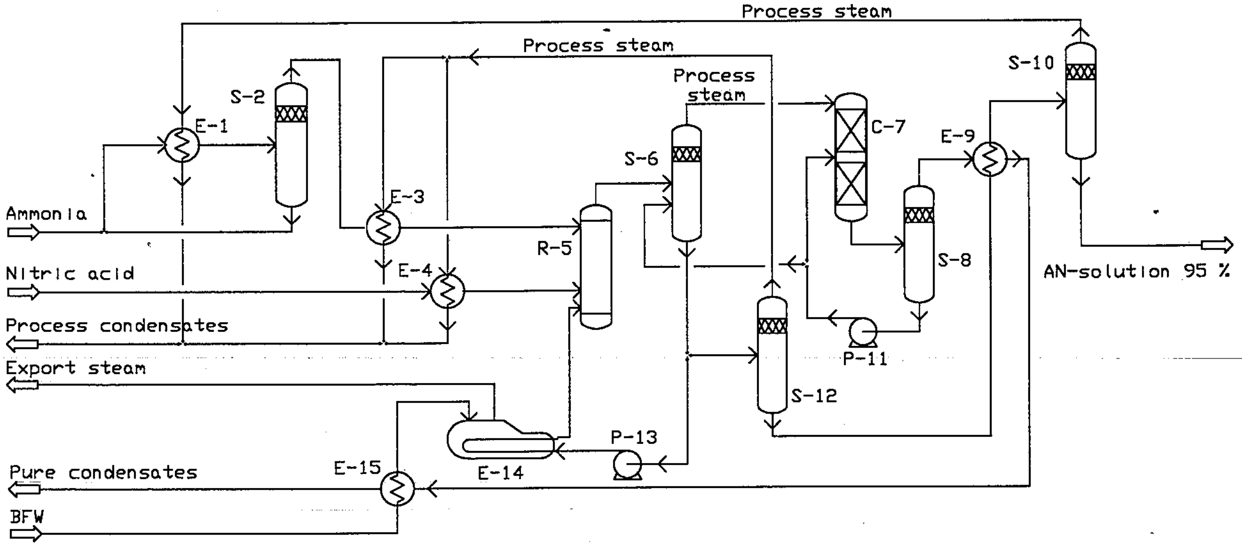


Legend:
R-1 Reactor
E-2 Ammonia preheater
P-3 Circulating pump
E-4 Heat exchanger
E-5, E-7, E-8 Flash evaporators
E-6 Reboiler

Figure 8.9. Uhde LP Neutralization Process With 0.4 MPa Steam Production.

Table 8.20. Uhde Pressure Neutralization Process Parameters

Flashing Pressure (MPa)	NH$_3$ (kg/t AN)	HNO$_3$ 100% (kg/t AN)	Final Concentration (%)	Steam Generation 0.45 MPa (kg/t AN)	Steam Consumption 1 MPa kg/t AN	Cooling Water Consumption (m^3/t AN)	Electric Power Consumption (kWh/t AN)
0.2	213	789	97	240	98	19.2	3.5
0.35	213	789	97	173	55	17.5	3.5



Legend:
E-1, E-3, E-4, E-9, E-15 Heat exchangers
S-2, S-6, S-8, S-12 Separators
R-5 Converter
C-7 Condensing column
S-10 AN-solution separator
P-11, P-13 Pumps
E-14 Utility boiler

Figure 8.10. Hydro Agri Medium-Pressure Neutralization Process.

8.3.6.4 The CARNIT Neutralization at 0.7-0.8 MPa – The CARNIT process (Kemira, S.A., Belgium) operates at 185°C at the reactor output pressure of 0.75 MPa.

The neutralization is carried out in two steps:

- Alkaline, where the low carbon stainless steel can be applied.
- Acidic, where the titanium reactor is installed.

The alkaline hot solution passes through a steam boiler and falling film evaporator made of low carbon stainless steel. Concentrated solution is recycled to the second reactor where additional nitric acid is added before flashing and scrubbing (Figure 8.11). The parameters of the process are given in Table 8.21.

8.3.6.5 The Pipe Reactor Neutralization (AZF) – In the AZF-Grand Paroisse process (Figure 8.12) the neutralization is carried out in a pipe reactor using gaseous ammonia and preheated nitric acid to give an ammonium nitrate melt of up to 97% concentration directly. The evolved steam is used to evaporate and superheat the feed ammonia and preheat the acid. The balance of the steam is condensed. The ammonia and acid, at pressure, are mixed at high velocity in the pipe reactor and are neutralized at a generated temperature of up to 200°C. The solution flashes into the separator operating near atmospheric pressure, and the resulting steam passes overhead directly to the ammonia evaporator or alternatively to be scrubbed with dilute AN solution to reduce ammonia and AN in the downstream condensates. Concentrated 95% - 97% AN solution overflows from the tank to the pump tank. If the AN solution is less than 96%, it is first concentrated in a falling film evaporator. The process parameters are given in Table 8.22.

8.3.7 Industrial Finishing Processes

8.3.7.1 The AZF-Grand Paroisse Prilling Process – The AZF-Grand Paroisse prilling process for fertilizer or industrial grade is shown in Figure 8.13. The ammonium nitrate solution from the pipe reactor neutralization step is first concentrated to 99.8% in an air-swept falling film evaporator, with steam condensing in the shell. If porous AN prills suitable for industrial explosives are to be made, then 95% solution is pumped directly to the mixing tank for redissolving recycled off-specification material. The solution concentration and pH are controlled by adding scrubbing liquor and gaseous ammonia respectively. The solution is pumped through sprays arranged in the top of the prilling tower. Fans located at the top ensure a countercurrent flow of cooling air against the falling droplets. Various options are available to clean the air before they are discharged

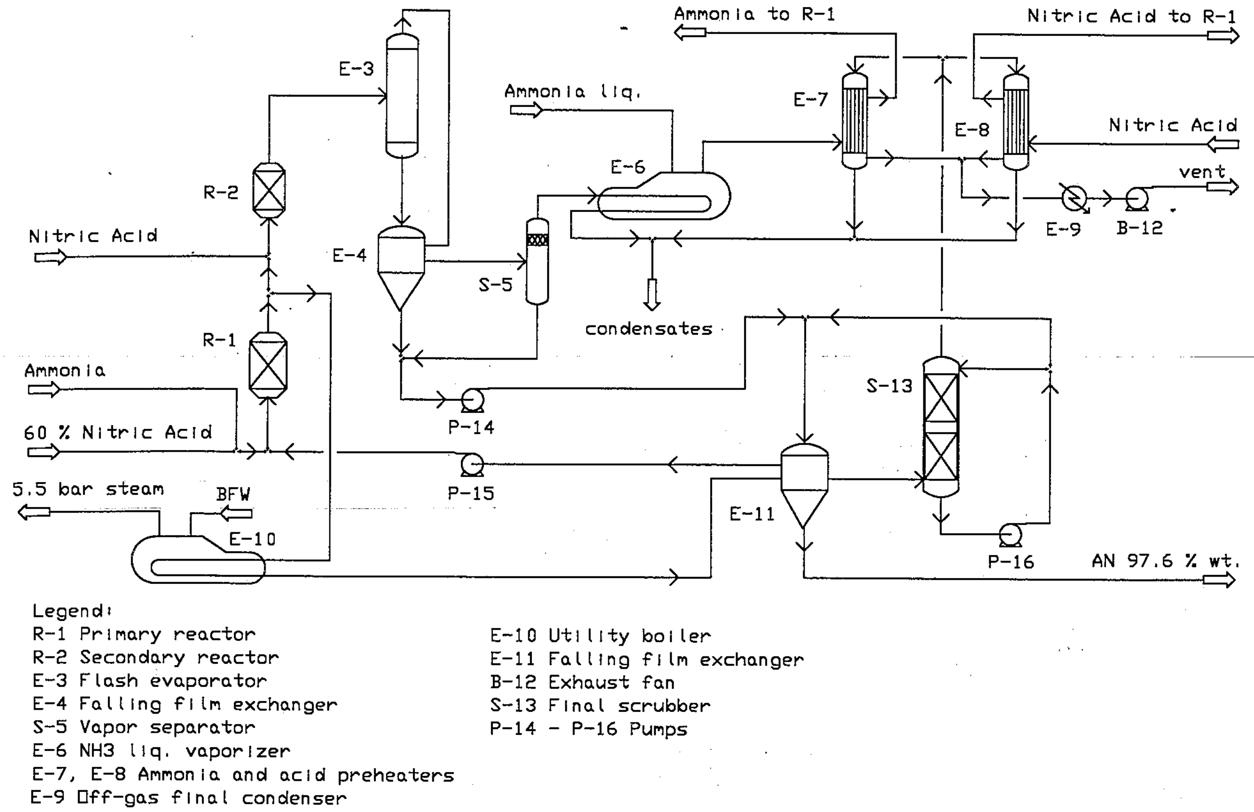


Figure 8.11. CARNIT Process Flowsheet.

Table 8.21. CARNIT Process Parameters

Parameter	Concentration (%)	Temperature (°C)	Pressure (MPa)
Feed			
HNO_3 liquid	60	30	0.95
NH_3 gas	100	30	1.1
Reactor input,			
HNO_3 liquid	60	65	0.9
NH_3 gas	100	65	0.95
Recycle solution	65.6	160	0.8
Reactor output,			
AN solution	65.6	185	0.75
Concentration section,			
AN solution from E-4	83-84	80-82	0.018
Product,			
AN solution from E-11	97.5	155	0.4

Flashing Pressure (MPa)	NH_3 (kg/t AN)	HNO_3 100% (kg/t AN)	Final AN Concentration (%)	Steam Generation 0.6 MPa (kg/t AN)	BFW (kg/t AN)	Cooling Water Consumption (m^3/t AN)	Electric Power Consumption (kWh/t AN)
0.018	212.5	787.5	97.5	128	133	11	1.85

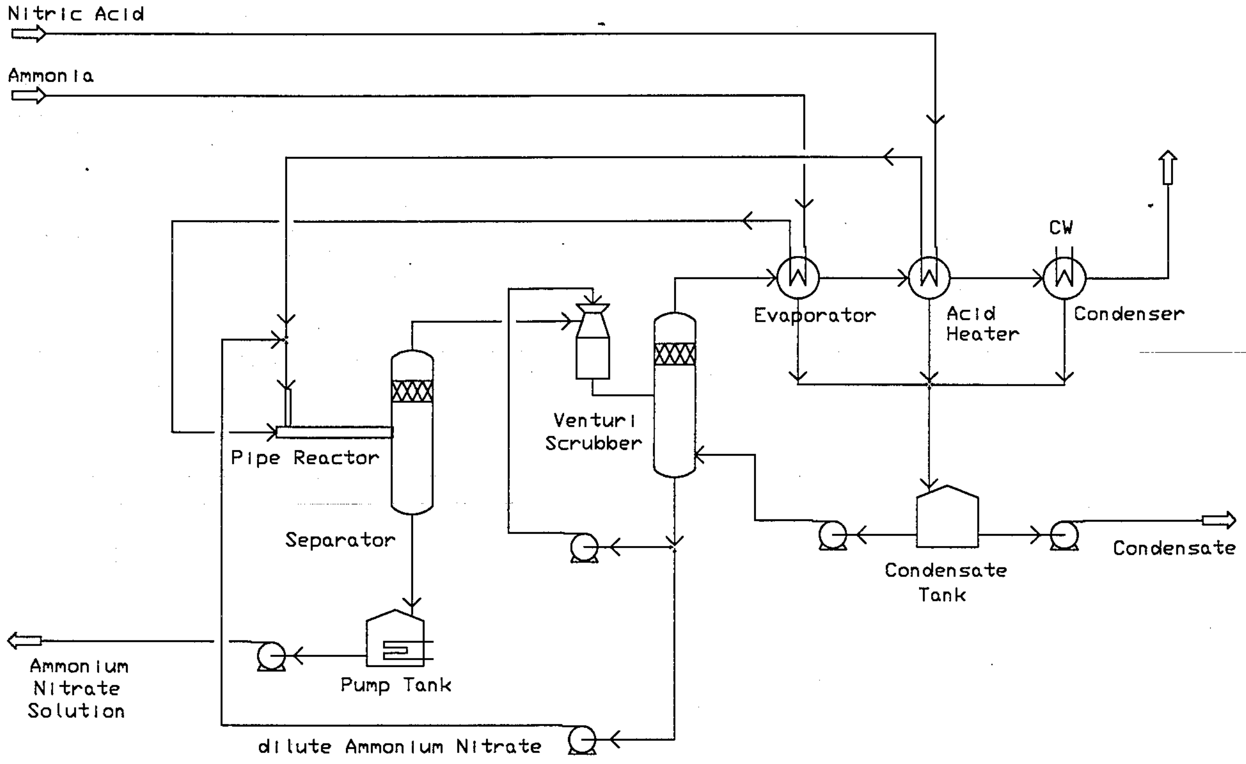


Figure 8.12. AZF Pipe Reactor Neutralization.

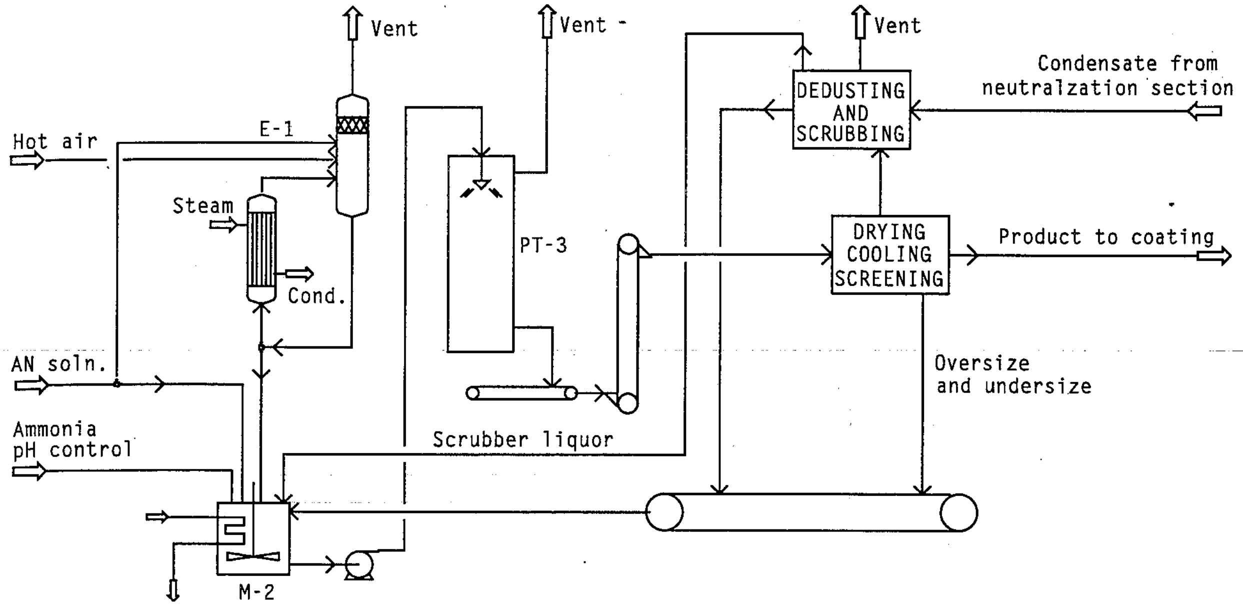
Table 8.22. Parameters of the AZF Pipe Reactor Process

Parameter	Concentration (%)	Temperature (°C)	Pressure (MPa)
Reactor input,			
HNO_3 liquid	51	80	0.6
NH_3 gas	100	160	0.6
Separator,			
AN solution	73	170	0.4
Concentrator,			
AN solution	95	132	0.03
Product,			
AN solution	97.5	155	0.04

to the atmosphere. The prills are collected at the bottom for discharge to the drying, cooling, and screening section. Recently (1990) the process was installed by GP-AZF in Mazingarbe, France, with a capacity of 500 tpd.

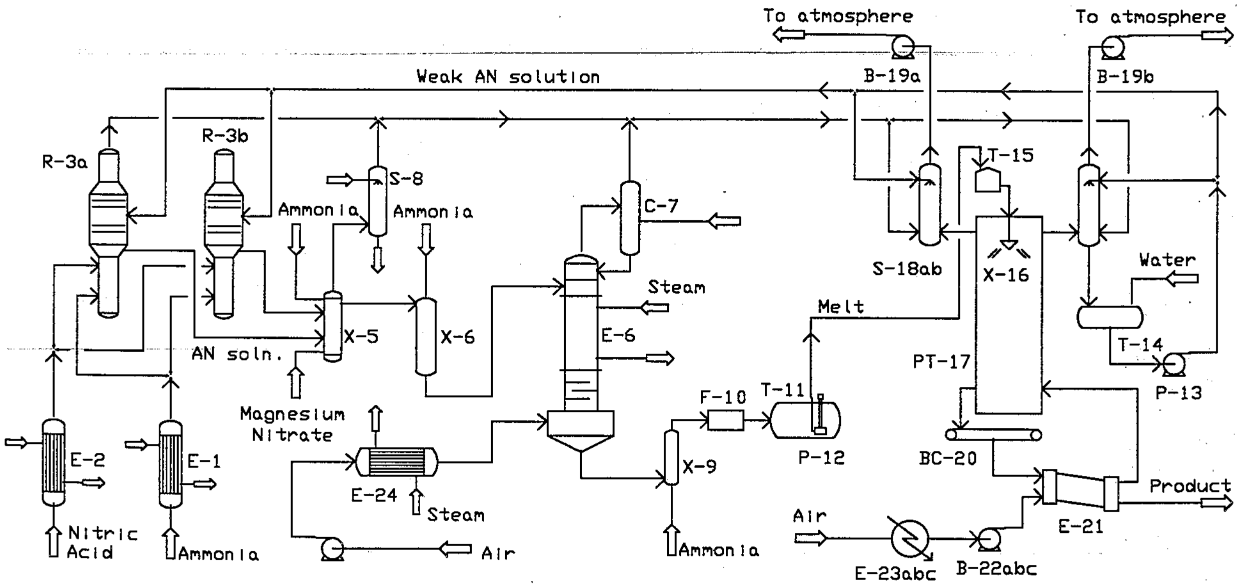
Some other companies, for instance, Imperial Chemicals Industries (ICI), have also offered high-density prilling processes. However, the main European producers of high-density prills are Russia and other republics of the CIS countries. In the CIS all ammonium nitrate fertilizer plants use the high-density prilling process.

8.3.7.2 GIAP Neutralization/Prilling Technology – Figure 8.14 presents a simplified flow diagram of



Legend:
E-1 Evaporator
M-2 Mixing tank
PT-3 Prilling tower

Figure 8.13. The AZF-Grand Paroisse Prilling Process.



Legend:
E-1, E-2 Preheaters of Ammonia and Nitric Acid
R-3a, R-3b Neutralizers
X4, X5, X9 - pH Adjusters
E-6 Final evaporator
C-7 Washer of steam-air mixture
S-8, S-18ab Scrubbers
F-10 Filter
T-11, T-15 Tanks for melt
P-12, P-13 Pumps
T-14 Tank for AN solution
X-16 Acoustic spray head
PT-17 Prill tower
B-19a, B-19b, B-22abc Fans
BC-20 Belt conveyor
E-21 Fluidized bed cooler
E-23abc, E-24 Air heaters

Figure 8.14. GIAP High-Density Prilling Process.

the GIAP high-density prilling process. A portion of the waste steam from the neutralizer is used to preheat the nitric acid to 70°-90°C; the remainder of the steam is fed to the prill tower air scrubber. The gaseous ammonia is preheated by a portion of the waste steam to 160°C. The concentration of the solution from the atmospheric-pressure neutralizer is as high as 89%-92%. The solution is further evaporated to a concentration of 99.7%-99.8% in the final evaporator and is fed to the spray heads of special design to form "uniform" ("monodispersion") prills. On Figure 8.14, item X-16 is a so-called "acoustic" spray head installed in the upper part of prill towers of many CIS plants. Several other designs of "monodispersion" spray heads were tried and are used at some plants. Such spray heads in conjunction with a fluidized cooling bed can provide up to 85% prills of 2- to 3-mm diameter. There is a choice of alternative stabilizers added to the AN solution before prilling. The prills are conditioned prior to bagging.

A distinguishing feature of this process is its simple operation and high reliability because most equipment, except for pumps and fans, is static and lacks moving parts. The high quality of the product (up to 85% of 2-3 mm prills) allows it to be bagged without screening. The product is screened only when it is sent to the adjacent warehouse for lengthy bulk storage [44].

The process has been operated at many CIS sites, for example, in Dorogobuj, Novgorod, Kirovo-Chepetsk, and others at capacities of up to 1,500 tpd [3].

The company also offers a proprietary low-emission prilling process with a closed circuit for prill tower cooling air. An original method for flow of cooling air through the system (without fans) is used in that process.

8.3.7.3 Granulation Processes – Prilling has the disadvantages of difficult emission control, limited product size, and lower product hardness. Granulation processes are flexible and allow easier emission control. Granulation plants can produce other products, for example, calcium nitrate (CN), ammonium nitrate sulfate (ANS), and NPKs. Granulation gives a coarser product than prilling, thereby minimizing segregation of bulk-blended fertilizers.

8.3.7.4 Production of Straight Granulated Ammonium Nitrate – Products with nitrogen contents in the range of 30%-34.5% are classified as straight ammonium nitrate. The following granulation processes are offered for straight ammonium nitrate production:

- Cold spherodizers
- Drum granulation
- Pugmill
- Pan granulation
- Fluid bed granulation
- Fluidized drum granulation

These processes are used for products containing up to 34.5% N. For products that contain up to 33.5% N, the pugmill, drum and cold spherodizers are used also [30,31]. These processes operate the same way as for CAN. However, the ammonium nitrate melt concentrations (wt. %) are different:

• Drum	96-96.5
• Pugmill	95.5-96
• Pan granulation	99.5
• Fluid bed granulation	99
• Fluidized drum granulation	97.5

With all methods, additives are obligatory for granulation and for improving storage properties. Process requirements for a granulation plant are given in Table 8.23.

Figure 8.15 shows the process flowsheet of a pan granulation plant [38]. Dry recycled material is fed at a controlled rate to the inclined rotating pan granulator. In the granulator a hot melt, which is virtually moisture free, is sprayed onto the moving bed of solids and solidifies on the cool particles. Round granules are formed by agglomeration, and, as their size increases, they move upwards in the rotating pan, finally rolling over the rim. The granulation temperature is controlled by the rate at which solids are fed to the pan. An optimum temperature range for agglomeration, within which a high growth rate of the particles is obtained, is 5°-25°C below the temperature at which the fertilizer melt solidifies. The recycle ratio under these conditions is about 0.5/0.7:1 for ammonium nitrate. Granules leaving the pan are plastic and have a somewhat irregular surface. They enter a polishing drum where they are exposed to mild mechanical forces and smoothed. A certain amount of cooling also occurs. Cooling to the desired product temperature is then performed in normal cooling equipment, such as a fluidized bed or a rotary drum. Depending on the climatic conditions at the plant site and the desired product temperature, the cooling air may be conditioned. Cooled granules are conveyed to a screen. Oversize material from the screen is fed to a crusher and the crushed material, undersize granules, and dust from the cyclones, are recycled to the pan.

Because of the high melt concentration and temperature, a "blue fume" of submicron ammonium nitrate – similar to the fume during prilling of high-density ammonium nitrate – has to be recovered for treatment. However, the air flow from the pan and polishing drum is relatively small. A wet scrubber may be used for

Table 8.23. Ammonium Nitrate Granulation Process Requirements

Product: Ammonium nitrate
Capacity: 1,400 tpd
Capacity utilization: 90%

Annual production: 415,800 tpy

Process: Pipe reactor/drum granulation
Investment cost:
– battery limits, US $31.6 million
– storage, US $7.0 million
Working capital, US $3.6 million

Cost Components	Unit	Unit/t
Raw materials		
Ammonia	t	0.210
Nitric acid (as 100%)	t	0.773
Stabilizer	US $	1.2
Utilities:		
Electrical energy	kWh	31.0
Process water	m^3	0.1
Cooling water	m^3	20.0
Steam	t	0.11
Labor	workhours	0.23

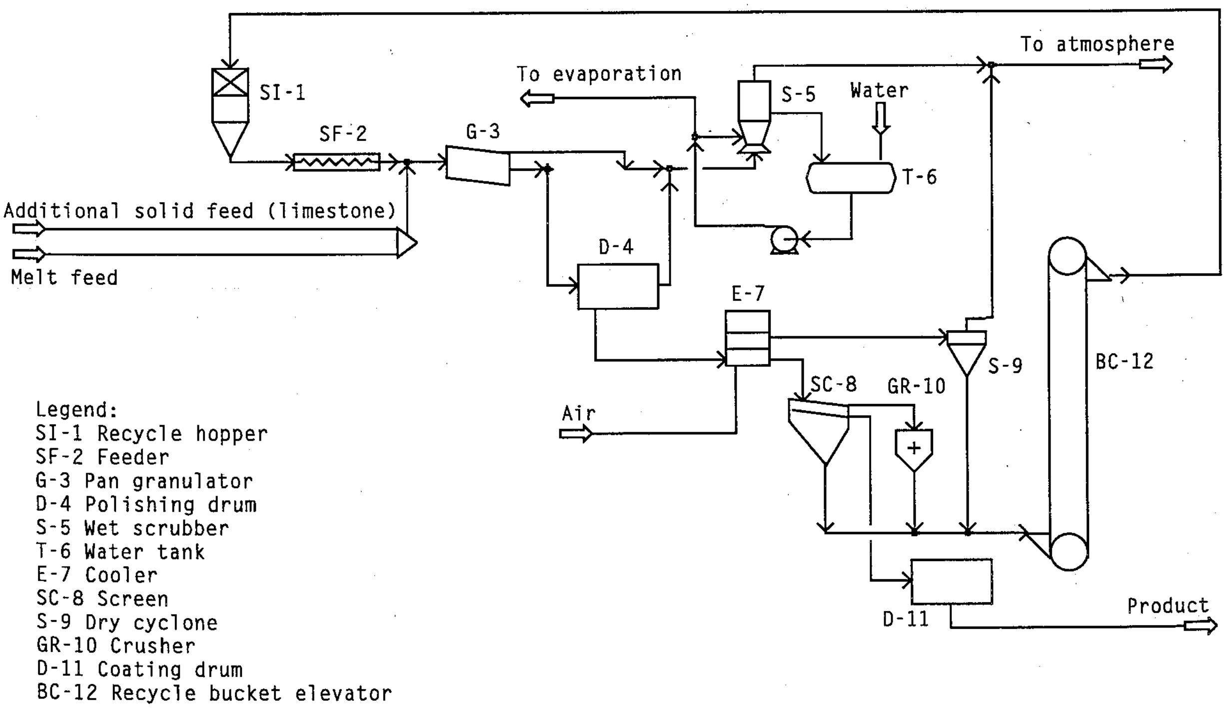


Figure 8.15. The Norsk-Hydro Pan Granulation Plant.

recovery; this is not usually practical in a prilling process with a high rate of air flow from the top of the prilling tower. The air from the product cooler is treated in wet or dry cyclones.

A rather new process is fluidized drum granulation [46], developed by the French company Kaltenbach-Thuring as shown in Figure 8.16 where the principle of the fluidized drum granulator is illustrated, and in Figure 8.17 where the flowsheet is given. The special granulator consists of a rotary drum fitted with lifters and a fluidized bed installed inside the granulator. It is swept with atmospheric or conditioned air according to the desired applications. Seed material fed to the granulator acts as recycle.

The seed material has to undergo a double operation in the granulator:

- Size increase.
- Cooling and/or drying as the case may be.

This is obtained in a series of cycles. Seed material lifted to the upper part of the drum falls to the surface of the fluidized bed. The product is cooled and/or dried on the perforated plate. The plate is inclined so that the product flows down along the plate and falls into the lower part of the drum. During this fall, the curtain is sprayed with melt or slurry. The lifters then deliver the coated granules to the fluid bed. The number of cycles needed to obtain the desired particle size is determined by the residence time in the drum and is controlled by an adjustable overflow threshold.

Various additives such as filler, micronutrients, or other specific additives can be added with the sprayed product. An external fan ensures the evacuation of the air out of the granulator. The heat balance and granulation behavior determine how much recycle material has to be dissolved in the feed ammonium nitrate melt and how much can be recycled as dry matter to the drum.

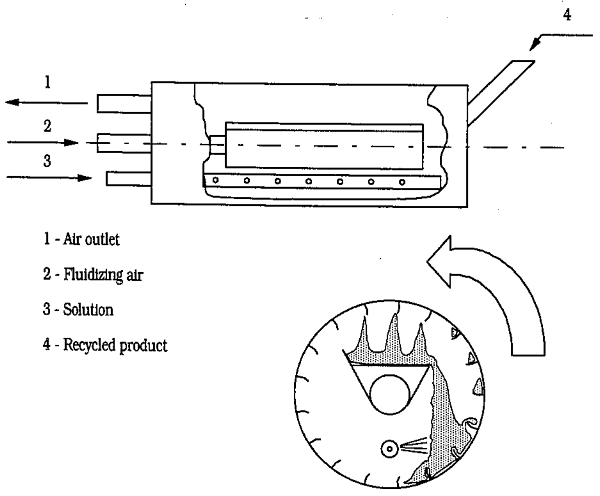


Figure 8.16. The Kaltenbach-Thuring Fluidized Drum Granulator.

8.4 Pollution Control

As in all industrial operations, pollution control requirements for AN and CAN plants have become more stringent in recent years. This has posed a difficult problem for high-density AN prilling because of the large volume of air exhausted from prill towers and because of the very small particle size of the fume in the air. Fuming is much more severe in high-density prilling because the AN melt must be at higher temperature (about 180°C) to keep it from freezing. At this temperature there is an appreciable vapor pressure of $NH_3 + HNO_3$ resulting from dissociation of AN, according to the equation:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$

The dissociation products recombine in the cooler air to form a blue haze consisting of AN particles of submicron size. Particles of this size are difficult to collect, and they present a highly visible and stable haze or "blue fume." The problem is much less serious with low-density prilling because of lower AN solution temperatures. It is less serious in granulation processes because of much smaller volumes of air in contact with hot solution.

A more detailed description of pollution abatement in AN plants is given in Chapter 19.

8.5 Production of Calcium Ammonium Nitrate

In countries where AN is not allowed for application, CAN is a substitute. CAN is preferred over AN for use on acid soils. In the early 1960s, the usual grade of CAN was about 21% N; this grade corresponds to 60% AN; the grade has been increased in most countries to 26% - 27.5% N (about 75% AN).

CAN is produced by mixing concentrated ammonium nitrate solution with ground calcitic or dolomitic limestone, chalk marl, or precipitated calcium carbonate from nitrophosphate production. The mixing should be done quickly to avoid decomposition of the ammonium nitrate:

$$2NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$$

Both technologies – prilling and granulation – can be used for production of CAN. In prilling CAN the AN solution is premixed with the ground limestone immediately before prilling. A rotating perforated bucket is the preferred type of drop-forming instrument. Prill towers

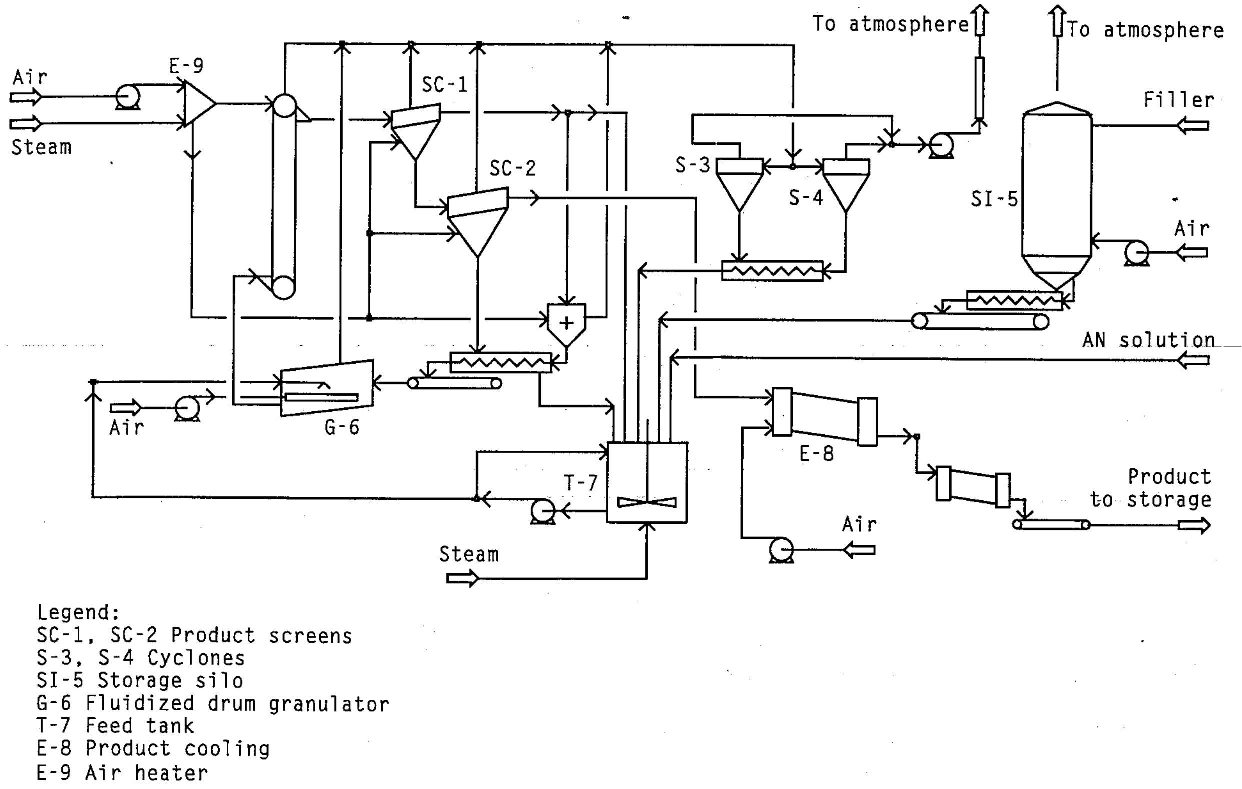


Figure 8.17. The Kaltenbach-Thuring Fluidized Drum Process.

are very high (30 m-50 m) depending on the AN solution concentration and cooling equipment used. Prilled CAN is conditioned with china clay, kieselguhr or calcined Fuller's earth in amounts ranging from 1% to 3%. In the prill tower mean particle size is 2 mm-2.5 mm. To obtain larger product, Hoechst and CDF Chimie (now AZF) have developed combined prilling-granulation technologies. The AZF process is shown in Figure 8.18.

The prilling tower produces only seed prills from about 35% of the ammonium nitrate solution. The prills are directed to the swelling drum where the rest of the AN and calcium carbonate are added to the AN solution. The fines are recycled.

The following granulation processes are available:

- Cold spherodizer.
- Fluid bed.
- Pugmill.
- Drum.

Pan granulation of CAN has proven difficult because the pan is very sensitive to heat and material balance factors. The product shape is irregular. The Spherodizer® processes and all other processes need additives:

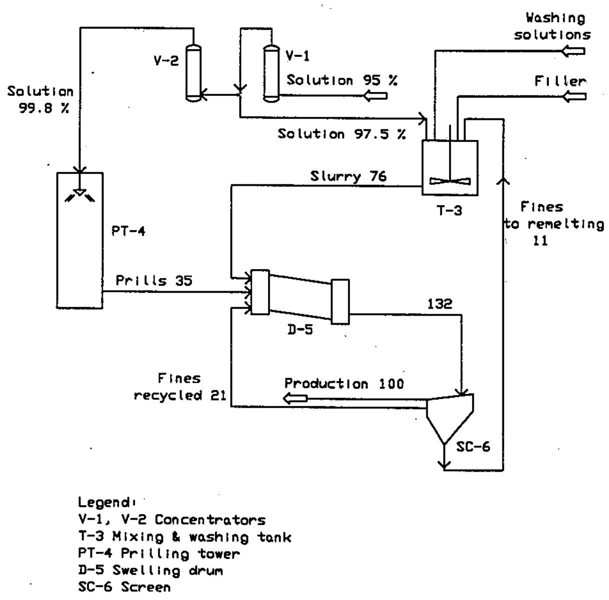


Figure 8.18. Combined Prilling/Granulation Process.

- Spherodizer®: ammonium sulfate, magnesium sulfate;
- Fluid bed: magnesium nitrate.

To improve product hardness, some manufacturers using the pugmill add ammonium sulfate – about 0.3%-0.5% of SO_4.

The melt concentrations are also different. These concentrations are as follows:

- Fluid bed: 98%-99% wt.
- Pugmill: 94.5%-95.5% wt.
- Drum: 93.5%-94.5% wt.

In the Hydro-Agri fluid bed granulation process, dedusting of the airstreams from the granulator and fluidized bed cooler is done by scrubbing with acidified weak AN solution. The scrubbing solution is mixed with the lime/AN mixture prior to final evaporation.

In pugmill granulation (Figure 8.19) [47] the AN melt and the lime are proportioned in ratio control to the pugmill. Dust, undersize product, and crushed oversize are recycled to the pugmill. The fresh, damp granules pass to a drying drum, and the granules are screened hot. For drying, the off-gas from the cooler is used. At full plant load the air heater for the dryer is turned off, and the plant operates autothermally. The drying air is dedusted in dry cyclones; final dedusting is performed in scrubbers. The onsize product is cooled in a fluidized bed cooler with conditioned air. Before storage or bagging the product is coated. Spilled product is returned to the granulation loop.

It should be mentioned that "forest grade" product can be manufactured. The same basic flow diagram is valid for drum granulation.

8.6 Other Nitrogen Compounds Used as Fertilizers

8.6.1 Sodium Nitrate

Before the availability of synthetic ammonia and its derivatives, sodium nitrate of natural origin was the primary source of nitric acid and chemical nitrogen for fertilizer purposes in many countries. Most of this nitrate originated in Chile, where it is found principally in a large ore body nearly 500 miles long and 10-15 miles wide on the eastern part of the Chilean coastal range. Nitrate production remains a primary industry in Chile.

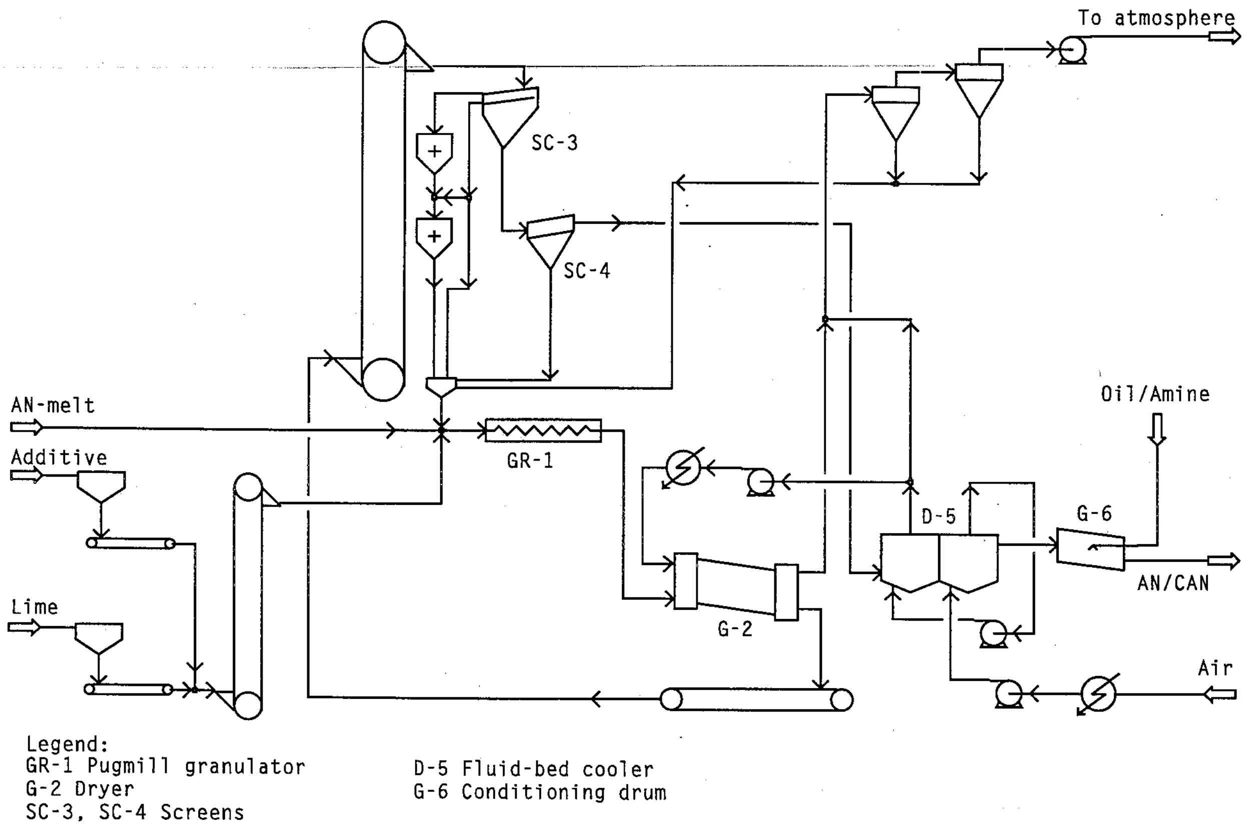


Figure 8.19. AN/CAN Pugmill Granulation Process.

Small deposits occur in other areas, e.g., Africa, Australia, Mexico. Substantial amounts of synthetic sodium nitrate were formerly made in Europe and the United States, but production declined after World War II, and now only insignificant amounts are produced from byproduct sources.

As a fertilizer, sodium nitrate has long been applied as a surface dressing for cotton, tobacco, and some vegetable crops. However, its use as a "straight" nitrogen fertilizer has declined considerably during the past century. For example, in the United Kingdom, some 20,000 tonnes of N was used in the form of sodium nitrate in 1899, but relatively none is used today. As with other nitrates, sodium nitrate is prone to leaching in the soil, but it has the advantage of possessing a metallic cation. Unlike ammonia and its derivatives, including urea, sodium nitrate will not promote cation losses in the soil and lead to unsuspected soil acidity.

Industrial applications include meat preservation, heat treatment of metals, and use as a flux in the ceramic and metallurgical industries.

8.6.1.1 Properties of Sodium Nitrate – Sodium nitrate is a white crystalline substance with an N content of about 16% and a sodium content of about 27%. Some properties of sodium nitrate are given in Table 8.24.

8.6.1.2 Commercial Form – Sodium nitrate is traded as crystalline, prilled or grained material.

Sodium nitrate produced by the Guggenheim method from caliche is usually a crystalline product about 48 mesh in size; the product contains approximately 3.5% of free moisture. Prilled product contains about 98% sodium nitrate and 0.2%-0.3% free moisture, and the size of the product is in the range of 10-20 mesh.

Table 8.24. Properties of Sodium Nitrate

Properties	Value
Solubility g/100 g of water	
– at 0°C	73
– at 10°C	96
– at 30°C	176
– at 100°C	180
Bulk density kg/m^3	
Pellets	1,202
Coarse material	1,282
Fine powder	1,363
Critical relative humidity, %	
– at 20°C	75
– at 30°C	74

Synthetic sodium nitrate produced in the CIS is a crystalline material. Two grades having standard properties and analyses that are produced (GOST-828-77) in CIS countries are listed in Table 8.25.

8.6.1.3 Storage and Transportation – Because sodium nitrate is a toxic product, some precautions (respirator, rubber gloves, and goggles) should be observed when handling it. Sodium nitrate can be stored and shipped in bulk, under conditions of low humidity, but should be packed in moisture-resistant bags when intended for use in damp or tropical climates. In some countries, it is regarded as a potential fire hazard and may necessitate special labeling, insurance, and other precautions as for ammonium nitrate and potassium nitrate. Materials such as bags or timber, when allowed to dry after impregnation with sodium nitrate, may quickly ignite if they are exposed to elevated temperatures and should be destroyed or thoroughly washed and fireproofed.

Table 8.25. Standard Analyses of Sodium Nitrate in the CIS

Content	Top Grade	1st Grade
$NaNO_3$, no less than	99.8%	99.5%
H_2O, no more than	0.5%	1.0%
Insoluble in water materials, no more than	0.03%	0.04%
Chlorides (as NaCl), no more than	0.15%	0.5%
Oxidizable material (as $NaNO_2$), no more than	0.01%	0.015%

8.6.1.4 Raw Materials – Only nitrate ore (caliche) is needed to produce sodium nitrate of natural origin. Caliche varies widely in composition and may range from 80% to virtually zero nitrate content although little high-grade material is available today. A typical analysis of run-of-mine ore might be the following (in percentages):

$NaNO_3$	7-10
NaCl	4-10
Na_2SO_4	10-30
Mg, Ca, K, Br, I_2	2-7
H_2O	1-2
Remainder (Gangue)	41-76

These components are present in the form of complex, mixed sulfates, e.g., darapskite ($NaNO_3 \bullet Na_2SO_4 \bullet H_2O$).

Different chemicals may be used to produce synthetic sodium nitrate: ammonia, soda ash, nitric acid, caustic soda, sodium chloride, and some others. Most of them are used to produce sodium nitrate in minor quantities (sometimes as a byproduct) for industrial applications.

8.6.1.5 Production From Natural Deposits – In Chile, production is based on the Guggenheim method, which permits ores containing under 10% nitrate to be profitably worked. Caliche is mined by open-pit operations, using draglines and power shovels, and is crushed to about 80% between 3/4 and 3/8 inches (1.9-0.95 cm). This product is leached at about 40°C with water in a series of vats; each vat has a capacity of some 10,000 tonnes of crushed ore. The underflow from each vat is heated before passing to the next since sodium nitrate has a negative heat of solution. After extraction and washing are complete, the residue is removed from the vats and transported to a waste dump.

Fine material from the crushers is pulped in a separate system, and the gangue is removed by means of Moore filters. The filtrates are combined with liquor from the leach tanks and are chilled in shell-and-tube units to precipitate crystalline sodium nitrate. Initial cooling is effected by heat-exchange with in-process leach liquor and final chilling by ammonia. The sodium nitrate slurry is dewatered and washed in batch centrifuges to yield a crystalline product. When a grained or prill-type product is required, the centrifuged salt is melted at about 325°C in reverberator furnaces, sprayed in large towers, cooled and screened to yield pellets in the 10- to 20-mesh size range.

8.6.1.6 Synthetic Sodium Nitrate – During the early part of the 20th century, several chemical processes for manufacture of sodium nitrate were developed. All these methods produce a sodium nitrate solution that is concentrated, crystallized, and centrifuged. In some cases, the dewatered and washed salt is dried in a rotary drier prior to screening, storage, and bagging; alternatively, it may be melted and grained or prilled.

Appreciable quantities of sodium nitrate have also been made in the United States by the salt process developed by the Allied Chemical Corporation. In this method (which is believed not to be currently in operation), nitric acid and sodium chloride are reacted to yield sodium nitrate, chlorine, nitrosyl chloride, and water, e.g.:

$$4HNO_3 + 3NaCl \rightarrow 3NaNO_3 + Cl_2 + 2H_2O + NOCl$$

The nitrosyl chloride can be used as an intermediate for other derivatives, or it can be reacted with sodium carbonate to yield additional sodium nitrate, sodium chloride, nitric oxide, and carbon dioxide:

$$3NOCl + 2\,Na_2CO_3 \rightarrow NaNO_3 + 3NaCl + 2NO + 2CO_2$$

The produced salts can be redigested and the nitric oxide used to make additional sodium nitrate (or nitric acid). Alternatively, the nitrosyl chloride can be oxidized to yield dinitrogen tetroxide and chlorine for further use, e.g.:

$$2NOCl + O_2 \rightarrow N_2O_4 + Cl_2$$

In 1934/35 Norsk Hydro developed a process to produce sodium nitrate from calcium nitrate (byproduct of nitrophosphate plants). It is based upon ion exchange, using zeolite exchange resin. The ion exchange takes place between calcium nitrate in water solution and sodium chloride contained in seawater, used as a regeneration agent [20]. Other methods used to produce sodium nitrate in minor quantities include reacting nitric acid with soda ash or caustic soda. Several double-decomposition reactions between various nitrates and alkali salts, for example, ammonium nitrate and caustic soda or common salt, have either been proposed or tested on a small scale.

In the CIS a method of manufacture of sodium nitrate and sodium nitrite from ammonia and sodium carbonate, developed by GIAP, and currently in operation, has been shown on Figure 8.20.

The method is based upon oxidation of ammonia in the presence of platinum catalyst at atmospheric pressure, absorption of the nitrogen oxides produced by water solution of sodium carbonate, and separation of sodium nitrate and sodium nitrite.

The nitrous gas after the burner is cooled in a wasteheat boiler to 210°-270°C and fed to the first absorber where nitrogen oxides are cooled further and partially absorbed by a water solution of sodium carbonate. Two reactions can take place:

$$Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$$

$$Na_2CO_3 + 2NO_2 \rightarrow NaNO_3 + NaNO_2 + CO_2$$

The solution leaving the absorber is fed to the crystallization section. The gas from the absorber is washed, compressed to about 0.4 MPa, and sent to the second absorber where the remaining nitrogen oxides are absorbed under pressure in a countercurrent stream of fresh sodium carbonate solution. The tail-gas from the second absorber is treated in an SCR NO_x abatement unit before it is vented. The solution from the second absorber is added to the circulating solution of the first absorber.

In the crystallization section the solution from the first absorber is filtered and evaporated. Crystalline sodium nitrite is separated from the solution in the primary centrifuge, dried in a rotary drum, and sent to storage. The mother liquor from the primary centrifuge is further

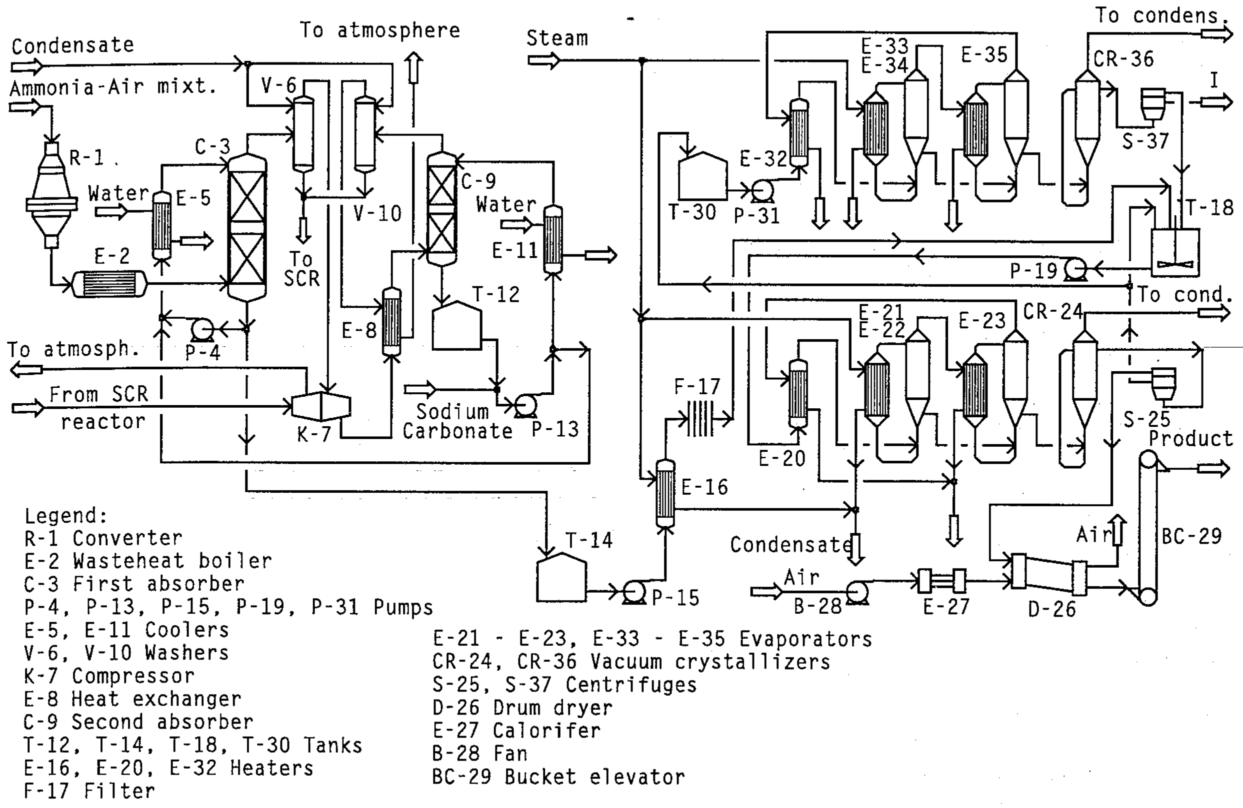


Figure 8.20. GIAP Sodium Nitrate Production Technology.

evaporated and centrifuged. The mother liquor from the secondary centrifuge is fed to a column reactor where the liquor is treated with nitric acid to convert $NaNO_2$ to $NaNO_3$:

$$3NaNO_2 + 2HNO_3 \rightarrow 3NaNO_3 + 2NO + H_2O.$$

Sodium nitrate is separated from the solution and dried in a rotary dryer.

This method of sodium nitrate/nitrite production is economically justifiable if there is an appropriate demand for sodium nitrite. Sodium nitrite has a wide range of applications: in the production of dyes and building materials, in the food industry, iodine industry, the machine-building industry and many others. The process is operated at Berezniki Joint-Stock Company "Azot," Russia.

8.6.2 Calcium Nitrate

Although simple methods are available for producing calcium nitrate, its use as a fertilizer is offset by its extreme hygroscopicity. As a fertilizer, calcium nitrate has special advantages for use on saline soils because the calcium displaces the sodium that is absorbed by clay in soils. For this reason, it may be preferred for use in areas with soil salinity problems. In addition, calcium nitrate has the advantage of being non-acid forming; it improves the physical properties of exhausted and acidified soils; and can be used as a topdressing [48].

Calcium nitrate is produced in large quantities at plants in:

- Norway by Norsk Hydro
- Egypt by Semadco
- Portugal by Quimigal
- Ukraine by Dnieprodzerzhinsk cokery
- Netherlands by Stamicarbon

Plant capacities of one single train range from 150 to 1,200 tpd. Its extreme hygroscopicity requires air-conditioned plants and good-quality, sealed, moisture-proof bags.

Other applications include explosives, pyrotechnics, and inorganic chemical operations. In some countries it is used in sizable tonnages as a de-icing agent (at airports).

8.6.2.1 Properties of Calcium Nitrate – The properties of pure calcium nitrate anhydride are given in Table 8.26.

Calcium nitrate forms four modifications:

- $Ca(NO_3)_2$
- $Ca(NO_3)_2 \bullet 2H_2O$ (H_2O = 18%)
- $Ca(NO_3)_2 \bullet 3H_2O$ (H_2O = 24.8%)
- $Ca(NO_3)_2 \bullet 4H_2O$ (H_2O = 30.5%)

Table 8.26. Properties of Calcium Nitrate

Formula	$Ca(NO_3)_2$
Appearance	White, crystalline
Molecular weight	164.10
Melting point	555.7°C
Density, 20°C	2.36 (anhydride)
Solubility:	
at 0°C	50.5%
at 100°C	78.4%
at 150°C	79.0%
Critical relative humidity [53]:	
at 20°C	54.8%
at 30°C	46.7%

By the addition of ammonium nitrate, the double salt $5Ca(NO_3)_2 \bullet NH_4NO_3 \bullet 10H_2O$ is formed. The melting point of the double salt is 100°-105°C; pH-value, 6-6.5.

8.6.2.2 Commercial Form, Storage, and Transportation – Calcium nitrate is traded as granulated, prilled, or flaked products. The trend is toward granulated products. Typical specification of fertilizer grade is as follows:

Total nitrogen	15.5%
$Ca(NO_3)_2$ - content	76.5-82%
NH_4NO_3 - content	4.5-7.2%
H_2O - content	12-17%

Hardness is as follows:

Prills	2.0 +/- 0.5 kg/grain
Drum granules	3.0 +/- 0.5 kg/grain
Pugmill granules	3.5 +/- 0.5 kg/grain

Screen analysis is as follows:

Flakes	95%-99% between 2 and 5 mm
Granules	90%-92% between 2 and 4 mm
Prills	93%-95% between 1 and 3 mm

Coating (only fertilizer grade): by oil-dissolved anticaking agents (water free)

Bulk density	1,050-1,100 kg/m^3
Packing	50-kg bags

Bulk storage is to be avoided at all costs. Immediate bagging in multilayered bituminoid paper bags, PE-lined jute bags, or mono-layer PE bags is mandatory.

As with other oxidizing nitrate fertilizers, precautions should be taken to avoid impregnation with organic material and contact with a heat source. Special storage and shipping regulations must be observed.

8.6.2.3 Production Technology of Calcium Nitrate – There are two principal methods of calcium nitrate production; they are as follows:

A. Neutralization of 50%-56% nitric acid by ground limestone; filtration of the 45%-52% solution, addition of ammonia to reach the correct ammonium nitrate level and to the correct pH value of about 4. Three-stage evaporation is used to concentrate the solution to about 79%-82%.

B. Use of calcium nitrate tetrahydrate byproduct separated from nitrophosphate processes. The separated tetrahydrate can be remelted in its own crystal water by wasteheat, which gives a solution of about 70%.

Finishing of product is mainly performed by granulation in a pugmill, drum granulator, or pan granulator. Older plants using flaking technology were modified to granulation. Because of effluent problems, most prilling plants have been replaced by granulation plants. Oil prilling was abandoned because of difficult-to-handle wastes.

The granulation technology for calcium nitrate is the same as for CAN with one exception; cooling must be done prior to screening and crushing.

Products intended for field application are coated with an anticaking agent of stearylamine (15%) and parafinic oil (85%). Products for greenhouse or drip irrigation and for explosives are not coated.

Due to the high solubility of calcium nitrate in water, wet scrubbing is used for the vapors from the evaporation section and for the air from the finishing section. Simple vertical or horizontal scrubbers are used to meet the 10-30 mg/Nm^3 requirement of dust in the exhaust. Scrubbing liquor and uncoated spilled product are reprocessed.

8.6.3 Ammonium Sulfate

8.6.3.1 Properties of Ammonium Sulfate – Ammonium sulfate was once the leading form of nitrogen fertilizer, but it now supplies a relatively small percentage of the world total nitrogen fertilizer because of the more rapid growth in use of urea, ammonium nitrate and, in some countries, UAN solutions and anhydrous ammonia. The main advantages of ammonium sulfate are its low hygroscopicity, good physical properties (when properly prepared), chemical stability, and good agronomic effectiveness. It is a good source of sulfur and nitrogen. Its reaction in the soil is strongly acid-forming, which is an advantage on alkaline soils and for some crops such as tea; in some other situations its acid-forming character is a disadvantage. Its main disadvantage is its lower analysis (21% N), which increases packaging, storage, and transportation costs. As a result, the delivered cost at the farm level is usually higher per unit of nitrogen than that of urea or ammonium nitrate. However, in some cases, ammonium sulfate may be the most economic source of nitrogen when the transportation distance is short, when it is available as a byproduct at low cost, or when a credit can be taken for its sulfur content.

Ammonium sulfate is available as a byproduct from the steel industry (recovered from coke-oven gas) and from some metallurgical and chemical processes. One large source is byproduct from the production of caprolactam. The bulk of ammonium sulfate produced in developed countries is a byproduct.

Table 8.27 shows the more important properties of crystalline ammonium sulfate.

8.6.3.2 Commercial Form, Storage, and Transportation – Fertilizer-grade ammonium sulfate specifications normally indicate a minimal nitrogen content, which is usually not less than 20.5%. Limitations on free acidity and free moisture are also generally demanded; typical figures are 0.2% for free H_2SO_4 and 0.2% for free H_2O. Occasionally, maximal values for certain organic or inorganic impurities may also be specified for byproduct material.

Crystal size-range specifications depend on customer requirements and the type of application. For direct application or bulk blending, large crystals, mainly in the range of 1-3 mm, are preferred although somewhat smaller crystals may be acceptable in some countries for direct application, such as 90% retention on an 0.8-mm screen. To obtain crystals of this size, considerable design and operating skill is usually needed, and in some plants additives are used to promote crystal growth or modify the crystal shape [49]. For use in the production of fertilizers, small crystals are acceptable. There is a trend toward the production of small crystals (mainly 0.2-0.8 mm), which are used by producers of granular compound fertilizers or are granulated by roll compaction for direct application or bulk blending.

Table 8.27. Properties of Pure Ammonium Sulfate

Formula	$(NH_4)_2SO_4$
Molecular weight	132.14
Nitrogen content	21.2%
Color	white
Density of solid, 20°	1.769
Specific gravity of saturated solutions	1.2414 at 20°C 1.2502 at 93°C
Specific heat of solid	0.345 cal/g-°C at 91°C
Specific heat of saturated solutions	0.67 cal/g-°C at 20°C 0.63 cal/g-°C at 100°C
Heat of crystallization	11.6 kcal/kg in 42% solution
Heat of dilution	6.35 kcal/kg from 42% to 1.8% solutions
Melting point	512.2°C
Thermal stability	Decomposes above 280°C
pH	5.0
Loose-bulk density	962 kg/m³
Angle of repose	28°
Critical relative humidity	
at 20°C	81%
at 30°C	81.1%
Solubility, g/100 g of water	
at 0°C	70.6
at 100°C	103.8

In the countries of the CIS, ammonium sulfate properties should comply with the specifications given in Table 8.28.

Several factors contribute to trouble-free storage of ammonium sulfate and other fertilizers. First, the product should be of uniform crystal size and should contain a low percentage of fines. It should be dry and preferably have below 0.1% free moisture. No free acidity should be present on the crystal surfaces. The product should be cooled with dry air under controlled conditions after drying, particularly when the ambient temperature and humidity are sufficiently high to cause subsequent moisture condensation after cooling in a bulk storage pile or in sealed bags. Ammonium sulfate is commonly shipped in polyethylene or paper bags.

8.6.3.3 Production Technology – Several different methods are used for ammonium sulfate manufacture, in accordance with available raw materials and local conditions.

The principal methods are as follows:

1. Reacting ammonia and sulfuric acid in a saturator-evaporator under vacuum or at atmospheric pressure and recovering the crystals via a centrifuge or filter.
2. Scrubbing coke-oven gas or town gas with sulfuric acid in saturator units of special design and recovering the crystals by centrifuging or filtration.
3. Reacting ammonium carbonate with anhydrite or gypsum derived from natural or byproduct sources, removing the calcium carbonate by filtering, evaporating, and crystallizing ammonium sulfate from the mother liquor prior to centrifuging.
4. Evaporating byproduct liquors containing ammonium sulfate produced from other processes and separating the nearly pure salt by: (a) crystallization and centrifuging or alternatively (b) recovering by slurry granulation in a moving bed and recycling in a drier-screening system to produce granules of the required size range.
5. Directly reacting gaseous ammonia with sulfuric acid in a spray tower to form a dry, amorphous product.
6. Simultaneously producing ammonium sulfate and other ammonium salts in granulated fertilizer processes to produce phosphate, nitrate, and nitrophosphate multinutrient fertilizers containing ammonium sulfate.
7. Using other miscellaneous processes, such as recovering ammonium sulfate from SO_2 in flue gas or in sulfuric acid tail-gas, which are in use or have been proposed.

Except in special cases, such as those described in subparagraphs 4, 5, and 6 above, crystallization is of primary importance in ammonium sulfate production. Fortunately, there are several publications reviewing the fundamental process and design features that control crystal formation and influence plant performance [50,51,52,53]. Some processes used to produce ammonium sulfate are described below.

Table 8.28. Standard Specifications of Ammonium Sulfate in CIS Countries

	Top Grade	1st Grade
Appearance	white granules or transparent crystals	not standardized
Content in Product, %		
Nitrogen, no less than	21	21
Water, no more than		
granulated	0.6	-
crystalline	0.2	0.3
H_2SO_4, no more than		
granulated	0.5	-
crystalline	0.03	0.05
Size Range		
granulated		
1-4 mm, no less than	90	-
crystalline		
+ 0.5 mm, no less than	80	not standardized
retention on 6-mm screen	absent	not standardized

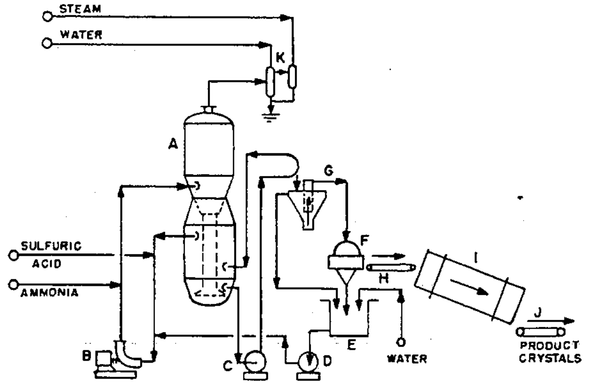
8.6.3.4 Combined Reaction-Evaporation Methods – Anhydrous ammonia and strong sulfuric acid are reacted in continuous saturator-crystallizer units operating either under vacuum or atmospheric pressure. In installations of the vacuum type, the heat of reaction is removed by evaporating water either present in the feed acid or added to the system for temperature-control purposes. This technique is also used for saturators of the atmospheric type; alternative cooling can be achieved in the latter by blowing large volumes of air through the slurry. The reaction between gaseous, anhydrous ammonia and sulfuric acid can be shown as follows:

$$2\ NH_{3(g)} + H_2SO_{4(l)} \rightarrow (NH_4)_2SO_4$$

The exothermic heat of the reaction given above is approximately 2,350 kcal/kg of N.

Units of the vacuum type are built in the form of a suspension vessel surmounted by a flash chamber. Ammonia and sulfuric acid are introduced via a slurry recycle line, wherein they react and superheat the recycling slurry, which is subsequently flashed in the upper chamber at a reduced pressure generally between 55 and 58 cm of mercury. The loss of water in this zone supersaturates the slurry, which recirculates to the lower suspension vessel via an internal pipe and comes into contact with small crystals and nuclei, thereby inducing further crystal growth in terms of size rather than in number. Slurry is recycled by a thermal syphon and/or by an external pump, and as it is brought into contact with newly added reactants, the exothermic heat that is produced destroys undesirable nuclei and fines. Skilled design of the suspension vessel and the means of slurry withdrawal permit considerable size classification to be attained in the unit, and proper instrumentation ensures long periods of uniform operation.

This type of crystallizer is generally known as the "Krystal" or "Oslo" unit and was developed in Norway by Isaacssen and Jeremiassen [54]. Figure 8.21 illustrates diagrammatically the use of forced circulation in conjunction with this design of crystallizer for ammonium sulfate production.



Legend

A	"Krystal" type of vacuum evaporator-crystallizer
B	Forced-circulation pump
C	Slurry-recirculation pump
D	Mother-liquor recycle pump
E	Mother-liquor tank
F	Continuous or batch centrifuge
G	Slurry concentrator
H	Drier conveyor
I	Rotary drier
J	Dried-product conveyor
K	Vacuum condenser-ejector unit

Figure 8.21. Ammonium Sulfate Crystallization.

During operation, it is important to control the pH within fairly close limits, e.g., 3.0-3.5, since a lower value yields undesirable, thin crystals. Excessive acidity also promotes an overgrowth of crystals, especially in pipelines, and necessitates frequent redissolving or "killing" with steam. Insufficient acidity, on the other hand, not only produces inferior crystals, which are difficult to wash and store, but may cause ammonia losses as well. For these reasons, some producers maintain a free acidity of 1.0-1.5 g of H_2SO_4/liter of solution.

Another popular type of reduced-pressure crystallizer is the draft-tube baffle unit, in which a vigorous upward slurry recirculation is maintained by means of an internal impeller and draft [55]. Growing crystals are brought to the surface of the flashing slurry, where supersaturation induces maximum crystal growth, and sufficient nuclei are present to minimize scale formation inside the unit.

Atmospheric pressure units are of several types and are preferred by some producers to the vacuum crystallizer, especially for small and medium outputs, because of their simplicity and somewhat lower investment costs. Ammonia can be added via a sparger tube or a jet-type mixer. In one proprietary process, a simple absorption column incorporating a few large slotted bubble-hoods is used. Another design employs a single vessel for both reaction and crystallization, and reaction heat is removed by evaporation of water, supplemented in many cases by air blowing. In other designs, separate neutralizing and crystallizing vessels are used to provide easier operation and closer control. An optimum balance between cooling-air energy and crystal yield is usually obtained when the crystallization temperature is controlled in the range of 63°-66°C.

In most cases, crystals are recovered from ammonium sulfate slurry by recycling through the continuous or the automatic batch-type centrifuge, wherein the product is screened and spin-dried, washed with water and weak ammonia, and again spin-dried before being conveyed to the drier. In some plants, continuous top-feed filters –

not centrifugal – are used. For small output, top-feed filters can sometimes be used with advantage since the product can be separated, washed, and dried in a single machine.

Ammonium sulfate liquors are quite corrosive, and wetted parts of the equipment are usually made of stainless steel or rubber-lined mild steel. Modifiers intended to improve crystal size and shape include small amounts of trivalent metallic salts. Corrosion inhibitors such as traces of phosphoric acid or arsenic compounds are also added in some cases.

8.6.3.5 Byproduct From Coke-Oven Gas or Town Gas Scrubbing – Typical bituminous coals used for gas and coke production contain about 1%-2% of nitrogen, and some 15%-20% of this can be recovered as ammonia, amounting to approximately 2.5-3.0 kg of NH_3/tonne of coal used. Most byproduct ammonia is usually associated with high-temperature carbonization units, e.g., coking plants for iron and steel production, where the amount of ammonium sulfate produced may be equivalent to about 20 kg/tonne of steel. However, in more recent years, world ammonium sulfate prices have fluctuated widely, and, from time to time, byproduct material from gasworks and coke ovens has been sold at price levels not much greater than the cost of the sulfuric acid needed as a raw material. As a result, some producers have converted their units to ammonium phosphate production, while some others intend to readjust their plants for recovery of ammonia as such. Other byproducts recovered from gas-washing units, because of necessity or additional financial return, include ammonium thiocyanate, ferrocyanides, pyridins, and tar.

Three principal methods are available for ammonia and/or ammonium salt recovery; they are known as the direct, indirect, and semidirect processes, respectively.

In the first method, the entire gas stream is cooled to remove as much tar as possible and is then passed through a saturator of the bubbler type (or, in more recent plants, a scrubber of the spray type), wherein it is washed with sulfuric acid. The ammonium sulfate slurry produced is withdrawn, centrifuged, washed, dried, and sent to storage. Advantages of this type of unit include high recoveries, relatively low investment and operating costs, low steam needs, and small effluent liquor volumes. Nevertheless, in many instances, the product is unavoidably contaminated with tar and pyridines and may be unacceptable unless, perhaps, it is recrystallized prior to sale. In addition, chlorides present in the fuel or water may react to form ammonium chloride and create additional corrosion problems unless linings of rubber or plastic material are used. Furthermore, except in cases where a separate crystallizer is employed, flexibility regarding size, shape, and purity of the product is likely to be very limited because it becomes difficult to maintain an optimum balance between the free acidity needed to suppress impurities and the optimum pH needed to promote good crystal growth.

Earlier problems of direct operation led to the development of the indirect method, whereby the gases are first cooled by contact with recirculating wash liquor, following in some cases by a further scrubbing with water. Combined liquors are sent to the upper section of an ammonia still of the bubble-cap type, in which contact with steam releases the "free" ammonia present as ammonium carbonate, ammonium sulfide, and other easily dissociated salts. The liquor then passes to an adjoining lime leg, where treatment with lime liquor decomposes the "fixed" ammonium salts, e.g., ammonium chloride. Steam passing upwards from the base of the column strips virtually all of the ammonia gas produced, which is recovered as a crude ammonia solution or is sent to a sulfuric acid washer for ammonium sulfate production. Advantages of this method include the production of a salt substantially free from impurities and also having considerable flexibility, plus an ability to make aqua ammonia and derivatives. However, operating costs are high, and effluent disposal problems may arise. In addition, ammonia losses may be appreciable, because of incomplete reaction and absorption.

The semidirect process offers a compromise between direct and indirect operation, whereby the gas is first cooled and washed to deposit tar and an aqueous condensate [56]. The latter is "sprung" in a relatively small ammonia still, and the released NH_3 is combined with the main gas stream, which is reheated to about 70°C and scrubbed with a solution containing nearly saturated ammonium sulfate and 5%-6% of sulfuric acid at about 50°-70°C in units either of the spray-absorber type or of the older saturator type incorporating a cracker pipe (or bubbling ring). Because this process gives ammonia recoveries that are greater than those attainable by direct operation and also produces a salt largely free from tar, pyridine, and other impurities, it has become the most popular for large installations. Figure 8.22 shows the basic flow diagram of a semidirect gas scrubber/ammonium sulfate unit.

Several varieties and modifications of these systems are found throughout the world; they are principally developed by the Koppers, Otto, and Wilputte organizations [57].

8.6.3.6 Ammonium Carbonate-Gypsum Process – This method, which is also known as the Merseburg Process, was originally developed in Germany and has long been used in Austria, India, Pakistan, and the United Kingdom [58]. It is based on combining ammonia and carbon dioxide to produce ammonium carbonate, which

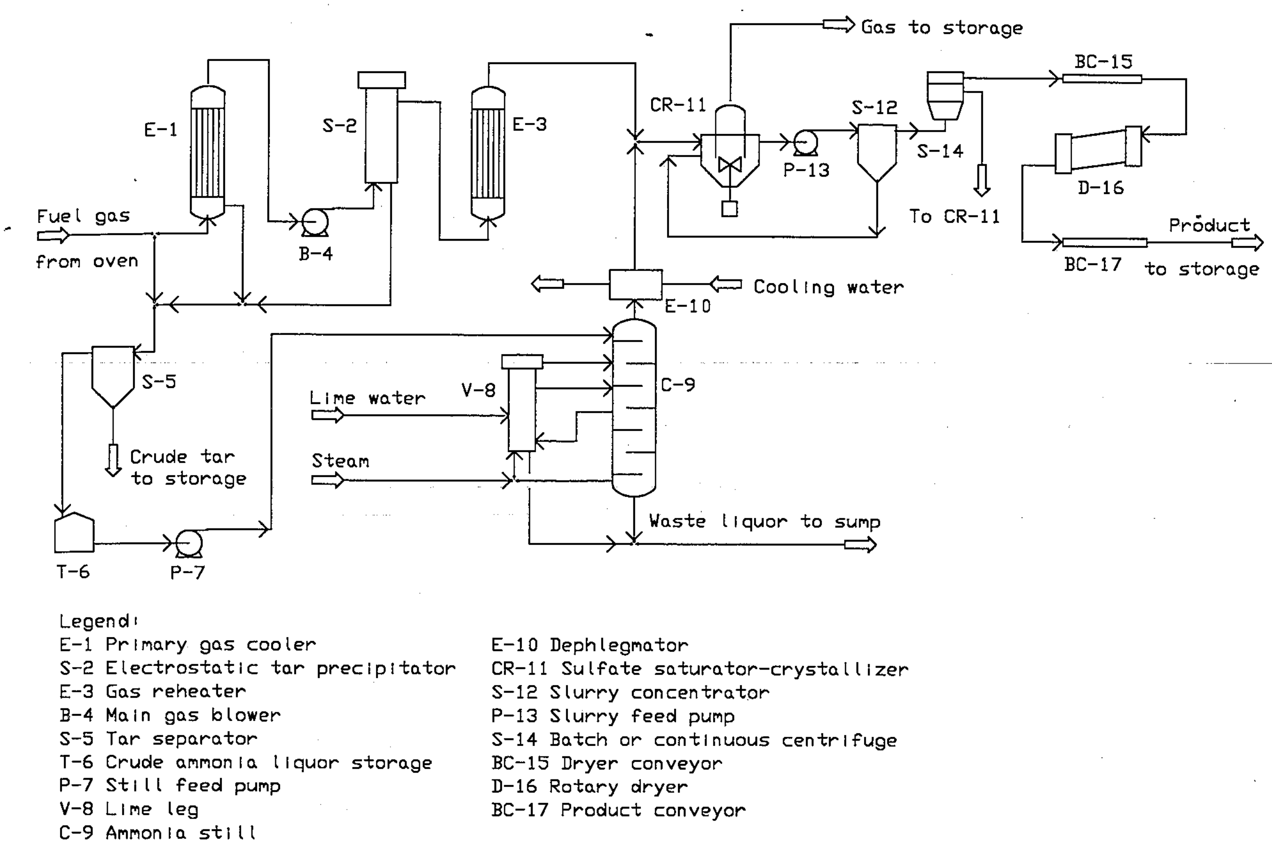


Figure 8.22. Semidirect Gas Scrubber/Ammonium Sulfate Production.

is then reacted with gypsum or anhydrite (of natural or byproduct origin) to yield ammonium sulfate and calcium carbonate, as follows:

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$2\ NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

$$CaSO_4 \bullet 2H_2O + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + 2\ H_2O.$$

All of the reactions are exothermic. Under certain circumstances, this process has several advantages, for example, countries that do not have indigenous sulfur supplies but do have natural or byproduct sources of gypsum (or anhydrite) can produce ammonium sulfate without purchasing sulfur from abroad [59]. In addition, the byproduct calcium carbonate can be used for cement production or other purposes, such as for agricultural lime or in calcium ammonium nitrate manufacture. One disadvantage is the large amount of energy (steam) required to recover solid ammonium sulfate from the relatively dilute solution.

In one Indian plant (Sindri), ammonia gas is absorbed in water and carbonated at a pressure of about 2.1 kg/cm^2 in two series-connected aluminum towers because this pressure allows a higher cooling-water temperature to be used than if atmospheric pressure were used. Carbon dioxide is introduced at the base of the primary tower, which is packed with 5-cm (2-inch) stoneware rings wetted with a solution of ammonium hydroxide and recycling ammonium carbonate. Final absorption is undertaken in the secondary tower, and reaction heat is removed by recirculating liquor through water-cooled heat exchangers in closed circuit with each tower. The preferred liquor strength corresponds to approximately 170 g of ammonia and 225 g of carbon dioxide per liter. Stainless steel is used for the wetted parts of pumps, and liquor piping is made of aluminum.

In another Indian plant (Fertilizer and Chemicals, Ltd., Travancore), jet absorbers were used to prepare both the ammonia solution and the ammonium carbonate liquor in conjunction with a carbonating tower. Cooling was undertaken by recycling liquor through water-cooled heat exchangers, and the heat of reaction vaporized the liquid anhydrous ammonia used in the process. When the desired strength was reached, the solution was sent to storage and subsequent reaction. The relation between liquor strength, moisture in the gypsum, and the resulting ammonium sulfate liquor concentration has been reported by George and Gopinath [60]. This plant was scrapped in April 1985.

When natural gypsum or anhydrite is used, it is crushed and ground before reaction. In one case, the preferred final size is about 90% through 120 mesh although, under certain circumstances, there are indications that a coarser size is permissible. When using byproduct gypsum of phosphoric acid plant origin, it may be preferable to remove impurities by repulping the filter cake in an agitated vessel (or, alternatively, by scalping in liquid cyclones) prior to washing and dewatering to the maximum extent on a drum or disc filter before reacting with ammonium carbonate.

Reaction can be undertaken either in a series of wooden vessels or mild-steel tanks fitted with steam coils and agitators, and the reaction train is usually designed to give a total retention time of 4-6 hours. The slurry produced is filtered and the calcium carbonate cake washed and dewatered on continuous vacuum machines of the traveling-belt type, or alternatively, on a two-stage drum-filter installation provided with intermediate repulping. (In some earlier plants, plate-frame filter presses were installed for this purpose.) Final clarification by pressure filtration or settling is sometimes employed to ensure maximum purity of product, followed by neutralization with sulfuric acid and heating to about 110°C to remove excess ammonia prior to concentration and crystallization. The evaporator feed-liquor usually contains about 500-520 g of ammonium sulfate and less than 0.1 g of ammonia per liter. Evaporation is undertaken in continuous multiple effect evaporator-crystallizers, and production can be supplemented, if desired, by adding ammonia and sulfuric acid to the crystallizer recirculating line. Crystals of the required size range are separated and washed in a centrifuge, dried in a rotary drier at 120°C, and sent to storage. Alternatively, a vertical tray type of dryer-cooler can be used since this is said to give reduced crystal breakage and dust formation, compared with the use of rotary dryer and cooler. A diagram of a gypsum-process ammonium sulfate plant is given in Figure 8.23.

8.6.3.7 Recovery From Industrial Byproduct Liquors – Byproduct units have been installed in many countries for producing ammonium sulfate from the waste streams of caprolactam, acrylonitrile, and certain other processes. In such cases, the waste liquor should normally contain at least 35% of ammonium sulfate in

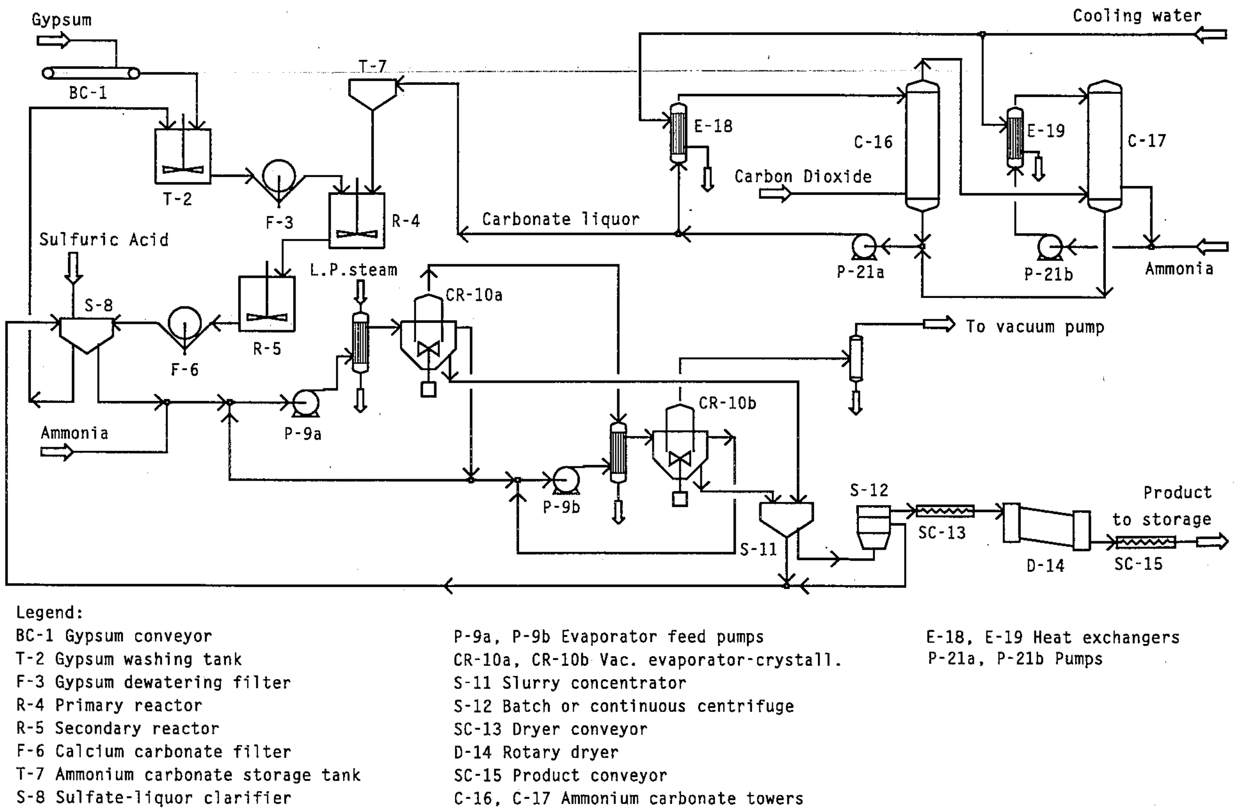


Figure 8.23. Gypsum Process of Ammonium Sulfate Production.

solution. Otherwise, recovery may not be justified except for the purpose of preventing stream pollution. The usual content of ammonium sulfate in the waste stream of the caprolactam process is in the range of 25%-42%. Since recovery often is unprofitable, processes have been developed recently for making caprolactam that produce less byproduct ammonium sulfate or none [61]. Most processes operating now produce 1.8-4.0 tonnes of ammonium sulfate per tonne of caprolactam.

Occasionally, spent sulfuric acid from petroleum refineries, petrochemical plants, and soap factories can be used for ammonium sulfate production if impurities do not cause insurmountable frothing or corrosion problems or render the product unacceptable. If the acid is too badly contaminated, it may be more expedient to burn off the impurities in a specially designed furnace and to produce fresh acid for ammoniation.

8.6.3.8 Spray-Tower Ammoniation – Substantial tonnages of ammonium sulfate have been made for many years in Japan in spray towers from the chamber or contact type of sulfuric acid and anhydrous ammonia. The acid is sprayed into ammonia vapor inside the tower, and the heat of reaction produces a dry, amorphous product primarily less than 300 mesh, which is continuously removed from the base of the tower by a screw conveyer. This form of ammonium sulfate is particularly suitable for use in granular compound fertilizers.

8.6.3.9 Double- and Mixed-Salt Production – By ammoniating mixtures of sulfuric and nitric acid or by combining their ammonium salts in special ways, it is possible to produce compounds containing both ammoniacal and nitrate nitrogen in the form of true double salts. Three double salts have been identified:

$(NH_4)_2SO_4 \bullet NH_4NO_3^-$

$(NH_4)_2SO_4 \bullet 2NH_4NO_3$

$(NH_4)_2SO_4 \bullet 3\,NH_4NO_3^-$

One German process produces an ammonium sulfate nitrate corresponding to approximately $(NH_4)_2SO_4 \bullet NH_4NO_3$ and containing 62% ammonium sulfate and 38% ammonium nitrate. Total nitrogen content is 26%; about three-quarters of this is present in the ammoniacal form and one-quarter as nitrate nitrogen. It is made by ammoniating the requisite mixture of sulfuric and nitric acids, evaporating to a moisture content of 3%, adding about 1% of ferrous sulfate (to reduce subsequent caking), cooling to 100°C, chilling, and flaking. After further conditioning by spraying with dilute ammonia solution, the double salt is granulated (sometimes with additional ammonium sulfate), dried, cooled, and bagged. In a simpler process, also of German origin, ammonium nitrate solution is evaporated under vacuum to 95% concentration, cooled to about 130°C, and reacted with solid ammonium sulfate in a pugmill granulator system having a recycle ratio of 2 or 3:1 of product until a pH of 4.0 is attained, after which the product is dried, cooled, and bagged. Processes for prilling the product have also been developed.

For several years, the Tennessee Valley Authority (TVA) produced an ammonium nitrate-sulfate, containing 30% N, mainly for use in sulfur-deficient areas. The process involved ammoniation of a mixture of nitric acid and sulfuric acid, followed by pan granulation of the resulting slurry. The product consisted mainly of the double salt $(NH_4)_2SO_4 \bullet 3NH_4NO_3$. Compared with ammonium sulfate, ammonium nitrate-sulfate of the usual grade (26% N) contains an additional 5% N. Its storage properties are superior to ammonium nitrate or a mixture of solid ammonium sulfate and ammonium nitrate since free ammonium nitrate is absent. However, the large-scale manufacture of urea and binary and ternary high-analysis fertilizers has diminished the importance of ammonium sulfate-nitrate in most countries.

When mixtures of sulfuric acid and phosphoric acid are ammoniated, a variety of mixed and double-salt products can be made. One of the most popular is "ammophos," containing 16% N and 20% P_2O_5. After ammoniation the slurry formed is granulated in a pugmill or drum unit, then dried and screened (and sometimes cooled) to give a water-soluble product containing about two-thirds ammonium sulfate and one-third ammonium phosphate by weight. This material has good storage properties under normal conditions.

8.6.3.10 Miscellaneous Processes – Numerous processes have been proposed or developed for recovering sulfur from flue gas. These processes are based on scrubbing with ammonia or injection of ammonia into the flue gas; ammonium sulfite, bisulfite, sulfate, or mixtures of these compounds result from the processes. Ammonium sulfate can be produced as a final product, and some commercial use has been reported in Japan. However, the demand for ammonium sulfate is small in comparison with the potential supply from flue-gas sulfur; therefore, most processes involve disposal of the sulfur as calcium sulfate or sulfite and recycling of ammonia.

8.6.4 Ammonium Chloride

8.6.4.1 General Information – Ammonium chloride is used for fertilization either as such or in a variety of compound fertilizers [62]. Examples are:

18 - 22 - 0 (ammonium-phosphate chloride)
16 - 0 - 20 (ammonium-potassium chloride)
14 - 14 - 14
12 - 18 - 14

Ammonium chloride is used in other grades of compound fertilizers in combination with urea or ammonium sulfate. Advantages of ammonium chloride are that it has a higher concentration than ammonium sulfate and a somewhat lower cost per unit of N (in Japan). It has some agronomic advantages for rice [63]; nitrification is less rapid than with urea or ammonium sulfate and, therefore, N losses are lower and yields are higher.

Although ammonium chloride is best known as a rice fertilizer, it has been successfully tested and used on other crops such as wheat, barley, sugarcane, maize, fiber crops, and sorghum in a variety of climatic conditions. Of particular note, however, is the use of ammonium chloride on palms; a linear response of coconut to chlorine in terms of copra yield per tree was shown [64].

Ammonium chloride is as highly acid-forming as ammonium sulfate per unit of N, which can be a disadvantage. Other disadvantages are its low N content compared with urea or ammonium nitrate and the high chloride content, which can be harmful on some crops or soils. Nevertheless, it is possible that ammonium chloride fertilizer could become a useful outlet for surplus chlorine or byproduct hydrochloric acid that arises from time to time in various countries. Another useful feature of ammonium chloride is that it can be applied to rice with safety in the presence of certain fungi, which would reduce ammonium sulfate to toxic sulfides. The industrial uses of ammonium chloride are worldwide although in relatively small tonnages. The main applications include dry-battery manufacture and use as a flux for soldering and brazing. As a fertilizer, ammonium chloride is notably popular in east and southeast Asia.

8.6.4.2 Properties of Ammonium Chloride – The properties of ammonium chloride are given in Table 8.29.

Table 8.29. Properties of Ammonium Chloride

Formula	NH_4Cl
Molecular weight	53.5
Nitrogen content	26%
Color	white
Density of solid, 20°C	1.526
Solubility, g/100 g of water at:	
Temperature, °C	
0	29.4
20	37.2
40	45.8
60	55.3
80	65.6
100	77.3
115.6 (boiling point)	87.3
Effect of heat:	Ammonium chloride begins to dissociate at 350°C and sublimes at 520°C
Crystal relative humidity	
at 20°C	79.2
at 30°C	77.5

8.6.4.3 Commercial Form, Storage, and Transportation – The fertilizer-grade product contains 25% N. The product can be in the form of either crystals or granules. Coarse crystalline or granular forms are preferred for direct application, whereas fine crystals can be used in compound fertilizers.

A typical analysis of the material produced by the dual-salt process is given in Table 8.30. The direct-neutralization method, in principle, may yield a purer material.

Table 8.30. Dual-Salt Process Product Specification

	%
NH_4Cl (minimum)	95.0
NaCl	1.5
Carbonates as CO_2	0.5
Sulfates as SO_4	0.3
Insoluble material	0.1

The same requirements as to ammonium sulfate should be observed. The product is to be packed in moisture-proof bags prior to storing or transportation.

8.6.4.4 Raw Materials – Principal raw materials are common salt (NaCl) and anhydrous ammonia in the case of the dual-salt process or anhydrous ammonia and hydrochloric acid (HCl) for the direct-neutralization method. To take advantage of byproduct CO_2, it is advisable to install the dual-salt process at a site where anhydrous ammonia is produced. For the direct-neutralization method, byproduct HCl may be used, e.g., byproduct HCl from the production of potassium sulfate by the Mannheim process. In addition, substantial amounts of byproduct HCl are available from other industries. HCl is a strong, highly corrosive acid; thus, special precautions should be observed when handling it.

8.6.4.5 Production Methods – Several methods for producing ammonium chloride are used; the order of importance is as follows:

1. The dual-salt process, whereby ammonium chloride and sodium carbonate are produced simultaneously.
2. Direct neutralization of ammonia with hydrochloric acid.
3. Miscellaneous methods.

8.6.4.6 The Dual-Salt Process – Most ammonium chloride used in India, China, and Japan for fertilizer purposes is produced by the dual-salt process as shown in Figure 8.24 [62] or in suitably modified Solvay plants.

In this method, ammonium chloride is salted out by the addition of solid, washed sodium chloride rather than decomposition by lime liquor to recover ammonia as in the Solvay ammonia-soda process.

In conventional Solvay plants, an ammoniated solution of about 30% sodium chloride is treated with carbon dioxide in large absorber towers to form ammonium carbonate:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

Additional carbonation produces ammonium bicarbonate:

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$$

The addition of sodium chloride yields sodium bicarbonate and ammonium chloride:

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

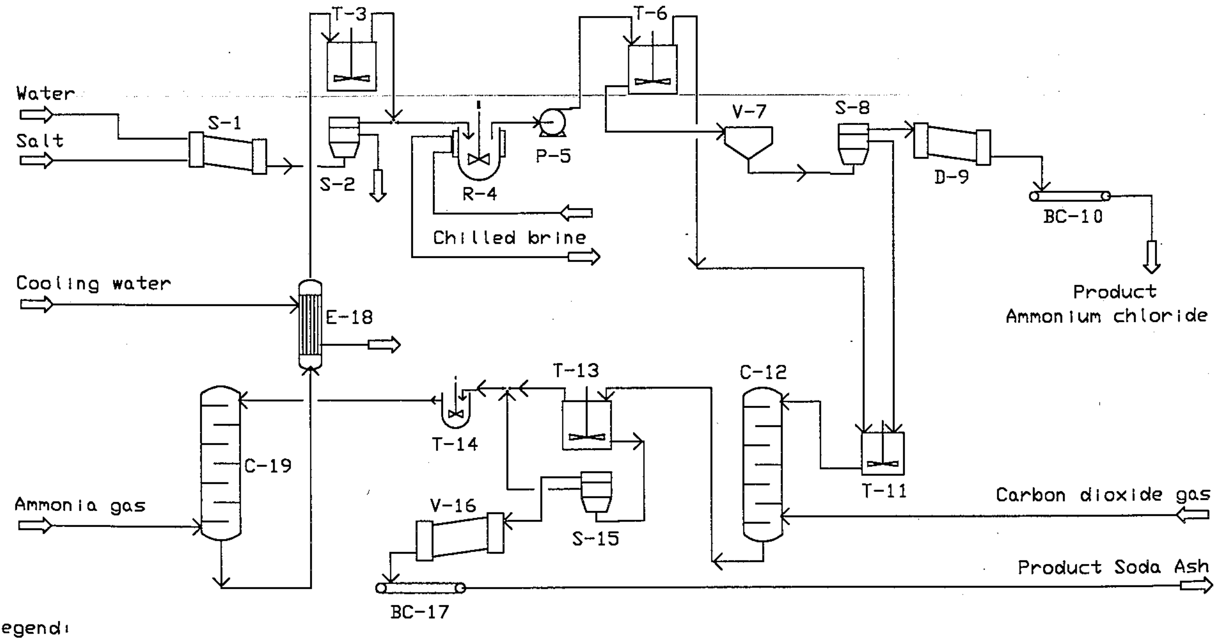
The sodium bicarbonate is separated by centrifuging or filtration and calcined to produce sodium carbonate and CO_2; the latter is recycled to the system. In the Solvay process, reaction reaches equilibrium at about 75% completion, and the mother liquor is reacted with lime liquor to recover ammonia for reuse in the process, i.e.:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The calcium chloride liquor can sometimes be sold but may have to be discarded in the absence of suitable markets.

In the dual-salt process (or the modified Solvay process), the mother liquor remaining after separation of sodium bicarbonate is ammoniated, cooled below 15°C, and salted out by adding washed, solid sodium chloride. The precipitated ammonium chloride is centrifuged, washed, and dried. The fine crystals can be granulated by roll compaction or used in compound fertilizers. In Japan, a method of producing large ammonium chloride crystals of rice grain shape, 2-3 mm in size, has been developed by undertaking cooling, nucleation, and crystallization of the ammonium chloride under closely controlled conditions in separate vessels of special design.

Slurry from the last crystallizer is centrifuged, washed, and dried to about 0.25% free moisture in a rotary drier



Legend:

S-1 Salt washer
S-2 Salt centrifuge
T-3 Ammoniated-brine tank
R-4 Salt reactor
P-5 Slurry pump
T-6 Ammonium chloride slurry tank
V-7 Ammonium chloride concentrator
S-8 Ammonium chloride centrifuge
D-9 Ammonium chloride dryer
BC-10 Ammonium chloride product conveyor
T-11 Mother-liquor tank
C-12 Carbonating tower
T-13 Bicarbonate slurry tank
T-14 Bicarbonate mother-liquor tank
S-15 Bicarbonate centrifuge
V-16 Soda ash calciner
BC-17 Soda ash product conveyor
E-18 Ammoniated-brine cooler
C-19 Ammoniation tower

Figure 8.24. Dual-Salt Ammonium Chloride Process.

at 105°C. After removal of ammonium chloride, the liquor is reammoniated and returned to the carbonating tower to produce further sodium bicarbonate and to commence a new cycle of operations. The ammonium chloride produced by this method, particularly when granulated or produced in coarse crystal form, is reported to have good physical properties.

The economics of the process must be evaluated in comparison with alternative methods for producing soda ash. This subject is discussed in a UNIDO publication [62]. In most countries the demand for nitrogen fertilizers greatly exceeds the demand for soda ash; therefore, ammonium chloride from this source is not likely to supply a large percentage of nitrogen fertilizer needs.

8.6.4.7 The Direct-Neutralization Method – Ammonium chloride of high purity is made in several countries by the direct reaction between anhydrous ammonia vapor and hydrochloric acid gas, according to the reaction:

$$NH3(g) + HCl(g) \rightarrow NH4Cl$$

The reaction is exothermic (42,000 cal/g-mole). In most cases, neutralization is undertaken at reduced pressures of 250-300 mm of mercury in one or more rubber-lined steel vacuum reaction vessels protected with an additional inner lining of inert brick. Concentrated hydrochloric acid gas is passed through an aspirator, wherein it is diluted with air to about 20% concentration and enters the reaction vessel via a vertical sparger tube. According to preference, ammonia gas is introduced either by a second sparger or by tangential nozzles in the base of the reaction vessel. Agitation is provided by the large volume of air entering the reactor with the hydrochloric acid vapor; thus, the need for a mechanical agitator with its additional power requirements and maintenance problems is avoided.

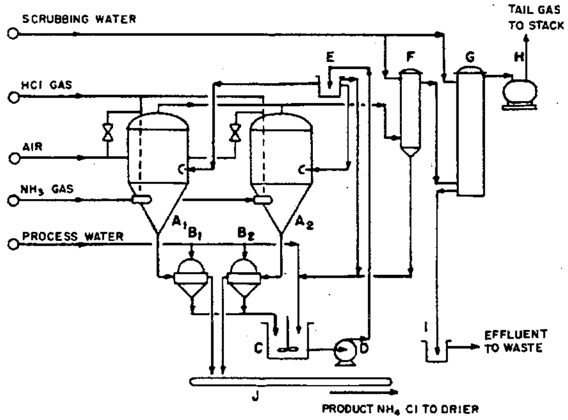
Similarly, operation under vacuum not only provides excellent cooling but simultaneously prevents escape of noxious vapors and eliminates the need for hydrochloric acid-vapor blowers, plus their attendant cost and maintenance charges. A reduced pressure of 250-330 mm of mercury and a corresponding slurry temperature of 75°-80°C represent typical operating conditions.

In most cases, it is normal to maintain a uniform acid feed for the desired output level and to control the ammonia addition to achieve a steady pH of 8.0. The control system should include an audible alarm and provisions for shutting off the acid if the pH falls below 7.0; otherwise, those components in the system not protected by rubber or plastic linings (e.g., the centrifuge) would be quickly damaged by corrosion. Slurry is withdrawn from the saturator at about 80% solids concentration, and the ammonium chloride crystals are separated and rinsed in stainless-steel centrifuges. In some cases, drying is also undertaken in the separator by blowing hot air through the crystal bed before discharge. Alternatively, a top-feed filter-drier can be used rather than centrifuges.

Mother liquor from the centrifuges is pumped back to the saturator(s) via a storage tank. Saturator offgases must be well scrubbed before entering the vacuum pump or ejector unit to prevent corrosion and to eliminate air pollution. A two-stage scrubbing system is usually employed and may consist of a direct, barometric scrubber-condenser followed by a wetted, packed tower. Liquor from the scrubber-condenser is returned to the mother-liquor tank and is evaporated in the saturator, thus providing a means of temperature control and acid recovery. Figure 8.25 shows the basic flow diagram for a typical direct-neutralization unit.

As with other processes involving reactions between hydrochloric acid (or chlorides) and ammonia, traces of free chlorine in the acid feed can lead to disastrous explosions caused by the formation of nitrogen trichloride in the saturator. Hence, adequate safety precautions must be installed whereby the HCl gas feed is monitored and the flow discontinued when chlorine is detected. This can be accomplished by such means as bypassing a small stream of gas through a photocell-calorimeter unit containing potassium iodide or using a modern continuous gas analyzer of the absorption or chromatographic type.

After separation and drying, the crystalline ammonium chloride is bagged as quickly as possible to minimize subsequent storage and application difficulties.



Legend

A_1, A_2	Neutralizer-crystallizers	F	Primary scrubber
B_1, B_2	Batch or continuous centrifuges	G	Secondary scrubber
C	Mother-liquor tank	H	Vacuum pump
D	Neutralizer feed pump	I	Seal-pot
E	Splitter feed box	J	Product conveyor

Figure 8.25. Ammonium Chloride Direct Neutralization Process.

Recent trials have shown that anticaking agents such as certain fatty acid derivatives or inert powders, either applied to the crystals after drying or added to the saturator, can be helpful in reducing caking tendencies after manufacture. Granulation by roll compaction would provide a good material for direct application.

In accordance with the purity of the feed materials (plus any reworked product) and provided the plant has been properly designed and maintained in good condition, the direct-neutralization method will produce ammonium chloride of high purity. For example, in one Indian plant a product of a quality well in excess of British Pharmacopea specifications can be achieved. Production of ammonium chloride could be a convenient way to use byproduct HCl which often has a low value and poses a difficult disposal problem.

8.6.4.8 Miscellaneous Processes – Ammonium chloride can be made from ammonium sulfate and sodium chloride according to the reaction:

$$(NH_4)_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2NH_4Cl$$

Another method is the use of SO_2 or sulfite liquor in conjunction with ammonia and sodium chloride, as shown below:

$$SO_2 + 2NH_3 + H_2O + 2NaCl \rightarrow 2NH_4Cl + Na_2SO_3$$

However, both methods are quite expensive and can be justified only for the manufacture of small quantities of pure material and not for large tonnage fertilizer production.

Although the deliberate production of ammonium chloride for fertilizer use is rare in regions other than east Asia, it is a very common constituent of compound fertilizers (granular or liquid) in Europe and North America. It is formed in NPK fertilizers by reaction of ammonium nitrate and/or ammonium sulfate with potassium chloride:

$$NH_4NO_3 + KCl \rightarrow NH_4Cl + KNO_3$$

$$(NH_4)_2SO_4 + 2KCl \rightarrow 2NH_4Cl + K_2SO_4$$

These reactions go substantially to completion in most granulation processes, in nitrophosphate processes, and in liquid compound fertilizer processes. Ando et al. found that ammonium chloride was one of the most common forms of nitrogen in representative grades of NPK granular fertilizers in the United States [65]. Thus, the production and use of compound fertilizers containing ammonium chloride is well established on a worldwide basis even though some people in the industry are not aware of it.

Licensers and contractors of the available processes for production of nitrates and ammonium salts are listed in reference [66]. Sites of the plants are listed in reference [67].

8.7 References

1. Aleinov, D. P. 1993. "The Russian Nitrogen Industry," Paper presented at the International Fertilizer Industry Association, Limited (IFA), 1993 Regional Conference for Europe, Vienna, Austria.
2. Chernyshov, V. I., and I. M. Kisil. 1993. "Platinum Metals Catalytic Systems in Nitric Acid Production, System Optimisation in Non-Concentrated Acid Plants," *Platinum Metals Review*, 37(3):136-143.
3. British Sulphur. 1993. The Competitive Performance of the Nitrogen Plants in the Former U.S.S.R., London, England.
4. *Ullmann's Encyklopadie der technischen Chemie.* 1972. 4th ed., 20:305-332.
5. Reference book of the nitrogen industry specialist, 2nd ed., V2, Moscow, Chimia, 1987 (in Russian), pp. 12-38.
6. *Fertilizer International*, No. 292, December 1990.
7. Harvin, R. L., D. G. Leray, and L. R. Roudier. 1978. "Single or Dual Pressure Nitric Acid – An Objective Comparison," Presented at the 71st Annual Meeting of American Institute of Chemical Engineers, Miami Beach, FL, U.S.A.
8. Hopfer, Klaus, and I. Dayanger. 1980. Lecture Series on "Recent Advances in Inorganic Acids Industry," Manufacture of nitric acid: Recent advances in ammonia conversion efficiency and NO_x reduction, Indian Chemical Manufacturers' Association.
9. Atroschenko, V. I., et al. 1985. Technology of Fixed Nitrogen. Kiev, Vischa Shkola (in Russian), 327 pp.
10. Graham, H. J., V. E. Lyons, and H. L. Faucett. 1964. "Concentrated Nitric Acid," *Chemical Engineering Progress* (New York), 60 (7):77-84.
11. "Urea as a Pollution Control Agent." 1975. *Nitrogen*, 93:32-36.
12. Rodier, L., N. Durand, and B. Mouille. 1982. "Nitric Acid Recovery From Waste Nitrous Gases by the COFAZ Process," Fert. Nitrogen: Proceedings, British Sulphur Corporation International Conference of Fertilizer Technology, pp. 561-569.
13. *Fertilizer International*, No. 300, August 1991.
14. Berkley, Neal E., and Franklin D. Cates. 1991. "New Filter Medium Improves Nitric Acid Process," *FINDS*, Third Quarter, Stokes Engineering, U.S.A.

15. Honti, G. D. 1976. *The Nitrogen Industry*. Properties. pp. 409-413, Akademia Kiado, Budapest, Hungary.

16. *Nitrogen*, No. 177, January-February 1989.

17. *Fertilizer Focus*, March 1990.

18. Zhukov, M. F., V. J. Smolyakov, and B. A. Uryukov. 1973. Electric Arc Heaters for Gas (Plasmotrones), Moscow, Nauka, 232 pp.

19. Ganz, S. P., and V. D. Parkhomenko. 1976. Production of Fixed Nitrogen in Plasma. Kiev, pp. 11-63.

20. Keleti, C.. 1985. *Nitric Acid and Fertilizer Nitrates*. Marcel Dekker Inc., New York, NY, U.S.A.

21. Landolt - Börnstein, Erg. Bd. II-b, p. 1495, 5th Ed., Springer Verlag, Berlin, Germany.

22. Hendriks, Posnjak, Kracek, 1932. *J. Am. Chem.*, 54:2766-2786.

23. Reference book of the nitrogen industry specialist, 2nd Ed., V2, Moscow, Chimia, 1987 (in Russian), p. 154.

24. Safety in Works. The Fertiliser Society of London, Proceedings No. 137, London, England.

25. The Development of Legislation Affecting the Production, Distribution, Storage and Use of Fertilizers. Fertiliser Society of London, Proceedings No. 267, London, England.

26. *Packing, Handling, Transportation, Bulk Storage and Use of Ammonium Nitrate Fertilizer*. The Fertilizer Institute, 1015 18th Street N. W., Washington, D.C., U.S.A.

27. Code for the Storage of Ammonium Nitrate. NFPA No. 490, National Fire Protection Association 60 Battery March Street, Boston, MA, U.S.A.

28. The Storage of Ammonium Nitrate, APEA - Technical Committee.

29. Olevsky, V. M., et al. 1978. Technology of Ammonium Nitrate, Moscow, Khimia, 312 pp. (in Russian).

30. Pagani, G., et al. 1981. NSM Ammonium Nitrate Plant. Paper presented at 4th International Conference on Fertilizer Technology.

31. Ulrichs, K. 1985. "AN-Neutralization," Paper presented at Ammonium Nitrate Pollution Study Group, Edmonton, Alberta, Canada.

32. Nebel, R. 1985. "Reduction of Nitrogen Losses in Plants for the Production of Ammonium Nitrate," *Fertiliser News*, pp. 41-47.

33. SPI Report No. 127 A1, Ma 1980.

34. Bovens, J. L., and F. van Hecke. 1992. "The CARNIT Ammonium Nitrate Process," Paper presented at the Fertiliser Society Meeting, London, England.

35. Indian Patent IN-170567, 11.04.1992.

36. Arion, N. 1986. "Fertilizer Plant Waste Water Treatment by Ion Exchange," *Nitrogen*.

37. Carter, R.W.R., and A. G. Roberts. 1969. *The Production of Ammonium Nitrate Including Handling and Safety*, The Fertiliser Society of London, England.

38. "The Granulation of Nitrogenous Fertilizers," *Nitrogen*, May-June 1981.

39. Bruynseels, J. P. 1981. "Granulate in Fluid Bed," *Hydrocarbon Processing*, pp. 203-208.

40. German Patent DE-3811913 C1, 12/10/1989.

41. Spanish Patent ES-553311, 24/03/1986.

42. United States Patent US-3,317,276, 02/05/1967.

43. United States Patent US-3,647,412, 07/03/1972.

44. Olevsky, V. M. 1992. "New Results and Modern Technologies for Nitric Acid, Nitrogen Fertilizers and Caprolactam Production," Paper presented at the International Meeting on Chemical Engineering and Biotechnology, ACHEMASIA'92.

45. Olevsky, V. M., and L. A. Taran. 1994. "The Effect of Certain Types of Insoluble Modifiers Introduced Into Nitrogen-Containing Fertilizer Melts on the Quality Performances of Prills," Paper presented at the International Meeting on Chemical Engineering and Biotechnology, ACHEMA - 94.

46. Vogel, E. 1986. "The Fluidized Drum Granulation Process," *Nitrogen*, 161:28-31, May-June.

47. "Opinion – AN/CAN Production Technology." 1986. *Fertilizer Focus*, Vol. 3, No. 9, October 1986.

48. Bertilsson, G. 1989. "Nitrogen Transformations and Nitrogen Balances in Scandinavian Soils," The Fertiliser Society of London, Proceedings No. 287, London, England.

49. Ettle, G. W. 1949. "Some Aspects of Ammonium Sulfate Production," Proceedings of the Fertiliser Society of London, No. 5, London, England.

50. Buckley, H. E. 1951. *Crystal Growth*, John Wiley and Sons Inc., New York, NY, U.S.A.

51. Keating, K. B. 1964. "Mechanisms of Crystal Growth," *Chemical Engineering Progress*

Symposium, Series 60, No. 48. American Institute of Chemical Engineers. New York, NY, U.S.A.

52. Rumford, F., and J. Bain. 1959. "Controlled Crystallization of Sodium Chloride," *Fluid Handling*, (117):284-186.
53. Palermo, J. A., and G. F. Bannet. 1964. "Crystallization," *Industrial and Engineering Chemistry*, 56(10):38.
54. Svanoe, H. 1940. "Krystal Classifying Crystallizer," *Industrial and Engineering Chemistry*, 32(5): 636.
55. Bennet, R. C. 1962. "Product Size Distribution in Chemical Crystallizers," *Chemical Engineering Progress*, 58(9):76-80.
56. *Nitrogen*, No. 168, July-August 1987.
57. Pratt, C. J. 1964. "Ammoniated Phosphate Type Fertilizers," "Ammonium Sulfate, Nitrate and Chloride Fertilizers," IN *Fertilizer Nitrogen*, Vincent Sauchelly (Ed.), pp. 196-200, 222, 232-236, Reinhold Publishing Corp., New York, NY, U.S.A.
58. Rao, D. G. 1977. "Technoeconomic Evaluation of Alternate Uses of Byproduct Gypsum," FAI-IFDC Fertilizer Seminar Proceedings.
59. Hardy, W. L. 1957. "Sulfur From Gypsum Not Feasible in United States but May Be Abroad," *Industrial and Engineering Chemistry*, 49(2):57a.
60. George, K. C., and N. D. Gopinath. 1963. "Manufacture of Ammonium Sulfate," Paper prepared for Conference on the Development of the Fertilizer Industry in Asia and the Far East, United Nations Economic Commission for Asia and the Far East, Bombay, India.
61. "Leaving the Byproduct Ammonium Sulfate Out of Caprolactam Manufacture." 1977. *Nitrogen*, 108:33-36.
62. UNIDO. 1969. "The Ammonium Chloride and Soda Ash Dual Manufacturing Process in Japan," Fertilizer Industry Series Monograph No. 4.
63. "Ammonium Chloride for More Crops." 1977. *Japan Chemical Week*, 18(7):875.
64. "Ammonium Chloride: A Minority Product, but Important in Asia." 1978. *Nitrogen*, 111:31-32.
65. Ando, J., J. P. Smith, M. R. Siegel, and J. E. Jordan. 1965. "Quantitative Analysis of Mixed Fertilizers by X-ray Diffraction," *Journal of Agricultural and Food Chemistry*, 13:186-195.
66. British Sulphur. 1992. *N-P-K-S Process and Plant Suppliers*, 3rd Edition, British Sulphur Publishing, London, England.
67. British Sulphur. 1987. *World Fertilizer Atlas*, 8th Edition, The British Sulphur Corporation Ltd., London, England.

Chapter 9. Urea

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Chapter 9. Urea

9.1 Introduction

Urea was first identified in 1773 when it was isolated by crystallization from urine. It was first prepared synthetically in 1828 by Wohler from ammonia and cyanuric acid [1]:

$$NH_3 + HCNO \rightarrow CO(NH_2)_2$$

This preparation was a milestone in science since urea became the first organic compound prepared by synthesis from inorganic materials. Previously it was believed that organic compounds could be produced only by living organisms. The present method of synthesizing urea from ammonia and carbon dioxide has been known in principle since 1868, but commercial production by this method started in 1922 in Germany, in 1932 in the United States, and in 1935 in England. However, there was some commercial production in Canada (by DuPont) starting in 1920 using calcium cyanamide according to the reaction:

$$CaCN_2 + 3H_2O \rightarrow CO(NH_2)_2 + Ca(OH)_2$$

Use of urea as a fertilizer developed rather slowly at first, partly because early processes were cumbersome and expensive and partly because of some doubt about its agronomic suitability. Urea has been considered a slow-release fertilizer in Europe since it must undergo two transformations in the soil before it becomes available to most crops [1]. The first transformation is hydrolysis:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

The second transformation is nitrification in which ammonia is oxidized in the soil by microbiological means first to nitrite and then to nitrate. These reactions proceed rapidly in warm, moist soil, but they are quite slow in cool soils, which are characteristic of temperate climates (northern Europe) in the spring season.

Under some circumstances urea can be phytotoxic, and many cases of severe damage to crops have occurred, especially when the urea was placed close to the seeds. These cases were mainly associated with "combine drilling," which is a common practice in some European countries. The practice consists of drilling fertilizer with small grain seed. The phytotoxicity may be caused by locally high concentrations of ammonia during the hydrolysis stage, or it may be caused by accumulation of nitrite during the nitrification stage. A possible third cause is the presence of excessive amounts of biuret as an impurity in urea.

Aside from toxicity, poor agronomic results may be caused by loss of ammonia to the atmosphere when urea is applied on the surface of the soil or as a topdressing to growing crops. This loss is caused by the formation of ammonia by hydrolysis under such conditions that part of it escapes to the atmosphere rather than being adsorbed by the soil. A primary use for straight nitrogen fertilizer in the United Kingdom and many European countries is for topdressing cereals and grass. Studies in England and the Netherlands have shown that on the average urea is only 80%-85% as effective as ammonium nitrate for this use.

For the reasons mentioned above, urea has been unpopular in most European countries, and it still finds little use in northern Europe as a straight nitrogen fertilizer. However, recent studies have shown that urea is as effective as ammonium nitrate when incorporated in the soil at or before planting time.

In the United States the general conclusion of agronomists is that urea is as good as any other nitrogen fertilizer **if properly used**. However, it is not recommended for some uses, such as in placements in contact with or near seeds.

Urea is generally satisfactory for rice and preferable to nitrates for flooded rice because nitrates are reduced to N_2O or N_2 in the anaerobic zone of the rice paddy and hence lost to the atmosphere. Furthermore, the rice plant, unlike most other crops, can utilize the ammonium form of nitrogen efficiently. In tropical, subtropical, and warm temperate zones, hydrolysis and nitrification (in aerobic soil conditions) are rapidly completed; thus, there is no delayed-release effect. For these reasons and because of its high concentration and favorable production cost, it has become the most popular nitrogen fertilizer in Asia and in many countries on other continents. An excellent discussion of the agronomic effects of urea has been presented by Tomlinson who concludes that urea can be used efficiently, but its use requires a higher degree of understanding than is the case with simple inorganic salts [2].

On a worldwide basis urea is the most popular solid nitrogen fertilizer, and its use grows much more rapidly than that of other materials. More than 50 million tonnes of urea is now produced annually. More than 16 million tonnes is produced in the Indian subcontinent, more than

10 million in China, and more than 4 million in Indonesia. More than 70,000 tonnes of daily capacity has been installed in the past 10 years.

Urea is used as a cattle feed supplement where it is a cheap source of protein. It is used both in prill form (microprill at 0.2/0.4-mm diameter) and as a liquid in a mixture of urea (±75% solution), molasses, and phosphoric acid. It is the feed material for melamine plastic and for various glues. The glues are either urea-formaldehyde or urea-melamine-formaldehyde. The latter is waterproof and is used for marine plywood.

9.2 Properties of Urea

Some properties of urea that are of interest for fertilizer use are as shown in Table 9.1.

Table 9.1. Properties of Urea

Molecular weight	60.06
Nitrogen content, %	46.6
Color	white
Specific gravity	1.335
Melting point, °C	132.7
Solubility in water, parts per 100 parts of water by weight at	
0°C	66.7
20°C	108.0
40°C	167.0
60°C	251.0
80°C	400.0
100°C	733.0
Critical relative humidity at	
20°C	81%
30°C	73%
Specific heat at 20°C, cal/g °C	0.320
Heat of solution in water (endothermic), cal/g	-57.8

The relatively low specific gravity, compared with that of other fertilizer materials, must be considered in calculating storage space requirements. For instance, storage space requirements per unit of nitrogen are about the same for urea as for ammonium nitrate because the higher analysis of urea is offset by its lower specific gravity. Urea is less hygroscopic than ammonium nitrate but more hygroscopic than ammonium sulfate; it requires protection from humid atmosphere in some climates. The coating of prilled urea with clay, oil, or Ureasoft™ gives relatively good protection. Many producers now add formaldehyde to the urea melt just before prilling and obtain very satisfactory results in storage.

If the product is dedusted and the producer has made good prills with high impact and crushing strengths, it is possible to ship uncoated bulk urea long distances with no problems (i.e., Houston to Brazil).

9.3 Process Operating Variables

Temperature – Conversion of ammonium carbamate to urea in the absence of excess ammonia increases with temperature to a maximum of about 50% at 170°-190°C when the pressure is sufficiently high to keep the reactants in the liquid state. The rate of reaction increases with temperature; it is slow at 150°C and below (with stoichiometric NH_3:CO_2 ratio) and quite rapid at 210°C. A satisfactory approach to equilibrium can be obtained in the temperature range of 180°-200°C in 0.3-1.0 hours or at lower temperatures with excess ammonia. Corrosion difficulties increase with temperature, and a range of 180°-210°C is generally accepted as optimum for most processes.

Pressure – At constant temperature, conversion increases with pressure up to the critical point which is the point at which the vapor phase is substantially eliminated and the reactants are in the liquid state. A further increase in pressure is not beneficial. The critical temperature is a complex function of the temperature and composition of the reactor's contents. For example, at 150°C a pressure of about 100 atm might be near optimum for a stoichiometric NH_3:CO_2 ratio, but at this temperature the rate of reaction is unacceptably slow. At the preferred temperature of 180°-210°C, pressures of 140-250 atm are commonly used.

Mole Ratio of NH_3:CO_2 – Excess NH_3 above the stoichiometric mole ratio of 2 favors the rate of the reaction. The percentage of CO_2 converted to urea is increased but, of course, the percentage of NH_3 converted to urea is decreased. Because recycling of excess NH_3 is relatively simple (as compared with that of CO_2, which remains as carbamate), most processes use 50% or more excess ammonia (a mole ratio of 3:1 or more). Today all processes account for a balance of both CO_2 and NH_3 conversion to reduce total recycling to a minimum plantwide (i.e., reactor and synthesis).

Other Factors – The presence of water decreases conversion; therefore, most processes are designed to minimize the amount of water recycled to the reactor. The presence of small amounts of oxygen decreases corrosion; all processes use this method of minimizing corrosion.

Optimum Conditions – It is generally not economical to maximize the percentage conversion in the reactor because this would require an excessive retention time. The aim therefore is to attain maximum quantity of urea production per unit of time with due regard to the cost of recycling unreacted CO_2 and NH_3 and the cost of increased reactor size and corrosion difficulties, which increase with temperature. Typical operating conditions are: temperature, 180°-210°C; pressure, 140-250 atm; NH_3:CO_2 mole ratio, 3:1-4:1; and retention time, 20-30 minutes.

9.4 Urea Processes

Basically all new plants use total-recycle processes. However, once-through or partial-recycle processes may still be preferred in some countries, and in some cases stripping can be considered a refinement of total recycle.

9.4.1 Once-Through and Partial-Recycle Processes

The once-through method is the simplest and least expensive (in both capital investment and operating costs) of the three basic types of processes. A typical unit flowsheet (synthesis section only) is given in Figure 9.1. Liquid ammonia and gaseous carbon dioxide are pumped into the urea reactor at about 200 atm. The reactor temperature is maintained at about 185°C by regulating the amount of excess ammonia; about 100% excess NH_3 is required, and about 35% of the total NH_3 is converted to urea (75% of the CO_2 is converted). The reactor effluent solution contains about 80% urea after carbamate stripping. The unconverted NH_3 and CO_2 are driven off at moderate pressures by steam heating the effluent solution in the carbamate strippers.

Even though this process is the simplest of the urea processes, it is the least flexible and cannot be operated unless some provision is made to utilize the large amount of off-gas ammonia. Thus, it must be used in conjunction with the coproduction of some other material, e.g., ammonium sulfate, ammonium nitrate, nitric acid, or ammonium phosphate, for which the ammonia can be used. One case in which the system can be used is the production of urea-ammonium nitrate solution; the unconverted NH_3 is used to make ammonium nitrate solution, which is then mixed with the urea solution. Even in this case, most new plants use a total-recycle process.

In the partial-recycle process, part of the off-gas ammonia and carbon dioxide from the carbamate strippers is recycled to the urea reactor. Recycling is accomplished by absorbing the stripper gases in a recycle stream of partially stripped urea effluent, in process-steam condensate, or in mother liquor from a crystallization finishing process. In this manner, the amount of NH_3 in off-gas is reduced. Any proportion of the unreacted ammonia can be recycled; typically, the amount of ammonia that must be used in some other process is reduced to about 15% of that from a comparable once-through unit.

The Mitsui Toatsu partial-recycle process flowsheet is typical of the first method and is shown in Figure 9.2. Liquid NH_3 and gaseous CO_2 are pumped to the urea reactor at 200 atm. The temperature of the reactor is maintained at about 185°C by proper balance of excess NH_3 and carbamate solution recycle feed. About 100%-110% excess NH_3 is used; about 70% of the NH_3 and

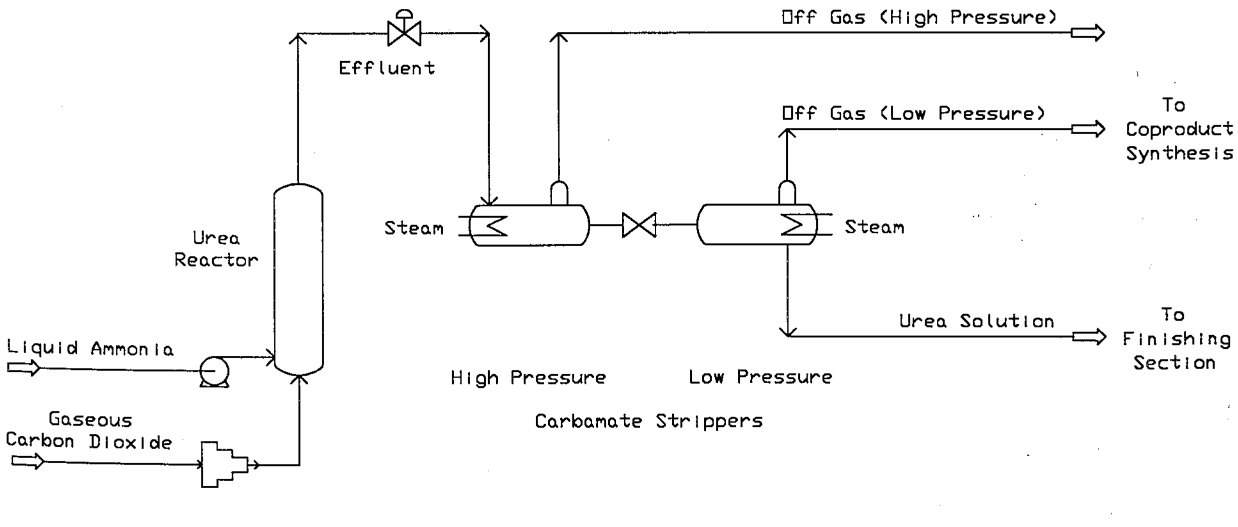

Figure 9.1. Typical Once-Through Urea Process.

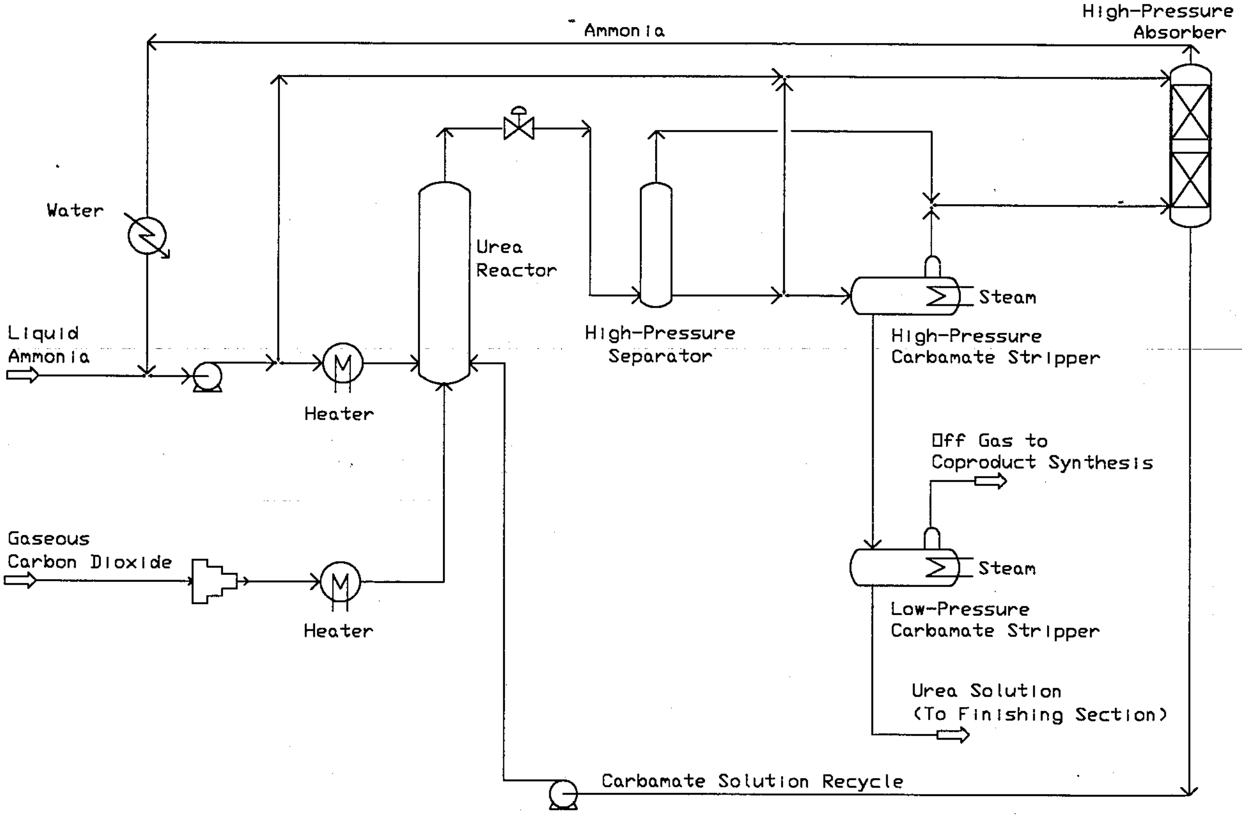

Figure 9.2. Typical Partial-Recycle Process.

87% of the CO_2 are converted to urea. The remaining 30% of the NH_3 must be used in some other process. The reactor effluent contains about 80% urea.

Unreacted NH_3 and CO_2 are separated from the urea solution in the high-pressure separator and in two to three steam-heated carbamate strippers at successively lower pressures. The off-gas from the separator and the first-stage stripper is absorbed in the high-pressure absorber by a side stream of partially stripped reactor effluent from the high-pressure separator. Heat evolved in the absorber reaction is removed (to increase absorption capacity) by the addition and expansion of part of the liquid ammonia feed at this point. Pure gaseous ammonia from the top of the absorber is also recycled to the urea reactor after being condensed.

Since the amount of ammonium carbamate that can be absorbed in the absorber solution described above is limited by its solubility in the system H_2O-urea-NH_3, part of the ammonia and carbon dioxide cannot be recycled and must be used in the production of a coproduct nitrogen material. As in the once-through process, the operation of the urea plant still must coincide with that of the coproduct plant.

Other partial-recycle processes differ in detail but accomplish similar results. Although the investment cost is somewhat lower than that for total recycle, this advantage apparently does not compensate for the inflexibility arising from the necessity of operating a coproduct plant with mutual interdependency problems. However, the partial recycle processes continue to find application, particularly where UAN solution is a coproduct.

9.4.2 Total-Recycle Processes

In total-recycle processes, all the unconverted ammonia-carbon dioxide mixture is recycled to the urea reactor (conversion is about 99%), and no nitrogen coproduct is necessary. This is the most flexible of the urea processes because it depends only upon the CO_2 and NH_3 supply from its supporting ammonia plant for operation. However, it is also the most expensive in investment and operating costs. Therefore, if the production of other materials requiring ammonia is planned, an integrated once-through or partial-recycle unit would have lower investment and perhaps lower operating costs. The disadvantages are decreased reliability arising from mutual dependence of two plants, inflexibility in proportions of coproducts, and difficulties in synchronizing the operation of two plants. Because of these difficulties, most manufacturers prefer a total recycle process, even when a second nitrogen product is desired.

The urea reactor effluent contains urea and water resulting from the synthesis reaction; it also contains unconverted carbamate and excess ammonia. These ingredients must be separated to give a urea solution reasonably free from the other materials and to recycle the CO_2 and NH_3 to the synthesis reactor. In order to separate carbamate from urea, it must be decomposed according to the equation:

$$NH_2CO_2NH_4 \leftrightarrows CO_2 + 2NH_3$$

This reaction is the reverse of the first step of the synthesis process and is strongly endothermic (37.7 kcal/g-mole). The decomposition is accomplished by various combinations of supplying heat, lowering pressure, and "stripping" which lowers the partial pressure of one or more ingredients. The NH_3 and CO_2 are removed from the urea solution as gases accompanied by some of the water in vapor form. Naturally the CO_2 and NH_3 will recombine (releasing heat) when the temperature is decreased or the pressure increased. Hence, condensing by cooling and/or compressing a gaseous mixture of CO_2, NH_3, and H_2O produces a carbamate solution.

Total-recycle processes can be classified in five groups according to the recycle principle: (1) hot-gas mixture recycle, (2) separated-gas recycle, (3) slurry-recycle, (4) carbamate-solution recycle, and (5) stripping. The first four groups use carbamate decomposition steps basically similar to those of the once-through and partial-recycle processes, whereas the last one differs even in this respect.

Hot-gas recycle of mixed CO_2, NH_3, and H_2O was used in Germany between the two World Wars by I. G. Farbenindustrie at Oppau. The hot gas was compressed in five stages by reciprocating compressors with interstage cooling to an end temperature of 260°-270°C and a pressure of 120-130 atm. It was then cooled to 160°C to condense the gases (with carbamate formation), and the heat was recovered as steam. The process was not very successful; when the plant was destroyed during the last war, it was not rebuilt. The idea was revived by Chemical Construction Company with the proposal that the compression be done with large centrifugal compressors that became available in the 1960s using new materials of construction that can operate at high temperature (400°-540°C) without interstage cooling. The proposed process seems technically sound, but centrifugal compressors of this sort are feasible only in such large sizes that the minimum scale would involve a urea plant of about 1,200-tpd capacity. Because smaller scale development was not feasible, no organization was willing to risk using the untried process on such a large scale.

The separate-gas recycle method was developed to overcome the difficulties of the mixed hot gas recycle process. The CO_2 and NH_3 can be compressed separately without difficulties caused by carbamate formation. Processes of this type were developed by Inventa (Switzerland) and CPI-Allied (United States). The principle of the processes is that CO_2 in the gas mixture from the decomposers is absorbed selectively in a solvent such as monoethanolamine (MEA). The NH_3 remaining after CO_2 removal is compressed and recycled to the synthesis reactor. The CO_2 is desorbed from the MEA solvent by heating, and it is recycled separately [3].

The process has the advantage that conversion is not reduced by recycling water to the reactor and that the problem of recycling corrosive solution to the reactor is avoided. Offsetting this is the difficulty in recovering heat and cost of MEA makeup. The number of plants using the method is relatively small, and it is not known to be in use in any of the large plants (1,000 tpd and up) built in recent years.

The principle of the slurry-recycle process is that the CO_2-NH_3-H_2O gas mixture goes to a reactor to which a light paraffin oil is added. Carbamate, formed in the reactor as an oil suspension, which contains 35%-40% solids, is pumped into the urea synthesis unit with fresh CO_2 and NH_3. The mixture then goes through the carbamate decomposers, and the oil is separated from the urea solution by decantation for reuse. The process was developed by Pechiney (France) and has been used by that organization.

The carbamate-solution-recycle system became the most popular of the original total-recycle processes. There were several proprietary processes (Stamicarbon, Mitsui Toatsu, Montedison, Snamprogetti, etc.) which have been offered by their developers and licensees. They differed mainly in engineering details, methods for heat recovery, and means for energy conservation. In general, all solution-recycle processes involve absorbing CO_2 and NH_3 in water and recycling it to the synthesis step as an aqueous carbamate solution. The amount of water must be kept to a minimum, however, because addition of water lowers the percentage of conversion to urea. In addition, the evaporation of additional water has a negative impact on the economy of the process.

Some years ago there was considerable variation in the design features of the various solution-recycle processes; these differences have gradually disappeared. Today most of the "conventional" processes are much the same. All use similar reactor conditions (temperature about 185°C and pressure about 200 atm), maintain an $NH_3:CO_2$ mole ratio of about 4:1 in the synthesis loop, and obtain about the same conversion (65%-67%)

of CO_2 to urea for each pass through the synthesis reactor. Overall conversion of NH_3 to urea is 99% or more. All reduce the reactor effluent pressure to an intermediate level and then pass the solution through two or three stages of decomposition (by heating) at successively lower pressure levels. In each stage, the evolved gas mixture is condensed (or absorbed in weak solution condensed in a later stage), and the resulting solutions are returned through the system to the reactor. The excess ammonia (from the excess used in the initial reactor feed) passes through the absorbers, is condensed, and is fed back to the reactor.

Although these primary steps are common to the various conventional methods, there is considerable difference in the carbamate solution-recycle systems – in pressure and temperature levels of the decomposition steps, equipment arrangement, and process flow. This phase of the development is still in a state of flux; even for a given company, the flowsheet for a current plant will likely be somewhat different from that of the immediately preceding one. The general design objectives are to:

1. Maximize heat recovery.
2. Minimize amount of carbamate solution recycled (smaller pumps and less power) and amount of water returned to the reactor (better conversion).
3. Minimize power requirement.
4. Maximize ammonia recovery (lower operating cost and less pollution).

Since another primary objective, of course, is to minimize investment, the problem becomes the usual one of finding the best balance between utility consumption and maintenance on the one hand and investment on the other.

Several parameters are involved in the design of the carbamate-solution-recycle system, and they are so interrelated and interdependent that it is difficult to analyze them separately. Changing one parameter in the direction of improvement almost always changes one or more of the others in an adverse direction, and the extent of the adverse effect can only be determined by somewhat complicated calculations. Hence, it is difficult to evaluate quantitatively the various schemes that have been developed.

One important consideration is the number of decomposition stages. Reducing the number lowers plant investment but increases the amount of water returned to the reactor, makes heat recovery less attractive (decomposer pressures generally lower), and results in higher ammonia loss in gaseous or liquid effluents. The current trend is to three stages as the optimum number. The third stage generally involves both decomposition of carbamate and evaporation of water, with vacuum applied to remove the ammonia down to a very low level as a means of minimizing atmospheric pollution. The flashed gas is passed through a water-cooled condenser, the condensate stripped of ammonia, and the stripped condensate preferably discarded rather than returned to the reactor. Such a procedure produces only traces of ammonia in the gaseous and aqueous effluents.

The point of heat recovery also varies. The main source of heat in the system is carbamate formation in the reactor. In some past designs, recovery or removal of heat directly from the reactor was practiced – by water coils in the reactor or a cooling jacket outside. Today, however, the recycled ammonia and carbamate solution take up the reaction heat and carry it out of the reaction zone.

In the decomposition section, heat must be added in order to get an adequate rate of carbamate decomposition. Much of this is heat released when the evolved gases are recondensed, and it is at this point that heat is usually recovered. The recovery is limited to the first decomposition stage, however, because the gases are at such a low pressure in the later stages that the condensation temperature is too low for economical recovery of the heat.

Thus, the usual source for heat recovery is hot condensed liquor from the first-stage absorber. Practice varies as to the stream used to absorb this heat. In some cases, water is heated and steam is produced: in other published flowsheets a process stream is involved.

Gas release procedure can have an important effect on the amount of water recycled to the reactor. The simplest arrangement – merely releasing pressure, flowing the solution into a vessel, heating it, and allowing the evolved gases to escape – is relatively inefficient because it gives maximum evaporation of water. Two systems have evolved, both of which minimize water evaporation. The first involves a sequence, in each stage, of (1) pressure reduction, (2) gas release, (3) heating, and (4) further gas release. The advantage is that gas evolved by release of pressure alone comes off at a lower temperature than in the heated decomposer. The partial-pressure relationships involved are such that this procedure gives less evaporation of water.

In the second system a rectifying column is used as the decomposer: relatively cold incoming solution flows downward in countercurrent flow to the hotter gas evolved in a heated section (or reboiler) at the bottom. Thus, the composition of gas leaving the column approaches equilibrium with the incoming solution, which has a relatively low partial pressure of water because of the reduced temperature.

Because of the large number of processes offered and frequent changes in flowsheets, it is not feasible to show flow diagrams for all processes. Figure 9.3 shows a flow diagram for the Mitsui Toatsu total-recycle process (Process C). No implication is intended that this process is necessarily superior to others.

9.4.3 Stripping Process-Based Plants

In 1966 Stamicarbon of the Netherlands introduced the CO_2 stripping process with a 220-tpd unit built for its parent company Dutch State Mines (DSM). In 1968 a 1,000-tpd plant was designed and built for DSM.

Shortly after this, Snamprogetti designed and built a small plant utilizing NH_3 as the stripping agent. (The company later switched to thermal stripping, which is possible due to the very high NH_3 ratio.) Next, Toyo Engineering Corp. of Japan utilized CO_2 for stripping.

Since that time, over 95% of all completed urea plants have utilized these three technologies. For that reason, these will be covered in this chapter. Over 140,000 tonnes rated daily capacity has been installed with stripping. Actually most of these plants are operated above their ratings and also are operated well over the 330 days usually used to calculate an annual capacity. A capacity of 50 million tpy from the stripping-based plants is conservative.

Plant sizes have increased drastically. Toyo's largest unit rating is 1,760 tpd, Snamprogetti has a 1,925 rated unit, and Stamicarbon has several 2,000-tpd units. (One of these is currently being revamped to 2,850 tpd.) After in-depth consultation with its equipment vendors (i.e., centrifugal compressors, centrifugal and reciprocating high-pressure pumps, and high-pressure vessels), Stamicarbon is prepared to offer units (single train) which have capacities up to 3,500 tpd.

Each of these three licensers has different approaches, and each has revised and improved its technology through the years. It is apparent that further improvements will be made.

All three processes closely approach stoichiometric values in raw material consumptions, and all have

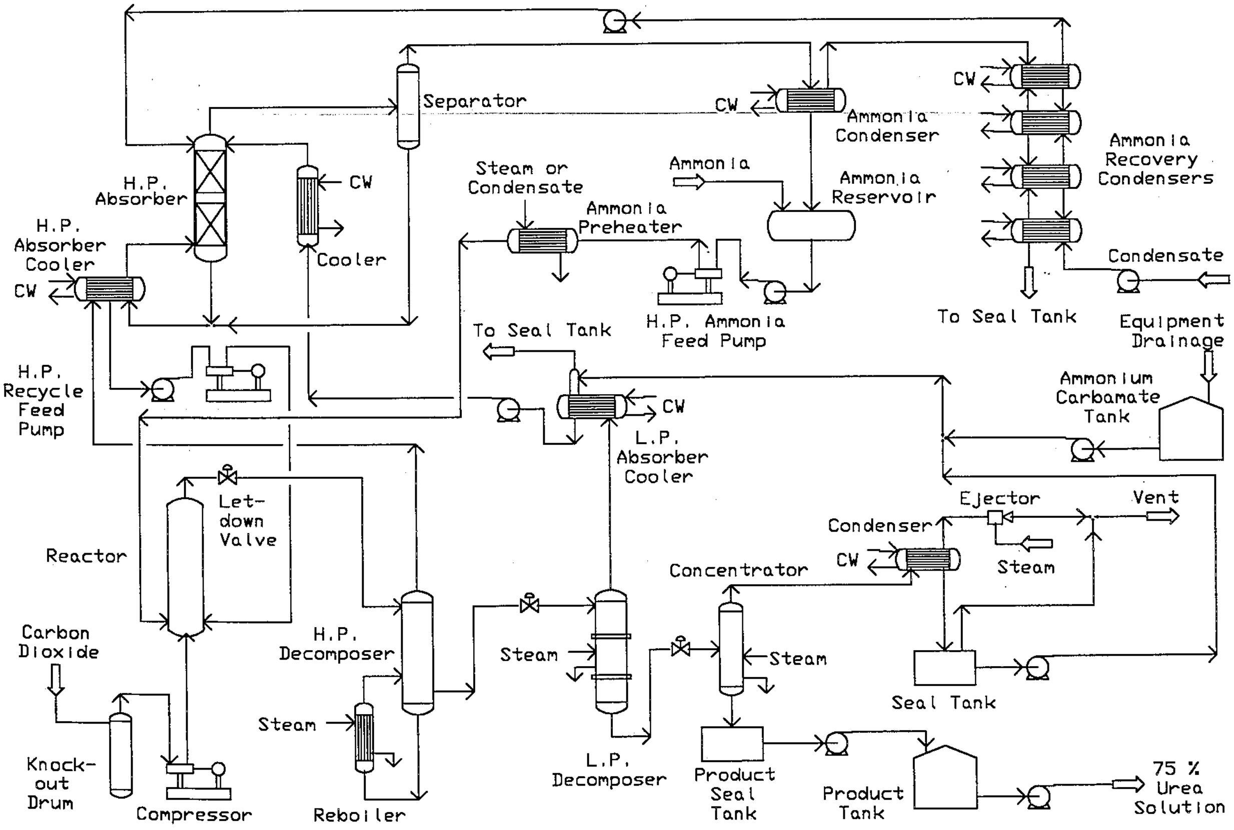

Figure 9.3. Typical Total-Recycle Urea Process (TVA Plant).

reduced their steam consumption to a minimum apparent economic level. (Steam use could easily be reduced further but with an unfavorable increase in capital costs.) The last avenues available for further improvements appear to be in reduction of capital costs, improved reliability and efficiency of mechanical equipment, and metallurgical advances.

Stamicarbon is presently prepared to offer technology that utilizes a pool reactor to reduce the number of high-pressure vessels from four to two. This drastically reduces both equipment and construction costs. The flow sheets shown in this chapter for the Stamicarbon, Snamprogetti, and Toyo processes (Figures 9.4, 9.5, and 9.6) are for the basic design used by each licenser in the past 10 years. As can be seen, Snamprogetti and Toyo, with their high NH_3/CO_2 ratios require two decomposition stages; Stamicarbon continues to use a single stage. The possible problem of more upsets due to one stage has been solved with a patented proprietary N/C ratio control instrument. Operating conditions and process requirements for the three principal synthesis processes are given in Table 9.2.

All processes still require use of oxygen for passivation in the synthesis loop. Metallurgical advances have reduced the amount required. Snamprogetti now utilizes a bimetallic zirconium/25-22-2 (Ni, Cr, Mo) tube in its stripper. The corrosion rate for zirconium in urea service is nil. Toyo utilizes a duplex alloy (ferrite-austenite), which requires less oxygen. Stamicarbon, working with the Swedish steel producer Sandvik, has patented a proprietary material called Saferex, which requires very little oxygen; future plants will use this new material.

A very good example of the results of these licensers' research and improvements can be shown by the fact that NH_3 emissions have been reduced from 8-plus kg/tonne of final product to 0.7 kg, and steam use has been reduced.

The best source of information on the very complicated thermodynamics and phase equilibria involved in the urea process is contained in the paper by Kaasenbrood and Chermin [4].

Interest in totally integrated NH_3/urea plants has dropped as most producers want to continue the flexibility

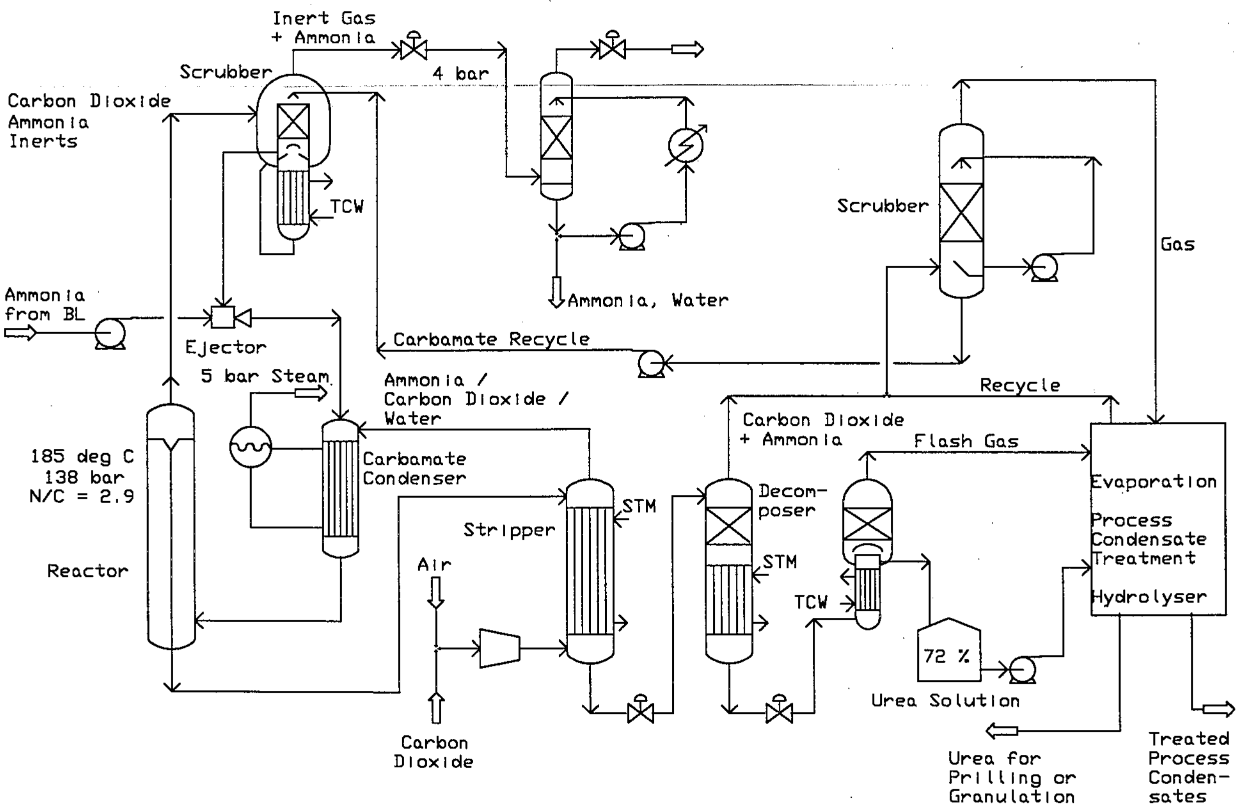

Figure 9.4. Stamicarbon CO_2 Stripping Process.

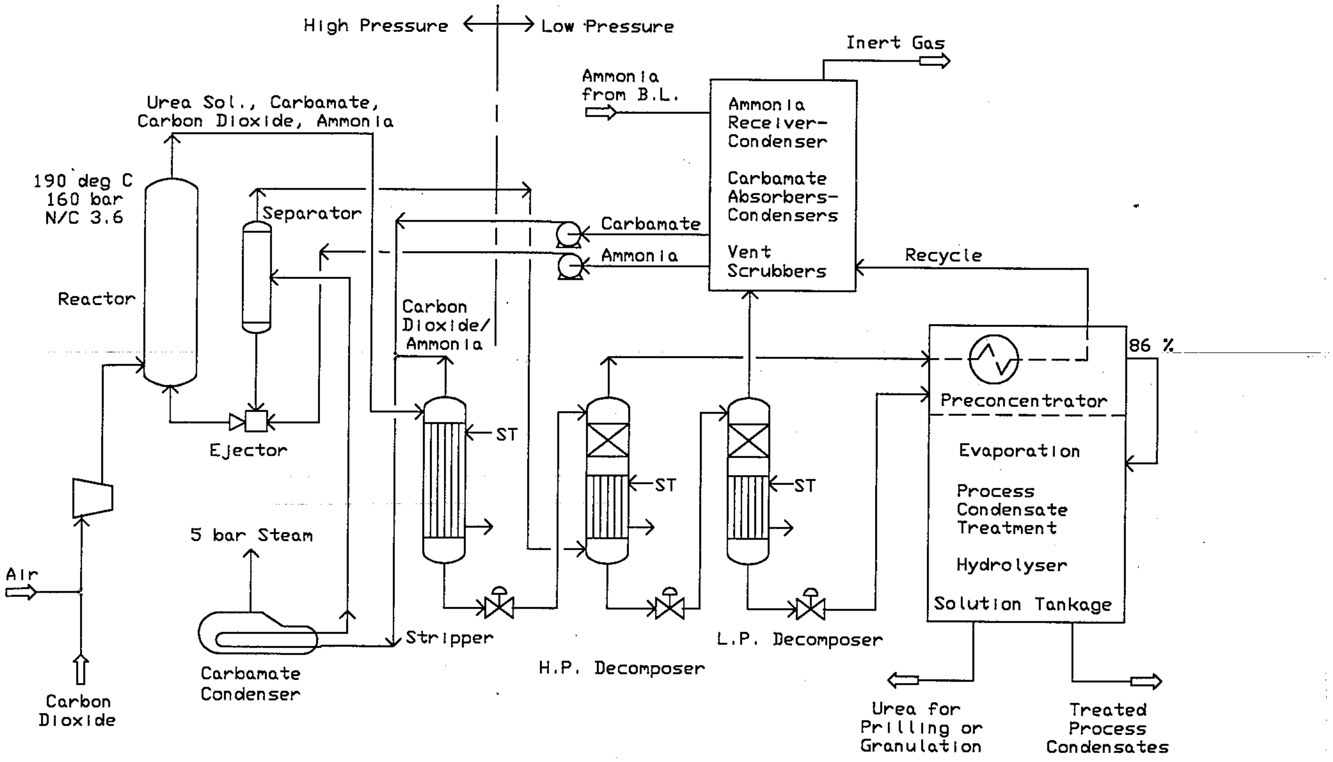

Figure 9.5. Snamprogetti Thermal Stripping Urea Process.

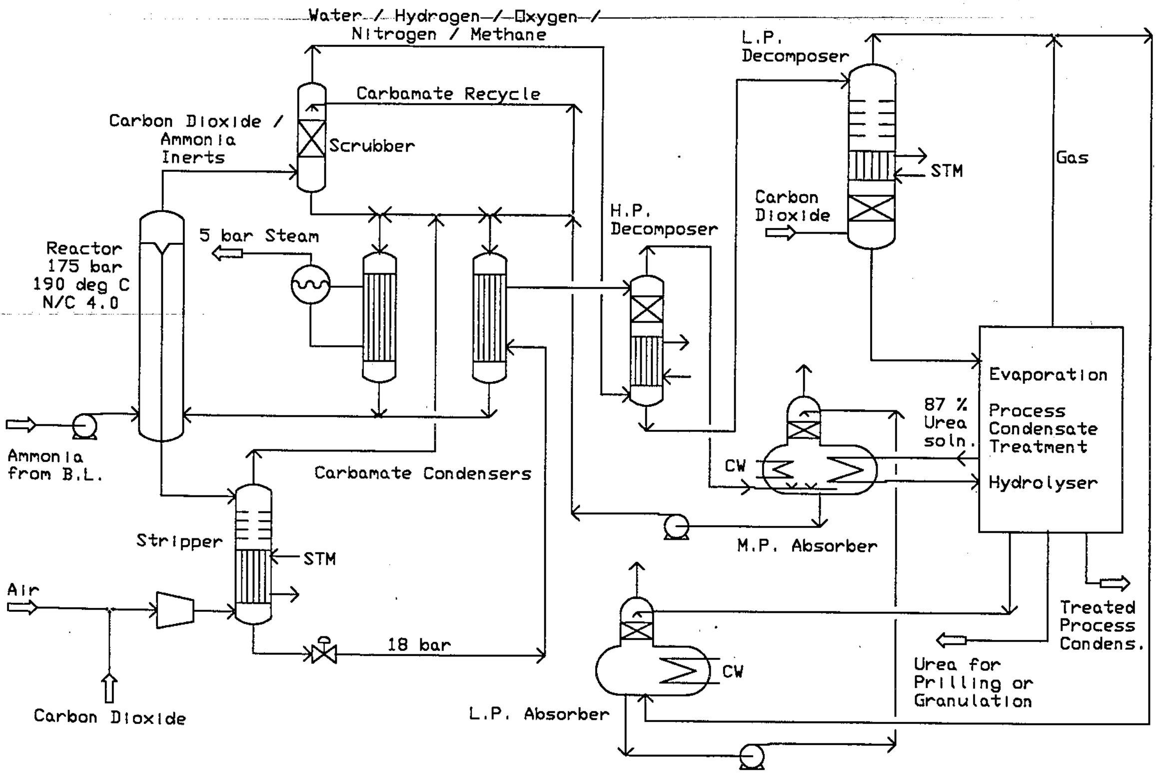

Figure 9.6. TEC ACES Process.

Table 9.2. Urea Process Operating Conditions/Requirements [5]

	Snamprogetti Thermal Stripping	Stamicarbon CO_2 Stripping	TEC ACES Process
Reactor pressure, atm	156	140	175
Reactor temperature, °C	188	183	190
Molar NH_3/CO_2 ratio	3.3-3.6	2.95	4.0
Molar H_2O/CO_2 ratio	0.5-0.6	0.39	0.6
CO_2 conversion in reactor, %	64	60	6.8
NH_3 conversion in reactor, %	41	36	34
CO_2 conversion in synthesis, %	84	79	NA
NH_3 conversion in synthesis, %	47	79	NA
No. of high-pressure vessels – synthesis	5	4	5
Recirculation – stages	2	1	2
NH_3 consumption, t/t	0.566[a]	0.566[a]	0.568
CO_2 consumption, t/t	0.735[a]	0.733[a]	0.735/0.740
Import steam, t/t[b]	0.950	0.920	0.80
Cooling water, t/t[b]	75	70	80
Electricity, kWh/t[b]	21-23	15	15
Liquid effluent			
Free NH_3, ppmw	2	1	5
Urea, ppmw	2	1	5
Hydrolyzer steam pressure, bar	38	25	25

Note: NA = not available.

a. Based on final product-urea granules containing ±4.5 kg formaldehyde/tonne product, using UF85 (urea+biuret 25%, formaldehyde 60%, water 15%).

b. Depending on plant location and available utilities, these figures can vary greatly. The plants can easily be designed for minimum steam or minimum electric power; the decision is on a cost basis.

they have with independent units. The few integrated units built have not been successful. There are some plant areas where integration appears attractive. An example would be in wastewater purification.

9.5 Urea Finishing Processes

Urea can be prilled, granulated, flaked, and crystallized. At the present time only prilling and granulation can be considered important. Most new plants that plan to ship internationally utilize granulation because of its far superior handling and storage qualities. Comparative product characteristics are shown in Table 9.3.

9.5.1 Prilling

Prilled urea is made by using a spinning bucket, shower heads, or acoustic vibration (19 plants). The most common method is the spinning bucket. Stamicarbon uses its own design for the buckets; Snamprogetti and Toyo both use the tuttle bucket, which was initially developed by Malcolm Tuttle and Premier Petrochemical (Pasadena, Texas) in 1964 and 1965. Toyo also will provide the acoustic vibration unit. In prilling, the urea melt is concentrated via vacuum evaporation to 99.8% and fed as quickly as possible into the bucket to minimize biuret formation. The liquid forms drops that then fall down a cylindrical concrete tower that has either induced, forced, or natural draft air flow. The prills solidify and are removed at the bottom by belt conveying to storage. Some plants have a fluidized-bed cooler in the prill tower bottom and others use an in-line cooler before storage. If low biuret product is to be produced, the urea melt from the last decomposition stage of the synthesis plant is first crystallized and the crystals are then melted just before prilling.

All prill towers have a dust problem, and even those with dust collection systems may have difficulties in meeting environmental standards. Properly designed prill towers utilizing natural draft can usually meet environmental standards without a dust collection system. Since prills are not as strong as granules in either crushing or impact

able 9.3. Urea: Comparative Product Characteristics

EC ACE
Process
.75
.90
4.0
0.6
6.8
34
NA
NA

	Prilled (Standard)	Granular (Bulk Blend)	Granular Large Granule[a]
oisture, %	0.30	0.20	0.25
iuret, %	0.90	0.70	0.70
ormaldehyde (injection), %	0.3-0.4	0.45	0.45
verage size, mm	1.70	2.50	Up to 8.0
rushing strength, kg	0.6 (2 mm)	3.0 (2.5 mm)	10.0 (6.3 mm)

. Used, for example, for forest application (3-5 mm size).

5
2
0.568
735/0.7
0.80
80
15
5
5
25
(urea+bi
an easil

rength, many of the new plants are using granulation rocesses for finishing.

If in order to improve the prill quality Stamicarbon ilizes a seeding system, fine urea dust is blown into the rill tower at a point about two-thirds above the bottom. his forms a nucleus for proper crystal growth. The re- ılting prill contains long interlocking crystals improv- ıg the crushing and impact strength greatly.

Many prill producers also add formaldehyde upstream f prilling in either the evaporators or to the melt. This nproves the quality greatly and reduces dust emission ıd caking tendencies in bulk storage. Other materials dded either before plant bulk storage or just before agging and/or bulk shipment are clays, Ureasoft™, or nineral oil.

9.5.2 Granulation

There have been many granulation processes developed and operated through the years. These include TVA pan granulation, C&I Girdler spherodizer spray-drum, Norsk Hydro pan granulation, and Fisons.

In the period from 1976 to 1979, NSM of the Netherlands developed a fluid bed granulation system that has been used in several plants. It produces excellent quality, and its single-train capabilities are up to the 3,500-tpd size that urea plant licensers are sizing up to. This process is now called the Hydro-Agri process.

In recent years Toyo Engineering Corporation developed a spouted-bed process, which was used in Japan and New Zealand. A few years ago they redesigned and

able 9.4. Granulation Process Requirements

	Hydro-Agri	Toyo Engineering	Stamicarbon
ectricity	37 kWh/tonne	23 kWh/tonne	38 kWh/tonne
P. steam	35 kg/tonne	not available	11 kg/tonne (4 bar) 21 kg/tonne (12 bar)
rocess water	0.2 m^3/tonne	not available	0.15 tonne/tonne
ooling water	none	none	none
ıgitive dust return	40 kg/tonne[a]	not available	69 kg/tonne[b]
ed solution	96% urea	98.5%	98.5%
F-85 additives (as formaldehyde)	0.45%	0.4%-0.5%	0.18
roduct			
Nitrogen content	46.2% wt.	46.2% wt.	46.4% wt.
Moisture	0.2%	0.23%	0.05%
Biuret	0.7%-0.8%	0.71%	0.80%
rushing strength (2.5-mm granule)[c]	+3 kg	3 kg	+3 kg
ulk density	780 kg/m^3	780 kg/m^3	780 kg/m^3

Dust returned as a 45% solution.
Dust returned as a 73% solution.
Hydro-Agri 6.3-mm granule = 10-kg crushing strength; others would be in the same range.

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now offer a spouted-fluid bed system (Figure 9.7). A 1,200-tpd plant has been very successful in Germany, and the New Zealand plant has been enlarged from 470 tpd to 750 tpd and converted to spouted-fluid bed. Toyo has considered 1,760 tpd as the maximum single-train size. Granulation process requirements are given in Table 9.4.

Stamicarbon developed a fluid bed system in 1976 and demonstrated its quality in a 50-tpd pilot plant. Due to various commercial matters, this system was never commercialized in a large-scale plant. With present commercial conditions, they are now prepared to license it with full guarantees on quality, quantity, and raw material/utility consumptions, etc. They also consider single-train units to 3,000 tpd no problem.

At this time fluid bed technology is the only one that can offer single-train units in sizes matching current urea plant sizes. In today's market, it can thus be considered the most acceptable type of granulation process.

Figures 9.8, 9.9, and 9.10 are flow sheets for the three available processes, Hydro-Agri, Toyo Engineering (spouted-fluid bed), and Stamicarbon.

Figure 9.11 shows the "heart" of the granulation plant; the granulator, as offered by Hydro-Agri.

9.6 Economics

The price of a urea plant with granulation varies greatly depending on client requirements, contractors' workloads, and vendor shop workloads at the time of bidding.

Recently five bidders submitted for a plant (urea/granulation) of +1,700 tpd. Three were utilizing one licenser and two were bidding with another. All five were using the same granulation technology.

For one process the three bids varied from about US $135 million to about US $165 million. For the other process they varied from about US $155 million to 185 million. All, of course, were bidding from the same client bid documents.

9.7 References

1. Honti, G. D. 1976. "Urea," IN *The Nitrogen Industry*, Akademia Kiado, Budapest, Hungary.
2. Tomlinson, T. E. 1970. "Urea-Agronomic Implications," *Proceedings of the Fertiliser Society* (London), No. 113.
3. Slack, A. V. 1969. "Urea Technology, A Critical Review," TVA Circular Z-4, *Proceedings of the Seminar on Fertilizer Technology*, New Delhi, India.
4. Kaasenbrood, P.J.C., and H.A.G. Chermin. 1977. "The Urea Stripping Process, Stripping Technology, Phase Equilibria, and Thermodynamics," *Proceedings of the Fertiliser Society* (London), No. 167.
5. Personal communications with the three process developing firms. 1996.

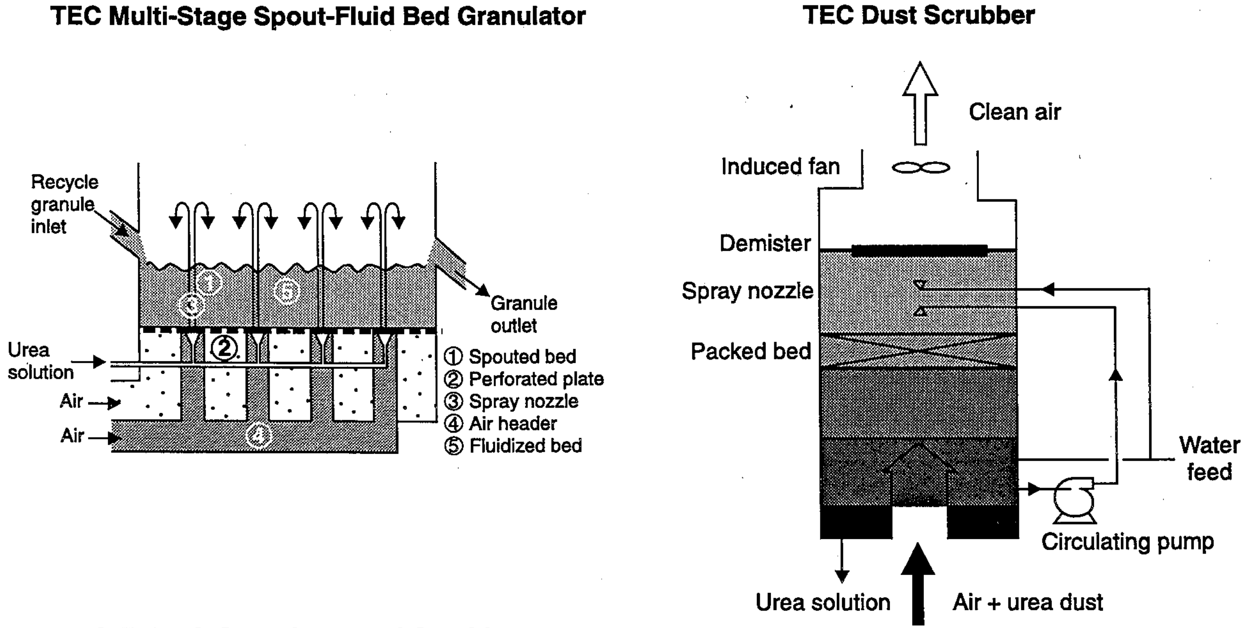

Figure 9.7. TEC Granulator and Scrubber.

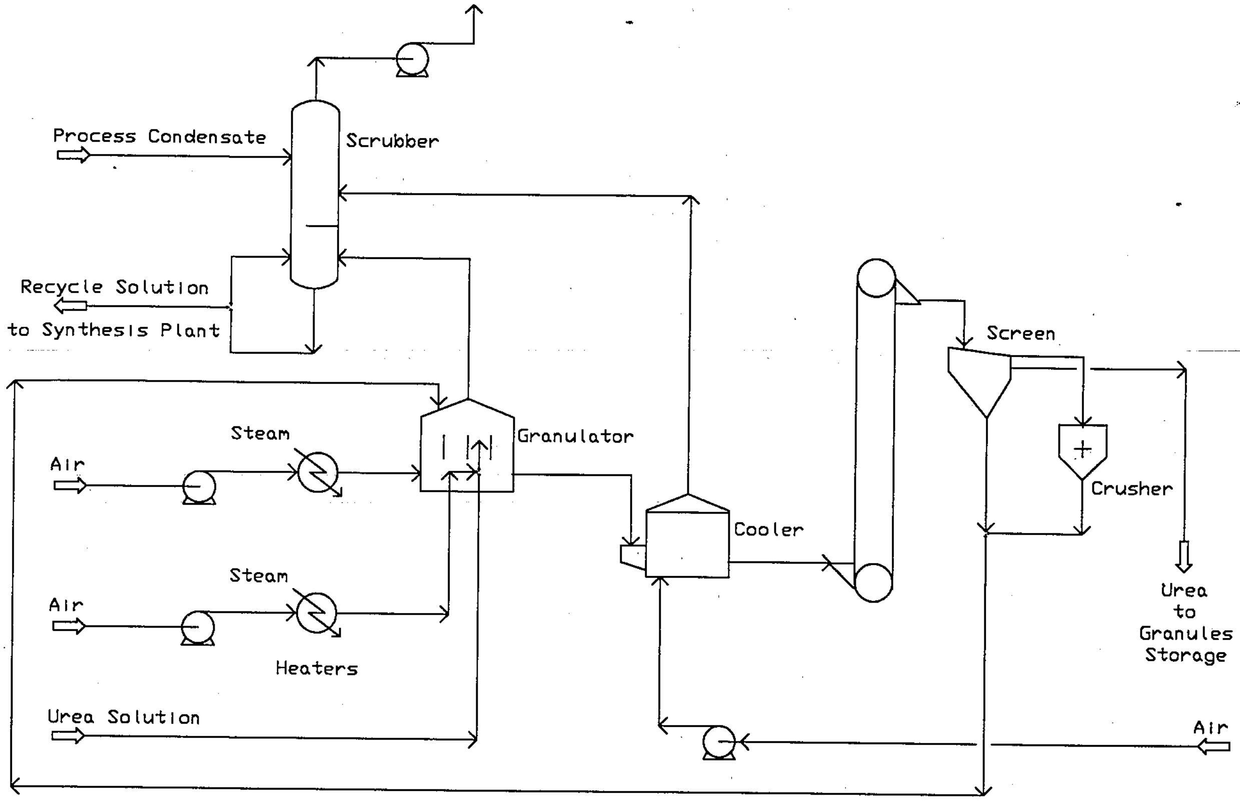

Figure 9.8. Hydro Agri Urea Granulation.

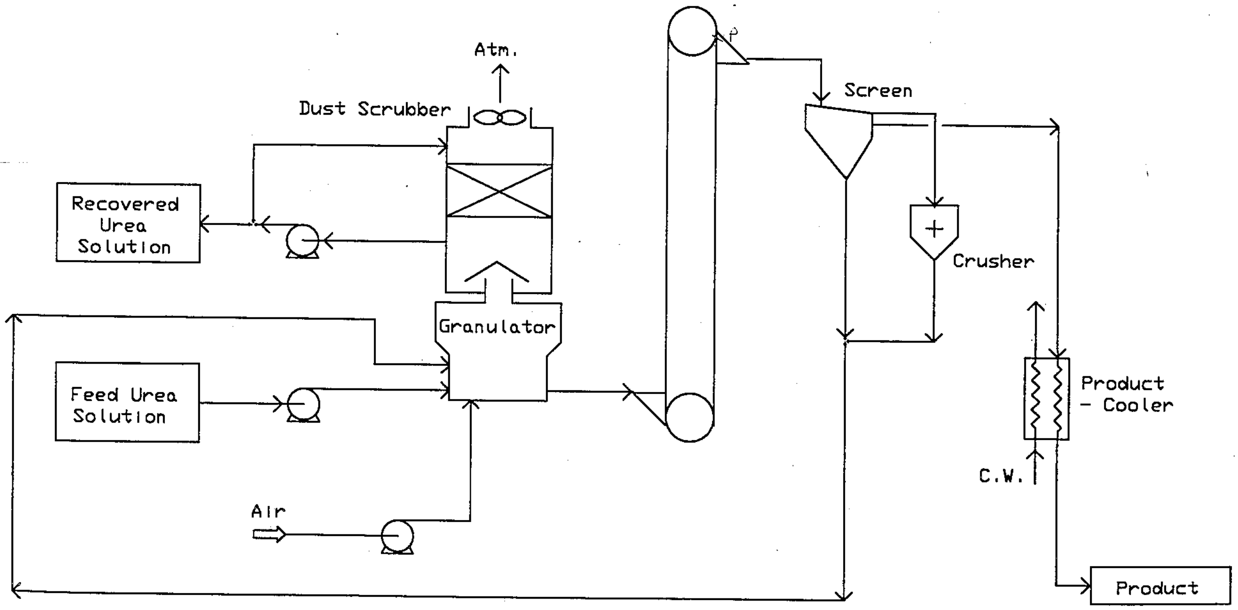

Figure 9.9. TEC Urea Granulation Process Flow Diagram.

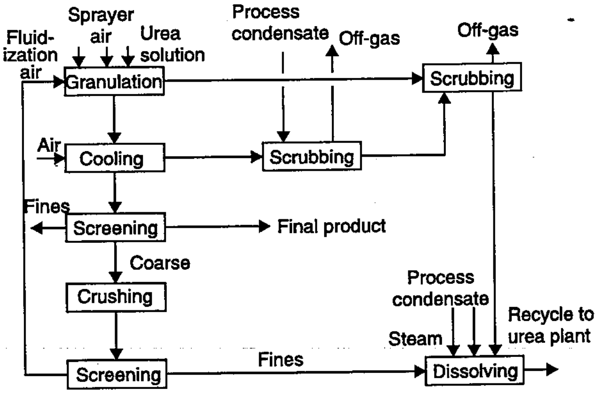

Figure 9.10. Stamicarbon Fluid-Bed Granulation.

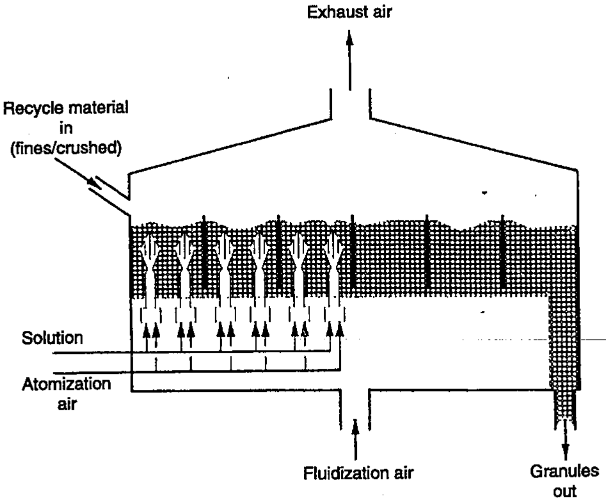

Figure 9.11. Hydro Agri Fluid-Bed Granulator.

Chapter 10. Liquid Fertilizers and Nitrogen Solutions

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Chapter 10. Liquid Fertilizers and Nitrogen Solutions

10.1 Introduction

The large-scale manufacture and use of fluid fertilizers began about 40 years ago. Fluids – the major source of nitrogen in the United States – are rapidly gaining popularity in France, United Kingdom, Canada, Spain, and Israel. Fluids are used to a lesser degree in Italy, Portugal, Denmark, Sweden, the Netherlands, Saudi Arabia, Brazil, and Colombia [1].

The former Soviet Union, now the Commonwealth of Independent States (CIS), was the second largest consumer of liquids; the CIS, however, comprises several different countries. The East European countries also consume significant amounts of fluid fertilizers.

Fluid fertilizers are usually divided into two distinct types: solutions and suspensions. Solutions are defined as fluids, the ingredients of which are in solution. Solutions may be clear or of a particular color. Sometimes a coloring agent is added so that a particular liquid can be distinguished from another liquid. Sometimes color is imparted by soluble impurities. The important factor is that all ingredients are in solution and it is necessary that they remain in solution. A suspension is defined as a saturated solution with small particles of nutrient-bearing materials suspended in the saturated solution. Gelling clays are used to cause conditions for good suspension of the particles in the fluid.

The term "fluid fertilizers" as used in this chapter refers to fertilizers such as anhydrous ammonia, aqua ammonia, nonpressure nitrogen solutions (28% to 32% N), liquid mixed fertilizer, and suspensions. Production of anhydrous ammonia, urea, and ammonium nitrate are presented in other chapters; however, the use of these materials to produce fluids and their application will be discussed in this chapter.

The fluid fertilizer industry started emerging as a significant industry in the United States during the early 1960s. By 1965 fluid consumption amounted to more than 5 million tonnes and represented about 18% of all fertilizers consumed. Table 10.1 gives the yearly consumption of fluids (anhydrous ammonia + aqua ammonia + nitrogen solution + solution mixtures + suspensions) during the period 1965-93.

Table 10.1. Fertilizer Consumption in the United States From 1965 Through 1993

Crop Year	Total Fluids	Total Fertilizer	Fluids,% of Total
	- - - -(thousand tonnes) - - - -		(%)
1965	5,352	30,315	17.7
1966	6,530	33,071	19.7
1967	7,676	35,324	21.7
1968	8,557	37,126	23.0
1969	8,937	37,280	24.0
1970	9,977	37,945	26.3
1971	11,132	39,564	28.1
1972	10,840	39,546	27.4
1973	11,124	41,823	26.6
1974	12,645	44,964	28.1
1975	12,189	40,606	30.0
1976	14,928	46,894	31.8
1977	15,680	49,098	31.9
1978	14,706	45,621	32.2
1979	16,328	49,342	33.1
1980	17,847	50,491	35.3
1981	18,887	51,760	36.5
1982	17,847	46,812	38.1
1983	14,402	40,428	35.8
1984	18,390	48,178	38.2
1985	18,514	47,127	39.3
1986	15,756	42,692	36.9
1987	15,928	41,272	38.6
1988	16,602	42,679	38.9
1989	16,592	42,762	38.8
1990	17,490	45,310	38.6
1991	17,880	44,588	40.1
1992	18,175	45,533	39.9
1993	18,294	46,586	39.3

These data show a major growth of fluid consumption from 1965 to 1985. In 1993, the consumption of fluids was about 18 million tonnes, representing about 40% of the total fertilizer consumed in the United States. From 1965 to 1993 fluid consumption in the United States tripled. Fluid fertilizer's percentage of total consumption more than doubled between 1963 and 1993. This healthy growth was partly due to the following reasons:

- Low-cost materials are used in the manufacture of fluid fertilizers.
- Because fluid fertilizers can be applied as starter fertilizers in row application or applied through irrigation systems, they allow the efficient use of plant nutrients to minimize environmental problems.

- Fluids are excellent carriers of micronutrients because a small amount of micronutrients can be homogeneously dispersed in the fluid; it is therefore easy to obtain uniform application of the micronutrient.
- Fluid fertilizers are excellent carriers of pesticides and are widely used in the application of herbicides. By using fluid fertilizer-pesticide mixtures, it is possible to reduce the number of applicator passes across the field. Because fluid fertilizers can be uniformly applied, it is possible also to uniformly apply the pesticide for uniform weed or insect control, which is not always possible when using granular fertilizers.
- Fluid fertilizers are usually much easier to handle than solid materials. For example, it would be much safer and easier to ship nonpressure urea-ammonium nitrate solutions and unload them than to ship either ammonium nitrate or urea.

However, fluids also have some disadvantages. The main disadvantages in using fluids are:

- They require special transportation, mixing, and storage equipment.
- Some of the fluids such as anhydrous ammonia and suspensions require special application equipment.

The United States uses the most fluid fertilizers. Table 10.2 summarizes fluid consumption by type in the United States during the period, 1960-93 [2]. These and other data indicate that in 1993 about 40% of the total fertilizers applied in the United States were in the fluid form; over one-half of the nitrogen was in the fluid form. The data also show that the most popular fluid in the United States is anhydrous ammonia; its use remained constant for several years and decreased slightly during 1993. The popularity of anhydrous ammonia for direct application is essentially nil in all other countries except Canada. The next most popular fluid in the United States is a nonpressure nitrogen solution that contains between 28% and 32% nitrogen (N).

The efficient use of fertilizers will continue to be stressed as a means of minimizing the effect of fertilizer on the environment. Two of the agricultural practices now being promoted are:

- Accurate measurement and placement of fertilizers to obtain maximum economic yield without adversely affecting the environment.
- Multiple application of nitrogen fertilizers to obtain more efficient use of nitrogen fertilizer.

A solution can be accurately measured, whereas it is difficult to accurately measure granular fertilizer. It is easier to accurately place fluids than to place solids. It is much easier to add fluids to irrigation units than to use solids for this purpose. For these reasons, the use of fluid fertilizers will increase, and their portion of the total consumed will also increase. In the United States, there will be a continued trend to use less anhydrous ammonia and more nitrogen solution. This shift is partly due to the precautions required in shipping, handling, and application of ammonia. A small amount of ammonia, which can cause a detectable odor, is released during handling at dealer locations. Therefore, it is expected that in the future the major source of fluid fertilizer nitrogen in the United States will be urea-ammonium nitrate (UAN) solutions (28%-35% N).

The use of nitrogen solutions is growing rapidly in other countries such as the CIS, France, United Kingdom, Canada, Spain, and Israel. The world consumption of nitrogen solutions increased by 112% between 1974 and 1990 [1]; it is expected to increase significantly during the next 5 years. However, nitrogen solutions still represent only about 2% of total world N consumption. In the United States in 1993 about 23% of total N was applied as nitrogen solution and about 32% of total N was applied as anhydrous ammonia. About 59% of the total N applied in the United States is in the fluid form. Phosphate solutions are reasonably popular in the United States, France, Canada, United

Table 10.2. Consumption of Fluids by Kind in the United States

	Thousand Tonnes of Material [2]				Nutrient
Materials	1960	1979	1992	1993	1993
Anhydrous ammonia	583	4,431	4,544	3,964	3,262
Aqua ammonia	387	443	295	300	60
Nitrogen solutions	590	5,444	7,356	7900	2370
Ammonia polyphosphate solutions	–	–	1,156	1,206	372

Kingdom, Spain, and some of the CIS states. Most of the phosphate solutions (11-37-0 or 10-34-0) are mixed with nitrogen solutions and potash to produce NPK solutions and suspensions. Usually when nitrogen solutions become acceptable, the use of fluid mixtures soon follows; fluids will become more popular as emphasis on efficient use of fertilizer increases.

10.2 Nitrogen

10.2.1 Anhydrous Ammonia

Some of the physical characteristics of liquid anhydrous ammonia are shown in Table 10.3.

In the United States 3.3 million tpy of nitrogen as anhydrous ammonia is consumed by direct application to the soil; the popularity of anhydrous ammonia for this purpose decreased from 40% of total N in 1980 to 32% in 1993. It is still the lowest priced nitrogen source, but because of safety and environmental problems many dealers are switching to other nitrogen sources. Those who continue to use anhydrous ammonia are fully aware of the dangers and difficulties of using this product. Liquid ammonia can cause severe skin, lung, and eye damage due to freezing and its caustic action and dehydration on tissue. It has been known to cause severe damage to the lungs and eyes.

Most users of anhydrous ammonia have found that safety problems can be avoided if the following ten agricultural safety commandments [3] are followed:

Table 10.3. Physical and Chemical Characteristics of Anhydrous Ammonia

Characteristics	Value
Boiling point[a]	-33°C
Freezing point[a]	-78°C
Latent heat of evaporation[a]	327.2 kcal/kg
Vapor pressure bars[b]	
-18°C	0.32
0°C	3.24
38°C	13.60
Specific gravity	
-18°C	0.6749
0°C	0.6385
38°C	0.5831
Explosive mixture	16%-25% NH_3 in air

a. At atmospheric pressure.
b. Gauge pressure.

1. Always have ample clean water available.
2. Always avoid hose and valve openings.
3. Always wear gloves and goggles when transferring ammonia.
4. Always close valves and disconnect hoses when a loading station is unattended.
5. Always ensure that pressure is relieved before disconnecting hoses or parts.
6. Never fill a tank to more than 85% of its capacity.
7. Never leave transfer operations unattended.
8. Never tamper with relief valves or other safety devices.
9. Use only approved ammonia equipment.
10. Never tow a trailer without secure connecting parts and safety chains.

Anhydrous ammonia is transported in the United States through gas pipeline systems, jumbo-size tank cars, refrigerated barges, and tank truck. Figure 10.1 is a photograph of a refrigerated barge [4]. Most regional storage tanks for anhydrous ammonia are of the atmospheric storage type. Usually the dealer storage tanks are of the pressure type.

10.2.1.1 Anhydrous Ammonia Dealer Operations – Usually most anhydrous ammonia dealers have pressure-type storage tanks varying in size from 45 m^3 to 114 m^3. The working pressure in these tanks should not exceed a gauge pressure of about 1.8 MPa. Liquid ammonia is transferred from the railway tank car to the storage tank by means of an ammonia compressor or a positive displacement pump. Use of an ammonia compressor is the most common method. Transfer is accomplished by removing vapor from the storage tank and pumping it into a railway car. Removing vapor from the storage tank causes its contents to cool; compressing the gas causes it to be heated; and hot gas causes the contents of the tank car to increase in temperature. These temperature changes cause a pressure differential between the railway tank car and the storage tank; this pressure differential allows the liquid ammonia to be easily transferred from the tank car to storage.

Pressure tanks having a capacity of 3.8 m^3 to 7.7 m^3 are often used to transport ammonia from a dealer's terminal to a farm. At a farm ammonia is transferred from nurse tanks to applicator tanks. Figure 10.2 is a photograph showing how a vapor transfer pump is used to transfer ammonia from a nurse tank to an applicator. Some farmers fill the applicator by bleeding ammonia gas from the applicator tank into the atmosphere. Thus, the vapor pressure of the ammonia in the tank causes

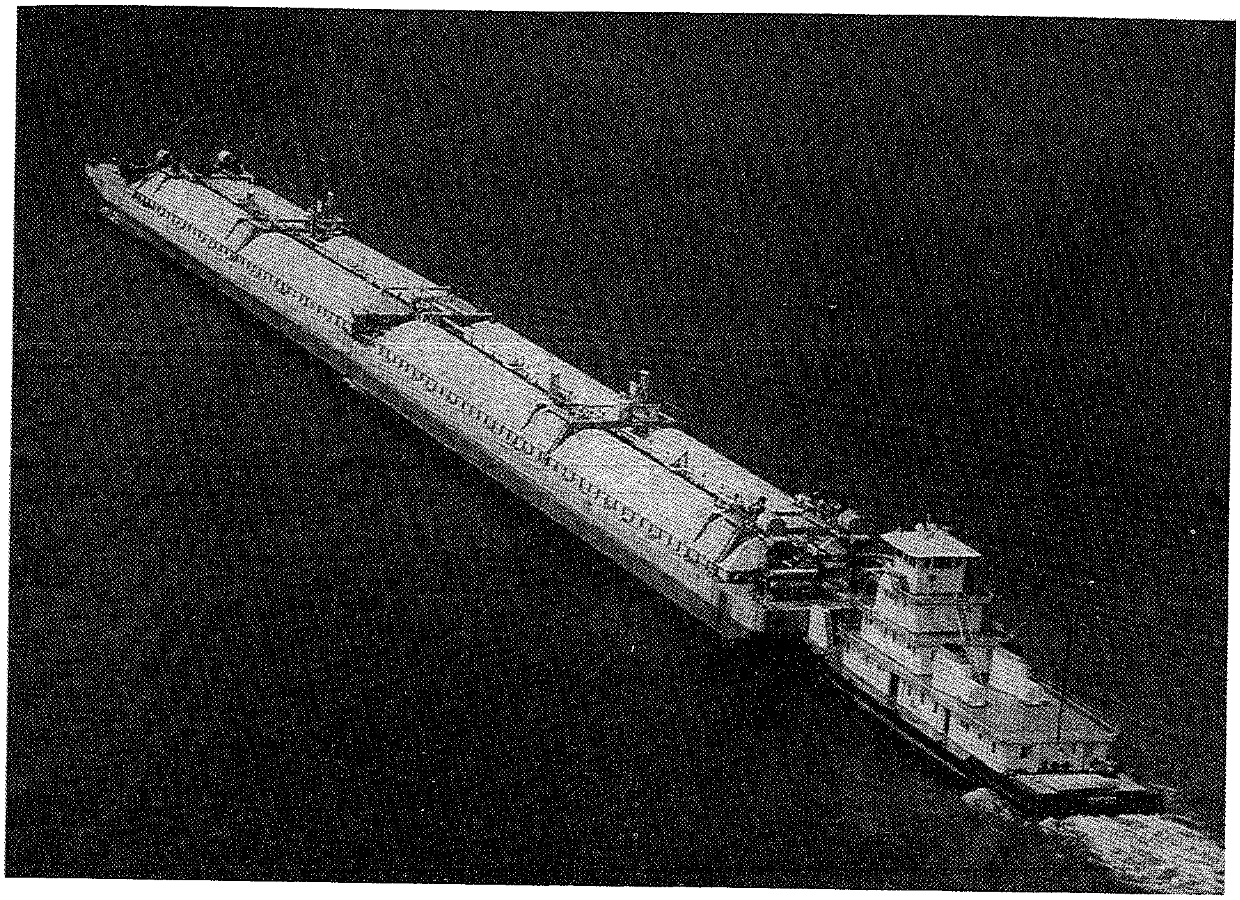


Figure 10.1. Anhydrous Ammonia Barge.

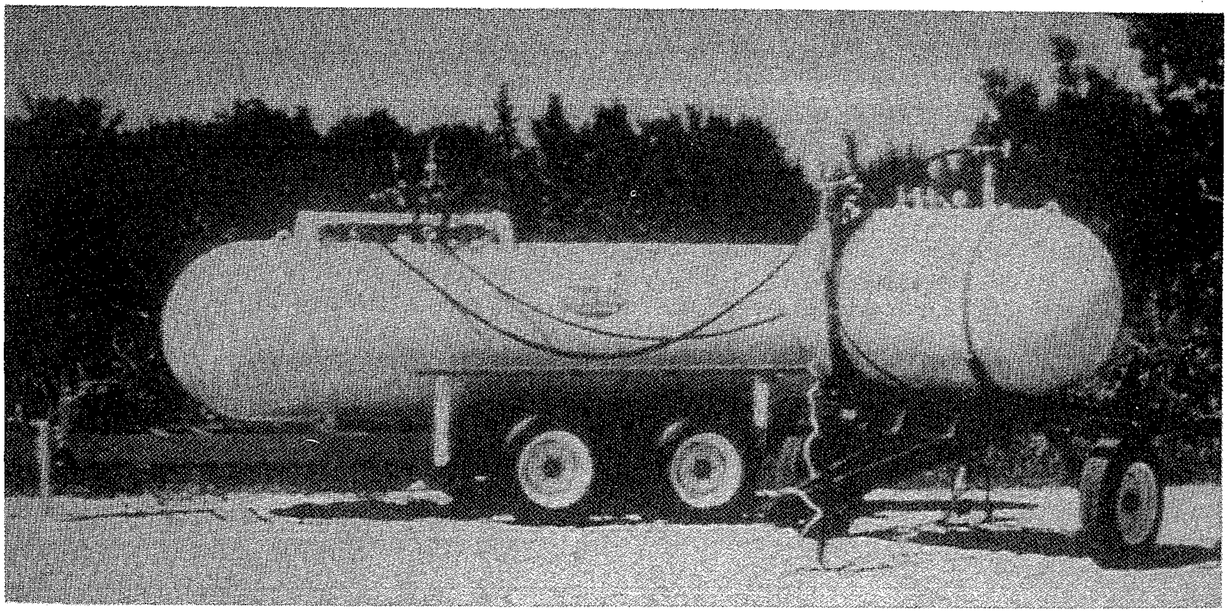


Figure 10.2. Transfer of Ammonia From Nurse Tank to Farmer's Applicator.

the liquid to be transferred to the applicator. However, the loss of ammonia, even though small in amount, has generally caused the dealer to start using gear pumps to transfer ammonia to the nurse and applicator tanks.

10.2.1.2 Application of Anhydrous Ammonia – Direct application of anhydrous ammonia started with rather humble equipment in the early 1940s. A horse-drawn applicator with a laboratory, 20-pound gas cylinder was used first. As the agronomic effectiveness of anhydrous ammonia was proven, more sophisticated equipment was developed and used.

Because it is applied as a volatile liquid, anhydrous ammonia must be injected 15 to 30 cm below the surface of the soil; this usually is accomplished by an application knife such as those shown in Figure 10.3. Often in sandy, loose soil ammonia is applied by an ammonia chisel, also shown in Figure 10.3. Anhydrous ammonia is usually metered by a variable orifice-type meter or by a piston pump. The rate of application using the orifice meter is determined by the speed of the applicator, the swath width, and the orifice opening. Piston pumps are usually actuated by a drive-chain operated by a sprocket attached to a wheel of the applicator. Application rate is changed by changing the length of stroke of the piston; the rate is independent of the applicator's speed.

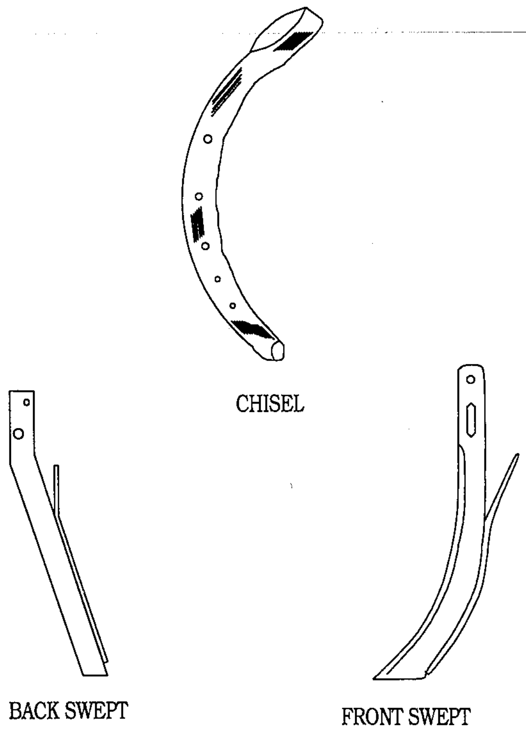


Figure 10.3. Sketch Showing Anhydrous Ammonia Application Knifers.

Ammonia applicators range in size from small 5-row rigs to large rigs that have swath widths up to 65 feet and are pulled by high-powered tractors as shown in Figure 10.4 [5]. The estimated application cost for anhydrous ammonia is about US $15/ha. This cost varies widely; however, most companies charge about twice as much for applying anhydrous ammonia as compared with applying nonpressure solutions.

10.2.2 Aqua Ammonia

Aqua ammonia is not as popular as anhydrous ammonia; however, interest in aqua ammonia is increasing because it is safer to use than anhydrous ammonia. The most popular aqua ammonia solution contains 20% N and exerts no gauge pressure at temperatures below about 36°C. It does lose ammonia when exposed to the atmosphere; therefore, aqua ammonia of this concentration is stored in covered nonpressure storage tanks. These tanks usually are constructed to withstand 0.35 bars gauge pressure and are equipped with pressure and vacuum safety valves, which are set to open at 1.051 and 0.991 bars absolute pressure.

Aqua ammonia is usually produced in a plant in which anhydrous ammonia and water are continuously mixed with recycled cool aqua ammonia in a simple pipe-type mixing chamber. Enough water is added to adjust the liquid's specific gravity to that of aqua ammonia containing 20% nitrogen or other desired concentrations. The product is usually cooled in a conventional heat exchanger or plate-type cooler. Usually a 45-tonne tank car of anhydrous ammonia can be converted to 187 tonnes of aqua ammonia in approximately 5 to 8 hours. The rate of conversion is dependent upon the cooling capacity of the plant.

Because aqua ammonia has a relatively low vapor pressure, it does not have to be injected as deeply into the soil as does anhydrous ammonia. Most operators have found that they can avoid excessive ammonia losses if they inject aqua ammonia about 6 to 12 cm beneath the surface. Applicators used for applying aqua ammonia are similar to those for anhydrous ammonia in that they have injection knives; however, since these knives penetrate about one-half the depth of anhydrous ammonia knives, much less power is required to operate them. Also, aqua ammonia can be applied at a much faster rate than anhydrous ammonia because deep injection of this solution is not required. Many operators have found that they can apply aqua ammonia in operations such as plowing, disking, etc., without high ammonia loss. One company uses large tank-type applicators and can apply aqua ammonia at a rate of 16 ha/hour.

Some companies apply aqua or anhydrous ammonia to ditch irrigation systems. This is done at very low

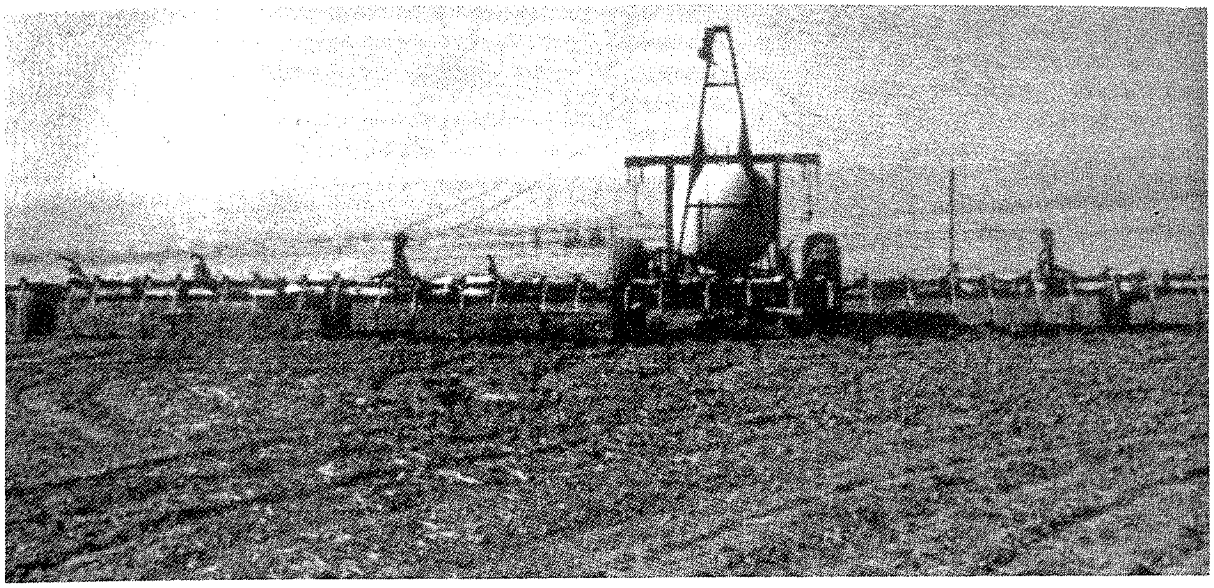


Figure 10.4. Anhydrous Ammonia Applicator With 65-Foot Swath.

concentrations and during the early spring when the temperature of irrigation water is low.

10.2.3 Nonpressure Nitrogen Solutions

These solutions are gaining in popularity in several countries. The reasons for the increased popularity are as follows:

- Safer to use.
- Easier to inject into various types of irrigation systems.
- Safer to handle and store. Special materials are not required for tanks and other equipment.
- Can be surface applied and uniformly applied at higher application speeds compared with those of anhydrous ammonia or solid fertilizer.
- Exhibit the same advantages as given for all fluids earlier in this chapter.

Nitrogen solutions are usually produced from urea, ammonium nitrate, and water. They usually contain a corrosion inhibitor and can be stored and used in mild steel (carbon steel) equipment. Solutions usually sold in the United States have three concentrations: 32%, 30%, and 28% N. Their salt-out temperatures vary directly with their plant nutrient concentrations. Some of the physical and chemical characteristics of the three nonpressure solutions are shown in Table 10.4 [5].

Table 10.4. Physical and Chemical Characteristics of Urea-Ammonium Nitrate Solutions

Grade, % N	28	30	32
Composition, % by weight			
Ammonium nitrate	40.1	42.2	44.3
Urea	30.0	32.7	35.4
Water	29.9	25.1	20.3
Specific gravity, 16°C	1.283	1.303	1.32
Salt-out temperature, °C	-18	-10	-2

One inhibiting agent that is frequently used in these solutions is a small quantity of anhydrous ammonia; usually about 5 kg of ammonia/tonne of product is added to adjust the pH of the solution to 7.0. Another effective inhibiting agent is ammonium phosphate; only a small quantity of ammonium phosphate (0.1% P_2O_5) is required to inhibit the solution. This phosphate material reacts with the mild steel tank to form an iron phosphate film, which is a barrier to further corrosion of the tank. There are several other inhibiting agents; they are listed in a handbook of specialty chemicals [6].

10.2.3.1 Production of Nonpressure Urea-Ammonium Nitrate Solutions – Two types of production processes are used – batch and continuous. Both are fairly simple; in each process concentrated hot urea and hot ammonium nitrate solutions are measured, mixed, and then cooled. In the batch process, solutions are weighed in a mix tank; the inhibitor is weighed separately and added to the mix tank. Finished product is cooled after it is mixed. The continuous process is similar except that the two nitrogen solutions, water, and inhibiting agent are metered and fed continuously to a mixing chamber similar to the simple baffled mixer shown in Figure 10.5. Product from the mixing chamber is cooled and pumped to storage.

The production of nitrogen solution from prilled urea and ammonium nitrate has sparked some interest. When producing solution from these solid materials in a batch mix tank, hot water is required to speed the dissolution of the materials. Usually enough heat is supplied so that all of the solid materials will be dissolved at the end of the 30-minute mixing time. About 23 kg of saturated steam per tonne of product is required for a reasonable mixing time. There is a mixing cost for this process; therefore, there must be special pricing policies that make it advisable to produce a nitrogen solution from solid materials.

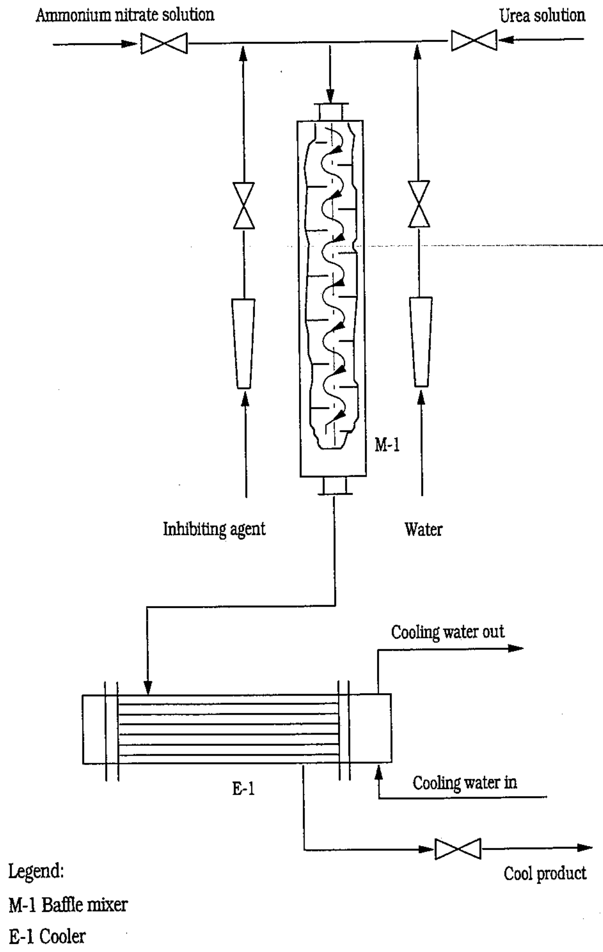


Figure 10.5. TVA Continuous Urea-Ammonium Nitrate Solution Plant.

One ammonia pipeline company that also has a river terminal close to the pipeline considers that it may be more economical to produce hot ammonium nitrate solution from ammonia at the pipeline and mix it with prilled urea received by barge. Anhydrous ammonia would be converted to nitric acid and then to hot ammonium nitrate solution. This hot solution could then be mixed with the prilled urea to produce the nonpressure UAN solution.

10.2.4 Application of Nitrogen Solutions

Most nitrogen solutions are used for direct application; however, a substantial quantity is used to produce fluid mixtures. Most are applied by broadcasting using various types of nozzles. Figure 10.6 is a photograph of the commonly used spray nozzles. The nozzle on the right is a fan-type that emits fine droplets.

Because they receive uniform response from the nitrogen and uniform kill of weeds, some applicator operators prefer fan-type nozzles to apply mixtures of nitrogen solution and herbicides. Other operators report that when the wind is blowing moderately, there is too much fertilizer drift with these nozzles; they prefer to apply the solutions through flooding nozzles such as that shown on the left side of Figure 10.6. Flooding nozzles emit droplets about the same size as that of average rain drops. There is little or no drip and a uniform application across the swath is obtained. This is the same type of nozzle that is used to broadcast fluid mixed fertilizers and suspensions.

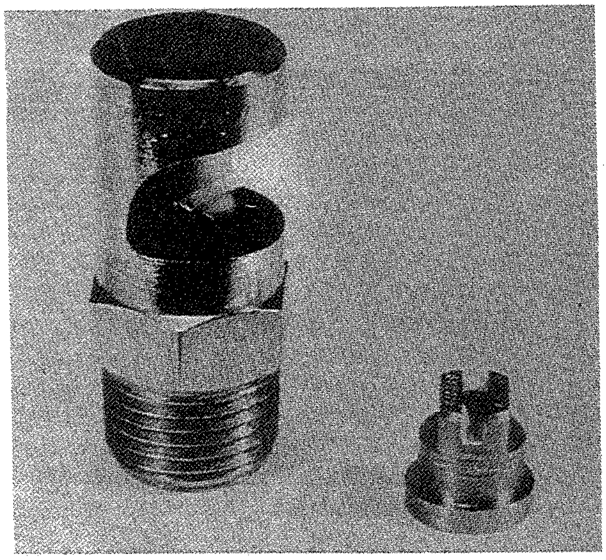


Figure 10.6. Liquid Fertilizer Spray Nozzle.

Applicator wagons used to broadcast nitrogen solutions vary in size from small ones pulled behind farm tractors to the large self-propelled high-flotation applicators (Figure 10.7).

High-flotation type tires minimize compaction of the soil during fertilizer application so that the fertilizer can be applied during wet periods. These large applicators are capable of applying fertilizer solutions at a rate of about 0.5 ha/min.

Nonpressure nitrogen solutions and other fluids are added through various types of irrigation systems such as sprinkler, gated pipe, drip tubes, and ditch. This practice often has been referred to as "spoon feeding" of the crop because the solution is added with irrigation water several times during the growing season. Apparatus for feeding these solutions to the irrigation unit usually consists of a storage tank and a piston-metering pump. The rate is varied by changing the length of stroke and speed of the piston pump.

Some nitrogen solutions are mixed with other clear liquids, such as ammonium polyphosphates of grades 10-34-0 and 11-37-0 and potash, to produce clear liquid mixtures. Nitrogen solutions are also used to produce suspension mixtures.

10.3 Fluid Phosphates

The use of fluid phosphate has not had the worldwide popularity of fluid nitrogen fertilizers (mainly UAN solution). However, fluids have captured a significant amount of the phosphate markets in the United States and to some degree in the United Kingdom, France, and to a much lesser degree in a few other countries. The usual pattern is for nitrogen solutions to first become established and to then be followed by the phosphate solutions.

10.3.1 Ammonium Polyphosphate Solutions

Ammonium polyphosphate solutions are the most popular phosphatic solutions now in use. The usual grades are 10-34-0 and 11-37-0. One company that uses a rather pure rock to produce phosphoric acid, which is used in the production of polyphosphate solution, has found it can produce a 12-40-0 grade of good quality. These ammonium polyphosphate solutions are used for direct application or as phosphate sources for NPK solution and suspension mixtures. Ammonium polyphosphate solutions are to the solution mixture industry as DAP is to the granular bulk-blend industry. This solution is usually produced in regional plants that sell to dealers. The dealer sells it to farmers who use it for direct application, or the dealer mixes it with nitrogen solution and potash to produce NPK fluids.

Most of the ammonium polyphosphate solutions are produced from wet-process superphosphoric acid, ammonia, and water. The reaction between the acid and ammonia is usually carried out in a Tennessee Valley Authority (TVA) pipe reactor [7] ("Tee" reactor). The superphosphoric acid is produced by concentrating merchant-grade orthophosphoric acid (54% P_2O_5) to superphosphoric acid in a vacuum or atmospheric concentrator. The superphosphoric acid usually contains

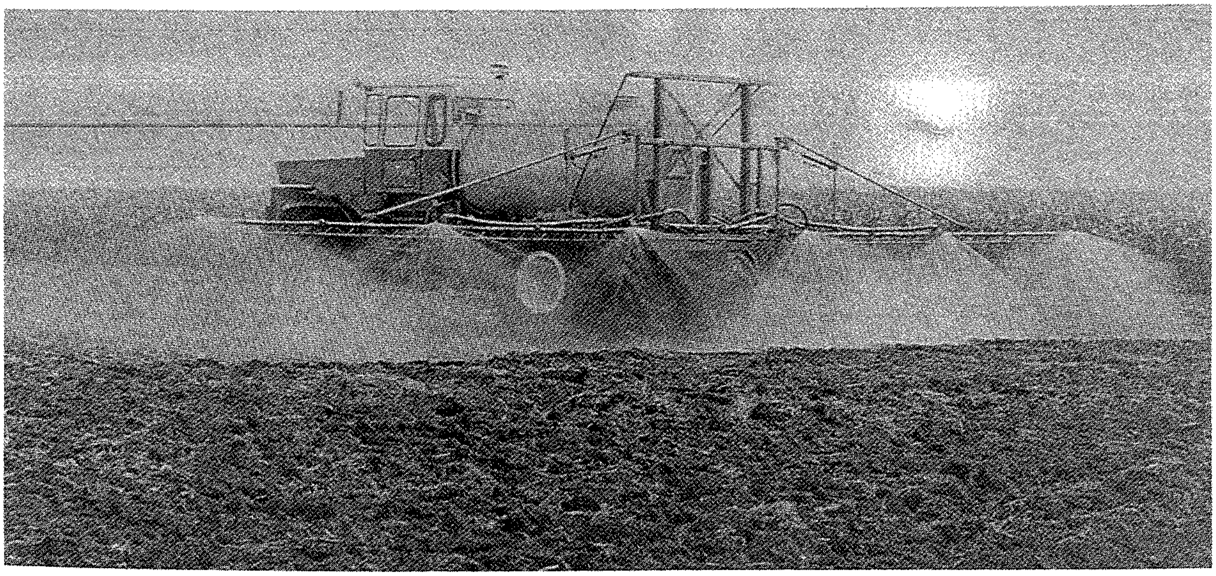


Figure 10.7. Self-Propelled-Type Applicator for Fluid Fertilizers.

about 68%-70% total P_2O_5 of which 20%-35% is present as polyphosphate. Physical and chemical characteristics of a typical superphosphoric acid are given in Table 10.5.

Essentially all of the polyphosphoric acid content of the wet-process superphosphoric acid is in the form of pyrophosphate; the remaining phosphate is present as orthophosphoric acid. Conversion to superphosphoric acid increases the cost somewhat, but with the long shipping distances in the United States, the higher analysis of the superphosphoric acid generates a saving on freight that reduces or eliminates the extra cost of concentrating phosphoric acid from 54% to 70% P_2O_5.

Table 10.5. Properties of Superphosphoric Acid

Total P_2O_5, %	70.0
Polyphosphate, % of total P_2O_5	30.0
Sulfate (SO_4), %	3.8
Aluminum (Al_2O_3), %	1.1
Iron (Fe_2O_3), %	1.0
Magnesium (MgO), %	0.4
Fluorine (F), %	0.27
Solids (Insol. in CH_3OH), %	0.15
Solids (Insol. in H_2O), %	0.01
Sp. gr. at 24°C, g/ml	1.96
Viscosity centipoises at 52°C	400

More than 100 U.S. plants use the pipe reactor process to produce an estimated 1.2 million tonnes of product per year. Two typical plants are shown in Figure 10.8; the plant on the left has a combination mix tank-cooler design.

The upper part of the tank consists of a section filled with plastic "Pall Ring" packing; liquid is recirculated to this section while air is drawn through the section to partially cool the liquid. Liquid from the bottom of the tank is passed through a heat exchanger, where it is further cooled before it is pumped to storage. Anhydrous ammonia is passed through this same heat exchanger, vaporized, and then passed into the tee section of the pipe reactor. Superphosphoric acid is pumped by a positive displacement pump to this same tee section where the acid and gaseous ammonia react to form a hot melt at 316°C. About 60% of the ammonia is added to the pipe reactor, and the remaining 40% is added to the hot well as aqua ammonia to adjust the pH of the liquid to 6.0 for the production of 10-34-0 or 11-37-0. The water content is controlled by the addition of water to the recirculation line and observing the specific gravity of the product.

The plant on the right of Figure 10.8 uses a separate mix tank and an evaporative cooler. The mix tank is used for mixing the hot melt from the pipe reactor with recirculating liquid and for the addition of ammonia or

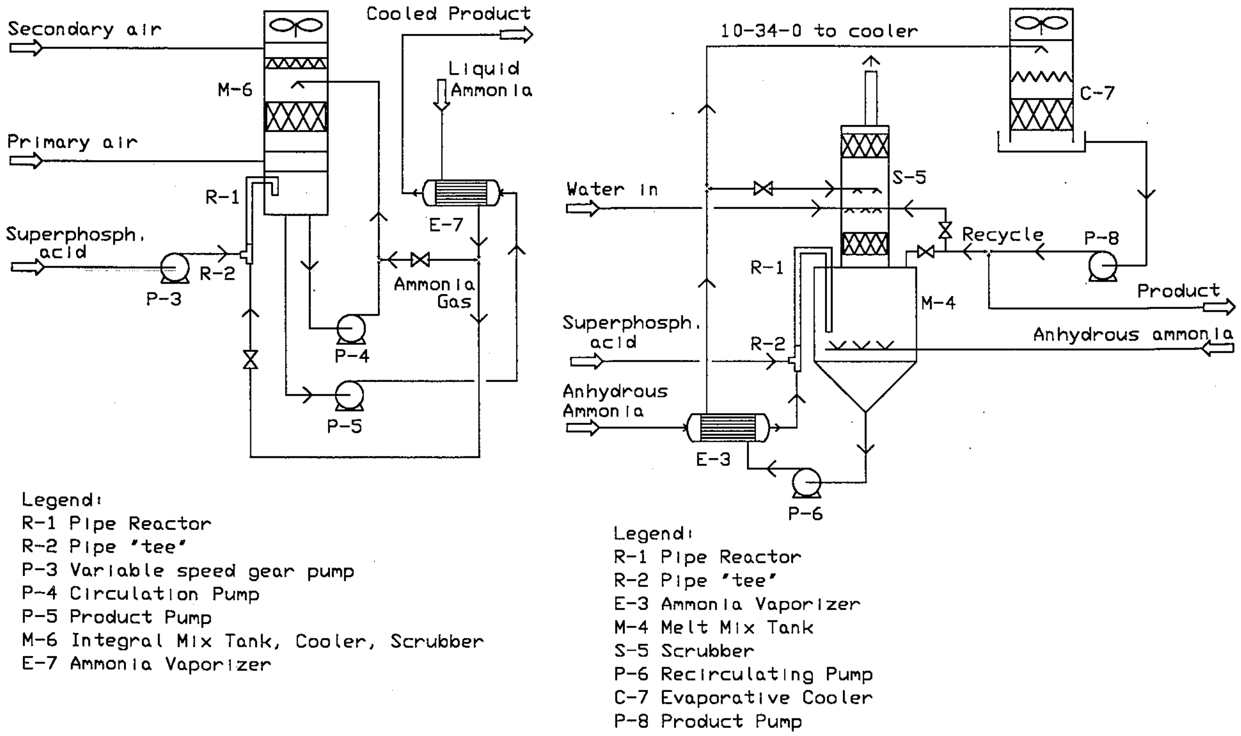


Figure 10.8. Typical Pipe-Reactor Plants for Production of Ammonium Polyphosphate Solution.

aqua ammonia. The separate mix tank allows a high liquid temperature, 180°F, to be maintained, which enhances mixing of the melt into the liquid and also provides hot solution to evaporate and superheat the anhydrous ammonia used in the pipe reactor. Data indicate that plants with a separate mix tank usually produce an ammonium polyphosphate liquid of slightly higher polyphosphate content than those with the combination mix tank-cooler, probably because of the high temperature of the ammonia used in the pipe reactor. Ammonia that is not added to the pipe reactor is usually added as liquid or aqua ammonia to the mix tank; this tank is equipped with a small scrubber in which cooled 10-34-0 is used to scrub the exit gases from the mix tank.

Both plants have efficient, inexpensive evaporative coolers. Essentially no contaminants are lost from either of the plants; a considerable amount of water is lost as steam and water vapor, which contains traces of ammonia. Some companies use plate- or pipe-type coolers in which the ammonium polyphosphate solution is passed through the inside of the plates or pipes and water on the outside surface of the pipe or plate. Cooling is accomplished by either air or evaporation of water from the outside surfaces of the pipe or plate. There is no loss of ammonia from these units because the cooling air does not contact the hot ammonium polyphosphate solution.

Physical and chemical characteristics of a typical ammonium polyphosphate solution of 10-34-0 grade made by this process are given in Table 10.6.

Phosphate base suspension will be discussed later in this chapter under a section on suspension.

10.3.2 Solution Mixtures

Most of the ammonium polyphosphate liquids (10-34-0 or 11-37-0) are used in small mix plants to produce NPK mixtures. A typical plant is shown in Figure 10.9. Ammonium polyphosphate solution is mixed with nitrogen solutions (UAN solution) and potash to produce various clear liquid grades such as: 7-21-7, 8-8-8, and 21-7-0.

Table 10.6. Physical and Chemical Characteristics of 10-34-0

Nitrogen, %	10
P_2O_5, %	34
Polyphosphate, % of total P_2O_5	65-70
Viscosity, centipoises at 24°C	75
Specific gravity at 27°C, g/ml	1.4
Salt-out temperature	< 0°C

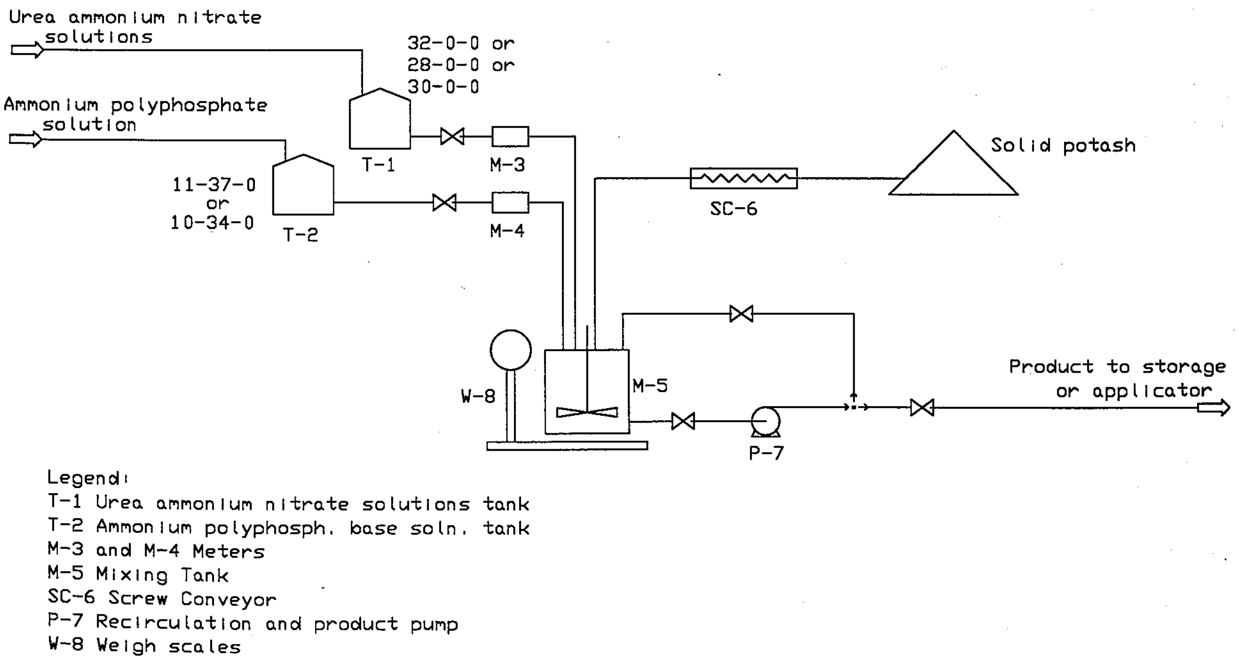


Figure 10.9. Liquid Fertilizer Mix Plant.

Formulas for these solution-type mixtures and others are given in Table 10.7.

The estimated salt-out temperatures shown in the above tabulation were calculated using the solubility curves shown in Figure 10.10 [8,9]. This is the conventional triangular solubility diagram with lines of constant solubility. The numbers on the contour lines represent the total percentage units ($N+P_2O_5+K_2O$) that will remain in solution at O°C. There are boundary lines (broken lines) to show the crystal phases at the various nutrient ratios and concentrations. The function on Figure 10.10 shows the solubility adjustment factors (coefficients) that are used to calculate the actual salt-out temperatures at various nutrient concentrations, which would have salt-out temperatures other than O°C.

Similar solubility systems have been developed in which other sources of supplemental nitrogen are used instead of UAN. Also, systems that use orthophosphate rather than polyphosphate have been developed. Some of these systems are:

Urea - ammonium polyphosphate - potash - water

Ammonium nitrate - ammonium polyphosphate potash - water

Urea - ammonium orthophosphate - potash - water

Ammonium nitrate - ammonium orthophosphate - potash - water

Urea - ammonium nitrate - ammonium orthophosphate - potash - water

References 5, 8, 9, and 10 give detailed instructions and examples concerning the use of these solubility systems.

Sometimes the liquid mix plant produces a potash base solution such as a 2-6-12 or 4-11-11 and transports it to a satellite station where it is mixed with nitrogen solution, containing 28%-32% N and 10-34-0 to produce NPK mixtures. At the satellite station each liquid is metered and mixed in the farmer's nurse tank.

Equipment used to broadcast solution-mixed fertilizers is essentially the same as that used to broadcast nitrogen solution. Sometimes a pesticide (herbicide or insecticide) is transported separately in a can to the farm and mixed with the liquid at that location. In this way the danger of transporting a pesticide-fertilizer mixture across roadways is avoided. Some applicators are equipped with a small eductor for the addition of pesticide to a recirculating stream of liquid from the applicator.

Many farmers in the U.S. Corn Belt and areas with short-growing seasons prefer to add some liquid mixtures, usually of grade 7-21-7, in the row with the seed to enhance early "pop up" of the crop. A substantial portion of the clear liquids used in the United States is consumed for this purpose. During planting, liquid flows from a constant head tank by gravity and through an orifice plate. Frequently part of the liquid is added directly with the seed and part is placed to the side of the seed.

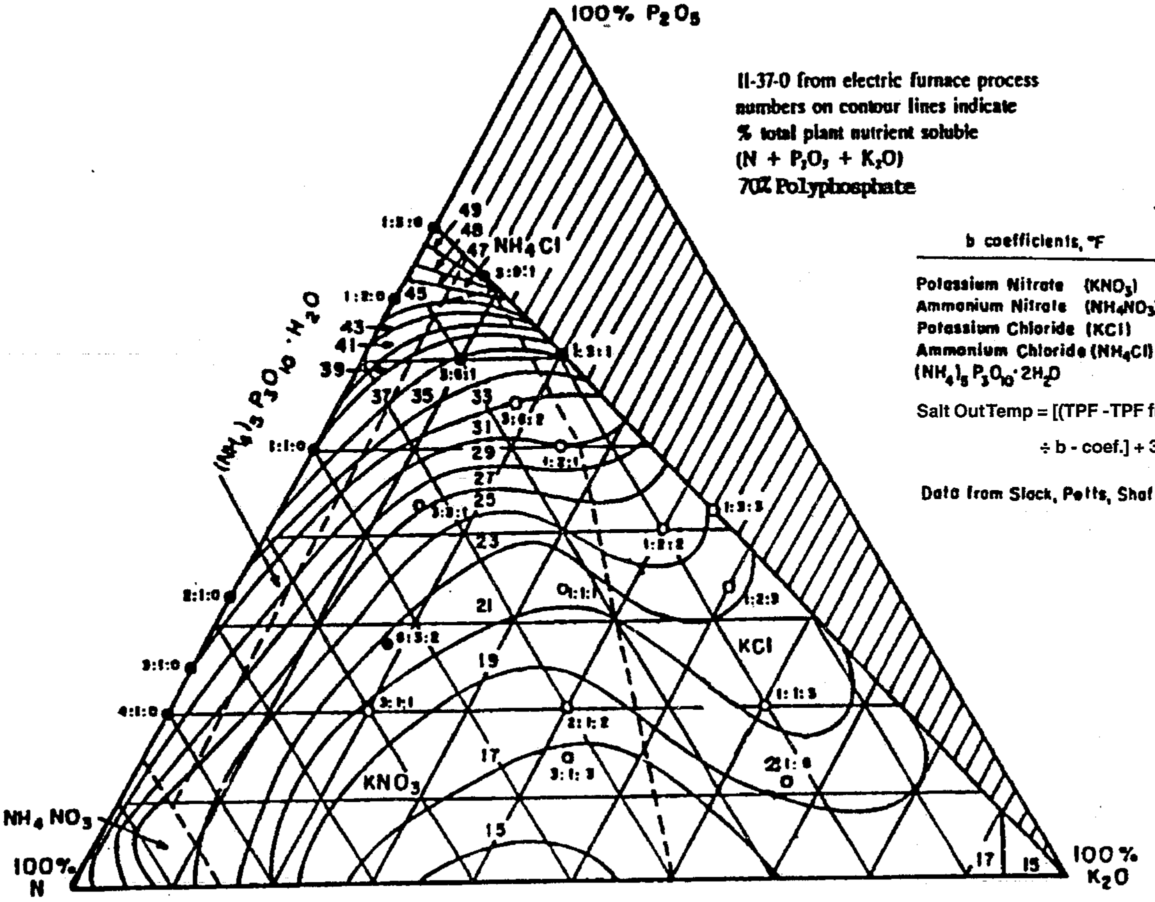
Figure 10.11 shows a barrel that has been adapted as a constant head tank for addition of solutions to ditch irrigation systems; sometimes, this barrel is used on farming equipment for dribbling liquids in the seed row.

This equipment is designed using the principle of "Marriott's bottle" and is similar to those used in laboratories. It has a breathing tube and an orifice plate at its discharge; with this equipment a constant head is maintained at the orifice plate. This metering equipment has

Table 10.7. Formulas for Solution Mixtures

$N:P_2O_5:K_2O$ Ratio	1-1-1	1-3-1	3-1-0	1-3-6	8-22-22
Grade	8-8-8	7-21-7	21-7-0	2-6-12	4-11-11
Formula, % total weight:					
UAN solution (32-0-0)[a]	17.6	2.6	59.2	0.8	2.4
10-34-0[b]	23.6	61.7	20.6	17.7	32.3
Potash	12.9	11.3	—	19.3	17.8
Water	45.9	24.4	20.2	62.2	47.5
Salt-out temperature, °C[c]	7	-6	<-20	-13	0

a. Urea-ammonium nitrate solution 32-0-0 grade.
b. Made from wet-process superphosphoric acid and ammonia.
c. Estimated using solubility curves, 70% polyphosphate.



11-37-0 from electric furnace process
numbers on contour lines indicate
% total plant nutrient soluble
$(N + P_2O_5 + K_2O)$
70% Polyphosphate

b coefficients, °F		
Potassium Nitrate	(KNO_3)	.21
Ammonium Nitrate	(NH_4NO_3)	.14
Potassium Chloride	(KCl)	.08
Ammonium Chloride	(NH_4Cl)	.05
$(NH_4)_5P_3O_{10}\cdot 2H_2O$		.05

Salt Out Temp = [(TPF - TPF from Fig.)
÷ b - coef.] + 32°F

Data from Slack, Potts, Shaffer

Figure 10.10. Solubility Equilibrium Curves, System 11-37-0, UAN Solution, KCl, Water at 0°C.

been used in Mexico and other countries to meter solutions into ditch irrigation units; it should have some application in other developing countries.

10.4 Suspension Fertilizers

Use of suspensions has grown very rapidly in the United States during the past 5 years. Some of the main reasons for their increased popularity are the same as for other fluids. However, some of the reasons they are used in preference to solution-type mixtures are:

- Cheaper, less pure materials can be used to produce suspensions.
- Higher analysis grades can be produced. This is particularly true when grades containing potassium are to be used.
- Usually larger quantities of micronutrients can be incorporated into suspensions than can be dissolved in solution fertilizers. Therefore, when suspensions are used, all of the micronutrient requirements can usually be applied with the suspension fertilizers.
- Powdered herbicides and insecticides that are not normally soluble in solution fertilizers can be suspended and uniformly distributed throughout the suspension.

The main reason for the early production of suspensions was to produce high potash grades for use in regions that require relatively large quantities of potassium. The most popular suspension grades are those that have a high potash content such as the 7-14-21, 3-10-30, and 4-12-24 grades. High nitrogen suspensions are also popular. Grades such as 14-14-14, 20-10-10, 21-7-7, and 24-8-0 are frequently produced. Surveys of fluid fertilizer manufacturers show that about 70% of the fluid fertilizer plants in the United States produce suspensions and 95% produce solutions. These plants use the materials listed in Table 10.8 to produce suspensions.

The most popular phosphate material for suspensions is still ammonium polyphosphate solutions. However,

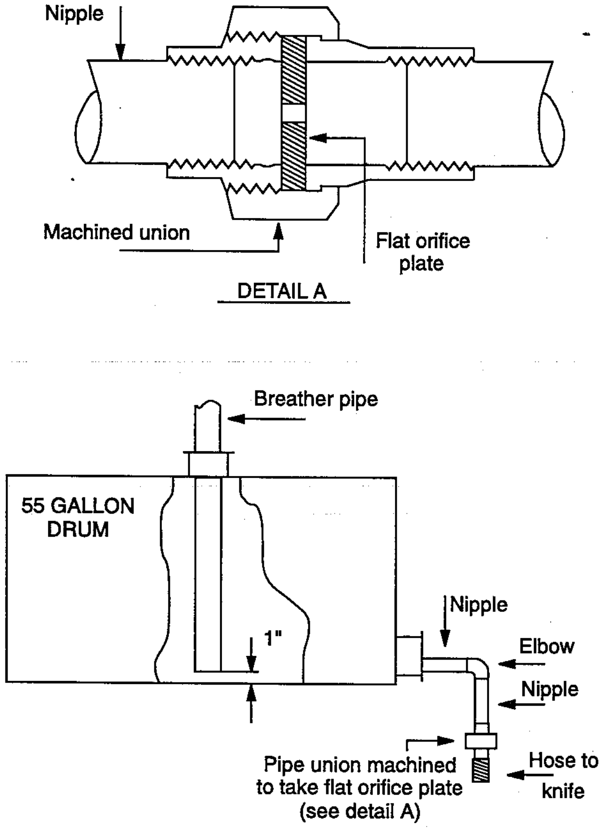


Figure 10.11. Barrel Adapted as a Constant Head Tank.

Table 10.8. Materials Used to Produce Suspensions

Materials	Grade
Potash	0-0-62
Nitrogen solutions	28-0-0 or 32-0-0
Ammonia	82-0-0
Ammopoly phosphate solution	10-34-0 or 11-37-0
Phosphoric acid	0-54-0 or 0-52-0
Solid phosphates (DAP & MAP)	18-46-0 or 11-52-0

economic pressures have encouraged the use of other low-cost materials. The next most popular phosphate source is monoammonium phosphate (11-52-0 MAP) followed by diammonium phosphate (18-46-0 DAP) and merchant-grade phosphoric acid (0-52-0 and 0-54-0). Many companies that formerly used 10-34-0 for the production of suspensions now plan to use either phosphoric acid or granular ammonium phosphate materials or combinations of these materials. Some of the smaller producers plan to use ammonium orthophosphate base suspension (10-30-0 or 11-33-0) for the production of their suspensions.

Companies that use ammonium polyphosphate solution 10-34-0 or an orthophosphate base suspension (10-30-0 or 11-33-0) use a simple plant such as the one shown in Figure 10.12. In this plant the base phosphate material (10-34-0 or 11-33-0) is mixed with nonpressure nitrogen solution, containing 28%-32% N and potash. All materials in the formulation are weighed and mixed in the mix tank. This plant has relatively low capital cost, and there are a number of them located throughout the United States. Probably the most economical source of phosphate materials for these plants is ammonium orthophosphate suspension of grade 10-30-0 or 11-33-0 produced from MAP and ammonia.

Most companies that use merchant-grade phosphoric acid (0-54-0) for suspensions use a batch ammoniation process for the production of base suspensions or NPK mixtures. They neutralize the acid with anhydrous ammonia and add dry potash [5]. A sketch of a typical batch plant that uses phosphoric acid and ammonia is shown in Figure 10.13. This process includes a stainless-steel (type 316) mix tank, stainless-steel recirculation pump, and a wooden evaporative cooler.

In using this process rapid cooling to 60°C is effected by the evaporative cooler. The mixture is recirculated with the pump while gelling clay. Acid is ammoniated to an N:P_2O_5 weight ratio of 0.33:1. With this procedure all of the crystals in the suspension are small DAP crystals. An example of the formulation for a 12-12-12 suspension produced in this type of plant is given in Table 10.9.

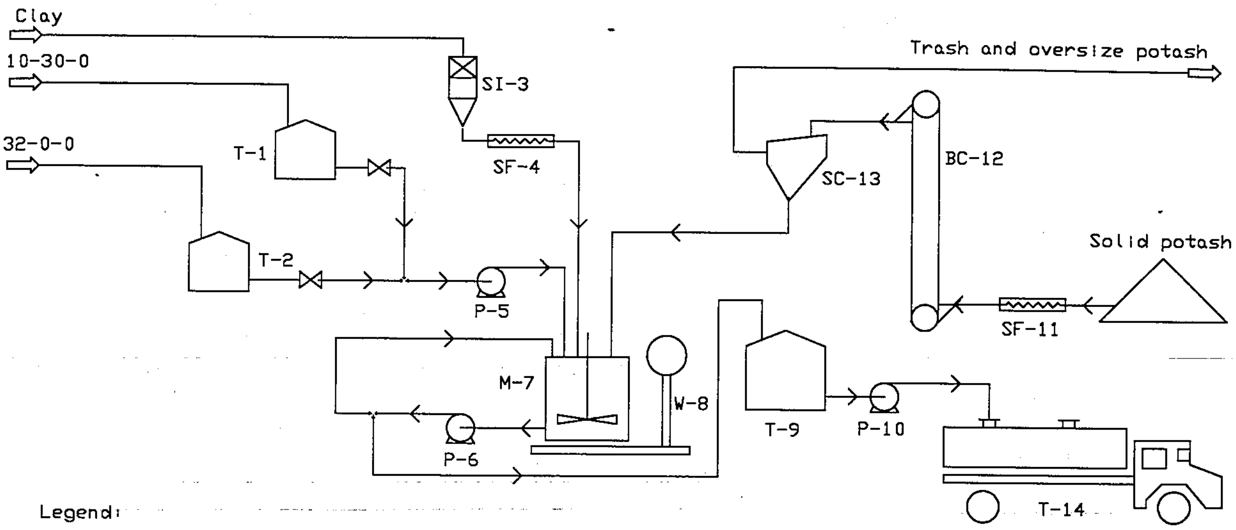
10.4.1 Use of Granular Materials in Suspension

The use of granular material for the production of suspensions is well established. Granular material such as MAP, DAP, and urea have been used.

Probably the main reason for using the granular materials is that they are usually the most economical source of phosphate delivered to the use areas. Also, when ammonia is added to the suspension the material cost usually is less than the comparable cost for bulk-blended (dry mix) materials. Other reasons given for the conversion of granular materials to fluids are:

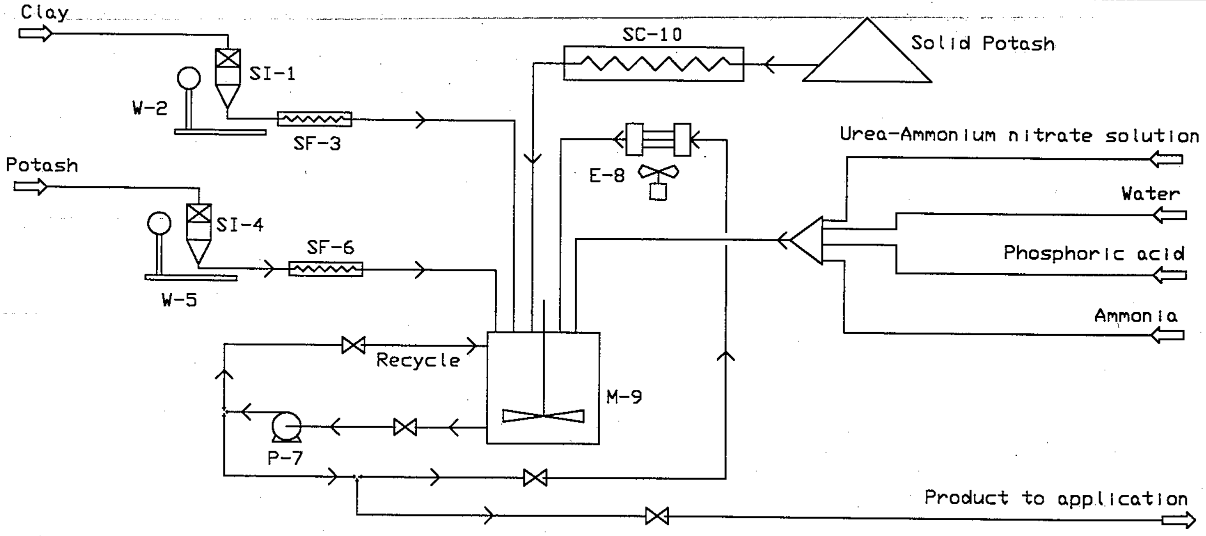
- Many merchants prefer to add the pesticide to the fertilizer mixture after it has been delivered to the farm. Pesticides can be safely mixed with fluid fertilizers on the farm.

- A fluid can be applied more uniformly and accurately than a granular mixture. This is important when



Legend:
T-1 Storage tank 10-30-0
T-2 Storage tank 32-0-0
SI-3 Clay hopper
SF-4, SF-11 Screw conveyors
P-5, P-6, P-10 Pumps
M-7 Mixing tank with agitator
W-8 Weigh scale
T-9 Product storage
BC-12 Bucket elevator
SC-13 Vibrating screen
T-14 Tankcar

Figure 10.12. Cold Mix Plant for Production of Suspension Mixtures.



Legend:
SI-1, SI-4 Storage bins
W-2, W-5 Weigh scales
SF-3, SF-6 Screw conveyors
P-7 Pump
E-8 Evaporative-type cooler
M-9 Mixing tank
SC-10 Screw Conveyor

Formulation for 12-12-12 suspension

Order of addition	Materials	#/ton
1	Water	531
2	Phosphoric acid (54 % P_2O_5)	445
3	Aqua-ammonia (20% N)	97
4	Clay	40
5	Potash (62% K_2O)	387
6	UAN (28% N)	500

Figure 10.13. Batch Plant Using Liquid Ammonia and Phosphoric Acid.

Table 10.9. Formulation for 12-12-12 Suspension

Order of Addition	Materials	Kg/t of Suspension
1	Water	266
2	Phosphoric acid (54%)	222
3	Aqua-ammonia (20% N)	49
4	Clay	20
5	Potash (62% K_2O)	193
6	UAN (28% N)	250

herbicide is incorporated into the fertilizer mixture since nonuniform application can cause toxicity in some spots in the field and ineffective weed control in others.

- Small quantities of micronutrients can be uniformly applied as fluid mixtures. This is difficult to accomplish with bulk-blended materials [11].
- Many companies report that they have fluid fertilizer application equipment for nitrogen solutions, and, in order to use it more effectively, they must convert solids to fluids.

A typical mix plant for the conversion of MAP and/or DAP to suspensions is shown in Figure 10.14. A dominant feature of this mix plant is the large pump used to recirculate liquid within the mix tank. Some plants have used liquid grinders while the others have high intensity agitators. The tank in Figure 10.14 is equipped for the addition of ammonia and phosphoric acid. This plant can readily convert solid materials such as MAP, DAP, ammonium sulfate, and urea to fluids.

Most suspension producers prefer to produce mixtures having the highest possible grade without exceeding practical viscosity limits. Application tests show that this viscosity should not exceed 8 g/cm-sec (800 centipoises) to avoid nonuniform application and difficulty in pumping and handling the suspension. Crystals formed in the suspension should be small and light enough to avoid excessive settling and plugging of nozzles during application. In producing suspensions, it would be desirable to adjust the N:P_2O_5 weight ratio to the point of highest solubility (0.3:1). However, it is more important that the suspensions be ammoniated to an

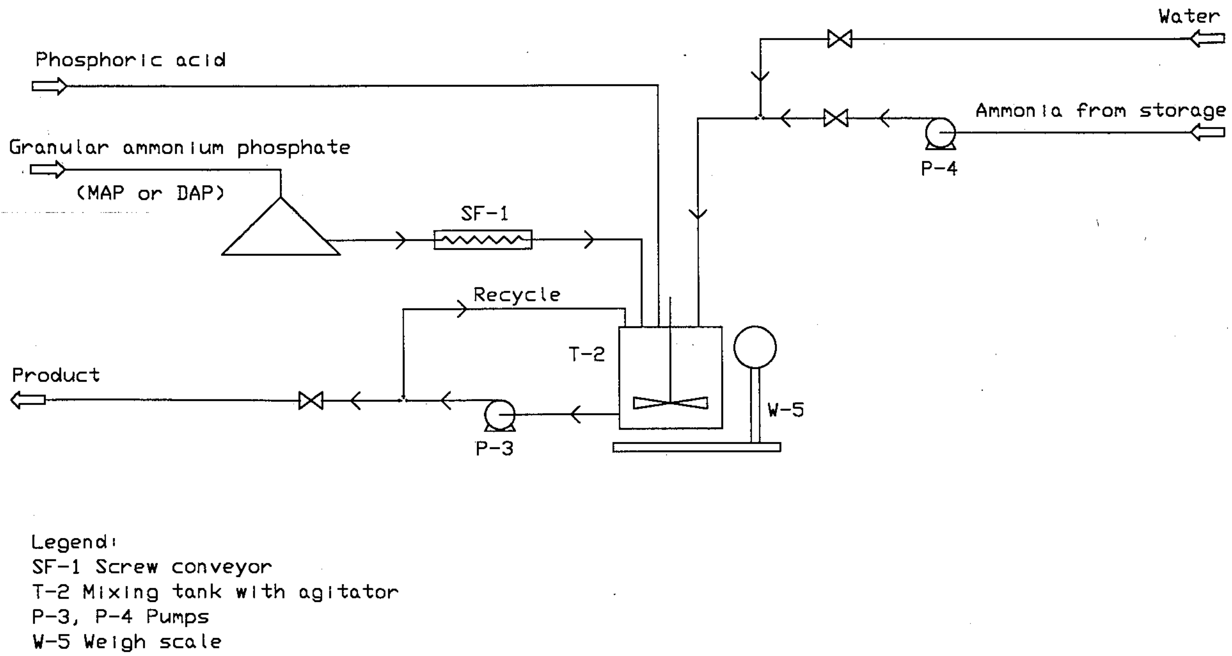


Figure 10.14. Mix Plant for Production of Suspensions From Granular MAP/DAP (12-Tonne Batch).

$N:P_2O_5$ weight ratio of 0.33:1 so that all of the crystals in the suspension are DAP. Figure 10.15 is a photograph of MAP and DAP crystals. It is obvious that DAP crystals would have less tendency to plug a nozzle. Also, DAP is lighter that MAP (densities 1.619 versus 1.803) and should have less tendency to settle during storage and transport.

Typical formulations for the production of 11-33-0 suspension from MAP, DAP, or APP are given in Table 10.10.

When either MAP or APP materials are used, only anhydrous ammonia is required to adjust the $N:P_2O_5$ ratio; however, when DAP is used, some phosphoric acid must be added to the formulation to lower the $N:P_2O_5$ ratio so that the solubility of the ammonium phosphate portion of the mixture will be improved. APP was formerly made by TVA and it contained about 20% polyphosphate. This polyphosphate shortened the mixing time and improved the storage qualities of the 11-33-0. A noncomplicated process is now available whereby basic phosphate producers can produce APP.

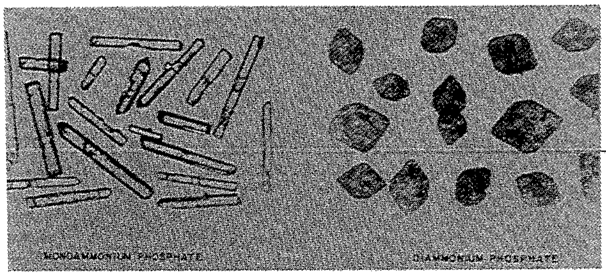


Figure 10.15. Microscopic Appearance of MAP and DAP.

10.4.2 Satellite Plants

Some companies produce NPK base grades (3-10-30, 4-12-24, and 7-14-21) and NPK base materials (13-38-0 or 11-33-0 suspensions or 10-34-0 solutions) and ship them along with nitrogen solutions to a satellite station such as that shown in Figure 10.16. In this plant base materials and nitrogen solutions are mixed and weighed in a small mix tank that is mounted on scales. With these base materials, it is possible for a small merchant to install an inexpensive plant for production of NPK suspensions or solution mixtures. Storage tests show that cone-bottom storage tanks are ideal for storage of suspensions; however, they are more expensive than flat-bottom tanks. Frequently companies use air spargers that consist of open-end pipes installed so that they introduce sparging air close to the bottom of the tank. Tanks that have cone bottoms also have spargers. Experience has shown that it is preferable to agitate the suspensions once a day by blasting 1.15 m^3 of air at 0.7 MPa into the suspension so that it becomes well mixed.

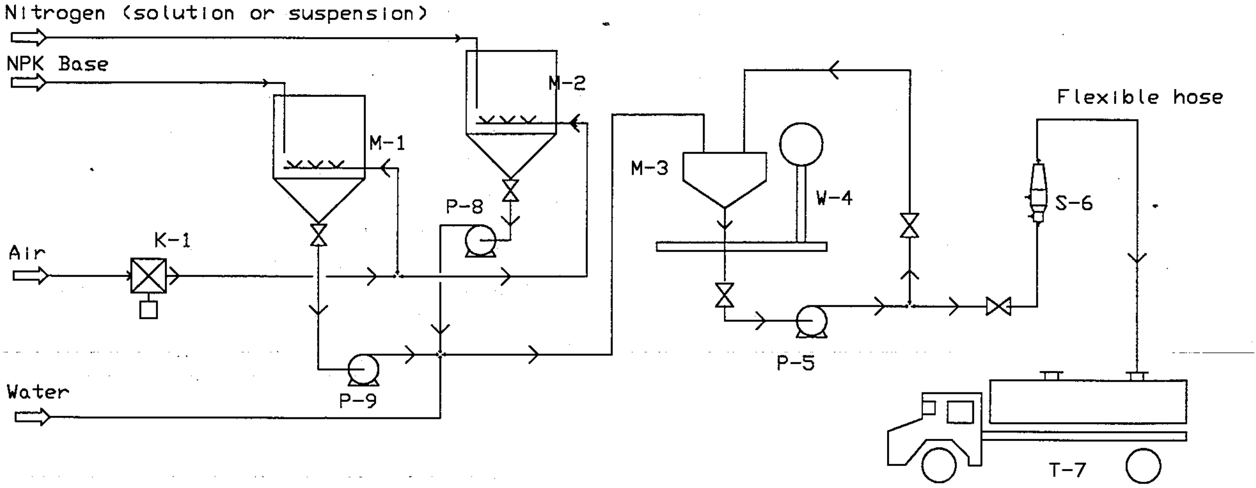
10.4.3 Transportation and Application of Suspensions

When suspensions were first introduced to the United States, they settled excessively during transport. It was found that some means of agitation during transit is desirable but not always necessary. Figure 10.17 shows a trailer truck that is similar to trucks used to transport powdered bulk cement.

The cone bottom of the truck is equipped with air spargers that can be used to re-suspend materials that

Table 10.10. Formula for 11-33-0 Suspension

Phosphate Material	MAP 11-52-0	DAP 18-46-0	APP 11-55-0
	(formulation, kg/tonne of product)		
11-52-0 (MAP)	634.5	–	–
18-46-0 (DAP)	–	502	–
11-55-0 (APP)	–	–	600.0
Phosphoric acid (54% P_2O_5)	–	183.5	–
Anhydrous ammonia	48.5	23.5	53.5
Water	302	276	330.5
Gelling clay	15	15	15
Total, kilograms	1,000	1,000	1,000



Legend:
K-1 Air compressor
M-1 NPK Base tank
M-2 Nitrogen tank
M-3 Mixing tank (scale-mounted)
W-4 Weigh scale
P-5 Pump
S-6 Strainer
T-7 Applicator truck with injector
P-8 Nitrogen soln. or suspension pump
P-9 NPK base soln. or suspension pump

Figure 10.16. Suspension Satellite Plant.

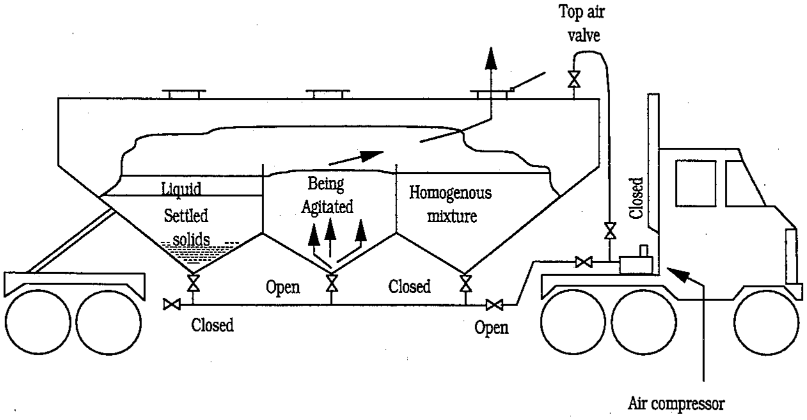


Figure 10.17. Cone-Bottom Transporter.

tend to settle during transport. Another type of transportation truck has a round bottom but is equipped with a recirculation sparger; the material that passes through the sparger sweeps the bottom of the tank and keeps the contents of the tank well mixed.

Applicators for suspensions are quite similar to the ones normally used for the application of nitrogen solutions; in many instances the same equipment is used. When suspensions are applied, a flooding-type nozzle must be used so that the nozzles will not become plugged. One of the larger applicators will apply suspensions at a rate of about 0.5 ha/minute.

10.5 Specialty Fluid Fertilizers

There are several types of fluid fertilizers and liming agents that deserve special discussion and application. The ones that will be discussed are:

10.5.1 Fluid limestone
10.5.2 Acid-type fluid fertilizer
10.5.3 Micronutrients in fluids
10.5.4 Solution using potassium hydroxide as a source of potassium
10.5.5 Fluids with sulfur

There are other specialty types of liquids, but these are the ones in which agriculturists have shown the most interest.

10.5.1 Fluid Limestone

Agronomists' studies have shown that to be effective, a liming agent must be of a fine size [5]. Industry agronomists report that to be 100% effective, limestone must be less than 0.2 mm with at least 75% less than 0.15 mm. It is generally agreed that the smaller the particle size of the liming agent, the quicker it reacts in the soil to adjust the pH to a suitable level for optimum crop growth. Problems occur with dusting and with drifting of the dust when this very small size material is applied. Obviously one way to avoid this problem with dust is to produce a suspension using it.

The mixing equipment normally used for the production of fluid limestone is the same as that used to produce other suspensions. Preferably, the mix tank is equipped with a large pump with a recirculation rate of about 1,900 liters per minute. Recirculating fluid enters tangentially to walls of the tank. Although the recirculating fluid causes most of the mixing, most operators also prefer to have an agitator to assist in mixing. Usually the fluid lime contains 50%-60% solids and 1%-2% gelling clay (attapulgite clay, sepiolite clay, sodium bentonite clay, zanthan gum, etc.). It is stored and applied in tanks and equipment used to produce suspensions.

A typical formulation for fluid limestone and some of its physical characteristics are given in Table 10.11.

10.5.2 Acid-Type Fluids [12]

These fluids are usually solutions and have a pH of less than 2.0. Some of the advantages of these acid solutions are: solution fertilizers can be produced from impure acids, larger quantities of micronutrients can be dissolved in them, they are less likely than neutral solutions to cause troublesome precipitates in irrigation systems that use water of high hardness, and it is possible to produce high nitrogen solutions that contain urea in a form that will not cause germination damage or lose its nitrogen when the solutions are surface applied [13].

Table 10.11. Formula for 10-Tonne Batch of Fluid Limestone

Material	Kg Per Batch
Limestone[a]	5,000
Gelling clay[b]	200
Water	4,800
Total	10,000
Suspended solid, %	50
Gelling clay, %	2
Specific gravity (20%), g/ml	1.44 to 1.68
Viscosity, g/cm-sec	<6.0

a. Particle size 100% <0.2 mm and 75% <0.15 mm.
b. Attapulgite clay.

The main disadvantage of these liquids is that they corrode mild steel and stainless steel. It is recommended that they be stored and handled in tanks, pipes, and equipment made of plastic (PVC, polyolefins, etc). In the production of NPK acid liquid mixtures probably the best combination of ingredients is UAN, solid urea, merchant-grade phosphoric acid, and potash. Typical formulations using these ingredients are given in Table 10.12.

The pH of all of these liquids is less than 2.0 and their specific gravities are close to 1.2 g/ml.

10.5.3 Micronutrients in Fluid Fertilizers

The need for micronutrients is growing in some countries because of intensive cropping, the shift to high-

Table 10.12. NPK Acid Solutions From UAN Solution, Urea, Phosphoric Acid, and Potash [10]

Ratio	1-1-1	1-2-1	1-4-1	1-3-1	1-3-3	3-1-2
Grade	8-8-8	7-14-7	5-20-5	7-21-7	3-9-9	9-3-6
	(Formulation, lb/tonne)					
Water	1,036	900	840	640	1,208	1,240
Urea (46% N)	232	200	144	200	76	256
UAN (32% N)	172	152	108	152	88	196
Phosphoric acid (54% P_2O_5)	300	520	744	780	336	112
KCl (62% K_2O)	260	228	164	228	292	196
Nitrogen from urea, %	83	83	83	83	79	83
Nitrogen from AN, %	17	17	17	17	21	17
Maximum mix temp, °C	27	27	29	27	27	27
Mixing time, min.	30	30	30	30	30	30
Crystal precipitation after 2 days at 0°C	No	No	No	No	No	No

analysis fertilizers that do not contain micronutrients, improved methods of identification of micronutrient deficiencies, and new crop varieties that have higher micronutrient requirements.

Correction of these micronutrient deficiencies may be accomplished by soil or foliar application. Boron, copper, zinc, manganese, and molybdenum are usually applied to the soil. Molybdenum is required in such small quantities that it is often dusted on seeds. Iron is usually added as a chelated material and is foliar applied.

Most micronutrients are mixed with the macronutrient materials (N, P, and K) and applied as a starter (banded close to the seed), a band between rows, through irrigation systems, or broadcast. Application with fluid fertilizers is a convenient method of uniformly spreading small quantities of micronutrients over a large area.

TVA conducted research to determine the solubility of micronutrients in fluids [5,14,15]. It was found that some sources form insoluble compounds that have low solubilities in liquid fertilizer and must be applied as suspensions. Generally, solubility data show that most micronutrients were more soluble in ammonium polyphosphate solutions than in conventional orthophosphate solutions. Table 10.13 gives a comparison of the

Table 10.13. Solubility of the Micronutrients

Solubility % by Weight of Element (Zn, Cu, Fe, Mn, B, Mo)

	Base Solution		
Material Added	11-37-0[a]	10-34-0[b]	8-24-0[c]
Zinc oxide	3.0	2.25	0.05
Zinc sulfate	2.0	1.30	0.05
Zinc carbonate	3.0	2.25	0.05
Cupric oxide CuO	0.7	0.53	0.03
Copper sulfate $CuSO_4 \bullet 5H_2O$	1.5	1.13	0.13
Ferric sulfate $Fe_2(SO_4)_3 \bullet 9H_2O$	1.0	0.80	0.08
Manganous-manganic oxide Mn_3O_4	0.2	0.15	0.02
Sodium molybdate $Na_2MoO_3 \bullet 2H_2O$	0.5	0.38	0.50
Borax $Na_2B_4O_7 \bullet 10H_2O$	0.9	0.90	0.90

a. 11-37-0 made from electric furnace superphosphoric acid; contains 70% polyphosphate.
b. 10-34-0 that contains 45% polyphosphates made from wet-process superphosphoric acid.
c. Made from electric furnace orthophosphoric acid; contains no polyphosphates.

amount of micronutrient elements (% by weight Zn, Cu, Fe, Mn, B, and Mo) that are soluble in three ammonium phosphate solutions, which are currently used or have been used to produce NPK solutions by mixing with other nutrient material such as UAN solution (28% to 32%) and potash (62% K_2O).

The 11-37-0 in Table 10.13 is an ammonium polyphosphate liquid made from superphosphoric acid, which was produced from elemental phosphorus. The 10-34-0 is the most common ammonium polyphosphate solution currently in use. It is produced from conventional wet-process superphosphoric acid, and the 8-24-0 liquid was produced from orthophosphoric acid made from elemental phosphorus.

These data show that the solubility of the micronutrients was substantially higher for the ammonium polyphosphate solutions (11-37-0 and 10-34-0) than for the orthophosphate solution (8-24-0). The 10-34-0 in these tests contained 45% polyphosphate. Later when it became possible to produce 10-34-0, which contained 70% polyphosphate using the TVA pipe reactor process, field tests confirmed that the solubilities shown for 10-34-0 in the above tabulation are conservative, and these are the values currently used. All of these liquids store well at 0°C.

These data are used to determine the quantities of micronutrients that will remain in NPK solutions made from 10-34-0 [16]. Plant-scale tests indicate that in most instances the solubilities in NPK solutions can be calculated using the quantity of 10-34-0 used in the formulation and the amount of the micronutrient that can be dissolved in 10-34-0. The operator can empirically calculate the amount of micronutrient soluble in the NPK solution according to the following example. In this example, determine the amount of zinc as zinc oxide that will remain in a 7-21-7 produced from 10-34-0, 32-0-0, potash, and water as follows:

1. The quantity of 10-34-0 used to produce a tonne of 7-21-7 is calculated to be 617.7 kg.
2. This 10-34-0 will dissolve 2.25% as zinc oxide.
3. The percentage of Zn as zinc oxide that can be dissolved in 7-21-7 is calculated as follows:

$$\frac{617.7 \times 0.0225 \times 100}{1000} = 1.39$$

A similar empirical method has been used to determine the amounts of several micronutrients that can be dissolved in liquids made from 10-34-0. The directives used are as follows:

- Never exceed the maximum amount of each micronutrient that can be dissolved in the 10-34-0.
- The sum of all the micronutrients should not exceed 3% of the amount of 10-34-0 used in the mixture.

With these criteria and the procedure used above, the operator can calculate the estimated amount of several micronutrients that can be added to solutions made from 10-34-0.

The amounts of micronutrients that can be added to a suspension without adversely affecting its uniformity of application must be determined through trial and error and small-scale tests. Application tests show that to avoid poor performance of a spray nozzle, the viscosity of the suspension must be less than 8 g/cm-sec (800 centipoise) and preferably less than 5 g/cm-sec (500 centipoise). At viscosities greater than these levels, the nozzle emits a nonuniform spray pattern. A test was conducted in which several micronutrient materials were added to a 15-15-15 suspension. The percentage of micronutrient material added and material used to supply this amount of element is given in Table 10.14.

Table 10.14. Suspensions With Micronutrients

Addition of Mixture of Micronutrients to 15-15-15 Suspension

% Micronutrient as Element	Material That Supplied Element
0.1 B	($Na_2B_4O_7{\bullet}5H_2O_1$ 14.3% B)
0.2 Cu	($CuSO_4{\bullet}5H_2O$)
0.6 Fe	($Fe_2SO_4{\bullet}9H_2O$)
0.6 Mn	($MnSO_4{\bullet}XH_2O$)
0.3 Zn	($ZnSO_4$, 36% Zn)

The freshly prepared 15-15-15 (0.1B-0.2Cu-0.6Fe-0.6Mn-0.3Zn) had a viscosity at 21°C of 2.00 g/cm-sec (200 centipoise) and after 1 day of storage it was 4.7 g/cm-sec. With further storage time, the viscosity increased beyond 8 g/cm-sec (800 centipoise), beyond the tolerance for accurate and uniform application.

These data show that the viscosity of the suspension increased with storage time. However, if it is applied soon after it is made (< one day), no problems with uniform application and pumping should occur. It is recommended that all suspensions that have micronutrients added to them be applied within one day.

Similar results were obtained when zinc oxide was mixed with 5-15-30 to produce a 5-15-30-2 Zn, 5-15-30-3 Zn, and 5-15-03-4 Zn. These results are given in Table 10.15. These data show that the 5-15-30-2 Zn is probably the best grade to produce, and it should be applied as soon as it is mixed.

10.5.4 Mixtures Using Potassium Hydroxide [5]

Tests have shown that when liquid mixtures are made from KOH and phosphoric acid (technical grade), one kilogram of K_2O as KOH will neutralize 1 kg of P_2O_5 from acid. For example, the 0-1-1 ratio is an 0-25-25 grade. For grades containing N, some or all of the nitrogen can be supplied by urea and/or ammonia.

In the production of a 1-2-1 grade, for example, there is insufficient KOH required to neutralize the acid, and some ammonia must be added to complete the neutralization.

When phosphoric acid that is produced from elemental phosphorus (furnace-grade phosphoric acid) is used to produce these liquids, the products have a clear appearance. The same is true when wet process superphosphoric acid is used. The grades are higher in analysis when superphosphoric acids are used in preference to orthophosphoric acid.

Typical grades of liquid fertilizers that have low-chlorine content and are made from superphosphoric acid and potassium hydroxide solution are given in Table 10.16.

The data show that it is possible to produce high-analysis mixtures with a wide range of nutrient ratios from these materials.

The main advantages of these clear solutions from KOH as compared to conventional solutions are:

- Higher analysis liquids.
- Possible to produce no-nitrogen and low-nitrogen to P_2O_5 ratios.
- Agronomic tests show that there is significantly less foliage burn caused by these liquids than by liquids made from potassium chloride.

10.5.5 Fluid Fertilizers With Sulfur

Much of the sulfur used in fluid fertilizers is added as ammonium thiosulfate solution (12-0-0-26S grade). This product is produced in a specially designed plant that produces the solution by the following steps:

- Burning sulfur with air to produce sulfur dioxide.
- Absorbing SO_2 in water to form sulfurous acid.
- Ammoniating this acid to form ammonium sulfite.
- Reacting ammonium sulfite with sulfur to produce ammonium thiosulfate.

This clear liquid is used to supply sulfur to clear mixtures such as an 8-20-5-5S or 26-0-3-3S. It is also used as a direct application of nitrogen and sulfur.

Another fairly common practice is to use ammonium sulfate solution of 8-0-0-9S grade, which is prepared by dissolving crystalline ammonium sulfate in water.

Sulfur is also added to suspensions. Small particle size elemental sulfur is suspended in a slurry using a gelling clay by the procedures described earlier.

10.6 Investment Costs

The investment costs of installations and equipment used in the production and application of liquid fertilizers

Table 10.15. Aging of Zn-Suspensions

	Viscosities of 5-15-30 XZn Mixtures (g/cm-sec at 21°C)			
Grade	Freshly Prepared	One-Day Storage[a]	One-Week Storage[b]	Two-Week Storage
5-15-30-2Zn	4.39	9.66	8.38	7.98
5-15-30-3Zn	6.79	14.36	12.90	12.34
5-15-30-4Zn	8.35	Too thick to measure or agitate by air sparging	–	–

a. Material not agitated prior to viscosity measurement.
b. Viscosity taken after agitation by air sparging.

Table 10.16. Low Chlorine Liquid Fertilizers

Typical formulations for low-chloride liquid fertilizers from superphosphoric acid and potassium hydroxide [5]

Ratio	Maximum Grade[a]
0:1:1	0-25-25
1:1:1	11-11-11
1:2:1	10-20-10
1:2:2	7-14-14
1:2:3	6-12-18
1:3:1	8-24-8
1:3:2	8-24-16
1:3:3	6-18-18
1:4:2	6-24-12
1:4:4	5-20-20
1:6:6	3-18-18
2:4:5	6-12-15

a. Maximum grade that was stored for 7 days at 0°C and 30 days at room temperature without salting out.

in Table 10.17 are based on information received from industry [17]. The Swift and Marshal index was used to adjust the costs to the 1994 level.

10.7 Summary

Fluid fertilizers are a major part of the fertilizer industry in the United States with about 60% of the total nitrogen and 20% of the mixtures being supplied in the fluid form. Other countries have also experienced growth in fluid fertilizer, particularly nitrogen solutions. It is anticipated that the use of nitrogen solutions will continue to grow throughout the world and that other fluids (phosphates and NPK mixtures) will soon follow in popularity. Fluids can be accurately measured and provide a means for efficient use of plant nutrients.

In the future, it is anticipated that fluids will be applied through the global positioning of applicators. The agri-services in the region or country, having all the necessary meteorological data, would be advised by a network applicator (farmer or service company) on grades, methods, and fertilizing intensity for particular crops to be applied at the optimum period of time.

10.8 References

1. International Fertilizer Industry Association. 1992. *Fertilizer Product Consumption Forecasts*, A/92/116 Paris, France.
2. Tennessee Valley Authority. 1994. *Commercial Fertilizer Consumption for Year Ended June 30,1993*, TVA NFERC 93/6 Bulletin-234.
3. The Fertilizer Institute. 1966. *Agricultural Anhydrous Operations Manual*, Washington D.C., U.S.A.
4. Achorn, F. P., and H. L. Kimbrough. 1977. "Latest Application Techniques for Applying Anhydrous Ammonia," TVA Fertilizer Conference, Kansas City, MO, U.S.A.
5. Achorn, F. P., Michael F. Broder, and Dan Henley. 1994. *ARA Professional Dealers Manual for Fluid Fertilizer*, Agricultural Retailer Association, St. Louis, MO, U.S.A.
6. Handbook on chemical specialties.
7. Meline, R. S., R. G. Lee, and W. G. Scott. 1972. "Production of Liquid Fertilizers with Very High Polyphosphate Content," *Fertilizer Solutions*, 16(2):32-45.

Table 10.17. Investment Costs of Equipment and Installations Used in the Production and Application of Liquid Fertilizers

Equipment and Installation (20 tph capacity)	Investment Costs (US $)
Typical pipe-reactor plants for production of ammonium polyphosphate solution	400,000 (limited storage)
Liquid fertilizer mix plant	275,000
Cold mix plant for production of suspension mixtures	400,000
Batch plant using liquid ammonia and phosphoric acid	400,000
Mix plant for production of suspensions from granular MAP/DAP	400,000
Suspension satellite plant	200,000

8. Slack, A. V., J. M. Potts, and H. B. Shaffer, Jr. 1965. "Effect of Polyphosphate Content on Properties and Use of Liquid Fertilizers," *J. Agri Food Chem.*, 13:165-71.

9. Slack, A. V., J. D. Hatfield, H. B. Shaffer, Jr., and J. C. Driskell. 1959. "Solubility Relationships in Liquid Mixed Fertilizer System," *J. Agri Food Chem.*, 7:404-408

10. Kachelman, D. L. 1989. *Fluid Fertilizer Reference Manual*, TVA Bulletin Y-210.

11. Achorn, F. P., and J. J. Mortvedt. 1977. "Addition of Secondary and Micronutrients to Granular Fertilizer," *Conference Granular Fertilizers and their Production*, pp. 304-332, International Conference, London, England, November.

12. Achorn, F. P., and C. A. Cole. "Production of Acid Fertilizer Solutions," U.S. Patent 4,531,926, Tennessee Valley Authority.

13. Gasser, J.K.P., and A. Penny. 1967. "The Value of Urea Nitrate and Urea Phosphate as Nitrogen Fertilizers for Grass and Barley," *Journal Agricultural Science*, 69:139-146.

14. Achorn, F. P. 1969. "Use of Micronutrients in Fluid Fertilizer," N.F.S.A. Conference, Kansas City, MO, U.S.A.

15. Giordano, P. M., and J. J. Mortvedt. 1966. "Zinc Availability and Concentration in Macronutrient Carriers," *Soil Science Society of America Proceedings*, 30(5):649-653.

16. Achorn, F. P. 1969. "Use of Micronutrients in Fluid Fertilizers," Presented at the Conference of the National Fertilizer Solutions Association, Kansas City, Missouri, July 22-23, Published in NFSA *Additives and Fluid Fertilizers '69 Round-Up*.

17. Personal communications with equipment manufacturers. 1990.

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Chapter 11. Sulfuric and Phosphoric Acids

11.1 Sulfuric Acid

11.1.1 Introduction

Sulfuric acid is an important raw material for phosphate fertilizer production and to a much lesser extent for nitrogen and potassium fertilizers. World production of sulfuric acid was about 158 million tonnes of H_2SO_4 in 1991 [1], from which 58% was used in fertilizer production.

About 65% of the world's production was based on elemental sulfur, 16% on pyrite, and 19% on other sources. Of the other sources, the principal one was byproduct sulfuric acid recovered from smelting operations.

The most important consumers of sulfuric acid are: North America (29%), Eastern and Central Europe and the Commonwealth of Independent States (CIS) (20%), and southeast Asia (18%).

In general terms, sulfuric acid is produced by catalytic oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3), which is subsequently combined with water to form sulfuric acid (H_2SO_4). In practice the SO_3 is absorbed in sulfuric acid that is kept at a controlled concentration (usually 98%) by water addition.

There are no major variations of commercial interest on this basic chemistry. There are alternatives regarding the source of SO_2 and the method of conversion to SO_3.

The two principal processes for conversion of the SO_2 are known as the chamber and the contact processes. The older chamber process, which was introduced in Europe near the middle of the 18th century, uses nitrogen oxides as oxygen-carrying catalysts for the conversion of SO_2 to SO_3 [2,3]. The reactions that produce the SO_3 and sulfuric acid take place within huge lead chambers (from which the process is named) or in packed towers that may be substituted for the chambers. Major disadvantages of the chamber process are limitations in throughput, quality, and concentration (usually 60° Bé or about 78% H_2SO_4). All known new plants use the contact process although some older chamber process plants may still be in use.

In the contact process SO_2 is converted to SO_3 by use of a metal or metal-oxide catalyst. Platinum was once widely used as a catalyst, but because of its excessive cost and susceptibility to "poisoning," it has largely been replaced by vanadium pentoxide. The SO_3 is passed to an absorption tower where it is absorbed in recirculating concentrated acid. There are many variations in the contact process depending upon the types of raw materials available and other considerations; also, a number of engineering variations are in use by the many different design/construction firms offering services in this field. The main advantages of the contact process are that concentrated acid (98% H_2SO_4) of high purity can be produced directly and that compact plants of quite high capacity have now become rather commonplace and capacities up to about 3,000 tpd are not unusual.

11.1.2 Production of Sulfuric Acid From Elemental Sulfur

Elemental sulfur, also called "brimstone," is the preferred raw material for sulfuric acid production whenever it is available at a reasonable cost. Elemental sulfur may be mined by the well-known Frasch process or recovered from volcanic ores, "sour" natural gas, or oil. It is also possible and sometimes commercially feasible to produce elemental sulfur from pyrites, other sulfide ores, and coal.

Commercial sulfur is usually 99.9% or higher in purity. "Dark" sulfur contains hydrocarbon impurities up to about 0.5%; "bright" sulfur contains less than about 0.1% (measured as carbon). Dark sulfur causes difficulties in some types of sulfur-burning plants. However, methods for using dark sulfur without difficulty have been developed. Another quality factor is the ash content, which should be quite low to avoid dust that will accumulate in the catalyst bed. Solid impurities can be removed from molten sulfur by filtration [4]. Alternatively, by using a hot gas filter, dust arising from ash in the sulfur can be removed from the hot gas leaving the sulfur burner.

Most sulfur-burning plants are designed to use sulfur in liquid form although plants with solid feed have been used. In many cases the sulfur is transported in liquid form by ships, barges, or railcars that are specially equipped for that purpose. In this case, the sulfur is stored in liquid form at the plant's receiving terminal until it is used. When the sulfur is received in solid form, it is usually melted before use.

In producing sulfuric acid from sulfur, heat is released in various steps of the process as noted in Table 11.1.

Some additional heat is released by dilution of the sulfuric acid to the usual concentration of 98% or 93%, but this is relatively small. The total heat released is equivalent to about 1.3 million kcal/tonne of H_2SO_4. Recovery of a maximum portion of this heat as usable

Table 11.1. Reactions in Sulfuric Acid Process

Reaction	Heat Released, kcal/mole of H_2SO_4
$S + O_2 \rightarrow SO_2$	70.9
$2SO_2 + O_2 \rightarrow 2SO_3$	23.5
$SO_3 + H_2O \rightarrow H_2SO_4$	32.8
Total reaction	
$S + 1\text{-}1/2\ O_2 + H_2O \rightarrow H_2SO_4$	126.2

energy is an important objective of the production technology.

Before describing particular industrial processes, it should be noted that each process is based on information supplied by a different engineering and construction organization. Each of the organizations offers a range of processes to meet various client needs. Several other companies offer sulfuric acid processes, and there is no intention to imply that processes offered by the companies mentioned by name are necessarily superior to those offered by other companies and does not imply any kind of endorsement by UNIDO or IFDC.

In a typical sulfur-burning, single-contact sulfuric acid plant (Figure 11.1), the molten sulfur is burned with dry air. The air is dried in a drying tower by contact with concentrated sulfuric acid. The sulfur is burned in a refractory-lined combustion chamber with excess air at a temperature of 950°-1100°C, a combustion gas containing about 10% SO_2 is produced.

The gas is cooled in a boiler, which generates steam, to about 420°C, the desired inlet temperature to the catalytic converter. Some of the excess air may be bypassed around the burner and boiler to control the combustion chamber temperature and to decrease the required size of the boiler. Alternatively, excess air may be added between catalyst beds to control the temperature during conversion.

Normal combustion of sulfur creates nitric oxides, which can be harmful to many processes. The formation of NO_x is proportional to the gas temperature, i.e., directly to the SO_2 concentration [3].

Figure 11.2 presents the formation of NO during normal combustion of sulfur. There are some special methods of sulfur combustion that minimize the formation of nitric oxides. The catalytic conversion of SO_2 to SO_3 usually is carried out in three or more steps (catalyst beds); the gas is cooled between steps to keep the temperature within the desired range of 420°-450°C. The conversion steps are carried out by contact of the gas with successive beds of vanadium oxide catalyst, which are often arranged in sections of a single tower.

The gas leaving the first catalyst bed may be at a temperature of 580°-600°C and must be cooled to a range of 420°-450°C to promote efficient conversion in the second bed because of unfavorable equilibrium at higher temperatures. Cooling may be done by injecting cool air or by heat exchange to produce more steam. Likewise, cooling between the second, third, and successive beds is required, but the temperature rise is less than that of the first bed.

The gas leaving the tower is cooled further in a heat exchanger (economizer) before entering the absorption tower where the SO_3 is absorbed in a recirculated stream of concentrated sulfuric acid. The sulfuric acid is maintained at the desired concentration (usually 98% H_2SO_4) by water addition, and its temperature is controlled in the desired range of 70°-90°C measured at the tower inlet by cooling the recirculated acid. Some of the

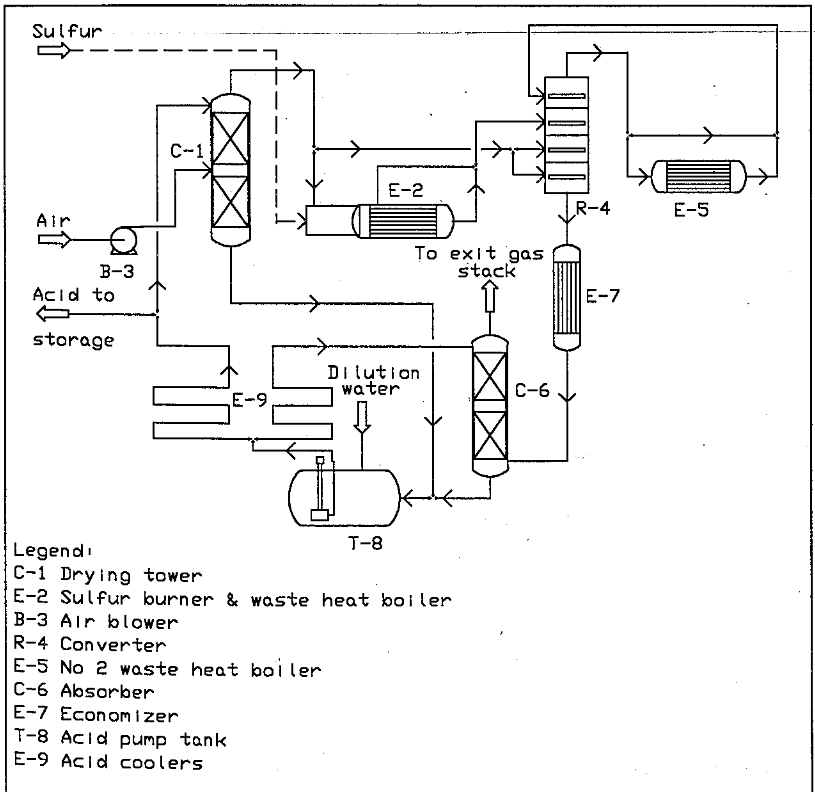
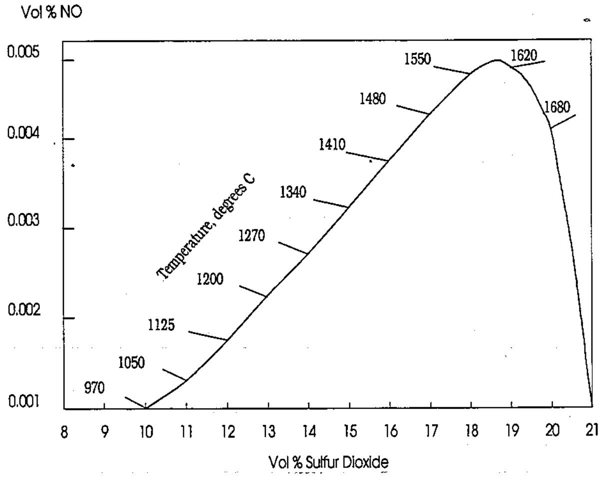


Figure 11.1. Sulfur-Burning Single-Contact Sulfuric Acid Plant.



Note:
Precise vol % NOx values may vary a little, because they depend also on the other parameters (particularly on dispersion of liquid sulfur being burnt and cooling conditions of resulting gases) therefore this figure is only a demonstrative one

Figure 11.2. Formation of NO During Combustion of Sulfur [3].

acid goes to the air-drying tower mentioned previously where moisture from the incoming air supplies some of the water needed in the reaction. In the above-described single-absorption process, the recovery of sulfur as sulfuric acid is 97%-98%; the remainder is lost to the atmosphere as SO_2. In most countries the discharge of this amount of SO_2 is environmentally unacceptable. Therefore, most plants use a double-contact, double-absorption (DC/DA) system as shown in Figure 11.3. The gas, after passing through three catalyst beds, goes to the first absorption tower where the SO_3 is removed. The gas is then reheated to about 420°C, passed through the fourth catalyst bed, and then cooled and sent to a second absorption tower. The theoretical principle of the double-contact process depends on the law of mass action:

$$K_p = \frac{P\,[SO_3]}{P\,[SO_2] \times P\,[O_2]^{1/2}}$$

Where:

- $P[SO_2]$, $P[O_2]$, and $P[SO_3]$ are partial pressures of the individual reactants in the gas phase, and
- Kp is the equilibrium constant.

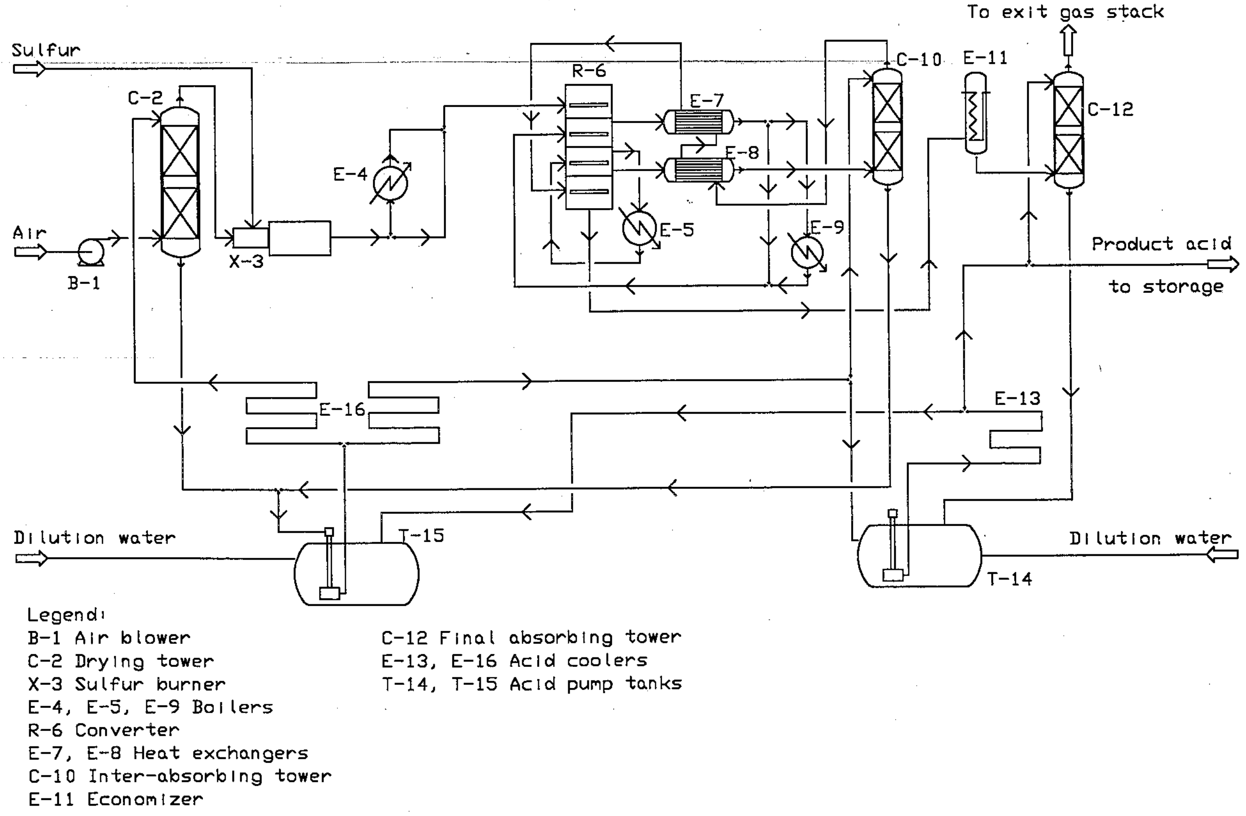


Figure 11.3. Sulfur-Burning Double-Contact, Double Absorption Sulfuric Acid Plant.

After a preliminary SO_2 conversion, the SO_3 formed at this stage is removed by intermediate absorption so that the equilibrium is shifted in favor of SO_3 formation.

The temperature-conversion functions for different steps of catalytic reaction are given in Figure 11.4.

The DC/DA process reduces the SO_2 loss to less than 2 kg of SO_2/tonne of H_2SO_4. High- efficiency mist eliminators are also required to limit the loss of H_2SO_4 mist to less than 0.05 kg/tonne of H_2SO_4. Thus, the recovery in a DC/DA plant should be at least 99.7%.

The use of the DC/DA system adds 10%-15% to the cost of the plant in comparison with the older single-absorption process. It also uses more energy and produces less steam or other recoverable energy. The residual quantities of SO_2 can also be removed by scrubbing the stack gases with an ammonia solution. The resultant ammonium sulfite/bisulfite solution is then acidulated with sulfuric acid to produce ammonium sulfate and SO_2.

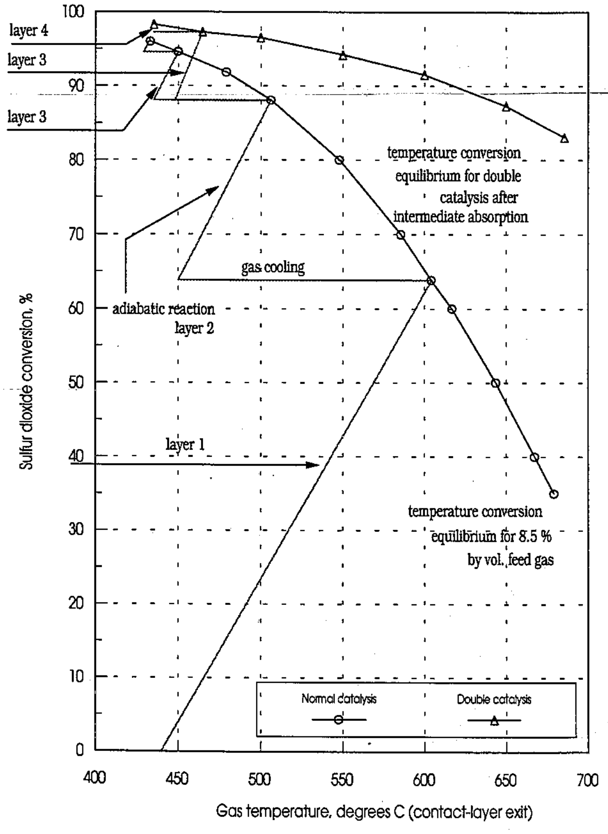


Figure 11.4. Diagram of Conversion Functions [4].

The liberated SO_2 is returned to the sulfuric acid plant, and the remaining concentrated ammonium sulfate solution may be used in a fertilizer plant.

Alternatively, the ammonium sulfite-bisulfite solution may be acidulated with phosphoric acid, producing an ammonium phosphate solution. There are numerous other tail-gas scrubbing processes that produce various byproducts or waste products [5].

Operation of a sulfuric acid plant under pressure has some advantages; the equipment is smaller and less expensive, less catalyst is required, and equilibrium conditions and reaction rates are more favorable in the conversion and absorption steps. The first pressure plant was built by Produits Chimiques Ugine Kuhlman near Lyon, France. It began operation in 1972 at a capacity of 550-575 tpd. The plant used a double-contact, double-absorption process and operated at 0.5 MPa pressure, measured at the air compressor exhaust. The conversion efficiency was 99.80%-99.85% during the first 5 years of operation. It was estimated that the investment cost was 10% less than for a conventional (nonpressure) plant, but for larger capacities up to 2,000 tpd, an investment saving of up to 17% was possible. About two-thirds of the energy required for compression was recovered by expansion of the reheated tail gas in a turbine that drives the compressor. Operating parameters are summarized below in Table 11.2 [6].

It was noted that the plant was designed in 1970 before the energy crisis, and some improvements in heat and energy recovery would still be possible and economically desirable under current conditions.

Another pressure process is called the CIL process (Chemetics International Ltd., Canada). The process operates at 0.8 MPa and uses a single-contact, single-absorption system. The unique feature of the process is that SO_2 remaining in the gas leaving the converter is absorbed in the sulfuric acid in the absorption tower. The acid containing dissolved SO_2 then goes to the air-drying tower where the dissolved SO_2 is stripped from the acid into the airstream and thereby recycled through the sulfur burner to the converter.

Table 11.2. Pressure Sulfur Plant Operating Parameters

Sulfur consumption	330 kg/tonne
Electric power	65 kWh/tonne
Byproduct steam (at 40 atm)	990 kg/tonne
Process and cooling water	Same as in conventional processes
Maintenance	3%-4% of capital cost
Operating labor	2 men/shift
Acid concentration	99.0%-99.5% H_2SO_4

The solubility of SO_2 in sulfuric acid increases with the increase of pressure and with the decrease in temperature. In a conventional plant operating at 1-atm pressure and with an acid temperature of 110°C, the solubility of SO_2 in sulfuric acid is only 8 ppmw. However, by increasing the pressure to 0.8 MPa and lowering the temperature to 49°C, the SO_2 solubility is increased to 190 ppmw. Under these conditions, a substantial amount of SO_2 can be transferred in the acid stream to the air-drying tower and then to the incoming airstream. Cameron et al. [7] point out that there is no theoretical limit to the amount of SO_2 that can be recovered and recycled; it depends on the rate of recirculation of acid between the absorber and air-drying towers. In a conventional plant, each tower has its own acid recirculation system (Figure 11.1) with only enough interchange between the systems to maintain the acid concentrations at the desired level.

In the CIL system [4], most of the recirculation is between the two systems. It is claimed that this system can readily attain or exceed the 99.7% efficiency that is required to meet U.S. pollution control standards.

The CIL process has the advantage of a pressure process, which was pointed out in describing the Kuhlman process, and the additional advantage of requiring only single-contact and single-absorption equipment, which would obviously decrease capital costs and simplify plant operation. However, maintaining the relatively low acid temperature (about 50°C in the absorber tower) would require more cooling. Even though the CIL process is technically interesting, no practical use has been found for it.

Before the energy crisis of the 1970s, the typical energy recovery from sulfur-burning interpass plants was 55%; steam production amounted to about 1.1 kg/kg of acid made. In the 1980s Monsanto Enviro-Chem [8] raised the energy recovery potential up to 70% and steam production to about 1.35 kg/kg of acid made. This was accomplished by the introduction of the following features:

- High SO_2 gas strength up to 12% for sulfur-burning plants and 14%-15% for metallurgical plants.
- A ring-type catalyst to reduce pressure drop by 50%.
- Low-temperature economizers.
- Boiler pressure of 6.0 MPa and steam superheat to 450°C.
- Suction drying towers.
- Boiler feedwater preheating.
- Improved mist eliminators.
- Economically optimized plant pressure drop.

These features have been introduced in new plants and can be made available in existing plants as the Retrofit Energy Enhancement Program (REEP). The payback period for these retrofits amounts to 1-3 years. In 1984 Monsanto Enviro-Chem patented the Heat Recovery System (HRS). The HRS is based on the discovery of a range or "window" of sulfuric acid concentration sufficiently wide to achieve high absorption efficiency and a low corrosion rate. This is to be accomplished while operating at a high temperature (over 120°C) in an absorption tower.

The process flowsheet, as shown in Figure 11.5, consists of a packed tower, recirculating pump tank (not shown), and boiler. The equipment is constructed of common stainless steel alloys; hence, anodic protection is not needed [9]. The tower is referred to as the heat-recovery tower (HRT) to distinguish it from the other towers in the acid plant. In a sulfur-burning interpass plant, the HRT is located after the economizer and replaces the interpass absorbing tower (IPAT). In a single-absorption plant, the HRT is located before the absorbing tower. As shown in Figure 11.6, sulfuric acid of controlled concentration enters the top of the HRT at point A. Absorption of sulfur trioxide increases the concentration and temperature and acid leaves the tower at point B. The hot concentrated acid is cooled by generating steam in a boiler, and the cooled acid exits the boiler at point C. Acid product is removed after the boiler, and the remaining acid is diluted with water prior to returning to the tower at point A. Points A, B, and C define the operating cycle [7]. Instead of 304 stainless steel, equivalent alloy steels may be used [10].

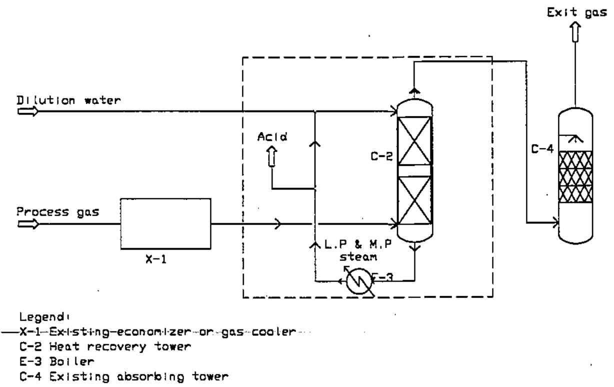


Figure 11.5. Monsanto Heat-Recovery System.

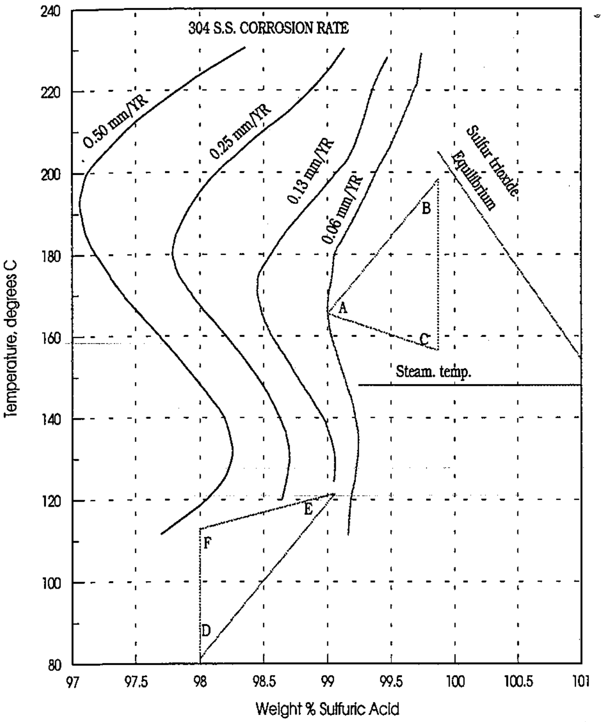


Figure 11.6. HRS Operation Cycle.

The HRS can produce steam at pressures up to 1.0 MPa from heat normally lost in acid cooling systems. About 0.5 kg steam/kg sulfuric acid can be made this way, thus boosting overall steam production in sulfur-burning plants to about 1.85 kg/kg of H_2SO_4 made. When this steam and the higher pressure steam from an energy-efficient sulfuric acid plant are used for co-generation, an additional amount of power may be produced as given in Table 11.3.

For new plants of different capacity, these figures can be scaled proportionally and will vary according to local plant conditions. There are a number of new major (over 1,000 tpd) acid plants based on sulfur burning using improved heat recovery technology including the HRS.

Table 11.3. HRS Energy Efficiency

Plant Capacity	Power Export	HRS Addition	Total Power
1,000 tpd	8.2 MW	3.1 MW	11.3 MW

11.1.3 Economics of Sulfuric Acid Production Capital Costs

The estimated capital cost of DC/DA sulfuric acid plants based on elemental sulfur is shown in Figure 11.7. The lower curve shows a battery-limits cost for a developed-industrialized country. The estimate is based on 1992 costs that include an allowance for a 4-week storage of sulfur and sulfuric acid [11].

The estimate does not include a cooling tower for reuse of cooling water. The upper curve is based on a battery-limits cost plus 50% to allow for auxiliary and support facilities, site preparation, etc.; these costs will vary with location and coexisting facilities. When the sulfuric acid plant is part of an industrial or fertilizer complex, this allowance probably is adequate. For a location in a developing country, costs should be increased by locational factor, e.g., 25% or more to provide for the increased cost of delivery and construction.

The plant normally produces enough steam to operate the main air supply compressor and boiler feedwater pumps and about 1.2 tonnes of additional steam per tonne of H_2SO_4. This excess steam can be used for generation of electricity, concentration of phosphoric acid, or other purposes.

Production Costs – An estimate of the major cost components of producing sulfuric acid from sulfur in a plant rated at 1,200 tonnes of H_2SO_4/day and operated at full capacity, 325 days/year, is given in Table 11.4.

Assuming a sulfur cost of US $75/tonne delivered at the plant, the estimated plant-gate production cost of sulfuric acid from an 1,800-tpd plant would be US $30/

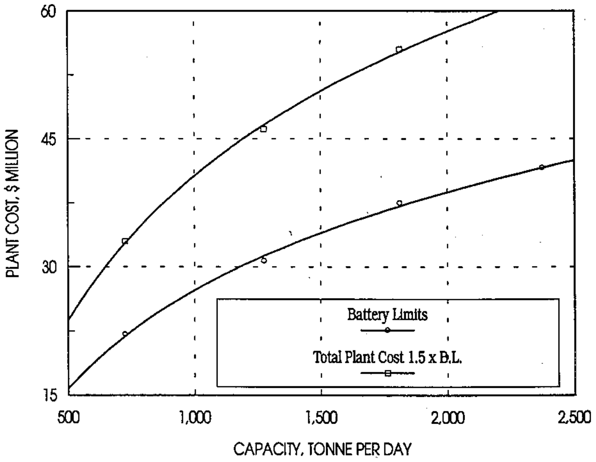


Figure 11.7. Investment Cost of Sulfuric Acid Plants.

Table 11.4. Process Requirements for Sulfuric Acid Production

Investment

Product	Process	Capacity	Investment Cost (BL) (US $ 10^6)
Sulfuric acid	Sulfur burning	390,000 tonne/year	28.5
Sulfuric acid	Iron pyrite gas	320,000 tonne/year	42.7[a]

Production

Cost Elements	Units	Value	
		Sulfur Burning	Iron Pyrite Gases
Elemental sulfur	t/t	0.33	-
Sulfur dioxide gas	t/t	-	0.66
Catalyst	US $/t	0.02	0.02
Electricity	kWh/t	(176)	52
Steam	t/t	(0.6)	(0.18)
Cooling water	m^3/t	75	65
Process water	m^3/t	0.6	0.5
Labor	workhours per t	0.32	0.38

a. Roasting excluded; only gas treatment.

Notes:
1. Capacity: in 100% H_2SO_4.
2. Operating days per year: 325 (sulfur burning, pyrite roasting).
3. Production level: 1,200 tpd of 93%-96% sulfuric acid calculated on 100% H_2SO_4 (sulfur burning).
4. Production level: 1,050 tpd of 93%-96% sulfuric acid calculated on 100% H_2SO_4 (pyrite gas treatment).
5. Basis: 1993 West European costs.

tonne of H_2SO_4 for a developed country location or US $34/tonne for a developing country, assuming that the plant capital cost is 25% higher. Cost estimates for different plant capacities are given in Table 11.5.

Even though sulfuric acid plants in general are not difficult to operate at full capacity for extended periods, maintaining a high capacity utilization depends on the reliability of production units that use the product and many other factors. Table 11.6 shows the effect of capacity utilization on transfer price, assuming a sulfur cost of US $75/tonne.

It is evident that low capacity utilization can increase the cost significantly. For instance, operation at 60% of capacity increases the transfer price by about US $14/tonne in comparison with operation at 90% capacity utilization for a 1,200-tpd plant in a developing country location. Since about 3 tonnes of sulfuric acid is required per tonne of P_2O_5 produced as phosphoric acid, the effect of low capacity utilization can be quite serious in a plant where the two units are interdependent.

11.1.4 Production of Sulfuric Acid From Pyrites or From Smelter Operations

When the source of the SO_2-containing gases is roasting of pyrites (FeS_2), pyrrhotite (approximately Fe_5S_6), or nonferrous sulfide ores, the sulfuric acid plant is similar to that described above (Figures 11.1 and 11.3) with the following differences [12,13]:

1. The sulfur-burning furnace is omitted.
2. The incoming gas must be cooled and scrubbed or otherwise cleaned to remove all impurities that might poison the conversion catalyst or clog the catalyst bed.
3. The gas must be dried in a tower that uses sulfuric acid as the drying agent.
4. The clean, dry gas must be heated to conversion temperature (about 420°C). There is usually enough heat generated in the conversion step to preheat the incoming gas by heat exchangers.

Table 11.5. Impact of Plant Capacity on Cost of Sulfuric Acid

		Developed Country			Developing Country		
Capacity	tpd	600	1,200	1,800	600	1,200	1,800
Investment cost (BL)[a]	US $ 10^6	19.5	30.0	37.5	24.5	37.5	47.0
Cost Elements	US $/tonne of sulfuric acid 100%						
Capacity, tpd		600	1,200	1,800	600	1,200	1,800
Raw materials		24.77	24.77	24.77	24.77	24.77	24.77
Utilities[b]		-14.64	-14.64	-14.64	-14.64	-14.64	-14.64
Labor[c]		8.71	6.60	5.62	8.71	6.60	5.62
Capital cost		18.25	13.24	11.70	22.93	17.55	14.66
Plant-gate cost		37.09	29.97	27.45	41.77	34.28	30.41
Sales cost		3.0	3.0	3.0	3.5	3.5	3.50
Transfer price		40.0	33.0	30.0	45.0	38.0	34.0

a. Investment cost in developing countries, assumed to be 25% higher than in developed countries.
b. Utilities; process and cooling water, electricity and steam produced.
c. Labor cost assumed to be inversely proportional to the 0.4 power of plant capacity increase.

Table 11.6. Effect of Capacity Utilization on Transfer Price of Sulfuric Acid[a]

Capacity utilization, % of nominal rated capacity, tpd	600	1,200	1,800
	(US $/t[b])		
100%	40	33	30
90%	43	35	32
75%	49	40	36
60%	58	46	42

a. Calculated from Table 11.5, assuming that labor and capital-related costs are constant on an annual basis, and raw material and utilities costs (credits) are constant on a per-tonne basis.
b. Values for developed countries; for developing countries multiply by 1.25.

5. Since the SO_2 concentration of the gas is often lower than that from sulfur burning, all equipment must be correspondingly larger.

As in the case of sulfur-burning plants, the sulfuric acid plant may use double-contact or tail-gas scrubbing to conform to pollution control requirements. A plant using sulfur dioxide from sulfide roasting is likely to cost about 50% more than a sulfur-burning plant including gas cleaning but excluding the roasting operation. Heat recovery depends mainly on how much heat can be recovered from the roasting operation. In general, the amount of heat recovered as steam or in other useful forms is somewhat less for a pyrites-based plant than for a sulfur-burning plant.

Pure pyrite (FeS_2) contains 53.4% S and 46.6% Fe. However, unlike sulfur, pyrite ores contain numerous impurities that affect their value, either positively or negatively. After mining and (usually) beneficiation, a commercial grade of pyrite may contain 40%-50% S. The most common valuable elements associated with pyrite are copper, lead, and zinc. However, the ore may contain many other elements (usually as sulfides) such as nickel, cobalt, cadmium, bismuth, arsenic, and small percentages of silver and gold.

An example of partial analysis of Spanish pyrite [12] is given in Table 11.7. The recovery of the valuable metals and iron plays an important part in the economics of

Table 11.7. Composition of Spanish Pyrite

	Crude Pyrite	Floated Pyrite
Sulfur (S)	48%	48%
Copper (Cu)	0.8%-1.2%	0.3%
Lead (Pb)	0.5-1.5%	0.3%
Zinc (Zn)	1.5-2.5%	0.4%
Gold (Au)	1 g/tonne	1 g/tonne
Silver (Ag)	30 g/tonne	30 g/tonne

processing pyrites. Arsenic is an undesirable impurity; during roasting it tends to form volatile compounds that foul heat exchangers and ducts. However, methods of dealing with this problem have been developed, of which the most important one is dearsenifying roasting.

When pyrites are relatively rich in copper or other valuable metals, the ore may be separated by beneficiation to provide a concentrate of nonferrous sulfides, which is treated separately. Alternatively, the cinder (residue) after roasting may be treated by one of several methods to extract valuable elements. Since the cinder mainly consists of iron oxide, it may be used by the steel industry as an iron ore. However, since several impurities are objectionable for use as iron ore, treatment after roasting may serve the dual purpose of recovering valuable elements and purifying the cinder for use in the steel industry.

Figure 11.8 shows a simplified flow diagram for production of sulfuric acid from pyrites. The diagram shows a single-contact, single-absorption process. In most locations either stack gas scrubbing or a second contact-absorption stage would be necessary to prevent atmospheric pollution. The treatment or disposal of the cinder, although important, is beyond the scope of this manual.

In spite of the large quantities of sulfuric acid offered, a well-defined demand exists for acid of special purity. This means low mercury acid with 0.1 ppmw Hg is at a premium (5 DM per tonne in 1994) over typical merchant-grade product, which has up to 0.5 ppmw mercury [11]. A specification for technical-grade sulfuric acid is given in Table 11.8.

The capital cost of the plant including the pyrite roasting step is about 2.6 times the cost of an equivalent sulfur-burning plant [12]. Based on the estimates in Table 11.5, the capital-related operating costs would be higher than for a sulfur-based plant by about US $20/tonne of H_2SO_4 for a 1,200-tpd plant in a developing country.

Labor and other costs would also be higher. Assuming a total differential is US $25/tonne of H_2SO_4, it is evident that, for equal production costs, the cost per

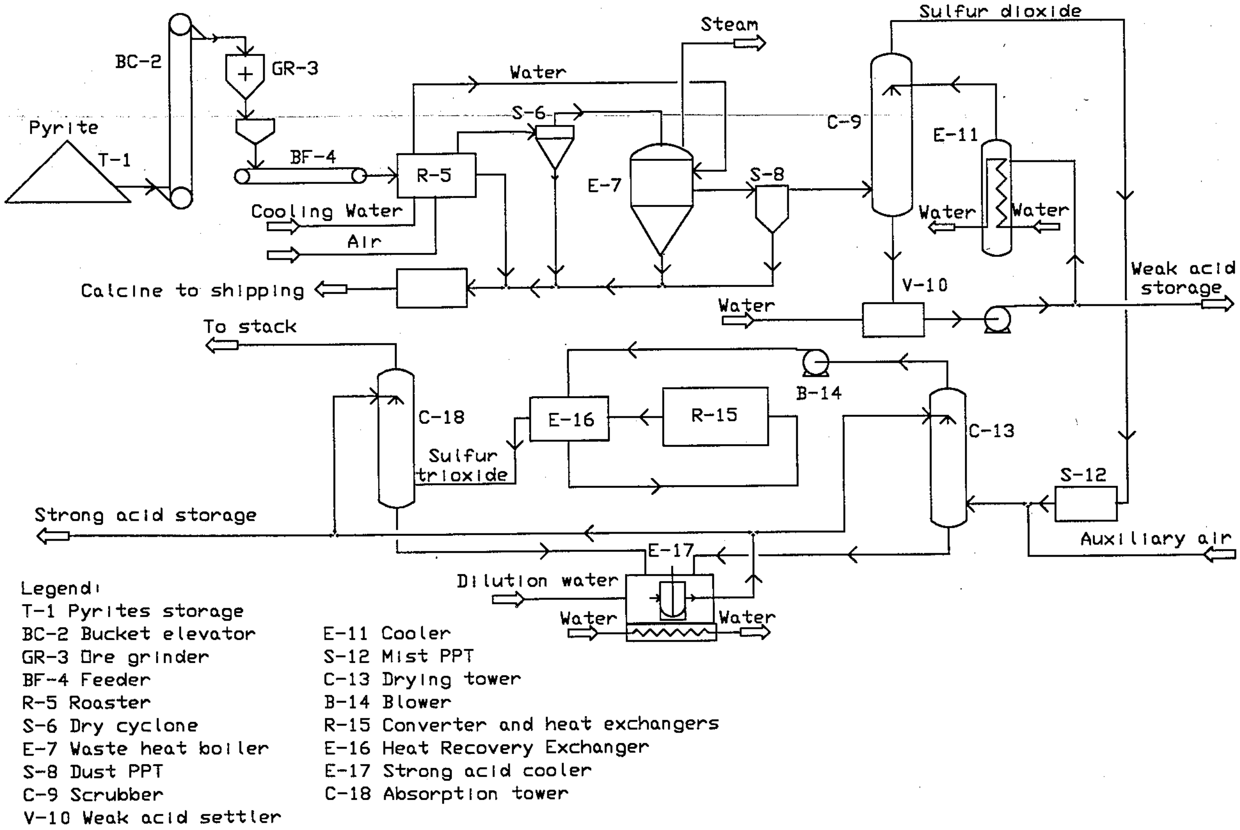


Figure 11.8. Production of Sulfuric Acid From Pyrites.

Table 11.8. Prevailing Sulfuric Acid Specification

Compounds	Units	Value
Sulfuric acid		
- summer season	%	>96
- winter season	%	92-96
Nitrogen oxides (N_2O_3)	%	<0.002
Dry residue	%	<0.003
Iron compounds as Fe	%	<0.006
Arsenic compounds as As	%	<0.0002
Lead compounds as Pb	%	<0.005
Chlorides as Cl	%	<0.01
Suspended matters	cm^3/dm^3	0.5

tonne of sulfur contained in pyrites would have to be US $75/tonne less than for elemental sulfur unless some value is assigned to the cinder.

Lasaosa presented data showing that the net cost of producing sulfuric acid from Spanish pyrites, after allowing credit for byproducts, was less than from sulfur in 1972 [12]. No generalized conclusion can be drawn because of the wide variation in quality of pyrites, value of byproducts, and local conditions. Typical process requirements for pyrite-based (and sulfur-burning) plants are shown in Table 11.4.

The recovery of byproducts from pyritic ores requires a high level of technology and may be a difficult undertaking for a developing country. Some countries that rely mainly on pyrites as a source of sulfuric acid are Finland, Norway, Sweden, Spain, Portugal, Italy, China, and the Commonwealth of Independent States. Some other countries, such as Japan, produce large quantities of sulfuric acid in smelting operations. The classification between pyrites and nonferrous ores is ill defined. In some countries a company that processes ore containing 1% copper might be classified as a copper smelter-producing byproduct sulfuric acid; a similar operation in another country might be classified as a sulfuric acid producer with byproduct copper production.

The Outokumpu process, which was developed in Finland, consists of flash roasting pyrites in a nonoxidizing atmosphere in a fluidized bed. About half of the sulfur content is recovered as elemental sulfur, and the remainder is in the residue, pyrrhotite, a magnetic iron sulfide. The pyrrhotite may be roasted in an oxidizing atmosphere to recover the remaining sulfur as sulfur dioxide.

11.1.5 The Production of Sulfuric Acid by Wet Catalysis

In contrast with the conventional contact sulfuric acid that operates with dry sulfur dioxide/air mixtures, wet gas is used in the wet contact process [13]. The hydrogen sulfide in the initial gas is first burned to SO_2 and H_2O. The sulfur dioxide is then converted to SO_3, which combined with the steam that is formed yields sulfuric acid. The process flowsheet is given in Figure 11.9.

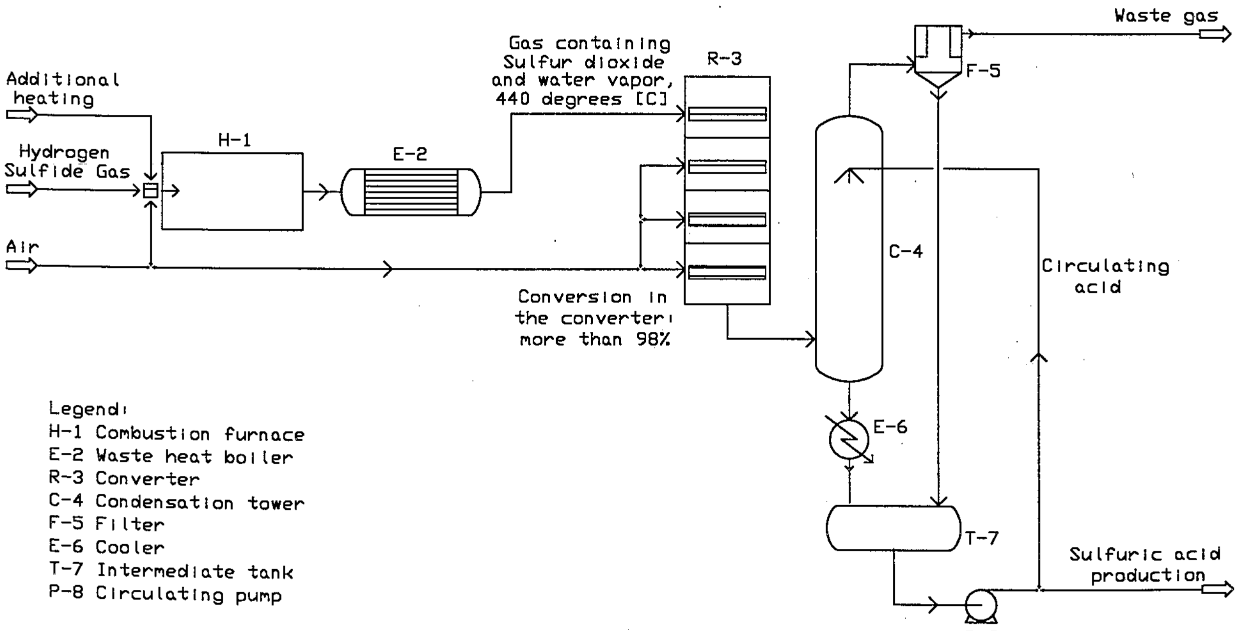


Figure 11.9. Wet Catalysis Sulfuric Acid Plant.

Waste gases containing at least 10% H_2S from various sources can be processed directly to sulfuric acid. These sources include cokeries, mineral oil refineries, fuel gasification or low-temperature carbonization plants, natural gas cleaning installations, carbon bisulfide production plants, and synthetic fiber plants. Gases with a lower H_2S content have to be burned with additional heating (e.g., with fuel gas, oil, or sulfur).

The sulfur dioxide and water vapor-containing gases enter the converter at about 440°C in which SO_2 is catalytically oxidized to SO_3 as in the conventional process (conversion efficiency above 98%).

The reaction temperature in each bed is maintained at a designated value by the addition of cold air to achieve an optimum conversion efficiency. The water vapor and SO_3-containing gas flows into a condensation tower sluiced with sulfuric acid. The condensation heat and the sensible heat are removed by coolers from the circulating sulfuric acid. Part of the circulating acid is continuously discharged as product acid. After passing through the condensation tower, the sulfuric acid mist is eliminated by using special filters. The concentration of the product sulfuric acid is 78%. This concentration corresponds to the H_2O/SO_3 ratio of complete condensation, but 93% H_2SO_4 can also be produced from wet gases by means of special equipment using the principle of hot condensation. The lifetime of the catalyst is up to 10 years [13].

11.1.6 Production of Sulfuric Acid From Calcium Sulfate

Sulfuric acid can be manufactured from calcium sulfates of all kinds including natural anhydrite, gypsum, and also phosphogypsum; portland cement is a byproduct of this process. Formerly the calcium sulfate-based process was used in several plants in some European countries and in South Africa, but these installations have been closed.

Nevertheless, the process based on calcium sulfate as a raw material has potential if its economics can be improved. A simplified flow diagram of the process is shown in Figure 11.10.

The process is carried out in a rotary kiln that is similar to cement kilns. When gypsum is used, it is first dehydrated in a separate kiln. When phosphogypsum is used, part of the fluorine is discharged and may be

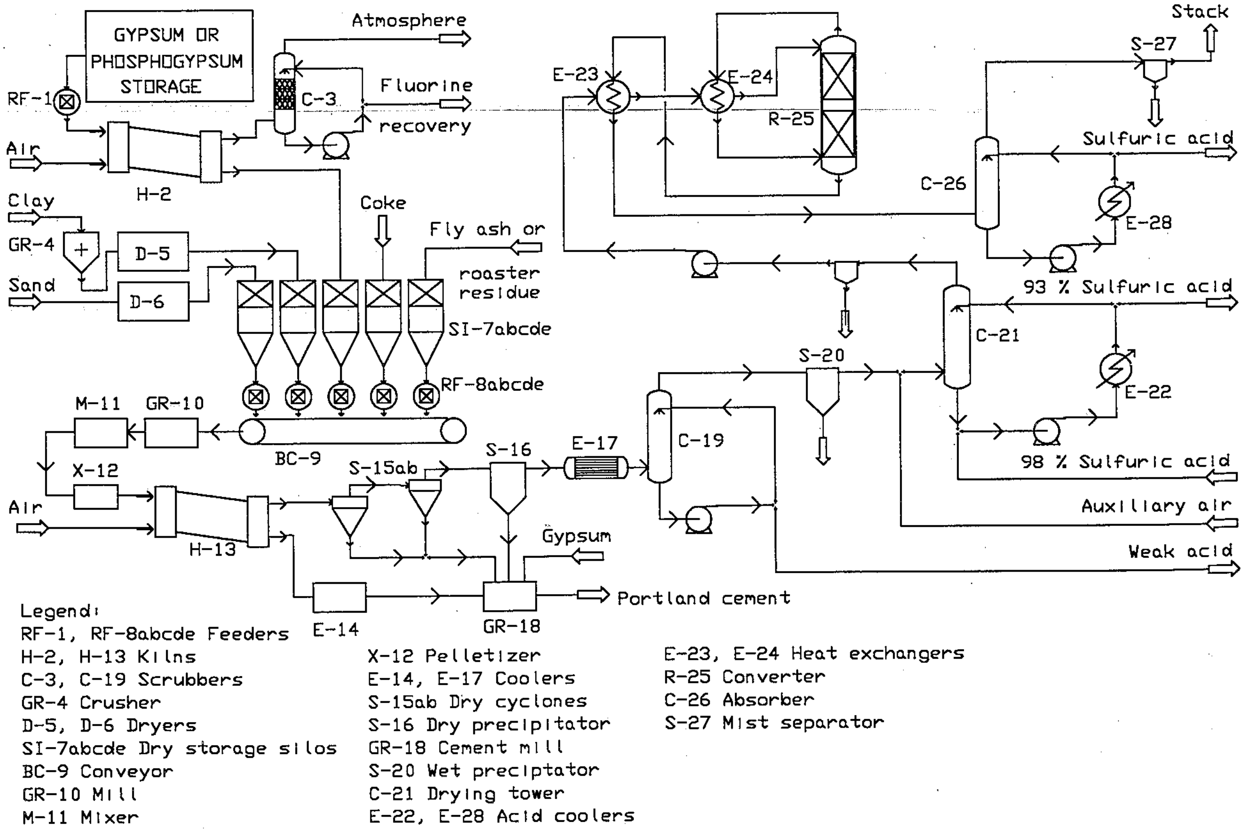


Figure 11.10. Sulfuric Acid Production From Gypsum [16].

recovered or disposed of. When anhydrite is used, the precalcination step is not necessary.

The charge to the rotary kiln consists of anhydrite (or calcined gypsum), coke, silica, and shale or other sources of iron and aluminum oxide. The charge must be proportioned precisely to give the required ratios of CaO, SiO_2, Al_2O_3, and Fe_2O_3 that are required for good quality cement.

The charge is mixed, ground, and pelletized to avoid dust losses. The kiln may be fired with coal, oil, or gas. The maximum temperature in the kiln is just short of fusion which may be approximately 1400°C. The cement clinker is discharged to a cooler and then finely ground and mixed with about 5% gypsum (a set retarder).

The sulfur is discharged as sulfur dioxide and emerges in the kiln exhaust gas, which also contains oxygen, nitrogen, carbon dioxide, water vapor, and a substantial amount of dust. The gas is cleaned and cooled in a system of cyclones, dry electrostatic precipitators, wet scrubbers, and wet electrostatic precipitators. Then air is added for oxidation of SO_2 to SO_3. At this point the SO_2 content of the gas is about 5.5%. The gas is dried, reheated to conversion temperature, and passed through the sulfuric acid plant which is similar to that described previously under "Sulfuric Acid from Pyrites." Because the SO_2 concentration in the inlet gas is lower, all equipment must be larger. The sulfuric acid is produced at the usual concentration of 96%-98% H_2SO_4 [14].

The overall reaction by which sulfur is volatilized from calcium sulfate is:

$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$$

The reaction is believed to proceed in two stages, First, part of the calcium sulfate reacts with the carbon (coke) to form calcium sulfide:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$

At somewhat higher temperatures the calcium sulfide reacts with the rest of the calcium sulfate:

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$$

At still higher temperatures, the CaO reacts with the other charge ingredients to form the desired compounds in portland cement, mainly tricalcium silicate, dicalcium silicate, tricalcium aluminate, and calcium ferrite.

The approximate consumption figures for the process are shown in Table 11.9 [15]. The process produces approximately equal quantities of cement and sulfuric acid. The largest kiln operating in 1968 at the Marchon plant, Whitehaven, England, had an annual capacity of 90,000 tonnes of sulfuric acid and the same quantity of cement [16]. The other plant, which used native anhydrite, had five kilns with a total production capacity of 400,000 tpy of sulfuric acid and cement. In the 1960s another large plant was in operation at Billingham, England, and a third in Wolfen, Germany, all based on anhydrite. A fourth plant located in Austria used natural gypsum or at times a mixture of natural gypsum and phosphogypsum, and a fifth in Poland was based generally on natural anhydrite with some admixture of phosphogypsum.

Table 11.9. Consumption Figures for Gypsum-Derived Sulfuric Acid

Inputs	Units	Value
Anhydrite ore	t/t	1.6-1.7
Gypsum[a]	t/t	2.0-2.2
Shale	t/t	0.29
Coke	t/t	0.10
Sand	t/t	0.06
Fuel for anhydrite	GJ/t	6.3
Fuel for gypsum	GJ/t	10.5
Cooling water	t/t	58
Electricity[b]	MWh	0.25
Labor	workhours	0.9

a. Does not include gypsum for addition to cement.
b. Includes 42 kWh for grinding cement clinker.

Capital cost: US $550 million for 1,000-tpd sulfuric acid plant.
Basis: West European location, 1976, battery limits [15].

At that time (1968) no plant was known to have used phosphogypsum exclusively for extended periods of operation although some plants had done so for short periods.

In commenting on the use of phosphogypsum in the cement-sulfuric acid process. Ashburner made the following points [16]:

a. The byproduct, phosphogypsum, usually contains 15%-25% free moisture in addition to about 21% combined water (dry basis). Thus, the weight ratio of water to $CaSO_4$ is between 0.38 and 0.58 (assuming no impurities). Removal of this water substantially increases the fuel requirement in comparison with anhydrite, which is quite dry as mined.

b. The P_2O_5 content of phosphogypsum should be quite low because P_2O_5 has a deleterious effect on the setting properties of cement. The upper limit is not precisely known, but a maximum level of 1% P_2O_5 in the cement has been set by one organization [15]. To attain this level the phosphogypsum should contain not more than about 0.5%. This level is difficult to reach in dihydrate plants but may be attained by recrystallization in dihydrate-hemihydrate or hemihydrate-dihydrate processes of phosphoric acid. Thorough washing to remove soluble P_2O_5 is necessary.

c. Fluorine is undesirable in the cement kiln charge since it lowers the melting point and may cause ring formation in the kiln. A specification of 0.15% F in the phosphogypsum is suggested [15]. Most of the fluorine may be removed by drying and calcining the phosphogypsum, which is necessary in any case to drive off the hydrated water. In addition, fluorine compounds in the kiln gases should be completely removed before they enter the sulfuric acid plant to prevent impairment of the effectiveness of the vanadium oxide catalyst.

d. Other impurities such as silica and aluminum compounds which are commonly present in phosphogypsum, are not objectionable, but they need to be considered in formulating the kiln charge, which must be controlled very precisely.

A grave objection to producing cement exclusively from phosphogypsum results from the radium content in phosphogypsum. For example, Central Florida phosphogypsum contains the equivalent of 25 - 30 picocuries/gram of radium Ra 226. Radium 226 disintegrates to produce radon gas, which has been related to lung cancer, and it is currently limited in building materials to 10 picocuries/gram in the United States. Since 2 tonnes of gypsum is required to produce one tonne of cement, the Ra 226 content in phosphogypsum would have to be less than 5 picocuries/gram [17]. The main advantage of sulfuric acid and cement from phosphogypsum is that the byproduct phosphogypsum is automatically available at a phosphoric acid plant at no cost, and also because the use of phosphogypsum solves a disposal problem.

The U.S. phosphate industry produces about 35 million tpy of phosphogypsum as the byproduct of wet-process phosphoric acid production. In Florida, which accounts for about 83% of U.S. phosphoric acid production, nearly all of this waste, roughly 800 million tonnes, accumulates in gypsum stacks. Six million tpy of sulfur is added to these stacks.

Furthermore, environmental regulations have made gypsum stacks increasingly expensive. IMC in the early 1990s paid US $7 million to prepare a new gypsum stack base, while Cargill Fertilizer, Inc., paid US $5.5 million to close a mature stack. The total cost for emplacement drainage, revegetation, and stack maintenance has been estimated at US $2-$4/tonne of phosphogypsum [18].

In countries where alternative sources of sulfuric acid are very expensive and fuel costs are low, the process might well be considered. In special cases there may be advantages favoring the use of phosphogypsum that are difficult to evaluate such as:

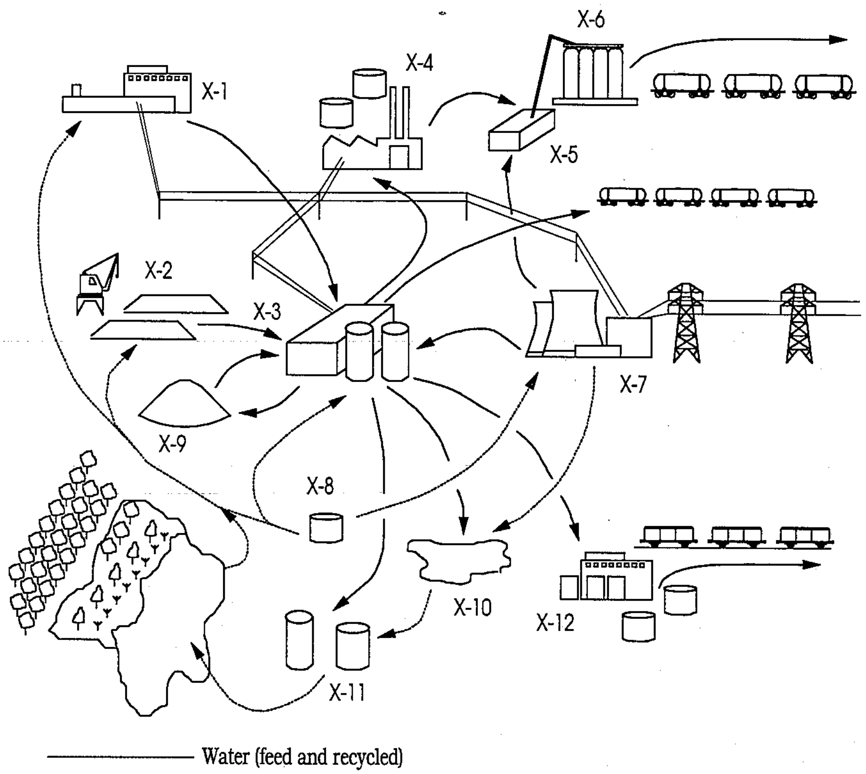
- Saving in foreign exchange.
- Independence from foreign sources.
- Stimulation of domestic employment.
- Lack of an environmentally acceptable alternative means for disposal of phosphogypsum.

The main disadvantages of the sulfuric acid cement process are the high capital cost and high energy (fuel) requirement. A comparison should be based on separate production of sulfuric acid and cement if both are needed. The fuel requirement for cement production from phosphogypsum is about 2.5 times that required for cement production from the usual raw materials (limestone, shale, etc.). Whereas production of sulfuric acid from sulfur produces a substantial amount of energy, usually in the form of byproduct steam, there is no export steam from the gypsum-based plant. No exact comparison of capital cost is available, but it is evident that the combination would be more expensive than separate plants since both the cement kiln and sulfuric acid plant would need to be larger and more complicated in the combined process than in separate production of cement from limestone and sulfuric acid from sulfur. Estimates of the total capital investment for the combined process range from a ratio of 5:1 to 10:1 when compared with sulfuric acid from sulfur.

The problem of using phosphogypsum as a raw material for combined sulfuric acid and cement production has drawn the attention of various companies. A cement/sulfuric installation was proposed in 1990/91 for the Pine Level Project at Consolidated Minerals, Inc. [17]. It was to be a part of the integrated complex comprising a 1.0 million tpy P_2O_5 phosphate fertilizer plant, a 2.35 million tpy portland cement plant, a 660-MW coal-fired power station, and a 4.5 million tpy preconcentrate phosphate mine, with 0.9 million tpy of sulfur equivalent recycled.

The idea of this project is shown in Figure 11.11. The integration is the key to the economic feasibility of such a cement-sulfuric acid type of sulfur recycle process. As shown in Table 11.10 [17], the integrated project saves considerable capital cost compared with the conventional approach of developing the capacities separately. The capital cost of the Pine Level Project was estimated primarily at about US $900 million. Hence the savings in capital costs alone amounted to 25%.

Science Ventures, Inc., has developed a new process for recovering the sulfur from phosphogypsum in the



X-1 Sulfuric plant
X-2 Phosphate mine
X-3 Phosphate processing plant
X-4 Sulfur recovery plant
X-5 Kilns
X-6 Cement plant
X-7 Power plant (600 MW export power)
X-8 Water well
X-9 Raw material storage
X-10 Slimes Pond
X-11 Sand-Clay mixing station
X-12 Solid fertilizer plant

Figure 11.11. Integrated Pine Level Industrial Complex.

Table 11.10. Cost-Effectiveness of Integrated Project

Area	Savings (US $ million)
Transport	120
Energy	20
Other infrastructure	160
Total	**300**

form of sulfuric acid; the process was named FLASC for Flash Sulphur Cycle. The process is carried out in a reactor resembling a flash copper smelter. Pulverized coal is premixed with calcined phosphogypsum and fluxing minerals and sprayed into a flame, where most of the desulfurization takes place. Excess fuel reduces the calcium sulfate to its oxide; thus, sulfur dioxide gas is released. The minerals fuse together and drain from the reactor as a molten slag. The slag is quickly quenched to form a hard glassy material, which resists leaching and radon emanation. Its hardness on the Mohs scale is 5.5

to 6, and it could be valuable as an aggregate for road construction [18].

There have been several attempts to recover sulfur from phosphogypsum by means of biochemical processes. Bacterial reduction to solid sulfur has generally been abandoned as being too slow. In India, where there are no known sulfur deposits, advances in biotechnology have revived interest in the possibilities of recovering sulfur from phosphogypsum by means of sulfate-reducing bacteria [19].

11.1.7 Sulfuric Acid Storage, Sea-Transport Prices

The terminals for maritime trading of sulfuric acid are located in practically all main ports throughout the world. They belong to various companies and their capacities vary notably from port to port.

The worldwide trading of sulfuric acid is dominated by three companies – Boliden Chemtrade, Interacid, and MG Chemical. In 1993 the Boliden group traded approximately 2.6 million tonnes of acid: of this about 1.4 million tonnes was seagoing. Boliden owns two terminals, in Tampa and in Rotterdam, each of which has a 40,000-tonne storage capacity.

Interacid traded about 2 million tonnes of acid in 1993. The company's terminal, operated by SATCO, in Tampa, has a storage capacity of 60,000 tonnes. The company plans to open another terminal having a 40,000-tonne storage capacity in northern Chile by late 1994.

In 1993 MG traded approximately 1.5 million tonnes of acid, some 60% of which was seagoing. Total storage capacity of the company in Europe is 150,000-200,000 tonnes with facilities at each of the company's production installations. From these sites the acid is taken by barge or rail either directly to the buyer or to a spot-chartered seagoing tanker.

Practically all sulfuric acid traders charter all or most of the vessels for seagoing transportation. These are tankers up to 35,000 tonnes. The shipping of sulfuric acid in bulk in ocean-going special bulk chemical carriers began in 1954. At present, a fleet of chemical tankers is available. The tanks are made of mild steel and lined with a plating of molybdenum-alloyed stainless steel or constructed entirely from this material. The freight rates and prices for sulfuric acid may vary significantly. In early March 1994, freight indications for sulfuric acid were: Helsingborg to S. Spain US $22-$23/tonne of cargo, 4,000-5,000 tonnes; Rotterdam to Venezuela US $30-$35/tonne of cargo, 7,000-7,500 tonnes. In September 1994 the prices of sulfuric acid were: ex-terminal Tampa (U.S.A.) US $25-$30/tonne, f.o.b. Mediterranean port US $30-$35/tonne, all calculated to 100% H_2SO_4.

11.1.8 Projections of Sulfuric Acid Production Trends and Technology Improvements

Forecasts made by McKinsey Co. in 1992 predict that the world production of sulfuric acid from all sources of sulfur will reach a level of 182.5 million tonnes (calculated to 100% H_2SO_4) in the year 2000. This is an increase of 15% over the production level of 1991.

The growth in sulfuric acid production in any country depends not on whether the country possesses natural sulfur deposits of any form but rather on how much it needs the acid for different industrial purposes. Of course, some increase in sulfuric acid capacity may result from waste sulfur dioxide recovery, promoted by more stringent environmental regulations affecting smelter operations, power plants, cokeries, and many other industrial activities. But most of all, growth will be dependent on the increase in wet-process phosphoric acid production. The most significant growth will occur in countries that implement programs of increased phosphate fertilizer production, based on phosphoric acid.

The regions where the production of sulfuric acid is to increase the fastest are: Middle East (Jordan, Iraq, Israel, Iran) from 4.0 million tonnes in 1991 to 9.6 million tonnes in 2000, increase 140%; North Africa (Morocco) from 15.0 million tonnes in 1991 to 21.1 million tonnes in 2000, increase 40%; Far East (China) from 29.1 million tonnes in 1991 to 36.9 million tonnes in 2000, increase 27%.

In North America the demand for sulfuric acid will remain at about the present level, and in Western Europe it is likely to decrease.

At present, the most common method used in sulfuric acid production is the double-absorption process based on oxidation of sulfur dioxide to sulfur trioxide on vanadium pentoxide catalyst. This process will remain the prevalent method of sulfuric acid production in the future. New sulfuric acid installations will be aimed mainly at increasing the output from production units, maximum heat recovery, and operational reliability of installation, particularly through precise selection of extra-resistant alloys and special noncorrosive materials. Further increases in SO_2 to SO_3 conversion efficiency would do little to improve emissions because the high efficiency of present processes already achieves very low SO_2 emissions.

Commercial development of sulfuric acid production based on utilization of phosphogypsum is not foreseen until sulfur from other sources is inaccessible. On the other hand, more and more sophisticated methods will be developed for use of sulfur dioxide contained in stack gases and from heat and power-generating plants for sulfur or sulfuric acid production.

Furthermore, it seems that the pressure method of sulfuric acid production, which appeared promising in the early 1970s, will not be successively developed, mainly due to the cost of compression energy and for construction reasons considering the large capacities of modern sulfuric acid installations.

11.1.9 Process Options

Practically all processes of sulfuric acid production presently in use are based on catalytic oxidation of sulfur dioxide to sulfur trioxide and subsequent absorption in recirculating sulfuric acid to form H_2SO_4. The process of oxidation is accomplished most commonly in multibed converters on vanadium pentoxide catalyst.

The principal difference in the various processes is the source of sulfur material that is processed in particular installations. From this point of view the installations for sulfuric acid production can be divided into four main groups.

1. Sulfur-burning installations

   At present all licensers offer very high rates of SO_2-conversion, up to 99.8%, and heat recovery as much as 90%. Production-scale capacities are usually between 1,000 tpd and 3,000 tpd. At the normal operating time of about 330 days per year this amounts to 330,000-990,000 tpy of sulfuric acid calculated as 100% H_2SO_4.

2. Installations processing outlet gases from iron sulfide roasting plants

   Dust-laden gases from a roasting plant may range from 5.5% to 12% SO_2 after cleaning, depending on the type of roaster and the process employed. The rate of SO_2-conversion may be as much as 98% or more. The installations' capacities differ according to the scale of the roasting operation, but installations up to 1,000 tpd are in use.

3. Installations based on gases from base metal sulfide smelter operations

   Installations vary from smelter to smelter depending on the technology used for the non-ferrous metal production.

4. Installations using waste hydrogen sulfide, based on wet-catalysis process

   This process can deal directly with gases containing at least 10% H_2S from cokeries and other operations. Gases with a lower H_2S-content have to be burned with additional heating (e.g., with fuel gas, oil, or sulfur). SO_2-conversion usually does not exceed 98%. Acid concentration is 78% and 93%, according to raw gas composition.

All licensers guarantee the lifetime of the catalyst for a minimum of 10 years and SO_3 absorption above 99.9% for sulfuric acid production from elemental sulfur. Concentrations of sulfuric acid produced may be, at the operator's discretion, in the range of 93%-98% of H_2SO_4. The surplus heat of reaction in sulfuric acid plants based on sulfur combustion is removed from the system in the form of high-pressure steam of 4.0-6.0 MPa pressure and a temperature of 400°-500°C.

In sulfuric acid plants based on roasting gases such a surplus of heat is not available since the total heat produced by the catalytic reaction is required to preheat the cold gases to the reaction temperature. Only at higher SO_2 concentrations, or if the HRS is installed, surplus heat can be available in the superheater or economizer to produce high-pressure steam in the boiler system. The heat available at a low temperature level in the absorbers, normally at an acid temperature of 70°-120°C, can be used for preconcentration of phosphoric acid, feed-water preheating, seawater desalination, or for integrated town heating systems.

Sulfuric acid processes are offered by the following engineering companies: Biprokwas, Chemetics, Haldor Topsoe, Hitachi Zosen, Hugo Petersen, Krebs, Lurgi, MHI, Monsanto Enviro Chem Systems, Monsanto Europe S.A., Nissan Engineering, Poseidon, Siry Chamon, Stratco, Tim J. Browder and others.

UNIDO would like to acknowledge receipt of information, which was useful in preparation of this chapter, from the following companies:

1. BIPROKWAS Engineering Ltd., 44-100 Gliwice, 11 Konsytucji Str., Poland.
2. LURGI Gesellschaft, D-6000 Frankfurt/Main, 17-19 Gervinusstrasse, Germany.
3. Monsanto Enviro-Chem, St. Louis, Missouri, 63178 U.S.A., and Monsanto Europe S.A., Avenue de Tervuren 270-272 B-1150, Brussels, Belgium, a wholly owned subsidiary of Monsanto Co.

11.2 Wet-Process Phosphoric Acid

11.2.1 Introduction

In the last three decades, phosphoric acid has become the most significant source of phosphate fertilizer production, and this trend is expected to continue worldwide in the foreseeable future. Growth is particularly expected in southeast Asian countries, which are implementing national programs to become self-supporting in the production of fertilizers.

World phosphoric acid production has stabilized in the past few years with, however, a slight decrease from 35.5 million tonnes P_2O_5 in 1990 to 33.6 million tonnes P_2O_5 in 1993. According to projections by the

International Fertilizer Industry Association (IFA), production of phosphoric acid will increase to 37.5 million tonnes P_2O_5 in 1999 and to 40.0 million tonnes P_2O_5 after 2000 [1].

The chief use of phosphoric acid is in the production of phosphate fertilizers, mainly ammonium phosphates (DAP and MAP). In 1993 the total world production of DAP and MAP amounted to 21 million tonnes P_2O_5, which represents 63% of phosphoric acid use. The above-mentioned forecast indicates that this pattern of phosphoric acid use will continue in the near future.

There are two basic types of processes for the production of phosphoric acid; furnace processes and wet processes. Furnace processes include the blast-furnace process and the electric-furnace process. The blast-furnace process has not been used commercially since 1938. The electric-furnace process is used extensively to make elemental phosphorus, most of which is converted to phosphoric acid for nonfertilizer uses. Since it is unlikely that furnace processes will be competitive for producing phosphoric acid for fertilizer use, except possibly in unusual circumstances, these processes will be described only briefly.

Wet processes may be classified according to the acid used to decompose phosphate rock. Sulfuric, nitric, and hydrochloric acid are used in commercial processes. Processes using nitric acid will be described under "Nitrophosphates" (Chapter 13). Processes using hydrochloric acid are not competitive for fertilizer purposes, except under unusual conditions, and will be described briefly in this chapter. Processes using sulfuric acid are by far the most common means of producing phosphoric acid for fertilizer use (and sometimes for other uses); therefore, these processes will be described in more detail. However, the scope of this manual precludes extensive detail of even the most important processes. For more detail, readers should consult *Phosphoric Acid*, edited by A. V. Slack [2], and other references listed at the end of this chapter.

11.2.2 Chemistry of the Wet Process

The main chemical reaction in the wet (sulfuric acid) process may be represented by the following equation using pure fluorapatite to represent phosphate rock:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4 \bullet nH_2O + 6H_3PO_4 + 2HF$$

where n = 0, 1/2, or 2, depending on the hydrate form in which the calcium sulfate crystallizes.

The reaction represents the net result of two stages. In the first stage, phosphoric acid reacts with the apatite forming monocalcium phosphate; in the second stage monocalcium phosphate reacts with sulfuric acid to form phosphoric acid and calcium sulfate. These two stages do not necessarily require two reaction vessels; they usually take place simultaneously in a single reactor.

As mentioned in Chapter 5, phosphate rock contains many impurities both in the apatite itself and in accessory minerals. These impurities participate in numerous side reactions. Most phosphate rocks have a higher $CaO:P_2O_5$ ratio than pure fluorapatite. The additional CaO consumes more sulfuric acid and forms more calcium sulfate. The HF formed by the reaction reacts with silica and other impurities (Na, K, Mg, and Al) to form fluosilicates and other more complex compounds. A variable amount of the fluorine is volatilized as SiF_4, HF, or both. The amount volatilized and the form depend on phosphate rock composition and process conditions.

As a result of side reactions, numerous impurity compounds (some of them very complex) are formed. For a complete discussion of the nature of impurities, see *Phosphoric Acid* by A. V. Slack [2].

11.2.3 Heat Released in Reaction

The reaction involved in producing phosphoric acid from fluorapatite and sulfuric acid by the dihydrate process may be represented by the following equation:

$$Ca_{10}F_2(PO_4)_6\ (s) + 10H_2SO_4\ (liq) + 20H_2O\ (liq) \rightarrow 10CaSO_4 \bullet 2H_2O\ (s) + 2HF\ (aq) + 6H_3PO_4\ (aq)$$

The heat of reaction may be calculated by using the heats of formation of reactants and products (Table 11.11) [3,4,5]. The heat of reaction so calculated is 256.94 kcal/g-mole of apatite which is equivalent to 255 kcal/kg of apatite or about 600 kcal/kg of P_2O_5. The heat required to raise the temperature of the gypsum ($C_p = 0.272$) and phosphoric acid (30% P_2O_5; $C_p = 0.703$) from 25° to 82°C is calculated to be 197 kcal/kg of P_2O_5 [6,7]. Thus, about 403 kcal/kg of P_2O_5 remains to be dissipated, and most processes provide a means of removing the excess heat. In practice, some of the heat is lost by convection and conduction. On the

Table 11.11. Heat of Formation (HF) of the Reaction Components

Compound	HF at 25°C (kcal/gmol)	References
$Ca_{10}F_2(PO_4)_6$ (s)	3,267.2	Farr and Elmore [3]
H_2SO_4 (l)	193.91	NBS [4]
$CaSO_4 \times 2H_2O$ (s)	483.06	NBS [4]
H_3PO_4 (a) 30% P_2O_5	308.25	Egan and Luff [5]
HF (aq)	75.56	NBS [4]
H_2O (l)	68.317	NBS [4]

other hand, some heat may be introduced by use of heated wash water, or if the wash water is not heated, some of the heat in the gypsum is transferred to the recycled weak acid and thus returned to the reaction. Additional heat will be generated by reaction of additional sulfuric acid with impurities in the rock. Most phosphate rock contains 10% - 20% more calcium than that required to form pure fluorapatite with the phosphorus in the rock, which may result from substitution of carbonate for phosphate in the apatite or presence of calcite or both. Reaction of this amount of calcium with sulfuric acid to form gypsum would increase the net heat of reaction per kilogram of P_2O_5 by about 11% -16%.

Hydrogen fluoride is shown as a product of reaction in the first equation. It reacts with the silica present as an impurity in phosphate rock to form fluosilicic acid which, in turn, forms fluosilicates and other compounds with impurities in the rock. The thermal effect of these reactions is negligible.

The net heat of reaction is influenced appreciably by the concentration of the sulfuric acid used as indicated in Table 11.12. If the conditions are such that the calcium sulfate crystallizes in the form of anhydrite or hemihydrate rather than gypsum, the excess heat to be dissipated is about 100 kcal/kg of P_2O_5 less than the values given above.

Table 11.12. The Net Heat of Reaction as a Function of Sulfuric Acid Concentration

Concentration of Sulfuric Acid (% H_2SO_4)	Net Heat of Reaction (kcal/gmol of apatite)	Excess Heat to be Dissipated (kcal/kg P_2O_5)
100	256.94	403
98	247.54	385
93	224.54	329
90	211.54	299
85	191.94	253
80	174.24	211
75	160.74	180

11.2.4 Types of Wet Processes

Commercial wet processes may be classified according to the hydrate form in which the calcium sulfate crystallizes:

Anhydrite – $CaSO_4$
Hemihydrate – $CaSO_4 \cdot \frac{1}{2}H_2O$
Dihydrate – $CaSO_4 \cdot 2H_2O$

Before starting to describe particular industrial processes, it should be noted that each process is based on information supplied by a different engineering and construction organization. Each of the organizations offers a range of processes to meet various client needs. In addition, several other companies, not mentioned, offer phosphoric acid processes, and there is no intention of implying that processes offered by the companies mentioned by name are necessarily superior to those offered by other companies and does not imply any kind of endorsement by UNIDO or IFDC.

The hydrate form is controlled mainly by temperature and acid concentration, as shown in Figure 11.12. This graph presents only approximation of production features because sulfuric acid concentration and impurities also have an influence.

At present there is no commercial use of the anhydrite process, mainly because the required reaction temperature is high enough to cause severe corrosion difficulties. Processes in commercial use are given in Table 11.13. From the very beginning, straight dihydrate processes are by far the most popular worldwide because they are relatively simple and adaptable to a wide range of grades and types of phosphate rock; hence they will be described in the most detail.

Hemihydrate processes have the significant advantage of producing phosphoric acid with a relatively high concentration without using any concentration step. There is also some interest in two-stage processes that involve crystallization in the hemihydrate form followed by recrystallization in the dihydrate form (or vice versa), with

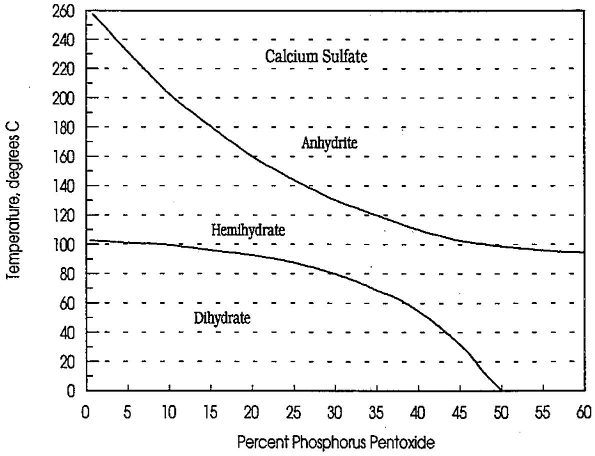


Figure 11.12. Dependence of Calcium Sulfate Crystallization on Temperature and P_2O_5 Concentration.

Table 11.13. Types of Commercial Processes

Crystal form(s)	Separation Steps[a]	Concentration of Acid, % P_2O_5	Reactor Temperature, °C	Recrystallizer Temperature, °C
Dihydrate	1	26-32	70-85	–
Hemihydrate	1	40-50	85-100	–
Hemihydrate-dihydrate	1	26-30	90-100	50-60
Hemihydrate-dihydrate	2	40-50	90-100	50-65
Dihydrate-hemihydrate	2	35-38	65-70	90-100

a. Filtration or centrifuging steps.

or without intermediate separation by filtration or centrifuging.

11.2.5 Description of the Dihydrate Process

The description of phosphoric acid production will be divided into the following steps:

1. Selecting phosphate rock.
2. Selecting source of sulfuric acid.
3. Receiving and storing raw materials.
4. Grinding and otherwise preparing the rock.
5. Reacting the phosphate rock and sulfuric acid.
6. Filtering to separate phosphoric acid from gypsum.
7. Concentrating and clarifying the phosphoric acid.
8. Sludge treatment.

Selection of Phosphate Rock – Many phosphoric acid plants are built in countries where phosphate rock must be imported. The plant is often designed on the basis of a single phosphate rock; however, it is often prudent to build into the plant sufficient flexibility to permit the use of rocks from different sources. This versatility will enable the producer to take advantage of competitive situations and to avoid disruption of supply when the intended source is inadequate or interrupted by hostilities, disasters, or other circumstances.

Many plants find it advantageous to use a blend of rocks from different sources. The extra expense of making the plant more versatile usually can be repaid many times over by savings resulting from freedom of choice in the world market. Some examples of steps to increase the versatility of the plant are:

1. Extra grinding capacity for harder rock.
2. Extra filtration capacity to provide for rocks that cause less rapid filtration or have lower P_2O_5 content.
3. Slurry handling systems that will cope with acid-insoluble impurities in the rock.
4. More corrosion-resistant construction for rocks that have corrosive impurities.

When the plant is built at or near the mine, there is still the likelihood that the rock composition will vary. In addition, there are other questions to be considered relating to the economic optimum balance between cost of extra beneficiation as compared with the cost of using lower grade rock [8].

The selection of phosphate rock source is sometimes viewed as a simple matter of obtaining a given amount of P_2O_5 in the rock delivered to the plant at the lowest price. However, phosphate rock is a complex raw material that affects plant operation in numerous ways, some of which may be unpredictable. Therefore, a thorough evaluation of all quality factors should be made before selecting a phosphate rock or changing from one source to another [9].

A complete chemical and mineralogical analysis of a phosphate rock is helpful in evaluating its usefulness for making phosphoric acid. However, this information is not sufficient in itself; trial runs in a plant or pilot plant are needed for a reliable evaluation unless the rock is one that has been used extensively in other similar plants with known results [10].

The following quality factors may provide a general guide for selecting phosphate rock for phosphoric acid production. The economic effect of many of the factors can be evaluated quantitatively to arrive at a comparative value of alternative sources of phosphate rock.

Starting with a standard grade of rock, the more common quality factors for wet-process phosphoric acid production and their effect are:

1. Lower grade (% P_2O_5) means that more tonnage must be purchased, transported, handled, and (usually) ground.

2. An increase in the $CaO:P_2O_5$ weight ratio increases the sulfuric acid requirement. (Any CaO present as $CaSO_4$ should be excluded in calculating this ratio.)

3. Magnesium oxide forms precipitates with fluorine in the reactor, which may blind the filter cloth; therefore, high MgO content is considered undesirable. When phosphoric acid is used to produce ammonium phosphates or polyphosphates, water-insoluble (but citrate-soluble) magnesium ammonium phosphate compounds may be formed. These compounds form troublesome impurities in liquid fertilizers.

4. Increases in the $Fe_2O_3 + Al_2O_3$ content above 2%-3% decrease the plant capacity, often decrease the P_2O_5 recovery, and cause post-precipitation problems (sludge). However, up to about 5% may be tolerable. From the other side Al_2O_3 and MgO are a bonus in some way because they reduce the corrosivity of the acid by forming complex ions with free fluorine ions.

5. It is desirable to have enough reactive silica (SiO_2) to form SiF_4 and/or fluosilicates to avoid formation of free HF, which is very corrosive. Excessive silica or other acid-insoluble impurities may cause erosion of equipment and possible accumulations in digestion vessels, depending on particle size, character, and plant design. In addition, a high percentage of silica in the rock would increase the required filter area.

6. Chlorine contents above about 0.03% cause increased corrosion of stainless steel especially in the case of the high-strength, high-temperature processes. More expensive alloys may tolerate Cl contents of 0.10% or perhaps higher.

7. High organic matter may increase foaming problems (by stabilizing the foam), increase viscosity, and hinder filtration. The effect depends on both the character and quantity of organic matter. Some rocks must be calcined to remove organic matter to make them usable.

8. Carbon dioxide (CO_2) contributes to foaming and increases consumption of antifoam reagents.

9. All commercial phosphate rocks contain fluorine (F); no special effect has been noted due to variations in fluorine content within the range of experience. Effects of fluorine on scaling, corrosion, and post-precipitation are related to other elements that combine with fluorine, including Na, K, Al, Mg, and Si.

10. Upon acidulation, some rocks that contain sulfides release hydrogen sulfide (H_2S), a toxic gas. These sulfides tend to increase corrosion.

11. Strontium and lanthanides (rare earths), found in igneous rocks, inhibit rehydration of the hemihydrate to gypsum, which can cause problems in certain phosphoric acid processes. Moreover strontium causes problems in the concentration sections because strontium sulfate has a minimum solubility in 40% P_2O_5 acid. An extremely thin film of $SrSO_4$ causes a very pronounced reduction in the capacity of the concentration unit.

12. High contents of toxic impurities in phosphate rock used (for example, cadmium compounds) may render the resulting phosphoric acid unsuitable for fertilizer production.

13. Hardness is a factor since harder rocks require more grinding capacity.

14. The particle size of the rock as-received affects the amount of crushing and grinding required. Very fine particle size may lead to dust losses in handling.

15. Low reactivity of the rock may require finer grinding.

16. Filterability of the rock-acid slurry is one of the most important characteristics of a phosphate rock for use in phosphoric acid production. Factors influencing filterability are complex and not completely understood. However, if a plant is to be designed to use a specific rock, an acceptable filtration rate can usually be attained through experimental means by adjusting operating conditions, addition of crystal modifiers, or pretreatment of the rock.

Table 11.14 gives the range of composition and median values of a group of 15 phosphate rocks from

Table 11.14. Typical Analysis of Commercial Phosphate Rocks

Constituent	Range of Content, %	Average Content, %
P_2O_5	29-38	33
CaO	46-54	51.02
SiO_2	0.2-8.7	2.0
$Al_2O_3 + Fe_2O_3$	0.4-3.4	1.4
MgO	0.1-0.8	0.2
Na_2O	0.1-0.8	0.5
CO_2	0.2-7.5	4.5
F	2.2-4.0	3.7
Cl	0.0-0.5	<0.02
SO_3	0.0-2.9	1.0
$CaO:P_2O_5$ ratio	1.35-1.70	1.5

commercial sources. Although the group is representative, compositions outside this range have also been used. Assuming 94% overall P_2O_5 recovery, the amount of phosphate rock required per tonne of P_2O_5 recovered as phosphoric acid is given in Table 11.15.

Calculation of Sulfuric Acid Requirement – Although the sulfuric acid requirement for the production of phosphoric acid from any given rock is best obtained experimentally, it is sometimes necessary to calculate it from the chemical analysis of the rock. For a first approximation the sulfuric acid requirement may be equated to that required to combine with the calcium in the rock to form calcium sulfate. This calculated value is often close enough for planning purposes. The requirement per tonne of P_2O_5 recovered should be adjusted according to the expected recovery. The overall recovery is seldom more than 94% if mechanical and sludge losses are included.

Table 11.15. Phosphate Rock Consumption as Function of Phosphate Rock Quality

Grade of Rock	P_2O_5 Content (%)	Rock Consumption (t/t of P_2O_5 in Acid)
Low	29	3.67
Median	33	3.22
High	38	2.80

If a complete analysis of the rock is available, a more exact calculation may be made. The method is illustrated in Table 11.16 and is explained below:

1. Assuming 94% overall P_2O_5 recovery, 1,064 kg of rock P_2O_5 is required per tonne of P_2O_5 recovered.
2. If the rock contains 33% P_2O_5, 3,224 kg of rock is required.
3. The CaO content of the rock is calculated. If the rock contains any other cation that forms an insoluble sulfate (such as barium), its CaO equivalent should be added.
4. The CaO equivalent of the SO_3 content (not total S) should be considered.
5. Typical filter cake contains about 3.3% of the input P_2O_5 in insoluble forms of which 1% may be unreacted rock and 2.3% $CaHPO_4$ cocrystallized with gypsum. The aggregate weight ratio of CaO combined with P_2O_5 is about 1.0.
6. The empirical assumption is that 15% of the fluorine combines with CaO to form CaF_2. Actual reactions are much more complex; $Ca_4SO_4SiF_6AlF_6(OH)\bullet 12H_2O$ is an example of a complex insoluble compound found in filter cake.
7. Items 4, 5, and 6 are totaled.
8. Item 7 is subtracted from 3 to give the net amount of CaO for reaction with H_2SO_4.

Table 11.16. Calculation of H_2SO_4 Required Per Tonne of P_2O_5 Recovered as Phosphoric Acid Using Median Rock Analysis

Step	kg/tonne of P_2O_5 Recovered
1. P_2O_5 required in rock at 94% recovery: 1,000/0.94	1,064
2. Kg of rock required per tonne of P_2O_5 recovered: 1,064/0.33	3,224
3. CaO in rock: 3,224 x 0.51	1,644
4. CaO equivalent to SO_3: 3,224 x 0.01 x 56/80	22.6
5. CaO combined with P_2O_5 in filter cake: 0.033 x 1,064	35.1
6. CaO combined with fluorine: 0.15 x 0.037 x 3,224 x 56/19 x 2	26.4
7. Total CaO not combined with sulfate	84.1
8. Net CaO for reaction with H_2SO_4: 1,644 - 84.1	1,559.9
9. H_2SO_4 required for $CaSO_4$: 1,559.9 x 98/56	2,729.8
10. Excess H_2SO_4: 1.5/30 x 1,000	50.0
11. Total H_2SO_4 required	2,779.8
12. H_2SO_4 required based on total CaO only: 1,644 x 98/56	2,877

9. The H_2SO_4 equivalent of the CaO is calculated.
10. The amount of excess H_2SO_4 is calculated by assuming that the 30% P_2O_5 acid contains 1.5% free H_2SO_4.
11. Total H_2SO_4 requirement is item 9 plus item 10.
12. For comparison, step 12 of Table 11.16 shows the H_2SO_4 requirement based simply on total CaO.

In Table 11.17 the sulfuric acid requirement for median-grade rock is taken from Table 11.16 (2.78 tonnes of H_2SO_4 per tonne of P_2O_5), and requirements for rocks of other Ca:P_2O_5 ratios are estimated in proportion to that ratio.

Table 11.17. Consumption of H_2SO_4 for Different Rock Grades

Grade of Rock	High	Median	Low
P_2O_5 content, %	38	33	29
Rock required, tonne/tonne of P_2O_5	2.8	3.2	3.6
CaO:P_2O_5 ratio	1.35	1.5	1.70
H_2SO_4 tonne/tonne of P_2O_5	2.50	2.78	3.15

Source of Sulfuric Acid – Although sulfuric acid production is discussed in section 11.1, some aspects of the source of the acid will affect plants for phosphoric acid production. Most, but not all, phosphoric acid plants have onsite facilities for producing sulfuric acid from sulfur or pyrites. In this case, heat is recovered from the sulfuric acid plants in the form of steam, which is available for concentrating phosphoric acid and other uses.

Finally, sulfuric acid from pyrites, smelter operations, or other byproduct sources may contain impurities that may or may not be deleterious for phosphoric acid production. In at least one case, zinc in smelter acid proved useful since the fertilizer produced from phosphoric acid contained enough zinc, mainly derived from the smelter acid, to improve crop yields in zinc-deficient areas. The same benefit applies to another micronutrient, copper.

Receiving and Storing Raw Materials – An efficient system for bulk handling and storing phosphate rock and other raw materials is necessary for a modern phosphoric acid plant. Other raw materials are discussed elsewhere. The criteria to be met are:

a. Rapid unloading of ships or other delivery units;
b. Negligible loss of rock;
c. Easy storage with the ability of separating shipments or blending shipments as desired;
d. Efficient retrieval from storage;
e. Protection against wind, rain, snow and freezing weather;
f. Protection from contamination with other raw materials, windblown dust, soil, etc.; and
g. Provision for expansion if future needs warrant.

When phosphate rock is received dry, it is usually desirable to keep it dry by covered storage, especially if it is to be used in a dry grinding system to avoid the expense of redrying. If open storage is used, wind or heavy rains can cause losses of rock that may amount to several percent if it contains much fines. However, relatively coarse rock can be stored in open piles, particularly if it is to be wet ground. The storage capacity should be at least 1½ times the largest shipment to allow for delays. Even larger storage capacity may be advantageous for blending shipments.

Rock Grinding and Preparation – The choices in rock grinding seem to be dry grinding, wet grinding, or no grinding. Several processes claim the ability to use rock without grinding if it is finer than 35-mesh or in some cases 20-mesh (Tyler) screen size (approximately equivalent to the standard 425 and 850 mm sizes listed in Chapter 18). Somerville suggests that such coarse rock is suitable for single-tank digester processes when sulfate control is good, but finer grinding is needed for multicompartment digesters and when sulfate control is poor [11]. Houghtaling states that older Prayon-type plants (which use multicompartment digesters) required grinding to 60% minus 200-mesh (0.074 mm). Newer plants of the same type specify only 25% minus 200-mesh, 60% minus 100-mesh, and all minus 35-mesh (Tyler) [12].

Most of the older plants and some of the new ones use dry grinding. Ring roller mills or ball mills are often used with air classification. The power requirement naturally depends on the initial size of the rock, its hardness, and the desired particle size. For grinding Florida rock to 55% minus 200-mesh, a requirement of 15-20 kWh/t of rock has been suggested, including air classification and pneumatic conveying to ground rock storage. Softer rocks may require one-half to two-thirds as much power.

There is a general tendency toward wet grinding in newer plants that are located near the mine. The wet grinding is done in a ball mill; a slurry containing 62%-70% solids is produced and fed to the digester via a surge tank. Advantages of wet grinding are 30%-40% reduction in power requirement and elimination of dust losses, atmospheric pollution by dust, and the necessity of drying the rock. The main disadvantages are somewhat faster wear of the balls and mill lining and a decrease in the amount of recycled wastewater that may be used in phosphoric acid production and which may contain some ions of value.

It is also necessary to maintain reasonably close control of the water: solids ratio in grinding. The power requirement for wet grinding 163 tph of Florida rock to minus 35-mesh was given by Shearon as 1,865 kW for closed-circuit grinding and 2,835-2,984 kW for open-circuit grinding [13]. The corresponding energy consumption is 11.4 kWh/t and about 18 kWh/t for closed- and open-circuit wet grinding, respectively.

There is some difference of opinion about the need for fine grinding of very unreactive rocks such as igneous apatite. Lutz and Pratt [14] suggest that such rock should be ground to 80% minus 200-mesh; whereas, Somerville considers that rock reactivity is not a major factor. According to Somerville, unground Meramec (Missouri) apatite (minus 150-mesh) is satisfactory. The explanation of this difference of opinion probably lies in the type of digester used [11].

Calcining of phosphate rock usually is considered part of beneficiation. However, some phosphoric acid producers who purchase rock also calcine it to eliminate organic matter or to decrease carbonate content or both. One purpose in calcining is to improve the color of products such as liquid fertilizer or nonfertilizer products such as sodium tripolyphosphate. However, Stern stated that one phosphoric acid plant was able to increase production by 30%-40% by changing from uncalcined to calcined rock [15]. A saving in foam-control reagents is another advantage.

Reaction System – There are so many types of reaction systems in use throughout the world that no attempt will be made to identify all of them. The objective in designing the reaction system is to carry out the reaction between phosphate rock and sulfuric acid so as to recover a maximum percentage of the P_2O_5 from the rock as product phosphoric acid in the simplest and least expensive manner. Since the filtration step is the most critical and expensive step in the process, a primary objective in the reaction step is to form gypsum crystals of such size and shape that the filtration and washing can be carried out rapidly and efficiently.

Maximizing recovery means minimizing losses. Three types of P_2O_5 losses are recognized: (1) unreacted phosphate rock, (2) P_2O_5 cocrystallized with gypsum through isomorphic substitution of HPO_4^- for SO_4^-, and (3) phosphoric acid lost in the gypsum due to incomplete washing. Perhaps a fourth source of loss should be mentioned – mechanical losses due to spillage, leakage, washing of filter cloth, piping, and equipment for scale removal, and losses as sludge.

The purpose of the reaction step is not only to extract the phosphate from the rock but also to ensure slow growth of gypsum crystals to a relatively large size. To attain this goal, reaction systems are designed to prevent direct contact between the two reactants, phosphate rock, and sulfuric acid. A high concentration of free sulfuric acid would result in coating the phosphate rock with calcium sulfate reaction product, thus blocking further reaction.

A serious case of "reaction blocking" in a phosphoric acid plant can take several hours or even days to correct. On the other hand, a high concentration of calcium ions (low sulfate) in the slurry will increase the amount of phosphate cocrystallized with the gypsum. Hence, the aim of designers and operators of reaction systems is to maintain a uniform composition of the slurry, avoiding pockets of high sulfate or calcium concentration. The liquid phase usually consists of phosphoric acid (about 30% P_2O_5) with about 1.5% free sulfuric acid; the optimum concentration of free sulfuric acid varies with rock composition. The solid phase is mainly gypsum. The proportion of solids in the slurry is about 35%-45%. Phosphate rock particles introduced into this slurry dissolve rapidly in the phosphoric acid in the liquid phase, which causes supersaturation with calcium sulfate and results in the growth of gypsum crystals.

To approach this ideal situation, the incoming streams of sulfuric acid and phosphate rock are mixed with the slurry (directly or indirectly) as rapidly and completely as possible, and the slurry in the reaction system is agitated to ensure homogeneity.

The phosphate rock may also be premixed with recycled weak phosphoric acid or with recycled reaction slurry. Sulfuric acid may be sprayed on to the surface of the slurry in the reactor vessel.

In many older plants, the sulfuric acid was diluted, sometimes to 55% - 60% H_2SO_4 and cooled in a heat exchanger before use. Most modern plants use the sulfuric acid at the concentration at which it is received, usually 96% H_2SO_4.

When strong sulfuric acid is premixed with weak recycled phosphoric acid, much heat is released, and this is accompanied by evaporation of water and volatilization of fluorine compounds (mainly SiF_4 and HF). In some plants this step is carried out in a flash vacuum cooler; a rich stream of fluorine compounds is provided in the vapor, which can be recovered as fluosilicic acid for sale or further processing.

The various dihydrate processes differ essentially in the reaction step. The reactor design generally falls into one of two categories, multicompartment reactors or single-tank reactors. Processes using more than one tank or compartment include the Prayon Mark IV dihydrate process, which led to the development of the Prayon pH range of hemihydrate processes and the Norsk Hydro dihydrate processes, from which the Norsk Hydro HH and HDH processes were developed. In the Prayon Mark IV dihydrate process, phosphoric acid is produced at a concentration of about 28% P_2O_5. The reactants are fed to the multicompartment attack tank (Figure 11.13), which is constructed of concrete and lined with rubber and carbon brick. Specially designed openings are provided in the attack tank inner walls so that the reaction slurry can flow from one compartment to the next. Each compartment is provided with a single agitator of special design to fulfil the functions of mixing, solids suspension, and foam breaking.

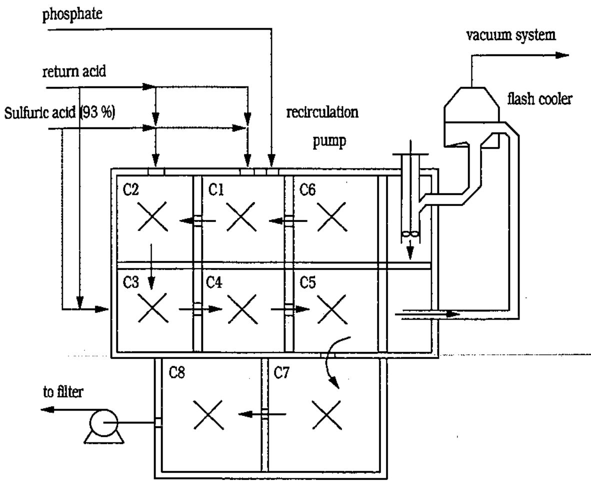


Figure 11.13. Reaction Section in the Prayon Mark IV Process.

The attack tank is cooled by circulating the slurry through a low-level flash cooler, in which the reaction slurry is cooled by evaporation of water under vacuum. Circulating power requirements are kept to a minimum by using an axial-flow circulation pump and by the low elevation of the flash cooler above the attack tank. The temperature in the attack tank is controlled by varying the vacuum applied to the flash cooler.

Slurry from the tank overflows to the digestion system, where the calcium sulfate crystallizes. The digestion section can be a single tank, depending on plant capacity. For larger plants it will comprise two or three digestion tanks of rubber-lined carbon steel; each is equipped with a single agitator.

Among processes using a single-tank reactor, some processes are the conventional type and others the so-called "isothermal" type. These first include Rhone-Poulenc's conventional dihydrate system containing a single, noncompartmental tank with a central agitator.

The reaction tank (Figure 11.14) is constructed of rubber-coated steel or concrete and is lined with carbon bricks. Baffles are fitted onto the walls to prevent the slurry from rotating bodily as a single mass inside the tank. The cover of the reactor is constructed of polyester or ebonite-coated panels. The phosphate rock is fed by a special duct within a cylindrical shroud at one or two points, according to the size of the tank, and into the turbulence zone of the central agitator on the opposite side to the gas extraction hood. The sulfuric acid is introduced into one, or several, independent discs fixed to the drive shafts of some of the surface coolers. The proprietary equipment distributes the acid so evenly over the entire surface of the tank that 98% acid can be introduced directly without prior dilution. There is no risk of local sulfuric acid concentration excess or temperature peaks, which can adversely affect the crystallization.

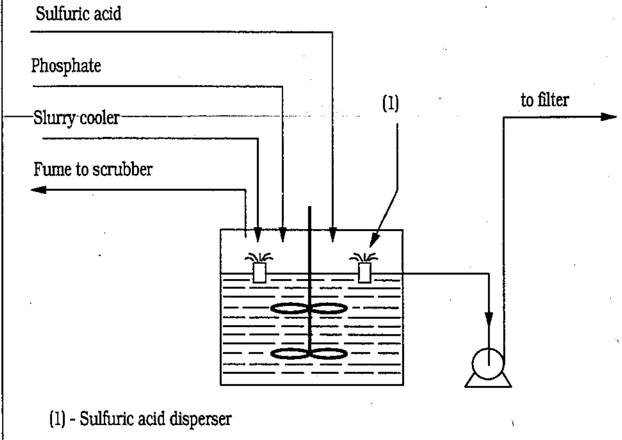


Figure 11.14. Rhone Poulenc Phosphoric Acid Reaction System.

Temperature control is provided by a flow of air over the surface of the slurry in the reactor. The tank cover, positioned between 1 and 1.2 m above the slurry level, is perforated to allow the entry of atmospheric air across about one-half the diameter of the tank and is fitted with a gas outlet hood on the opposite side of the tank. A fan provides the circulation of air. Rhone-Poulenc's DIPLO process [16] is a variation of the single-tank process (Figure 11.15). It is based on the same principles

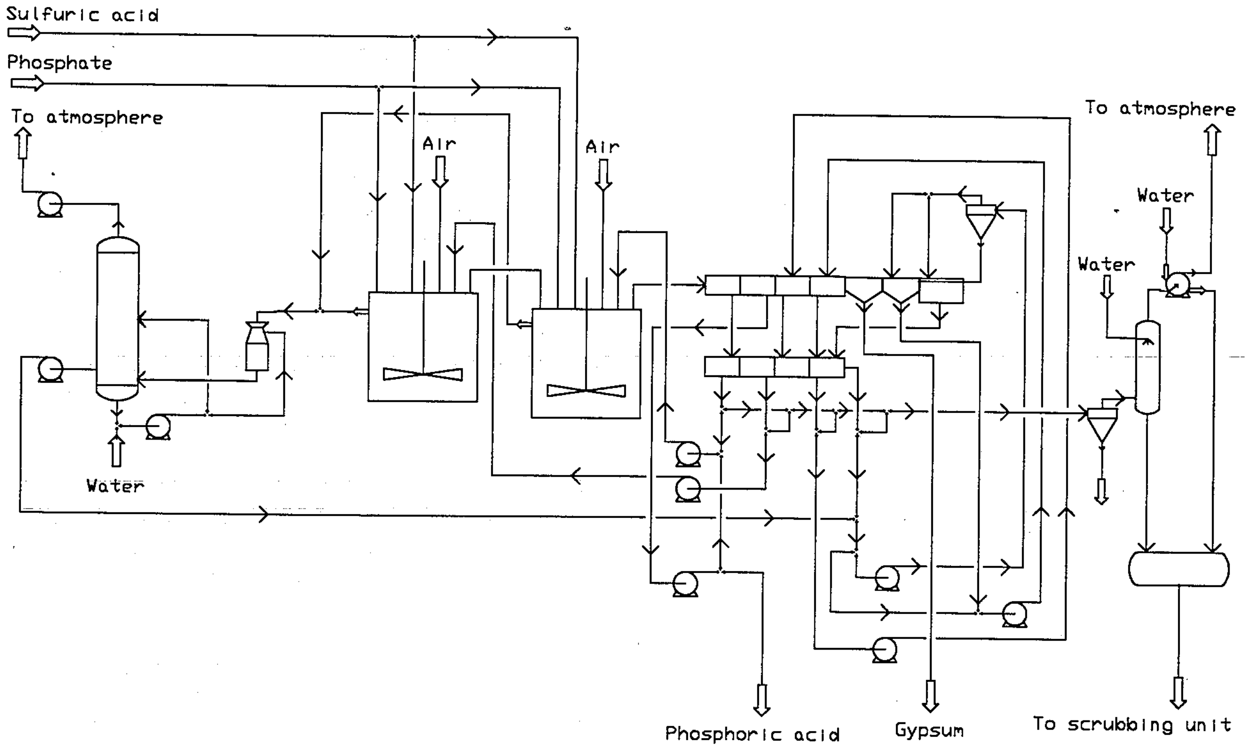


Figure 11.15. The Rhone-Poulenc Speichim DIPLO Phosphoric Acid Process.

as the single-tank process but differs in that two attack tanks are employed in series with no recirculation between them. The process has been developed to handle low-grade, less-reactive, or unground phosphates. The two processes (single-tank and DIPLO) developed by Rhone-Poulenc were acquired by Speichim, which offers them as Speichim - Rhone-Poulenc processes.

Similar in some respects to the above-described Rhone-Poulenc system is the process developed by Société Industrielle d'Acide Phosphorique et d'Engrais (SIAPE, Tunisia), which also features a single tank in the reaction section although its construction is somewhat different. The reaction system comprises a cylindrical tank divided into a central compartment, (into which the phosphate rock, sulfuric acid, and returned acid are fed), and an outer ring-shaped compartment. The tank is usually constructed of concrete and is coated on the bottom and sides with rubber, which is then covered with carbon bricks.

The process was specially developed to use the low-grade Gafsa rock, which has a relatively high carbonate content. The carbon dioxide released in the attack section promotes slurry circulation. Because of the high gas concentration, a slurry low-density zone is created. By having one opening at the bottom, a natural draft is set up, which moves the slurry out in a continuous flow. This circulation is further enhanced by an axial-radial double-impeller agitator working as a pump.

Since the quality of indigenous rock has continued to decrease, SIAPE has modified its process by adding a digestion tank with two agitators (Figure 11.16). Slurry at 78°-80°C is fed from the outer section of the reactor to the digestion tank, where it is cooled to 72°-73°C before being returned to the central compartment of the reactor. This arrangement allows a temperature gradient to be maintained between the recycle slurry and the slurry in the attack tank, which is necessary for good crystal growth [17,18].

Another type of single-reactor system is Jacob's dihydrate phosphoric acid process comprising an annular reactor with separate cooler seal and filter feed compartments [18]. The reactor design allows phosphate rock and sulfuric acid to be added at several points. The reactor is equipped with multiple agitators, and cooling is generally provided by low-level flash coolers (Figure 11.17). The combined action of the cooler circulation pumps and back-mixing from agitator to agitator provides the necessary degree of recirculation in the reactor.

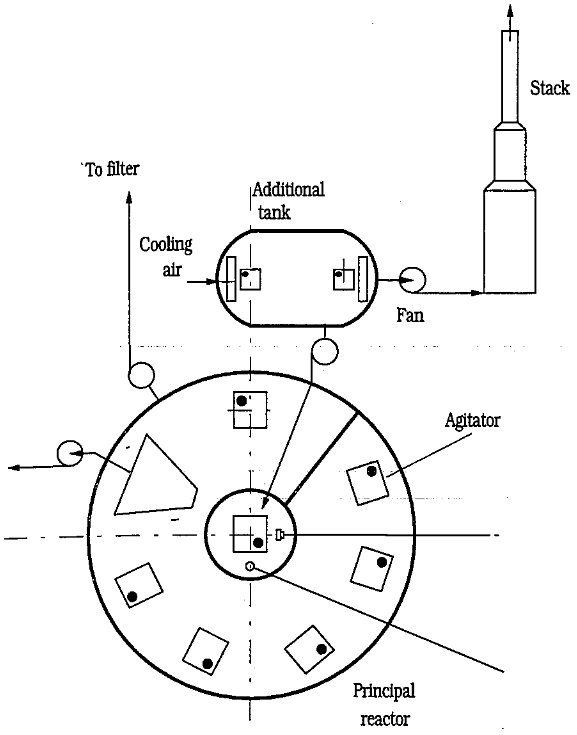


Figure 11.16. **SIAPE Phosphoric Acid Reactor With Additional Tank.**

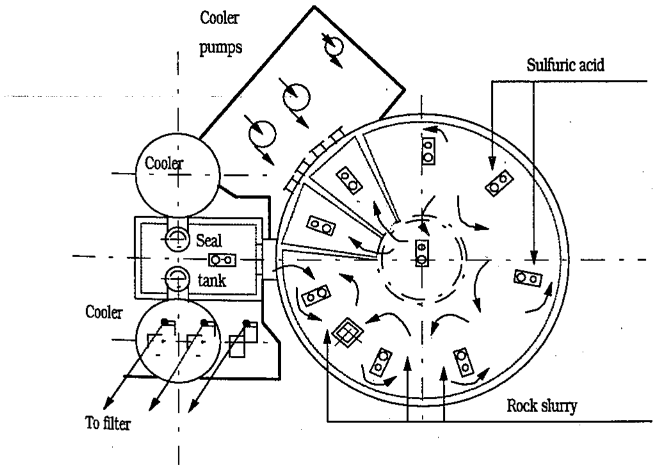


Figure 11.17. **Jacobs - Dorco II Phosphoric Acid Reactor System.**

The system allows easy sulfate control, good crystal growth, and low nucleation rates.

A good example of an isothermal process is the Raytheon Isothermal Reactor process. The temperature in the reactor is maintained at a constant value – hence the name "Isothermal" – by keeping the contents in rapid circulation. These reaction conditions give rise to a number of advantages in comparison with more conventional reactor conditions: raw material use efficiency is enhanced, and sulfate and product compositions are easier to control. The slurry solids concentration in the reactor, and thus the filtration rate, are more stable. The reactor consists of one reaction compartment containing a draft tube and a single circulating impeller (Figure 11.18). Rock slurry is pumped from a storage tank or premix tank and introduced at the bottom of the reactor near the center of the draft tube, which surrounds the impeller. This feed point is most suitable because the rock is dispersed very efficiently into the circulating slurry as it flows up through the impeller.

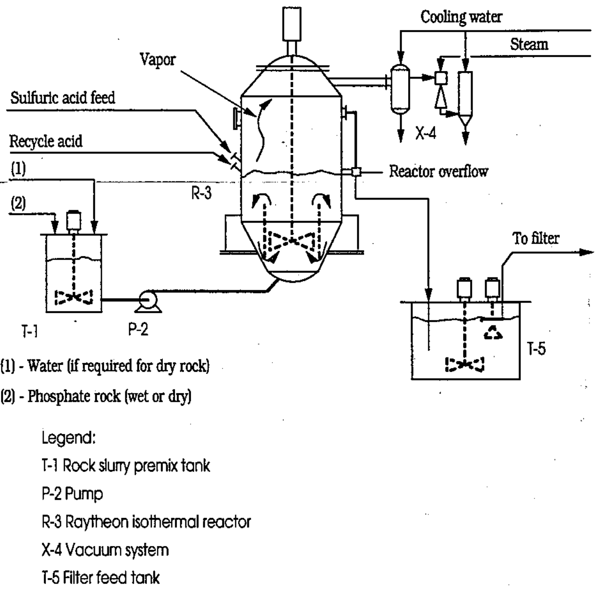


Figure 11.18. **The Raytheon Isothermal Reactor.**

A controlled flow of 93%-98% sulfuric acid is introduced to the reactor inside the draft tube, just above the propeller. The turbulent flow at this point ensures maximum dispersion of the acid. The slurry temperature is maintained by regulating the reactor pressure, which is maintained by either a steam ejector or vacuum pump through the vacuum system.

The reactor slurry level is fixed by an overflow nozzle located on the shell of the reactor above the top of the draft tube. The resulting slurry, containing 29% P_2O_5 and 38%-40% solids, overflows through a self-venting pipe, which is sealed below the liquid level in the filter feed tank. The filter feed tank and a surge tank are between the reactor and filter.

The high circulation rate in the reactor is maintained by a propeller-type, top-mounted agitator equipped with a specially designed vacuum shaft seal at the reactor top and an externally mounted steady bearing at the reactor bottom. The impeller is within the draft tube, near its bottom. The specially-designed, water-cooled, high-durability rubber steady bearing is used to maintain precise centering of the circulator shaft.

The circulation ratio of the isothermal reactor is about ten times that occurring in most conventional multicompartment reactors. The large difference in circulation rate results in uniform temperatures, uniform sulfate concentration, and larger gypsum crystals [18]. Previously known as the Swenson (Gulf) Isothermal Reactor and offered by Badger, it is now offered by Raytheon Engineers and Constructors, U.S.A.

Two processes somewhat related to the isothermal process are the Kellogg - Lopker process and the process proposed by R. L. Somerville.

In the Kellogg - Lopker process the reaction system comprises two vessels – a dissolver and an evaporator (cooler) (Figure 11.19). The phosphate rock and recycle phosphoric acid are introduced into the dissolver, which works under atmospheric pressure, and sulfuric acid is introduced into the vacuum evaporator. Neither vessel contains an agitator; the necessary turbulence is provided by circulation of the slurry, which is pumped from the bottom of the dissolver and injected tangentially into the evaporator just below the liquid level, inducing a swirling motion. It then returns under gravity to the dissolver and is injected in the same way to maintain a similar vortex. The difference between the liquid levels in the two vessels corresponds to the difference in their operating pressures. The Kellogg-Lopker system is distinguished by being able to accept very coarsely ground phosphate rock and for its low residence time (1½ hours compared with 8 hours for the Prayon process).

In the Somerville process (Figure 11.20) phosphate rock is introduced into an agitated digester containing slurry under atmospheric pressure and is then drawn by vacuum into the cooler, which is a stirred evaporator. Sulfuric acid and recycle phosphoric acid are added and the slurry is then pumped back into the digester.

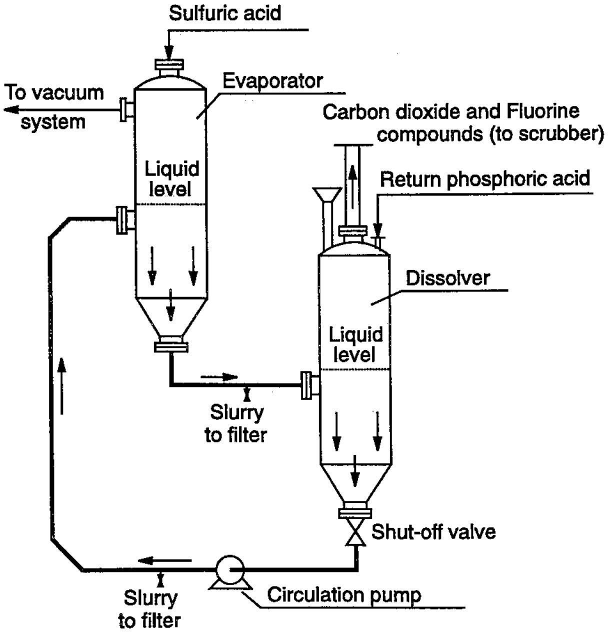


Figure 11.19. Kellogg - Lopker Reaction System.

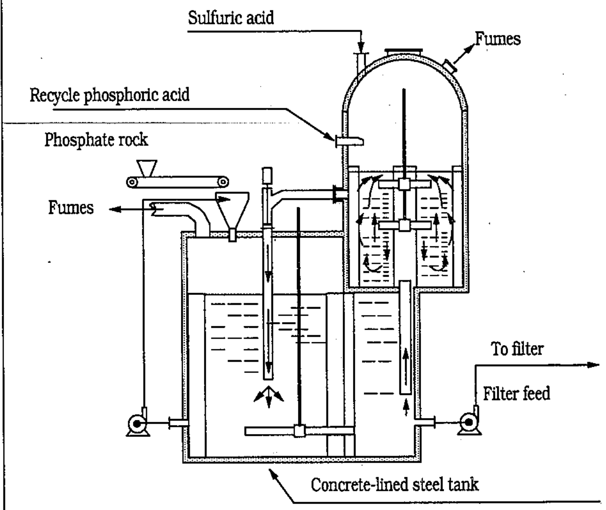


Figure 11.20. Somerville Phosphoric Acid Reactor.

The processes described above are believed to be fairly representative of dihydrate processes. While most plants operate with a small excess of sulfuric acid, it is possible to operate with a deficiency of sulfuric acid but with an excess of SO_4 by replacing part of the sulfuric acid with an equivalent amount of ammonium sulfate (or other soluble sulfate). About 10%-15% of the sulfuric acid can be replaced by ammonium sulfate. This process modification may be advantageous for using small amounts of byproduct ammonium sulfate. A further advantage is lower corrosion rates. A disadvantage is longer reaction time (up to 18 hours). The phosphoric acid produced by this process contains ammonium phosphate; therefore, its use is limited to production of ammonium phosphate or compound fertilizers.

Reaction Time and Retention Time – Somerville states that the average life of a phosphate rock particle in a typical reaction system may range from 15 seconds to 3 minutes. Nevertheless, retention times in industrial plants range from 1.5 to 12.0 hours or more [11]. One of the reasons relates to the formation of good gypsum crystals, as discussed previously. Another reason is the difficulty of close control of free sulfuric acid (SO_4^{-2}) content of the liquid phase when the reaction time is short. Close control of this value is extremely important. Although the optimum level of control may depend on the character of the rock, a level of about 1.5% is typical. Serious upsets can occur when the SO_4^{-2} level varies appreciably from the optimum. Obviously, the shorter the reaction time, the faster (and more often) problems can arise. The success of the 1½-hour reaction time in the Kellogg-Lopker process is likely related to the use of an automatic sulfate analysis instrument that permits close control and rapid adjustments.

Filtration – The function of the filtration step is to separate the gypsum (and any insoluble materials derived from phosphate rock or formed in the reaction) from the phosphoric acid product as completely, efficiently, and economically as possible. All modern plants use only continuous horizontal vacuum filters.

The most popular types of filters are the tilting-pan rotary filters, rotary table filters, and belt filters. In each of these filters, the cycle proceeds through the following steps: (1) deposition of the phosphoric acid-gypsum slurry on the filter, (2) collection of product acid by application of vacuum, (3) two or three countercurrent washes to complete the removal of phosphoric acid from the gypsum, (4) discharge of the washed gypsum, and (5) washing of the filter cloth to prevent accumulations of scale-forming materials. The sequence of operations is illustrated in Figure 11.21. In the washing sections, successively weaker solutions of phosphoric acid are collected. The last wash is with fresh water or sometimes with water recycled from a gypsum pond or from sumps that collect cloth-washing water and spillage or drippings.

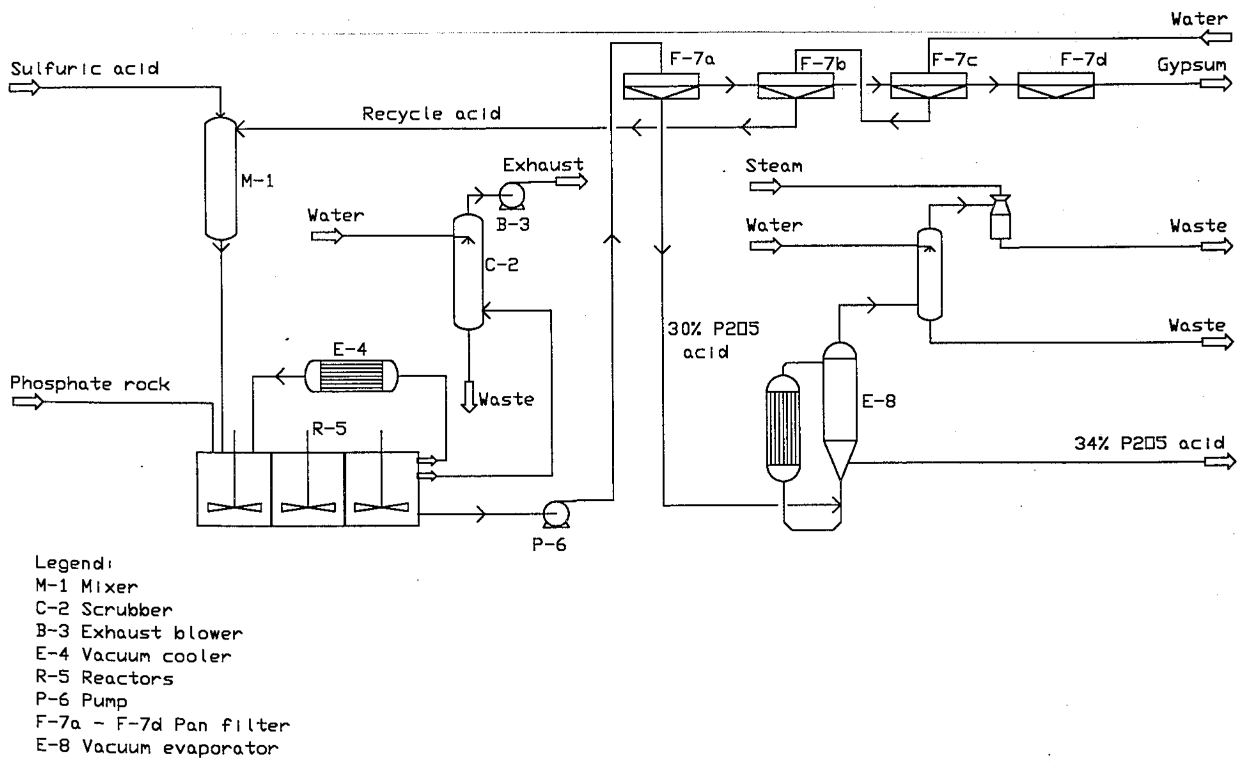


Figure 11.21. Typical Wet-Process Phosphoric Acid Plant.

The very weak acid collected in the last section is returned to the preceding section with the filtrate from the first wash being recycled to the reaction vessels. Some of the product acid also may be recycled to the digestion step to control the percentage of solids in the slurry at a manageable level, usually 35%-45%.

Filters are usually rated according to their active surface area, which may range up to about 320 m^2. The rate of rotation (in a rotary filter) or the rate of travel (in a belt filter) is variable to permit adjustments as required by the filtration characteristics of the slurry and other factors.

The only types of filters that are suitable for phosphoric acid production (that can perform the sequence of all operations desired in the process of filtering gypsum) are the horizontal belt vacuum filters, which are offered by companies such as Fimco, Delkor, and Pannevis; the Bird tilting-pan vacuum filters, offered by Bird and Profile, and the UCEGO rotating-table vacuum filters, offered by Rhone-Poulenc.

The production rate may vary widely, but a common design factor is 6.5 tonnes of P_2O_5/m^2/day. The filtration rate is affected primarily by the size and shape of gypsum crystals which, in turn, are affected by conditions in the reaction section including the type of phosphate rock, use of crystal shape modifiers, control of reaction conditions, etc. Insoluble impurities in the rock, such as clay, may affect filtration rates adversely [19]. The filtration rate is also affected by the temperature, concentration, viscosity of the acid, and the desired recovery. While many plants strive for maximum recovery, in specific plants there is often an economic optimum operating rate at which increased production is attained at some sacrifice of recovery.

Filtration rates also depend on the design of the filter, amount of vacuum, and numerous other factors. Moraillon et al. give illustrations ranging from 2 to 18 tonnes/m^2/day [20]. Shearon mentions rates ranging from 7.8 to 9.8 t/m^2/day for Florida plants [13].

Concentration and Clarification – Phosphoric acid produced by most dihydrate processes contains 26%-32% P_2O_5 (filter acid). Acid of this concentration can be used in some fertilizer processes, but for most purposes it is economically preferable to concentrate it by evaporation of part of the water content. The desired concentration depends on the use; the requirements are given in Table 11.18. The above concentrations are merely guides to standard practice; it is quite possible to use other concentrations in most cases. For instance, 30% P_2O_5 acid has been used for TSP production by a process requiring extensive drying of the product. However, energy is usually more efficiently used by concentrating the acid than by drying the product with high rates of recycle. This is especially true when energy is available in the form of steam from an adjacent sulfuric acid plant.

Table 11.18. Phosphoric Acid Concentrations Required in Downstream Processes

Application	Acid Concentration (% P_2O_5)
Triple superphosphate – den process	50 - 54
Triple superphosphate-slurry process	38 - 40
Diammonium phosphate	about 40
Monoammonium phosphate (depending on process)	40 - 54
Shipment (merchant grade)	54[a]
Superphosphoric acid for shipment or liquid fertilizer production	68 - 70

a. Although 54% P_2O_5 is the usual standard for merchant-grade acid, variations are in the range of 50%-60%.

Precipitates form in phosphoric acid before, during, and after concentration. Compounds precipitating before concentration are likely to be mainly calcium sulfate and fluosilicates. A wide variety of compounds may form during and after concentration, depending on acid concentration. These compounds are collectively known as "sludge" and cause many difficulties in handling and use of the acid. They also form scale in evaporators. Therefore, many manufacturers clarify the acid and either recycle the sludge or use it in fertilizer products where it causes the least trouble. Acid for shipment, in particular, should be well clarified. Phosphoric acid produced by hemihydrate processes (40%-50% P_2O_5) is reported to be relatively free from sludge.

The amount of fluorine removed during concentration from 30% to 54% P_2O_5 may be 70%-80% of that originally present in the acid, most of which is volatilized and recovered in the condensate. Much of the fluorine is volatilized during evaporation and must be recovered to prevent pollution. In some cases saleable fluorine byproducts are produced such as fluosilicic acid, fluosilicates, cryolite, aluminum fluoride, hydrofluoric acid, and even liquid hydrogen fluoride.

Phosphoric acid concentrators may be classified as direct-fired or indirectly heated. In direct-fired evaporators, combustion gases come into direct contact with the acid, as in a spray tower or submerged combustion evaporators. Use of this type of evaporator has been abandoned because of the difficulty of cleaning the exhaust gases to recover acid mist and fluorine compounds.

Most phosphoric acid concentration processes heat the acid with steam in a heat exchanger under vacuum (Figure 11.22). When hot water from heat recovery in sulfuric acid plants is to be used, an acid can be concentrated in two stages from 28% to 35% P_2O_5 with hot water and further with steam. Commonly used are tubular evaporators with forced circulation; the tubes can be of graphite or stainless steel. The impregnated graphite tubes are cheaper but are fragile and crack during operation. There was an opinion of users that over a period of a few years the capital and replacement costs for both systems were about the same. Now the situation has changed somewhat in favor of graphite tube exchangers because better materials are being used. The other type of exchanger is the carbon block. Concentration from 30% to 54% P_2O_5 using steam heating may be carried out in one, two, or three stages, sometimes with interpass crystallizers, to decrease scale formation in the heat exchangers.

Concentration from 30% to 54% P_2O_5 requires about 1.9 tonnes of steam per tonne of P_2O_5 in the acid concentrated. This amount is usually available from the sulfuric acid manufacture if the acid is produced by burning sulfur. Electric power requirements may range from 11 to 16 kWh/tonne of P_2O_5, depending on the scale of operation. About 6 tonnes of cooling water per tonne of P_2O_5 is required for condensing the water evaporated from the acid.

Utilization of Sludge – As mentioned previously, sludge impurities precipitate in phosphoric acid before, during, and after concentration. If the acid is used onsite for fertilizer production, it may be possible to use the acid without separating the sludge. However, in some cases the amount of sludge may be so great as to lower the grade of fertilizer products below that desired.

Sludge solids that form in filter acid (30% P_2O_5) are mainly gypsum and fluosilicates and may, in some cases, be returned to the phosphoric acid production unit without serious interference with its operation. Sludge forming after concentration is likely to contain a high proportion of iron and aluminum phosphate compounds. One example is $(Al,Fe)_3KH_{14}(PO_4)_8 \bullet 4H_2O$. Lehr has identified 38 distinct crystalline compounds occurring in sludge from wet-process acid [21]. The return of iron and aluminum compounds to the acid-production unit is likely to cause some difficulty. When this sludge must be separated, as is usually the case for shipment, it is often used for the production of TSP. Most of the P_2O_5 in the sludge solids is citrate soluble but not water soluble; therefore, this solution is not advantageous when the TSP is sold on the basis of water solubility.

The sludge may be used in the production of nongranular monoammonium phosphate (MAP) which, in turn, is used as an intermediate in the production of compound fertilizers. There is no standard grade for MAP

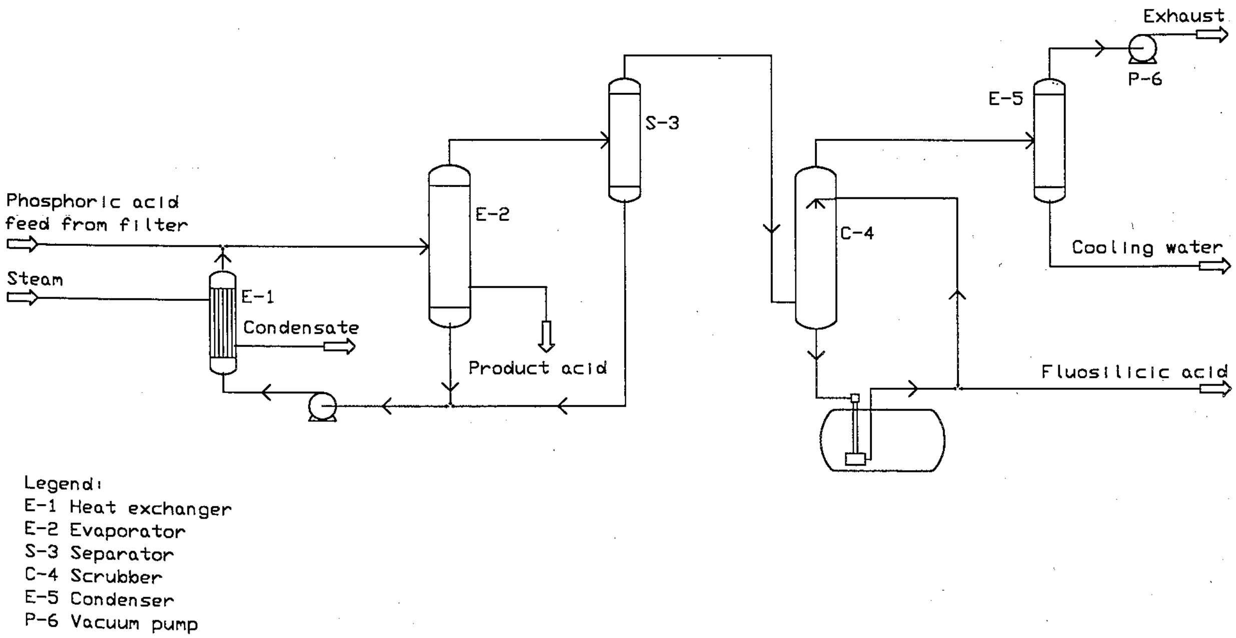


Figure 11.22. Typical Phosphoric Acid Concentration Unit.

to be used as an intermediate; the user can formulate compound fertilizers on the basis of actual analysis. In this case also, the iron, aluminum, and magnesium compounds are not water soluble. In fact, there is no economical method for using sludge solids in countries where phosphate fertilizer is sold on the basis of water solubility.

Precipitation after concentration to 54% P_2O_5 is slow and never so complete but that more precipitate will form on further storage. However, clarification methods are available that reduce the sludge problem in merchant-grade acids to manageable levels.

Dihydrate Process Requirements – Raw material and utilities requirements vary among dihydrate processes, but the values shown in Table 11.19 may be considered mid-range values.

11.2.6 Hemihydrate and Two-Stage Processes

As with dihydrate processes, there are a number of hemihydrate and combined systems developed by various companies, and no attempt is made to describe them all in detail. However, for simplicity it may be taken as a rule that the basic equipment for both hemihydrate and combined processes is the same, and differences exist only in technical parameters, additional equipment, general layout, and to some extent in materials of construction used.

Hemihydrate Process (HH)

The hemihydrate reaction proceeds in two distinct zones. It is therefore necessary to have at least two separate vessels or compartments in the reaction section. The preferred volumetric ratio is 2:1. The first zone is often divided into two identical compartments or vessels, 1A and 1B.

Phosphate rock is fed to reactor 1A; sulfuric acid and dilute phosphoric acid from the filter are fed to reactor 2 (Figure 11.23). Slurry from reactor 2 is recycled through a flash cooler to reactor 1A, thus exposing the phosphate rock to sulfate ions under controlled chemical conditions. Slurry overflows from compartment 1A to 1B. Heat is removed by vacuum cooling (or by air with omitting flash cooler) to maintain the reaction slurry temperature at 98°-100°C.

The product acid at between 40% and 50% P_2O_5, depending on downstream requirements and hemihydrate gypsum, is separated by a horizontal vacuum filter

Table 11.19. Process Requirements of the Dihydrate Process

Product: Phosphoric Acid	Process: Dihydrate
Capacity: 534 tpd (52% P_2O_5) 160,000 tpy Operation time: 82% Working capital: 5.5 US $ million	Investment cost: (BL) Grinding: US $1.5 million Process: US $30.0 million Concentration: US $6.0 million Total: US $37.5 million

Inputs	Units	Consumption Per Tonne of P_2O_5
Phosphate rock (32% P_2O_5)	t/t	3.29
H_2SO_4 (100%)	t/t	2.80
Lime	t/t	0.15
Antifoaming agent	US $/t	0.5
Electric power:		
– Grinding	kWh/t	20
– Process	kWh/t	70
– Concentration	kWh/t	10
Steam:		
– Process	t/t	0.15
– Concentration	t/t	1.75
Cooling water	m^3/t	70
Process water	m^3/t	7
Labor	workhours/t	0.38

Basis: 1993 West European costs.

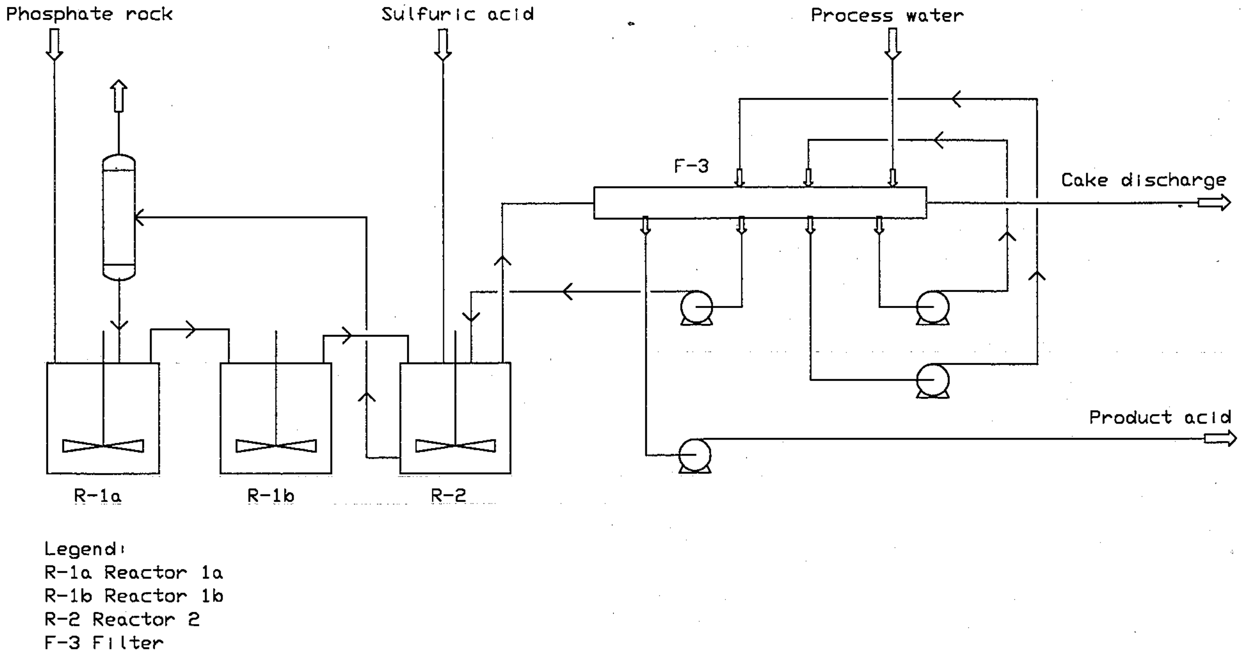


Figure 11.23. The Hydro HH Process.

with three countercurrent wash stages. The product acid from the filter passes directly to storage. It does not require clarification or solid removal and may be used directly as concentrated acid without evaporation.

However, there are some disadvantages that have tended to restrict the popularity of the hemihydrate route, among them the following:

Filtration rate:	Hemihydrate crystals tend to be smaller than those from dihydrate processes; hence, hemihydrate slurry can be more difficult to filter.
P_2O_5 losses and water balance:	The water balance is more critical; thus the amount of wash water that can be used is restricted. Amounts of both soluble and cocrystallized P_2O_5 remaining in the filter cake are greater because of the higher P_2O_5 concentration of the slurry being filtered.
Scaling:	Hemihydrate is not a stable form of calcium sulfate, and it tends to revert to gypsum even before the acid has been filtered off. During washing, conditions are even more in favor of rehydration, which may lead to scaling of piping and equipment.
Corrosion:	At the higher temperature and acid concentration in a hemihydrate reaction system, there is more rapid wear of equipment, particularly of agitators and slurry pumps.

However, apart from the reduction or elimination of the evaporation heat requirement, the process has certain advantages:

Capital saving:	Less evaporation equipment is needed, if any.
Purer acid:	The acid contains substantially less free sulfate and suspended solids than the evaporated dihydrate-process acid of the same strength and somewhat lower levels of aluminum and fluorine contents.
Lower rock grinding requirements:	Under more severe reaction conditions, phosphate rock feed reacts much more quickly, and a satisfactory rate of reaction can be achieved from much coarser rock.

Three single-stage hemihydrate processes have been in use in commercial-scale plants. They are the Norsk Hydro Licensing (formerly Fisons Fertilizer) Process, Prayon Process, and the Occidental Process. Average process inputs for hemihydrate processes are shown in Table 11.20.

Hemidihydrate Processes

Hemihydrate-dihydrate processes without intermediate filtration, so-called hemihydrate with recrystallization (HRC), are widely used in the countries of East Asia and Oceania. The plant layouts for these processes resemble those of multiple-reactor dihydrate processes. An exception is that the attack and digestion reactors operate under hemihydrate conditions while succeeding reactors operate under conditions favoring the rehydration of hemihydrate to gypsum, which is encouraged by seed dihydrate crystals recycled in slurry from the filter feed. The product acid is not any more concentrated than that obtained from the dihydrate process because of the need to crystallize easily filterable crystals in the presence of the product acid, but the gypsum is much purer and therefore of greater use in, for example, plaster manufacture or as a cement-setting retarder. This advantage is important for countries where natural gypsum is scarce, wholly or partly imported, and expensive.

The process also provides a very high recovery of P_2O_5 from the rock since losses in the gypsum are very low. The value of the 2%-3% increase in P_2O_5 recovery depends on the cost of the rock. The disadvantages are the higher cost and increased complexity of the process. Also some phosphate rock contains impurities that stabilize the hemihydrate, thereby preventing recrystallization to gypsum at an acceptable rate.

This process was developed in Japan by Mitsubishi Chemical Industries Ltd., Nippon Kokan KK, and Nissan Chemical Industries Ltd. The Nissan "H" process is typical.

Hemihydrate-Dihydrate Process With Intermediate Filtration (HDH)

The first stage of the process is almost identical to the HH process already described. In the transformation stage the hemihydrate cake is discharged from the filter into an agitated vessel (Figure 11.24). The operating conditions are controlled to ensure complete transformation

Table 11.20. Process Requirements of the Hemihydrate Process

Product: Phosphoric Acid	Process: Hemihydrate
Capacity: 534 tpd (52% P_2O_5) 160,000 tpy Operation time: 82% Working capital: 5.5 US $ million	Investment cost: (BL) Grinding: US $0 Process: US $33.0 million Concentration: US $3.0 million Total: US $36.0 million

Inputs	Units	Consumption Per Tonne of P_2O_5
Phosphate rock (32% P_2O_5)	t/t	3.29
H_2SO_4 (100%)	t/t	2.78
Lime	t/t	0.17
Antifoaming agent	US $/t	0.5
Electric power:		
– Grinding	kWh/t	0
– Process	kWh/t	70
– Concentration	kWh/t	10
Steam (LP):		
– Process	t/t	0.11
– Concentration	t/t	0.49
Cooling water	m^3/t	22
Process water	m^3/t	4
Labor	workhours/t	0.42

Basis: 1993 West European costs.

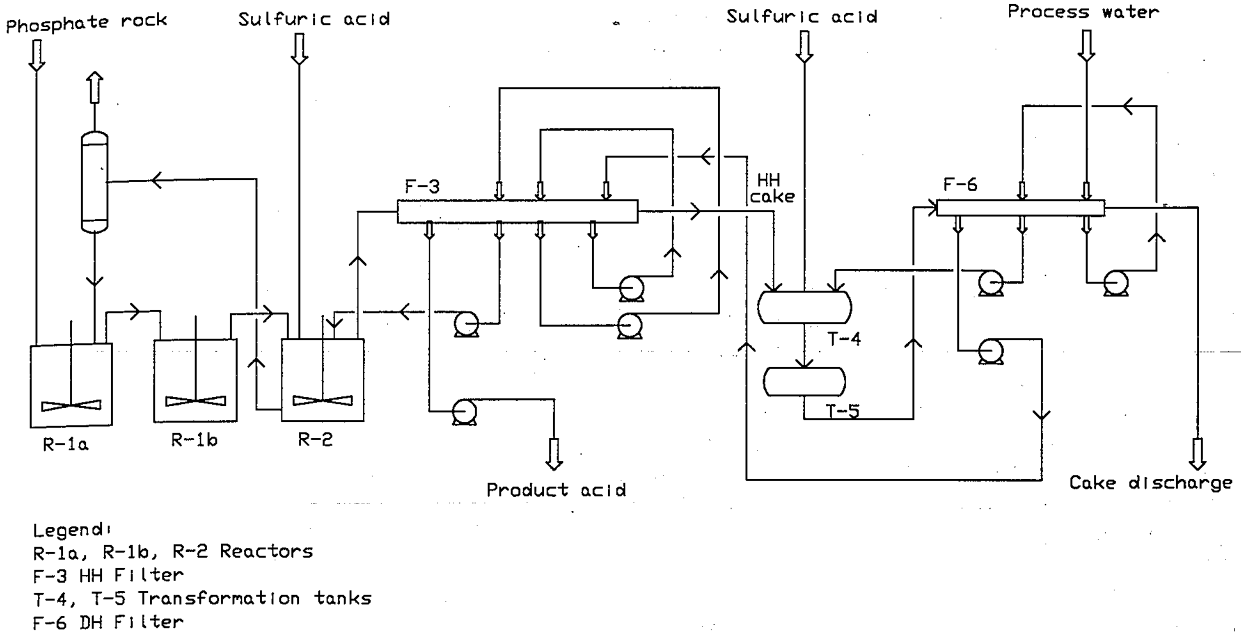


Figure 11.24. Nissan "C" Hemihydrate-Dihydrate Process.

of hemihydrate gypsum to dihydrate and to allow sufficient time for the dihydrate crystals to grow.

The rate of transformation is increased by the addition of a small feed of sulfuric acid. Nearly all the lattice P_2O_5 co-precipitated with the hemihydrate is released into the liquid phase. The dihydrate gypsum is then filtered off and the cake washed with process or pond water. The filtered and the released P_2O_5 is returned to the hemihydrate reaction stage as the last wash on the hemihydrate filter.

The extra filtration step increases the cost and complexity of the plant, but this disadvantage may be offset by decreasing or eliminating the concentration step because of the high P_2O_5 concentration of about 45% in the phosphoric acid produced.

Moreover, the dihydrate gypsum obtained is much purer than that from HH or DH processes and similar to HRC gypsum and may be used in the production of building materials.

Such a solution has been adopted in the Singmaster and Breyer, Prayon, Fisons Fertilizers, Norsk Hydro Licensing, and Nissan "C" ("New Nissan") processes and a later development of the Nippon Kokan process. In commercial use are the Fisons HDH process, the Nissan "C" process, and a whole scale of Prayon's PH three-stage processes: PH2, PH3, PH11, PH12 with very pure hemihydrate, anhydrite II, or a mixture of the two [22]. Impurity distributions in the acid and filter cake are shown in Table 11.21 for the Norsk Hydro processes. Median hemidihydrate process requirements are given in Table 11.22.

Dihydrate-Hemihydrate Process (DHH)

Although the attack and digestion sections are run under dihydrate conditions, it is not desirable to effect a very high degree of P_2O_5 recovery during the separation of the acid from the dihydrate because the succeeding dehydration stage requires about 20%-30% P_2O_5 and 10%-20% H_2SO_4. A centrifuge is therefore used instead of a filter to produce a thickened slurry of gypsum in phosphoric acid of the correct concentration, and it is not of critical importance to produce highly filterable crystals in the first stage. Thus, it is possible to make a product of up to about 35% P_2O_5, compared with a maximum of about 32% for the ordinary dihydrate process. The transformation of dihydrate into hemihydrate is not hindered by the impurities in Kola apatite and other igneous rocks for which the process is very suitable.

The dihydrate-hemihydrate process has about the same advantages and disadvantages as hemihydrate-dihydrate except that the hemihydrate byproduct may be more useful than gypsum in some cases. On the other hand, the product acid concentration is somewhat lower.

Table 11.21. Raw Material and Product Analyses for Norsk Hydro Fertilizers Phosphoric Acid Processes (wt %)

Components	Rock[a]	DH+C Acid	DH+C Cake[b]	HH Acid	HH Cake[c]	HDH Acid	HDH Cake[b]
P_2O_5	31.6	50.0	0.7	50.0	1.4	50.0	0.2
CaO	45.8	0.2	30.9	0.2	34.4	0.2	30.8
SO_4	1.2	4.8	52.8	2.0	54.5	2.0	52.5
F	3.6	1.3	1.1	0.7	0.7	0.7	0.7
SiO_2	7.5	0.1	4.3	0.1	4.28	0.1	3.78
Fe_2O_3	1.18	1.77	0.15	1.75	0.14	1.78	0.06
Al_2O_3	1.4	1.76	0.2	0.9	0.6	1.49	0.32
MgO	0.45	0.65	0.05	0.65	0.04	0.67	0.01
Na_2O	0.55	0.08	0.3	0.08	0.26	0.09	0.032
K_2O	0.1	0.08	0.08	0.09	0.07	0.1	0.02
Water	1.0	-	25	-	20	-	25
Solids	-	4.3	-	< 1	-	< 1	-
Na_2O	0.55	0.08	0.3	0.08	0.26	0.09	0.032

Note: DH+C - Dihydrate process and concentration
HH - Hemihydrate
HDH - Hemidihydrate

a. Florida 68% BPL, 100% through 1.6 mm.
b. Gypsum, dry basis.
c. Hemihydrate, dry basis.

Table 11.22. Process Requirements of the Hemidihydrate Process

Product: Phosphoric Acid	Process: Hemidihydrate
Capacity: 534 tpd (52% P_2O_5) 160,000 tpy	Investment cost: (BL) Grinding: US $0
Operation time: 82%	Process: US $38.0 million
Working capital: 5.5 US $ million	Concentration: US $3.0 million
	Total: US $41.0 million

Inputs	Units	Consumption Per Tonne of P_2O_5
Phosphate rock (32% P_2O_5)	t/t	3.17
H_2SO_4 (100%)	t/t	2.74
Lime	t/t	0.12
Antifoaming agent	US $/t	0.5
Electric power:		
– Grinding	kWh/t	0
– Process	kWh/t	90
– Concentration	kWh/t	10
Steam:		
– Process	t/t	0.10
– Concentration	t/t	0.49
Cooling water	m^3/t	27
Process water	m^3/t	6
Labor	workhours/t	0.42

Basis: 1993 West European costs.

This route has been investigated by Marchan (later Albright and Wilson), but the only commercial process is that developed at first by the Japanese Central Glass Company and Société de Prayon, of Belgium and subsequently jointly finished as the Central-Prayon Process.

Plant Engineering/Construction

Three companies provided information on recent phosphoric acid plant activities.

1. The Raytheon Isothermal Reactor process described above is offered by Raytheon Engineers and Constructors, Tampa, Florida. Single-train capacities available are 80,000 to 330,000 tpy P_2O_5. The 54% P_2O_5 product acid contains less than 1% suspended solids, with further clarification available. Wet grinding of rock is preferred if grinding is needed. One highlight is a drier gypsum cake containing only 25% water. Raytheon has built 7 plants, revamped at least 12 and is now building two plants of 400 and 950 tpd P_2O_5 capacity.
2. The various Prayon processes, as summarized in Table 11.23, are offered by Kvaerner Process Technology, London, England. Since 1984 Kvaerner (formerly Davy McKee) has engineered six plants of 100- to 1,310-tpd P_2O_5 capacity and provided engineering and supervision of construction for up to 59 wet-process acid plants in prior years.
3. BIPROKWAS Engineering, Ltd., Gliwice, Poland, offers a single-reactor dihydrate process with capacities of 30,000- to 200,000-tpy per train. The product is 54% P_2O_5 acid containing about 1.5% F. BIPROKWAS has built eight phosphoric acid trains and revamped two, the latest a 160,000-tpy unit.

11.2.7 Materials of Construction

Choice of construction materials is very important since it will affect the degree of maintenance and downtime of a phosphoric acid plant.

Corrosion rates in a plant are variable and depend largely on the chloride and free fluoride content of the acid.

Typical materials of construction for various items of equipment are as follows [23].

Reactors:	Concrete, with acid-resistant aggregate such as siliceous sand and gravel, rubber lined or RLMS (rubber-lined mild steel) protected by carbon bricks.
Vessels:	RLMS, propylene, FRP (fiber-reinforced polypropylene).
Pipework:	Polypropylene, FRP, rubber.
Agitators:	Alloy 20, 904 L, HV9, Sanicro 28, Ferralium 255, 317L, Uranus B6.
Pumps:	Alloy 20, alloy 28, HV9, Sanicro 28, high-density polyethylene, ferralium 255, 317 L, Hastelloy C.
Heat exchangers:	Impregnated graphite reinforced with carbon fiber as Diabon (Sigri), Bigilor, Graphilor BS (Le Carbone-Lorraine).

Alloy materials commonly used in phosphoric acid service are given in Table 11.24.

The most vital and vulnerable portions of the phosphoric acid plant are agitators, pumps, and filters.

Table 11.23. Features of the Prayon/Davy Processes

Process/Features	Dihydrate (DH)	Hemihydrate (HH)	Hemidihydrate (HDH)
P_2O_5 efficiency, %	96.5	93.0	98.5
Phosphate rock	All grade sedimentary and igneous	Selected, coarser grinding acceptable	Igneous not suitable, coarser grinding acceptable
Rock feed	Dry or wet	Only dry	Dry or moist
Reactor system	Multi-compartment with separate sections for attack and digestion	As for DH with high and low temperature attack zones	Two-reactor system: and 1. as for HH 2. for recrystallization HH to DH
Unit capacity, tpd P_2O_5	Up to 1,800	Up to 1,300	Up to 1,300
Filter acid strength, % P_2O_5	29	42	45
Quality: acid and phosphogypsum	Standard	Acid of high purity	Gypsum of high purity

Table 11.24. Alloy Materials Used in Phosphoric Acid Equipment

Alloy	Cr	Mo	Cr+Mo	Matrix
Lewmet 25	29	4.5	33.5	Austenitic
Lewmet 15	28.5	2.25	30.75	Duplex-austenitic and ferritic
Sanicro	27	3.5	30.5	Austenitic
CD4MCu	26	2.0	28.0	Duplex austenitic and ferritic
Ferralium	25	2.5	27.5	Duplex austenitic and ferritic
Hastelloy G	22	6.5	28.5	Austenitic
Incoloy 825	21.5	3.0	24.5	Austenitic
Jessop 700	21	4.5	25.5	Austenitic
Carpenter 20 Cb-3	20	2.5	22.5	Austenitic
Alloy 20	20	2.5	22.5	Austenitic

Note: The above table ranks alloys according to their chromium plus molybdenum content in descending order from top to bottom.

Corrosive conditions are the most severe for agitators; however, agitators can be replaced with relative ease and low cost. Filters, on the other hand, are large and expensive and not so easily replaced or repaired. Corrosive conditions are somewhat less severe for filters than for agitators because the average temperature is lower and erosion is a lesser factor.

For many years, 316L stainless steel has been a common construction material for agitators, filters, and the other equipment coming in direct contact with wet-process phosphoric acid or reaction slurry. However, there is a growing tendency to use more resistant alloys in new plants, particularly when the rock source may be subject to change or more severe conditions of operation are provided.

Obviously these improved alloys are more expensive; for example, the cost of the alloy 317L has been about 10% higher than 316L; Ferralium, 25% higher; and UB6, 50% higher. However, this extra cost can easily be justified by longer life, fewer delays for repairs, and greater flexibility in choice of rock and operating conditions.

11.3 Superphosphoric Acid

Phosphoric acid when concentrated above 54% P_2O_5 forms superphosphoric acid (SPA). This name is given to phosphoric acid in which an appreciable proportion, usually 30% or more, of the P_2O_5 is in the form of condensed or polyphosphoric acids [general formula $H_{n+2}(P_nO_{3n+1})$]. A variety of concentrations of SPA can be manufactured from wet-process phosphoric acid; generally they are in the range of 69%-76% P_2O_5. Essentially, production of SPA first involves removal of physical water from the weaker acid and then the removal of chemically bound water. The latter step can be represented by the equations:

$$2H_3PO_4 + \text{Heat} \rightarrow H_4P_2O_7 + H_2O\ (g)$$

$$H_3PO_4 + H_4P_2O_7 + \text{Heat} \rightarrow H_5P_3O_{10} + H_2O\ (g)$$

where H_3PO_4 is orthophosphoric acid, $H_4P_2O_7$ is pyrophosphoric acid, and $H_5P_3O_{10}$ is tripolyphosphoric acid. At an SPA concentration of about 70% P_2O_5, the conversion of H_3PO_4 to other forms is of the order of 25%-45%.

For concentration from 54% to 70% P_2O_5, about 1 tonne of high-pressure steam (about 2.7 MPa pressure and 230°C temperature) is required per tonne of P_2O_5. Power requirements are about 24 kWh/tonne of P_2O_5. When a Dowtherm heat transfer medium is used, the fuel requirement is about 2.7 GJ/tonne of P_2O_5.

Several types of evaporators may be used for SPA production, but the most popular is a forced-circulation system (Figure 11.25) developed by the Swenson Evaporator Co. In production of superphosphoric acid (69%-72% P_2O_5) by concentrating wet-process acid, most of the fluorine is volatilized so that the acid contains only 0.2%-0.3% F. By adding reactive silica during evaporation to enhance fluorine volatilization, the fluorine content can be further decreased to about 0.1%. Such acid is suitable for the manufacture of animal-feed supplement products, such as dicalcium phosphate or ammonium phosphate, and is used for that purpose. Other advantages of superphosphoric acid are:

a. Savings in freight per unit of P_2O_5 compared with 54% acid.

b. Sludge is eliminated. The polyphosphoric acids sequester most common impurities; however, in some acids, titanium or magnesium pyrophosphates may precipitate.

c. Superphosphoric acid is much less corrosive than acid of lower concentrations.

d. Superphosphoric acid is suitable for production of clear liquid fertilizers (ammonium polyphosphate solutions) because the polyphosphate sequesters impurities that otherwise would precipitate upon ammoniation.

e. Superphosphoric acid is suitable for production of clear liquid fertilizers with micronutrients because of the ability to sequester metal ions.

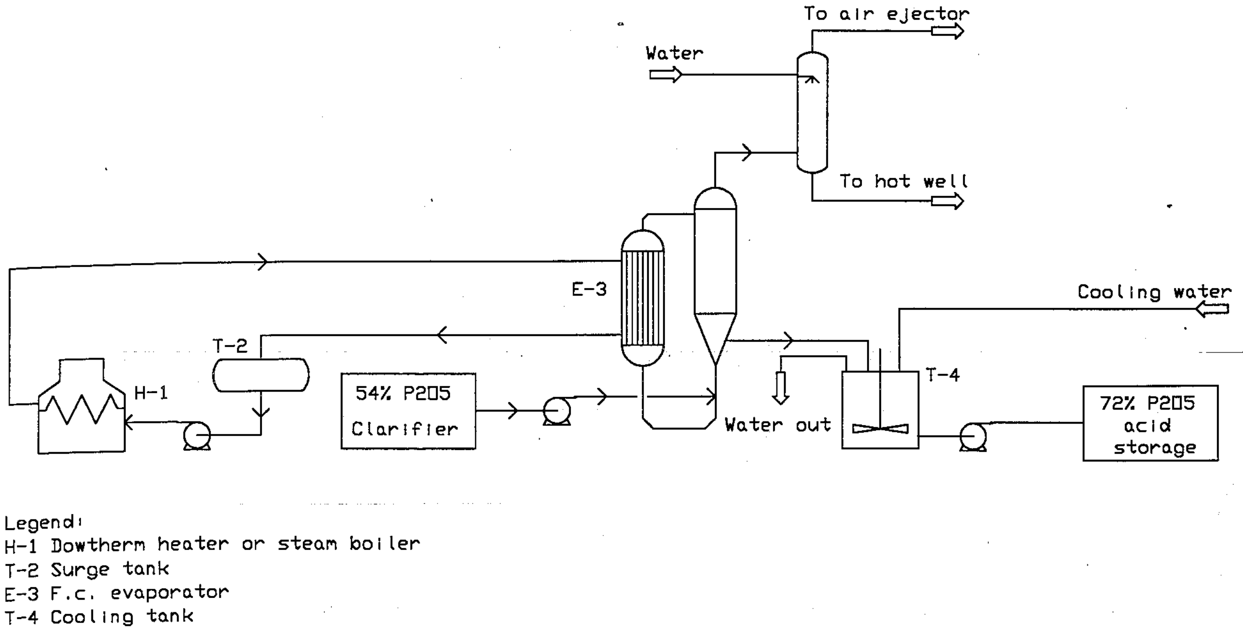


Figure 11.25. Swenson System for Wet-Process Superphosphoric Acid.

The main disadvantages of superphosphoric acid are the energy requirement, corrosion in some types of evaporators, and high viscosity. The viscosity depends on temperature, concentration and impurity content; some superphosphoric acids must be heated to 60°C or higher to permit pumping with centrifugal-type pumps. An example of viscosity variations due to impurities and temperature is shown in Figure 11.26.

The compositions of superphosphoric acids produced from several types of phosphate rock are shown in Table 11.25.

11.4 Shipment of Phosphoric Acid

Until the early 1970s, phosphoric acid trade was largely confined to sales between companies in the United States and trade among countries in Western Europe. During the period 1973 to 1978 the volume of merchant-grade phosphoric acid more than tripled from 1.03 million tonnes of solution in 1973 to more than 3.5 million tonnes in 1978. Since 1978 world trade in phosphoric acid has continued to expand; annual trade volumes increased in each subsequent year until 1985 when trade was reduced to 80% of the previous year's

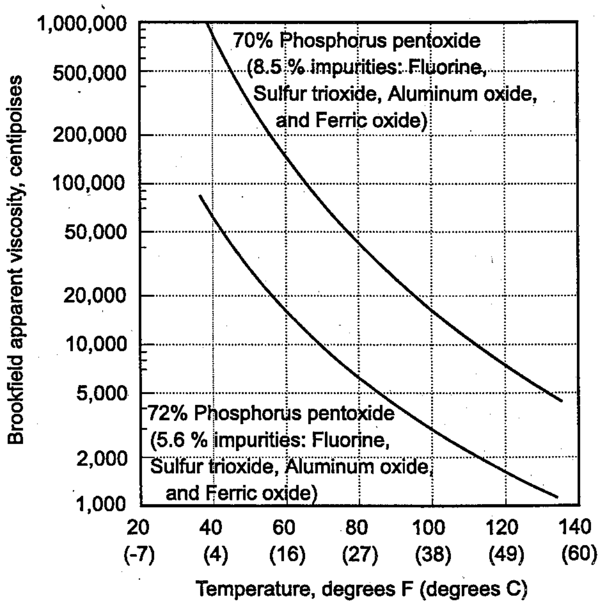


Figure 11.26. Effect of High Impurity Content on Viscosity of SPA.

Table 11.25. Chemical Composition of Superphosphoric Acids

Type of Rock	Florida	Western U.S.A.	North Carolina	Morocco	Togo	Taiba
Calcination	No	Yes	Yes	No	No	No
Total P_2O_5, %	72.9	69.5	71.2	72.4	73.0	72.1
Ortho P_2O_5, %	31.3	53.5	37.6	25.1	35.3	27.1
Fe_2O_3, %	2.2	0.9	1.4	0.6	1.9	2.4
Al_2O_3, %	1.8	2.5	1.3	0.4	0.9	0.5
F, %	0.3	0.5	0.4	0.1	0.1	–
SO_3, %	2.0	2.1	3.4	2.7	1.7	3.3
MgO, %	0.3	0.3	0.6	1.1	0.1	0.1
Color	Black	Green	Green	Green	Dark	Dark
Polyphosphate content, % of total P_2O_5	56	23	47	65	52	62.5

level as a result of the recession in fertilizer markets. In 1987, however, trade reached a new high of 6.25 million tonnes as demand for downstream phosphate fertilizers resumed its increase. Seaborne trade accounted for more than 85% of merchant-grade acid trade in 1987. After 1987 the level of trade became rather stable with some limited fluctuations. In 1992 world trade totaled 3.7 million tonnes P_2O_5 (about 7 million tonnes solution) and in 1993 – 3.3 million tonnes P_2O_5 (about 6.2 million tonnes solution). Morocco was the largest phosphoric acid exporter in 1993 – 1.4 million tonnes P_2O_5 (43.5% of total), Tunisia – 0.5 million tonnes P_2O_5 (15.0%), and United States – 323.5 thousand tonnes P_2O_5 (the sum of merchant-grade acid and superphosphoric acid, 9.8%). In 1993 the main importers were China – 1.1 million tonnes P_2O_5, France – 0.27 million tonnes P_2O_5, and Turkey – 0.21 million tonnes P_2O_5 [24].

Advantages of phosphoric acid as a source of P_2O_5 are versatility, rapid loading and unloading of ships, and high concentration. Phosphoric acid may be used to produce any desired phosphate or compound fertilizer to meet local needs; TSP or ammonium phosphates are less versatile.

Most of the acid shipped overseas has been of 54% P_2O_5 concentration although some "superphosphoric" acid, 69%-72% P_2O_5, has also been shipped.

Compared with importing raw materials, 1.0 tonne of P_2O_5 as phosphoric acid requires shipment of only 1.85 tonnes of 54% P_2O_5 or 1.43 tonnes of 70% P_2O_5 acid versus about 4.3 tonnes of raw materials (3.3 tonnes phosphate rock plus about 1 tonne of sulfur).

Rapid loading and unloading decrease costs by saving labor, decreasing port time, and decreasing congestion in ports. Handling of phosphoric acid (or any liquid) is dust free, thereby avoiding atmospheric contamination by dust and minimizing losses.

Some disadvantages are the requirement for specially equipped ships and special terminals with pumps and storage tanks at both shipping and receiving points. The need for further processing by the importer limits the market to countries that have sufficient demand to warrant such facilities.

Phosphoric acid for shipment should be relatively free of sludge-forming solids, preferably less than 1%. To meet this requirement the acid usually must be clarified, as discussed previously in this chapter. The amount of sludge depends on the composition of the phosphate rock and the phosphoric acid production process and, in some cases, clarification is unnecessary.

Two means of protection against the corrosion of tank walls are currently in common usage:

- the lining of mild steel tanks with sheets of self-vulcanizing chloroprene - based rubber;
- the lining of mild steel tanks with a plating of molybdenum-alloyed stainless steel (mainly 317L) or constructing the tank itself entirely from this material.

Trends in choice of containment system are difficult to discern since both have their merits and drawbacks. In general, the cheaper construction cost, anticipated long-term employment in phosphoric acid, and restrictive shipping schedules have made vessels with rubber-lined tanks more appealing to the producer-exporter while the cargo flexibility of stainless-steel plating has proved attractive to the independent parcel tanker owners.

Approximately 2.2 million tonnes of world shipping capacity (stainless steel and rubber-lined tanker ships) was available by the late 1980s for the transportation of phosphoric acid (although phosphoric acid obviously competes with other cargoes, such as acetic and nitric acid, phenol, ethanolamine and formic acid for space in stainless tanks). Rubber-lined tanks can carry only phosphoric acid; at the end of 1987, stainless-steel capacity amounted to some 94% of the total [25]. For long distance shipment, large vessels are preferred, up to 40,000-tonne capacity.

A report issued by IFA in 1991 lists 270 ships that are suitable for transport of phosphoric acid (and other corrosive liquids); cargo capacities range from 500 to 39,000 tonnes. Table 11.26 shows the number of ships in various capacity ranges.

Table 11.26. Shipping Potential for Phosphoric Acid

Cargo Capacity in Tonnes	Number of Ships
950 - 2,000	17
2,001 - 5,000	70
5,001 - 10,000	90
10,001 - 20,000	46
20,001 - 30,000	31
over 30,000	16
Total	270

Under the International Maritime Organisation (IMO) bulk chemical code, merchant-grade phosphoric acid requires a moderate degree of containment due to its corrosive nature and its high specific gravity (typically 1.7). In addition, a vessel must have a double bottom and wing tanks on the side if the tank section is to be used for acid. Because impurities in the acid tend to form a thick, viscous sludge, which is difficult to remove, tanks used for transport (and storage) must also be equipped with agitators to keep the acid in motion.

Superphosphoric acid is usually heated during transit to avoid a long period of reheating prior to discharge; thus, tankers for SPA transportation require heating equipment.

Fertilizantes Mexicanos (FERTIMEX) was the first phosphoric acid producer to invest in its own ships with the acquisition of a 23,400-DWT vessel in 1968, but the fleets of Marphocean, the acid shipping arm of OCP, Morocco, and Tunisia's Gabes Chimie Transport are of greater significance today. There are other captive phosphoric acid fleets, among others in Brazil, India, the United States (Occidental), and the Commonwealth of Independent States.

Three major chemical ship operators dominate the noncaptive fleet for phosphoric acid transportation. Stolt-Nielsen, Odfjell-Westfal Larsen, and Jo Tankers together operated over one-half of some 1.2 million tonnes of stainless-steel capacity, i.e., potential phosphoric acid carrying capacity, at the end of 1987.

Freight rates for ocean shipment of phosphoric acid are not published; the larger cargoes are moved under long-term contracts in custom-designed vessels. It is reasonable to assume that freight costs are higher for phosphoric acid than for bulk solid cargoes because of the special construction required. A study made in the past assumed that the cost would be 40% higher for a short haul (north Africa to northern Europe) and 25% higher for a long haul (United States to India). Now, because there is a much larger number of ships, the differential may be lower. Obviously, the storage capacity at terminals must be at least equal to the size of the largest shipment although ships may load and unload at more than one terminal. A survey issued by IFA in 1991 listed 124 maritime terminals with an aggregate storage capacity of 3.0 million tonnes.

For construction of storage tanks, rubber-lined steel is common although stainless-steel linings may be used. In some cases, ponds or lagoons are used for storage. The ponds are lined with heavy sheets of rubber or plastic underlaid with gravel with drainage to a sump so that any leakage can be detected and returned to another pond. One such installation near Tampa consisted of four ponds with a total capacity of 11,000 tonnes. The ponds had inflatable plastic covers to protect them from rain or other contamination. Most storage tanks have facilities for agitating the acid occasionally to prevent settling of solids.

It is difficult to compare the terminal cost for phosphoric acid with that for solid products such as triple superphosphate (TSP) or monoammonium phosphate (MAP). The cost of storage facilities for the same number of tons of solids (30,000 tonnes) has been estimated to be about 40% of the cost for phosphoric acid [26]. However, a substantial investment in mechanical equipment would be required to reclaim bulk solids from storage and convey them to a ship. In addition, a substantial amount of labor would be required for operating the equipment; whereas, loading and unloading costs are negligible for phosphoric acid. For a developing-country receiving terminal that may not be well equipped with mechanical devices, the total of unloading and port storage costs may well be higher for solids. On balance, it seems likely that overall terminal storage and handling costs may be about the same for acids as for bulk solids.

11.5 Use of Byproduct Gypsum

In the production of wet-process phosphoric acid, 4.5 - 5.0 tonnes (dry basis) of byproduct gypsum is produced per tonne of P_2O_5 recovered as phosphoric acid. The global output of 40 million tonnes P_2O_5 per year in the form of wet-process phosphoric acid is equivalent to the production of about 150 million tonnes of phosphogypsum, of which only about 15% is reused.

Phosphogypsum retains at least 20% of free water by weight. The disposal of this material as a waste product is discussed in Chapter 19. This chapter will briefly review ways for using the byproduct. The principal means for using phosphogypsum are to:

- Make ammonium sulfate by reaction of the gypsum with ammonia and carbon dioxide (discussed in Chapter 8).
- Make cement and sulfuric acid by calcining the gypsum with coke and clay or shale (discussed in section 11.1).
- Make plaster or plasterboard for building materials or make pressed or cast blocks for construction purposes.
- Use in cement as a set retardant.
- Use as a fertilizer filler.
- Use for direct application to farmland when the soil requires it.

11.5.1 Use for Building Materials

Plaster consists mainly of gypsum that has been dehydrated to hemihydrate ($CaSO_4 \bullet 1/2\ H_2O$) under carefully controlled conditions so that it will rehydrate rapidly when mixed with water. The dehydrated gypsum usually is finely ground and sometimes mixed with a filler before use. Phosphogypsum must be purified for this use: the extent of purification depends on the amount and character of the impurities and how the plaster is to be used.

When plaster is used as a coating on interior walls, a bright white color is often desired. Organic impurities originating from some phosphate rocks may cause an undesirable dark color. Some phosphogypsum may be purified sufficiently by slurrying in water and passing the slurry through a hydrocyclone to recover the coarser fraction; the undersize has a high impurity content and is discarded. When the gypsum is sufficiently pure, simple washing to remove residual acid may be sufficient. The last trace of acid may be neutralized with lime and the wash water separated by filtration.

For wallboard production, rapid setting is especially necessary, and phosphogypsum with a high P_2O_5 content is unsuitable. Gypsum produced by a hemihydrate-dihydrate process usually has a sufficiently low P_2O_5 content for this purpose.

Aside from impurities, the main disadvantage of phosphogypsum for use as plaster is the high moisture content, which results in a high fuel cost for drying. For this reason there has been comparatively little use of phosphogypsum for building materials in countries where natural gypsum is abundant. In Japan, where there are no domestic supplies of natural gypsum, phosphogypsum has long been used as a plaster and cement additive. More recently the rising cost of environmentally acceptable disposal methods has caused some European countries to undertake utilization. The literature on the subject of production of plaster products from phosphogypsum is voluminous.

In general, the processes consist of purification of phosphogypsum including, in some cases, the addition of chemicals such as lime to neutralize acidity, thermal treatment to convert gypsum to hemihydrate or anhydrite or some combination of the two, and preparation for the market, which may include grinding or agglomeration and, in some cases, drying.

11.5.2 Plaster - Board Products

About 14 million tpy of gypsum is used for making plaster or products based on plaster.

Hemihydrate exists in two crystalline forms. The alpha form is produced when wet phosphogypsum is heated under pressure in an autoclave to about 130° - 160°C. The beta form is prepared by drying and calcining at about 140°C under controlled conditions. Either form can be used for making plaster products, but the alpha form produces denser and harder plaster. Most calcination processes are likely to produce a mixture of beta hemihydrate and anhydrite, but such mixtures are acceptable for most plaster uses and may be preferred for some.

Several processes for making plaster products from phosphogypsum are known. Some of these processes were used commercially in several European countries. The C&F Chemie process was used in France in a plant of 130,000-tpy capacity mainly to make plasterboard. Phosphogypsum was wet screened to remove large particles such as quartz, washed to remove soluble and organic impurities, neutralized with lime water, and dewatered by filtration. It was then dried and calcined in a series of three cyclones with hot air and ground to a fine powder. Another process, developed by Rhone-Poulenc, was used in two plants in France with a total capacity of about 300,000 tpy.

Purification procedures depend on the character of the phosphogypsum; a minimum treatment involves separation of larger particles, washing to remove soluble impurities, neutralization with lime, and dewatering by filtration or centrifuging. For phosphogypsum with more impurities, repeated washing with slime removal or flotation may be used. The purified material is dried and calcined in one step or two. An advantage of the two-step process is that some of the dried phosphogypsum can be removed after the first (drying) step for use as cement additive. Either a direct-fired calciner or a fluidized-bed calciner heated with hot air may be used.

The Knauf processes were offered by the West German company, Gebrueder Knauf Westdeutche Gipswerke. Three different processes were used in two plants in Germany and one in Belgium with a total capacity of nearly 1 million tonnes of various plaster products including gypsum partition blocks. The three processes differed mainly in the degree of purification. For example, one of the processes received hemihydrate from the Central Prayon process, which is already quite pure. The extent of purification is minimized by additives that precipitate phosphates in an inert form. This reaction is slow and is carried out in a reaction silo after partial dehydration of the dihydrate. One unusual feature is that products intended for construction plaster are pelletized in a pan granulator to a particle size of at least 20% plus 0.2 mm after adding a small amount of water to rehydrate some of the hemihydrate. This coarse particle size is preferred for construction plaster.

The Centre d'Etudes et de Recherches des Phosphates Mineraux (CERPHOS) process was used in a plant of 30,000-tpy capacity in Senegal. It appears to be very similar to the CdF Chemie process except that more extensive purification of the phosphogypsum was used, and this involved wet screening, flotation, two washes, and calcium carbonate addition. The product was dried with heated air in a flash dryer and calcined in an indirect-fired kiln.

The ICI process was used in two large plants in England, but both were closed because of difficulties resulting from changes in composition of the phosphate rock. The process used standard methods of washing and neutralization to purify the phosphogypsum followed by calcination to beta hemihydrate. The company also developed a wet-phase dehydration process to produce alpha hemihydrate, but it was not used commercially.

Other processes, not known to be in commercial use, have been developed by FCI (India) and Allied Chemical (United States). The latter process, which is intended specifically for plasterboard manufacture, includes the unusual feature of neutralization of acid components of the phosphogypsum with ammonia.

Processes used in Japan for making plaster products are influenced by the prevalence of hemihydrate-dihydrate phosphoric acid processes that produce an unusually pure gypsum; therefore, the purification step can be simplified.

From the above brief summary, it is apparent that processes to make plaster products by the dry (beta hemihydrate) route may vary widely depending on the impurity content of the phosphogypsum which, in turn, depends on the composition of the phosphate rock and the process used to convert it to phosphoric acid. The general tendency toward use of lower-grade rocks is likely to result in more complicated phosphogypsum purification processes. A substantial portion of the phosphogypsum may be lost in the purification process; the recovery may be as low as 70%.

For the above reasons process requirements vary widely, but those given in Table 11.27 as average requirements for the Rhone-Poulenc process may be illustrative [27].

The only known commercial process for producing alpha hemihydrate from phosphogypsum is the Giulini process that was developed in West Germany [28] and was used in two plants in that country and one in Ireland. As mentioned previously, alpha hemihydrate is formed by dehydration of gypsum in an aqueous suspension in an autoclave.

The purification step of the Giulini process, as with other processes, depends on the impurity level of the incoming phosphogypsum and the type of plaster product to be made. It may consist of washing or flotation or both. After purification, the gypsum is pumped to an autoclave as a slurry, which is operated at 120°C and a pH of 1-3. The temperature is maintained by injection of steam. Dehydration and recrystallization occur in the autoclave, releasing cocrystallized impurities (mainly phosphate), which dissolve in the liquid phase. The size and shape of the alpha hemihydrate crystals that are formed in the autoclave are important and are controlled by additives. The slurry is withdrawn from the autoclave continuously and sent to a filter where the crystals are washed and dewatered to 10%-20% moisture. The filtrate contains an appreciable amount of P_2O_5 and may

Table 11.27. Consumption Figures in Gypsum Plaster Production

Inputs	Units/t of Plaster	Consumption
Phosphogypsum	kg	1,500
Lime	kg	5-10
Electric power	kWh	50
Water	m^3	3
Fuel oil	kg	45

be returned to the phosphoric acid plant. The treatment of the wet crystals from the filter depends on the desired end product. Cast building blocks are produced by adding a controlled amount of water to the filter cake and pouring the slurry into molds where it solidifies as the hemihydrate rehydrates to dihydrate. For production of dry plaster powder, the crystals must be dried and ground after which the powder can be stored for use as plasterboard or various other plaster products.

The main process requirements per tonne of alpha hemihydrate are given in Table 11.28. If a dry product is required, an additional 10 kWh of electric power and 200,000 kcal of fuel are needed per tonne of product.

Table 11.28. Consumption of Inputs Per Tonne of Alpha Hemihydrate

Inputs	Units/t	Consumption
Steam (LP)	t/t	0.4-0.6
Hot water (90°C)	m^3	0.5
Process water	m^3	2.0
Electric power	kWh	25

The ICI alpha hemihydrate process, which has not been used on a commercial scale, is generally similar to the Giulini process. However, it uses two autoclaves in a series, which are operated at 150°C, and the product crystals are separated from the liquid phase by centrifuging. As does the Giulini process, it makes use of crystal modifiers to control the size and shape of the crystals.

Plaster blocks are usually cast with smooth faces of about 1/3 square meter and 75 to 100 mm thick. They are tongued and grooved to allow a smooth-surfaced wall, to be constructed using plaster "glue" to bond them together. The blocks have limited load-bearing capacity and are generally used for internal walls within framed buildings. In Europe there were three commercial operations using phosphogypsum for plaster blocks, but all have been closed or reverted to natural gypsum.

Plasterboard consists of a sandwich of gypsum between sheets of paper or cardboard. The thickness is about 10 mm, and sheets of about 2 m^2 are produced. The boards are used for internal walls or ceilings, usually nailed to a wooden frame. In Europe there is only one plasterboard plant using phosphogypsum. However, in Asia, notably in Japan, a large proportion of the plasterboard is based on phosphogypsum, which is often imported. Other plaster products, for example, spray plaster, tunnel linings, and dental products have been manufactured using phosphogypsum.

Most phosphate rocks, particularly of sedimentary origin, contain minor concentrations of uranium, and part of this passes to phosphogypsum. Uranium decays to radium, which in turn decays to the radioactive gas radon. Radon is released in very small quantities from plaster products. This is of greatest concern from plaster blocks, which contain a larger mass of plaster per unit of wall area. For buildings having limited ventilation radon concentrations have been detected at levels above those considered safe. This has been used as an argument against phosphogypsum building materials although similar levels occur naturally in certain locations.

11.5.3 Use as Cement Additive

Introduction of phosphogypsum as an additive to cement accounts for about 4 million tonnes per annum. Portland cement usually contains about 5% gypsum, which is added to control (retard) the setting time. Phosphate, fluoride, and organic impurities in the phosphogypsum are undesirable and should be reduced to acceptable levels. Material from double crystallization phosphoric acid processes is satisfactorily employed in Belgium and Japan.

A process for treating phosphogypsum from dihydrate processes to make it suitable for use as cement additive (and other purposes) has been described [29]. It consists of calcining the phosphogypsum to hemihydrate and then rehydrating it with addition of limewater, $Ca(OH)_2$. Recrystallization during dehydration releases the cocrystallized P_2O_5, and the lime converts the P_2O_5 to inert forms. The lime also converts fluorine compounds to inactive forms. Requirements for the process per tonne of treated gypsum are:

Quick lime (CaO)	55 kg
Fuel oil	45 liter
Electricity	15 kWh

As a variation in the process, the lime may be added to the gypsum before calcining, which eliminates fluorine evolution during calcining. The product may be granulated during rehydration for convenience in handling.

11.5.4 Agricultural Use

Small amounts of phosphogypsum are used as a filler or additive to compound fertilizers. Calcined gypsum is sometimes added to assist in granulation or to increase granule strength. In other cases the purpose may be to supply sulfur for agronomic reasons. Granular gypsum is available in some countries for use in bulk blends.

Gypsum is used in fairly large amounts on some soils to combat the effects of salinity or alkalinity or to reclaim soil that has been inundated by seawater. Clayey soils tend to retain sodium from salt water; use of gypsum replaces sodium with calcium. Gypsum is also a good source of sulfur for use on sulfur-deficient soils.

Some crops, such as groundnuts, benefit from soluble calcium in gypsum. Wet phosphogypsum is difficult to handle and apply; the cost of drying is an economic disadvantage that often leads to a preference for natural gypsum. In dry climates the phosphogypsum can be air-dried in the sun. Drying to about 6% moisture is sufficient to make it free flowing.

Despite the numerous uses mentioned above, only a small percentage of the phosphogypsum is actually used on a worldwide basis; in most cases it seems to be economically preferable to dispose of the byproduct in ponds, in other land disposal areas, or in the sea.

11.6 Utilization of Fluorine

Most phosphate rocks of the fluoroapatite - type contain a significant quantity of fluorine, usually 3%-4% F by weight. In some cases up to 60% of this can be evolved during the manufacture of wet-process phosphoric acid. The remainder of the fluorine is retained in the gypsum (depending mainly on the rock composition), and most of the remainder is in the filter acid [30]. The fluorine is evolved from various stages of phosphoric acid processes: from the reactor slurry surface, in the flash cooler, and in the concentration plant. In a dihydrate process the proportions are:

Slurry surface:	3% - 5%
Flash cooler:	8% - 10%
Concentration plant: (up to 45% P_2O_5)	15% - 20%

In hemihydrate or hemidihydate processes (producing 45% P_2O_5 acid at the filter) the proportions are:

Slurry surface:	12% - 15%
Flash cooler:	15% - 20%

In a typical case, about 50 kg of F is volatilized per tonne of P_2O_5, usually as SiF_4 or HF, or some mixture of the two. The compositions of the vapors emitted from the reaction/filtration section and the evaporator are different. During acidulation of phosphate rock, the fluoride is first converted to hydrogen fluoride, which subsequently reacts with active silica to form silicon fluoride:

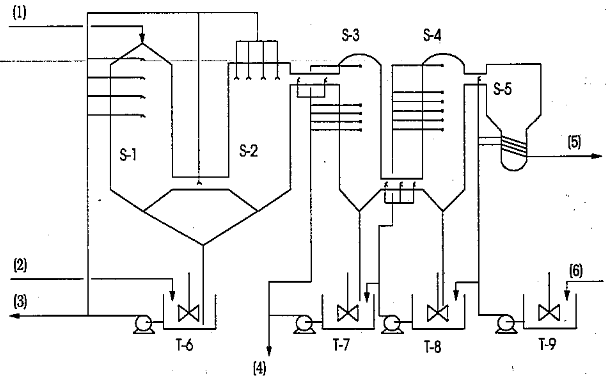
$$4HF + SiO_2 = SiF_4 + 2H_2O$$

This is partially emitted as vapor in preference to hydrogen fluoride because of its higher vapor pressure. The remainder reacts further to form fluosilicic acid, which remains in the product acid, or insoluble fluosilicates, which are removed in the filter cake.

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

If the silicon tetrafluoride vapor leaving the reaction section is washed with water, this reaction will take place in the scrubber also and insoluble silica will form. The silica will cause scaling and eventually plug the scrubber. Therefore, the usual procedure is to scrub with a dilute solution of fluosilicic acid, in which silica remains in colloidal suspension. A scrubber design, such as cyclone or venturi, that is virtually free of internal obstructions, which might become fouled, must be used in the first stage to remove the bulk of the fluorine. A second, highly efficient stage, such as a spray tower or tower with movable packing, removes most of the remaining traces of fluorine and avoids fouling (Figure 11.27). More dilute vapors such as air from the hood over the first filter stage and from the first filtrate separator can be introduced directly into the second-stage scrubber.

About two-thirds of the fluorine in the filter acid is volatilized when the acid is concentrated to merchant strength (50%-55% P_2O_5). Under the conditions of high temperature and reduced pressure obtained in vacuum evaporators, the fluosilicic acid decomposes and both silicon tetrafluoride and hydrogen fluoride are evolved.



(1) - GASES EX FLASH COOLER
(2) - MAKE-UP FSA
(3) - CONTAMINATED FSA TO REACTOR
(4) - TO FIRST STAGE STORAGE TANK
(5) - C/T GASES TO FLASH COOLER CONDENSER
(6) - LIQUOR FROM FINAL STAGE COOLER

Legend:
S-1 Venturi scrubber
S-2 Droplet separator
S-3 First stage scrubber
S-4 Second stage scrubber
S-5 Droplet separator
T-6 - T-9 Seal tanks

Figure 11.27. Norsk Hydro Licensing's Two-Stage System for Fluorine Scrubbing.

$$H_2SiF_6 = 2HF + SiF_4$$

However, at acid concentrations of less than 50% P_2O_5, more silicon tetrafluoride is evolved (creating silica in circulated fluosilicic acid) owing to the relationship between its vapor pressure and that of hydrogen fluoride.

At acid concentrations of 50%-55% P_2O_5, the molar ratio HF : SiF_4 is approximately 2, while at higher acid concentrations hydrogen fluoride predominates [30]. There is least danger of problems with silica deposition in the scrubber if the HF : SiF_4 ratio is at least 2, since the only product of scrubbing will be fluosilicic acid, while it is undesirable to allow it to exceed 2 by too much, since the product will then contain free hydrogen fluoride. Because the scrubbing solution used is fluosilicic acid, it is desirable to maintain a high concentration from the point of view of transport costs and use of the product. To avoid dilution by the water from the evaporator, the scrubber, which is interposed between the evaporator and the condenser, must be operated at a high temperature at which water will not significantly condense. In practice, this sets a maximum of about 18%-22% H_2SiF_6 on the concentration of the scrubbing medium because at higher concentrations the equilibrium vapor pressures of hydrogen fluoride and silicon tetrafluoride are too high for efficient fluorine removal.

The void spray tower type of scrubber, originally developed by Swift and Co. and further developed by Fisons and others, is often used. The scrubber is conveniently mounted atop the evaporator and receives vapors from the entrainment separator, which returns any droplets or mist particles of phosphoric acid to the acid system. Fluorine scrubbers typically operate at an efficiency of 90%-93%; the remainder of the fluorine vapors is largely removed in the condenser into which the vapors subsequently pass. The condenser is usually of the barometric direct-contact type, but after cooling the water must be directed to a wastewater treatment installation to remove the contamination.

Numerous processes for recovering saleable fluorine compounds have been proposed and developed experimentally; some of these processes are used on an industrial scale. A description of all of these processes is beyond the scope of this manual.

Fluorine is usually recovered in the form of an aqueous solution of fluosilicic acid, H_2SiF_6. The concentration may be as high as 20%-25%. In some countries the fluosilicic acid is used directly for "fluoridation" of municipal water supplies to prevent tooth decay. The acid is shipped to various municipalities in rubber-lined railcars. Salts of fluosilicic acid, such as sodium, potassium, and ammonium fluosilicates, have various uses and can be readily produced from the acid. Sodium fluosilicate is used for fluoridation of municipal water supplies, but fluosilicic acid is generally preferred.

Processes have been developed for making aluminum fluoride (AlF_3) and cryolite (Na_3AlF_6) from fluosilicic acid, which are used by the aluminum industry in substantial quantities. However, these materials must be quite pure for this purpose; in particular, the silicon and phosphorus must be very low. This requirement complicates production from byproducts of the phosphate industry. Calcium fluoride may be produced and used instead of natural fluorspar for production of hydrogen fluoride (HF), which is the basic material for producing numerous organic and inorganic fluorine compounds or for metallurgical purposes [31]. There are also processes to produce hydrofluoric acid solutions or anhydrous hydrogen fluoride from fluosilicic acid solutions.

In general, the economics of producing chemical-grade fluorine compounds from byproduct fluosilicic acid is marginal to unfavorable for small phosphoric acid plants. However, large plants may find recovery profitable. Where several phosphoric acid plants are operating within an economical shipping distance, the crude fluosilicic acid may be shipped to a central point for production of refined fluorine compounds. For more details on fluorine use, see reference [30].

11.7 Uranium Extraction

Uranium occurs in most phosphate rocks, but its concentration varies from deposit to deposit. Some sedimentary rocks show notably higher concentrations than most igneous rocks. The most uranium-rich rocks found to date are those of Florida (up to 300 ppmw U), Morocco (up to 230 ppmw U), and Jordan (up to 240 ppmw U) [32,33]. In comparison, conventional uranium deposits such as pitchblende typically have a uranium content of 1,000-3,000 ppmw. When the phosphate rock is acidulated, up to 80% or 90% of the uranium passes into solution in the phosphoric acid. The exact amount of PR acidulated depends on its characteristics and the parameters of the phosphoric acid process employed. Examples of the uranium contents of different phosphate rocks and of phosphoric acids produced from them are indicated in Table 11.29.

The first commercial plant to recover uranium by precipitation in a sodium phosphates operation was built in Illinois, U.S.A. in 1952. Subsequently, in 1955 IMC built a commercial plant based on solvent extraction in Florida; another was operated by U.S. Phosphoric Products.

In the early 1970s, several factors stimulated new interest in uranium recovery. Among these factors were the growth of nuclear programs in the United States

Table 11.29. Typical Uranium Contents of Phosphate Rocks and Phosphoric Acids (30% P_2O_5)

Rock Source	U_3O_8 ppmw in Rock	U_3O_8 ppmw in Acid
Algeria	110-140	130
Brazil	80	80
Israel	50-150	165
Jordan	120-150	165
Morocco	90-140	140
Tunisia	50-100	80
Florida	180-150	190
N. Carolina	80	80

and other countries, the steep and continuing increase in the cost of conventional hydrocarbon fuels since 1973, and a significant increase in the capacity of individual phosphoric acid plants. The price of uranium peaked at about US $95/kg in mid-1978, after having remained static at US $15.5/kg for several years until 1975.

In the early 1980s eight commercial plants in the United States and one in Canada were recovering uranium from wet-process phosphoric acid. At about the same time, a commercial uranium facility was constructed at the Chimie Rupel subsidiary of Societe de Prayon in Belgium, and others were planned in France by Rhone-Poulenc and APC, using their own technologies, and in Japan by a consortium headed by the Power Reactor and Nuclear Development Corporation, using its own process.

The technology for the commercial plants is based on solvent extraction although other methods have been developed. Much of the development work on solvent extraction was done by the U.S. Government-owned Oak Ridge National Laboratory (ORNL) in Tennessee [34,35]. Most of the processes use either octyl pyrophosphoric acid solvent (OPPA), as in the earliest processes in the United States, or various combinations of solvents, developed later by ORNL, di(2-ethylheksyl) phosphoric acid (DEPA), trioctyl phosphine oxide (TOPO), and octylphenylphosphoric acid (OPAP).

The ORNL research program resulted in the development of two basic processes. These processes are similar as far as equipment is concerned, and they differ only in the solvent used [36]. Uranium extraction is achieved in a process that comprises two cycles (Figure 11.28). In the first cycle, uranium is extracted from phosphoric acid with an organic solvent in five stages and then stripped from this solvent with fresh phosphoric acid.

Because the phosphoric acid from the stripping section is more concentrated in uranium than the original acid, it passes to the second cycle where extraction with an organic solvent is again performed to separate the uranium, which is finally recovered as U_3O_8. According to the process, the solvent used in the second cycle is the same as that used in the first cycle and is either a synergistic combination of DEPA and TOPO in kerosene or a mixture of mono- and dioctylphenyl phosphoric acid (OPPA), also in kerosene [37].

The different commercial processes can be generally divided into three categories:

1. Those using only OPPA as solvent included the IMC and U.S. Phosphoric Products processes, but recently only Gardinier, Inc., has used this extractant.
2. Those using a DEPA/TOPO mixture include the IMC/Prayon, Freeport Uranium Recovery Co., Wyoming Mineral Corp., and COGEMA-APC processes.
3. Those in which a DEPA/TOPO mixture is used in one cycle and OPPA in another, such as the UNC Recovery Corp. and the Earth Sciences, Inc., processes. Several other companies have also considered processes of this type.

UNC Recovery Corp. developed a single-stage process that uses an alkyl pyrophosphoric acid extractant; this process was intended for commercial use by Prodeco Inc., a wholly-owned subsidiary.

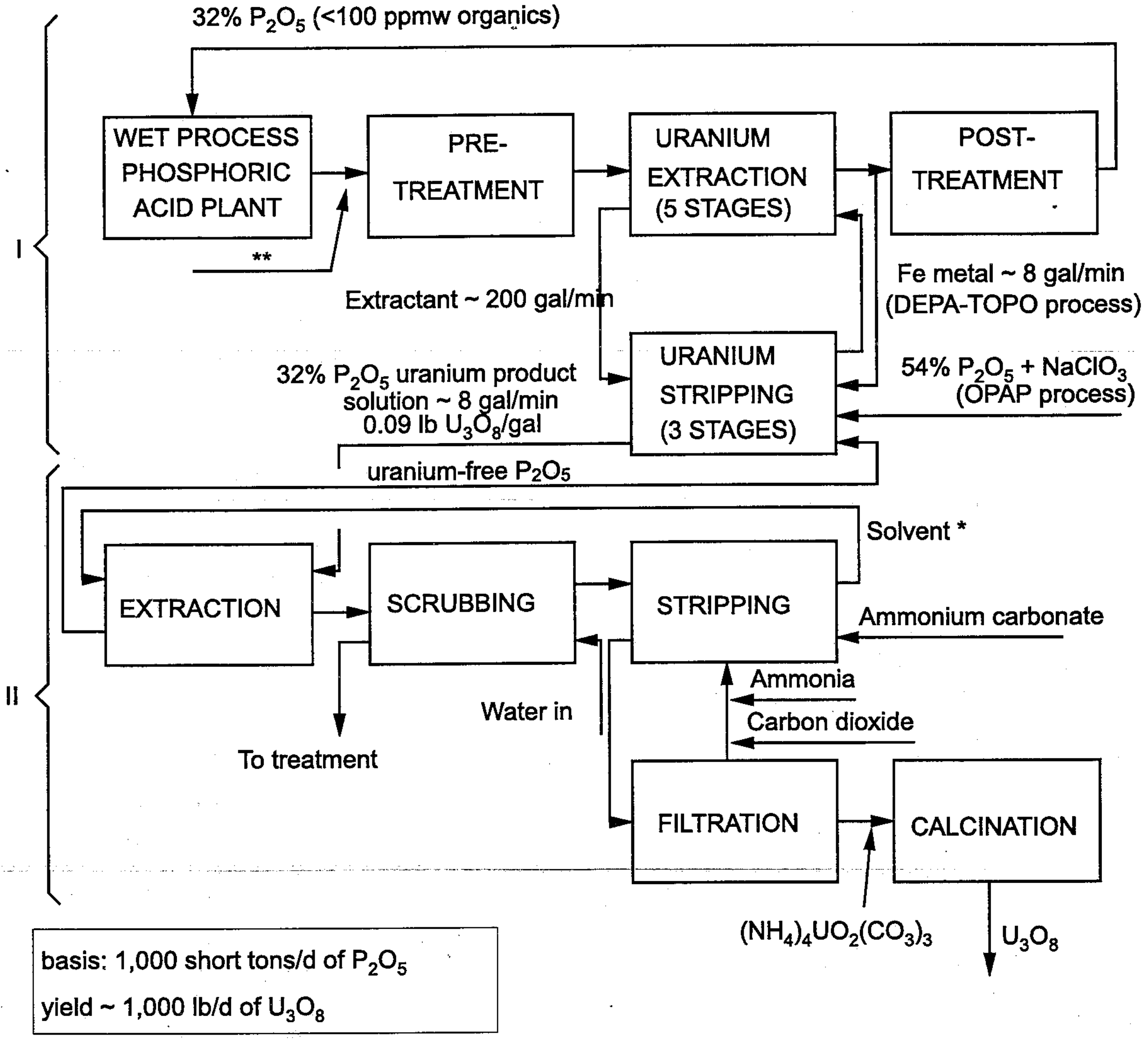
11.8 Purification of Phosphoric Acid

For most fertilizer production processes, purification of wet-process phosphoric acid is not necessary. However, there are two common fertilizer uses that may call for partial purification:

a. "Merchant-grade" acid that is shipped by rail, barge, or ocean vessels and is often stored at shipping and receiving terminals should be purified sufficiently so that formation of insoluble precipitates (sludge) during shipping and storage is minimized.

b. Phosphoric acid to be used in the production of liquid fertilizers, such as ammonium polyphosphate solution, sometimes requires partial purification to prevent formation of precipitates upon ammoniation or during storage of the ammoniated solution.

Although ammonium polyphosphate sequesters most of the common impurities, excessive amounts of some impurities (especially magnesium and organic matter) cause precipitate formation. Superphosphoric acids usually do not form sludge, but magnesium and titanium have been known to cause sludge-forming precipitates.



* - Solvent: 0.3 M DEPA + 0.075 M TOPO in refined kerosene

** - 32% P_2O_5, 400 gal/min (0.0017 lb U_3O_8/gal)

I - First cycle

II - Second cycle

Figure 11.28. Flow Diagram of the Oak Ridge Uranium Extraction Process.

A major fraction of sludge in most merchant-sludge acids is the compound $(Fe,Al)_3KH_{14}(PO_4)_8 \bullet 4H_2O$. It precipitates slowly over a period of several weeks; therefore, long storage periods are required to ensure reasonable completion of the precipitation reaction.

In the production of sodium tripolyphosphate and other condensed phosphates for use as builders in detergents, the whiteness of the product and all metal ions (without sodium and potassium) are the principal concern. For use in human food processing and animal feed supplement production, the content of toxic impurities must be diminished to insignificant levels. These include fluorine, arsenic and any heavy metals that are present in the phosphate rock and sulfuric acid. When purified acid is required only for the production of phosphates, impurity removal is facilitated by neutralization, since many impurities are rapidly precipitated as insoluble phosphates. When it is not permissible to neutralize the acid, it is necessary to rely on physical treatment such as solvent extraction or ion exchange, with or without chemical treatment. Phosphoric acid manufacturers purifying phosphoric acid for sale have inclined towards this type of treatment, usually based on solvent extraction. In most cases when chemicals are used (e.g., in the case of removing arsenic), they react with the impurity alone and do not chemically alter the phosphoric acid.

11.8.1 Removal of Organic Materials

In the oxidizing and dehydrating environment of the attack section, organic impurities tend to be decomposed to carbon; if the rock has a relatively high organic content, the resultant acid will be black. Two methods of removing this discoloration include calcining the rock, which destroys a good proportion of the organic matter, and treating the acid with active carbon, with or without a flocculating agent. Conducting the latter treatment at a moderate temperature (60°-80°C) increases the efficiency of organics removal to the extent that it may be possible to avoid calcining some high-organic rocks. Other techniques that have been proposed rely on using a special flocculating agent or hydrogen peroxide in the presence of a mixed, metal oxides catalyst.

11.8.2 Defluorination

Even if wet-process phosphoric acid is concentrated to the superphosphoric acid stage, it still contains too much fluorine for production of feed phosphates although the other impurity levels may be acceptable for animal feed. For animal feed preparation, it is desirable that the phosphorus: fluorine ratio should be at least 100 P : 1F, but normal wet-process phosphoric acid has a P : F ratio of between 15 : 1 and 54 : 1, depending on its concentration, the composition of the rock from which it is made, and its production conditions.

Several procedures have been proposed to remove fluorine from phosphoric acid based on volatilization or chemical precipitation, in the latter case with or without other impurities. A commercial technique developed by Occidental Chemical Co. involves feeding silica and steam into hot 54% P_2O_5 phosphoric acid and removing the volatilized fluorine compounds by scrubbing with fluosilicic acid.

11.8.3 Solvent Processes

Precipitation – In this type of process, a large amount of water-miscible organic solvent is added to the phosphoric acid, which causes settling of many of the dissolved impurities out of solution and enables the acid-solvent mixture to be separated.

Particularly, if methanol is used, alkali metal or ammonium ions must be present in sufficient quantities to convert the sludge impurities into less-soluble double salts. Other solvents that could be used include acetone, methyl ethyl ketone, other lower alcohols, and dioxane.

Various processes of this route have been reported; these processes include Chemische Fabrik Budenheim, TVA (methanol/ammonia), Goulding (methanol/potassium dihydrogen phosphate), and Rupel (methanol/potassium chloride).

The inconvenience of this type of process is that the phosphoric acid must be separated from a large volume of solvent, usually by stripping, which is expensive.

Extraction – The alternative method of purifying phosphoric acid by means of organic solvents is liquid/liquid extraction; crude phosphoric acid is brought into countercurrent contact with a partially or substantially water-immiscible solvent in a series of mixer-settlers. In general, the partition coefficient of phosphoric acid between the aqueous solution and the solvent is very unfavorable; thus the crude acid is usually concentrated before processing and only a relatively small proportion of the acid is extracted. The remaining partially depleted raffinate, containing most of the impurities, is usually disposed of in fertilizer manufacture.

Depending on the degree of purification required, the extract may be washed with purified phosphoric acid and is then usually contacted with water, into which the majority of the acid passes. The end product is a somewhat weaker but much purer acid than the original crude acid and a depleted solvent phase, which is recycled.

In the Prayon process (Figure 11.29), acid purification is carried out using a mixed organic solvent, diisopropyl ether (DIPE) and tri-n-butyl phosphate (TBP) after pretreatment of the acid to remove these impurities that affect the coefficient of distribution between the organic and aqueous phase (F, SO_4 and As). Acid purification involves four operations: solvent extraction; re-extraction; separation of solvent from purified acid; and color clarification. Concentration follows purification. Four volumes of solvent (50%-95% DIPE/5%-50% TBP by volume) are contacted countercurrently with one volume of acid at 5°-25°C. This yields two phases; one is an aqueous raffinate, containing most of the impurities, which is stripped in an evaporator to release, for recycle, any ether it contains and to provide a raffinate return acid stream that is sent to fertilizer-grade acid storage. The second phase is organic and contains the solvent and acid. The purity of acid in the organic phase is further increased by washing this phase with water.

Re-extraction of the acid is favored by a slight temperature increase and involves countercurrent washing with water to produce a purified acid. The final steps in the process are stripping to remove residual traces of solvent, addition of a solid chemical absorbent, filtration

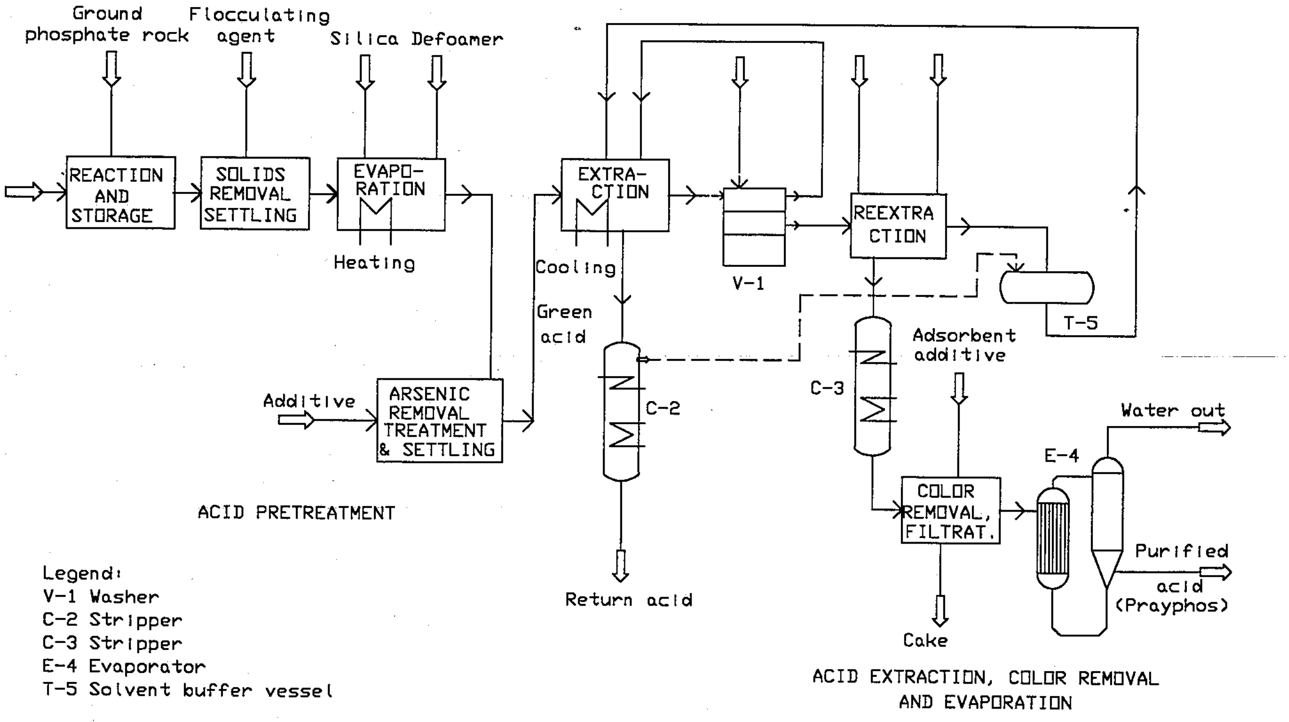


Figure 11.29. Prayon's Process for Phosphoric Acid Purification.

to remove any organic matter (which gives a yellow discoloration), and concentration (which is effected in a vacuum concentrator). The resultant technical acid, Prayphos P, after defluorination gives a food-grade acid, Prayphos P5. A pharmaceutical grade is also possible.

The firm, Albright and Wilson, is an early pioneer of solvent-extraction technology in the United Kingdom. Its first designed plant (40,000 tpy P_2O_5) began operation in 1976. The company's second plant (90,000 tpy P_2O_5), intended mainly for sodium tripolyphosphate (STPP) manufacture, began operation in 1979. The third plant, which came into operation in 1987, produces food-grade phosphoric acid. All three plants are at Whitehaven, where a wet-process phosphoric acid plant is located. The first U.S. plant based on the solvent-extraction process began production in 1990 at Aurora, N.C. Owned by Purified Acid Partners, this unit is a joint venture of Texasgulf Inc., Albright and Wilson Ltd., and Olin Corporation. The construction costs for the unit, which has a capacity of 109,000 tpy P_2O_5 of purified acid, amounted to US $40 million [38,39].

The industrial phosphoric acid used in Aurora requires no purification for organics or sulfate removal, but fluorine must be removed by further evaporation in the presence of active silica.

In the Albright and Wilson process the impure acid is concentrated to the level of 74%-80% of total acidity (% H_3PO_4 + % H_2SO_4, 54% - 57% P_2O_5) and then clarified. Next, it is contacted with 1.2-1.6 parts by weight of methyl isobutyl ketone (MIBK) in a reactor to give an organic extract of phosphoric acid while leaving most of the impurities and a proportion of the P_2O_5 in the aqueous phase or raffinate (Figure 11.30).

Multistage countercurrent extraction is carried out in a vertical cylindrical column equipped with rotating-disc agitators and stator rings. Acid enters near the top of the column and solvent near the bottom; the acid-laden solvent leaves the top of the column and a dense aqueous phase is discharged at the bottom. The organic extract, which contains 50%-60% (by weight) of P_2O_5, is scrubbed with a relatively pure aqueous solution of phosphoric acid in a multistage countercurrent scrubbing system, using 0.3-0.5 units of P_2O_5 for each unit of P_2O_5 in the extract.

The used scrub liquor passes back to the first stage, the extraction column, where it enters near the top and emerges in the aqueous impurity-containing raffinate. The raffinate is then stripped to recover the MIBK, and the impure phosphoric acid is used in the phosphatic

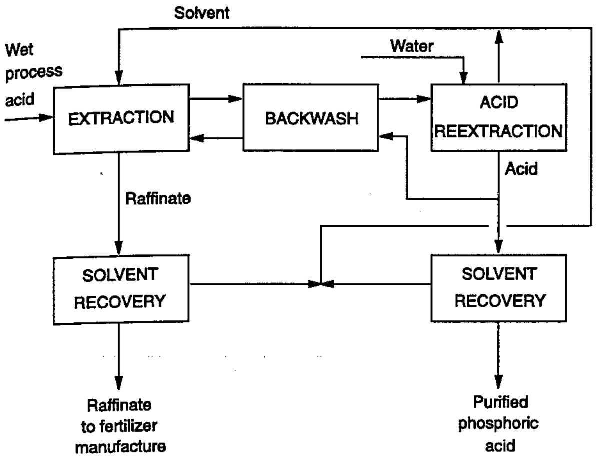


Figure 11.30. Purification of Wet-Process Phosphoric Acid by Solvent Extraction.

fertilizers. About 0.4 tonne of P_2O_5 is found in the raffinate for each tonne of P_2O_5 in the impure feed acid. The solubility of MIBK in phosphoric acid is low, less than 2%, so that little steam is required for stripping. The scrubbed organic extract is re-extracted with water in a two-stage system to give the required purified phosphoric acid product, which also needs stripping for solvent removal. In addition, evaporation is necessary to concentrate the pure acid for sale. The MIBK solvent, after P_2O_5 recovery, is recycled to the extraction stage. However, the solvent gradually accumulates impurities, and occasionally a quantity is removed from circulation for distillation; which consists of evaporation and condensation without reflux.

When there are no possibilities to use raffinate in fertilizer production, it must be strongly acidified with sulfuric acid before additional extraction; most of the P_2O_5 is driven into the solvent phase. Impurities remain in the acidified aqueous phase, which is neutralized with lime before disposal as waste.

11.9 Production of Phosphoric Acid Using Acids Other Than Sulfuric

Phosphate rock can be dissolved by several organic and inorganic acids to produce phosphoric acid. The use of nitric acid for this purpose is described in Chapter 13. Commercial nitrophosphate processes produce phosphoric acid that contains nitrates; hence, these processes are used to produce compound NP or NPK fertilizers. It is technically feasible to produce phosphoric acid that is substantially free of calcium or nitrates by separation methods involving solvent extraction. One such process using tertiary amyl alcohol as the solvent was developed in Finland and described by Lounamaa [40]; however, no commercial use has been reported.

Several processes using hydrochloric acid have been developed or patented, but only that developed by the Israel Mining Industry (IMI) has been used commercially [41]. The IMI process has been described in a UNIDO publication [42]. A brief description of the main stages of the process follows.

1. Dissolution of phosphate rock by hydrochloric acid, which results in an aqueous solution of calcium chloride and phosphoric acid;
2. Liquid-liquid contacting in a number of solvent extraction steps to obtain a solution of substantially pure phosphoric acid; and
3. Acid concentration to obtain 95% H_3PO_4 (69% P_2O_5).

The raw materials and reagents used are as follows:

1. Phosphate rock (any commercial grade). The P_2O_5 recovery is more than 98%.
2. Hydrochloric acid for acidulation can be used as a solution of 20% HCl or higher or in gaseous form by combining absorption with reaction. For economic reasons, concentrated acid is preferred because most of the water accompanying the acid must be evaporated in a later stage of the process. HCl consumption is dependent on the composition of the rock. Acid consumption for Florida rock of 34% P_2O_5 is about 2 tonnes HCl (calculated as 100%) per tonne of P_2O_5.
3. Solvent. Several solvents can be used for extraction. Those preferred are technical isoamyl alcohol (IAA), n-butanol, or a mixture of both. Solvent makeup is 4 kg/tonne P_2O_5.
4. Process water.
5. Auxiliary reagents. Depending on the type of rock and the method of separation of insoluble residue from dissolution liquor, minor quantities of filter aids or flocculating agents may be required.

11.9.1 Dissolution and Mechanical Separation of Insoluble Residue

The dissolution of phosphate rock is essentially decomposition of fluorapatite by HCl according to the following equation:

$$Ca_{10}F_2(PO_4)_6 + 20\ HCl \rightarrow 2\ HF + 6\ H_3PO_4 + 10\ CaCl_2$$

Other acid-soluble components of the rock, such as $CaCO_3$, decompose simultaneously.

The rock is dissolved by hydrochloric acid. The insoluble residue amounts to a small percentage of the rock feed and consists mainly of silica, silicates, and insoluble organic matter. The insoluble matter can be separated from the dissolution liquor by filtration, followed by washing of the cake or by sedimentation in a thickener, followed by countercurrent decantation washing of the sediment. The choice of the proper method of separating solids depends on the character of the insoluble residue and on economic considerations. The dissolution liquor is fed to the subsequent section.

Figure 11.31 shows a typical flowsheet of the HCl phosphoric acid process.

11.9.2 Liquid-Liquid Contacting

This stage consists of several operations: extraction, purification, washing, and stripping.

Extraction – Extraction is performed by a countercurrent contact of dissolution liquor with the selected solvent. Phosphoric acid transfers selectively from the aqueous dissolution liquor to the organic solvent phase; the resultant extract and calcium-chloride brine (raffinate) contain substantially all the impurities, such as fluorine and iron.

Purification – The solvent extract, which contains small amounts of Ca^{++} and some other impurities, is purified further by countercurrent contact with an aqueous phase.

Washing – The acid of the purified extract is transferred into water. The solvent that leaves this stage is virtually free of acid.

Stripping – The acid-free solvent stream extracts the residual acids present in the raffinate and is recycled to extraction. The spent calcium-chloride brine is stripped by steam to recover any dissolved solvent.

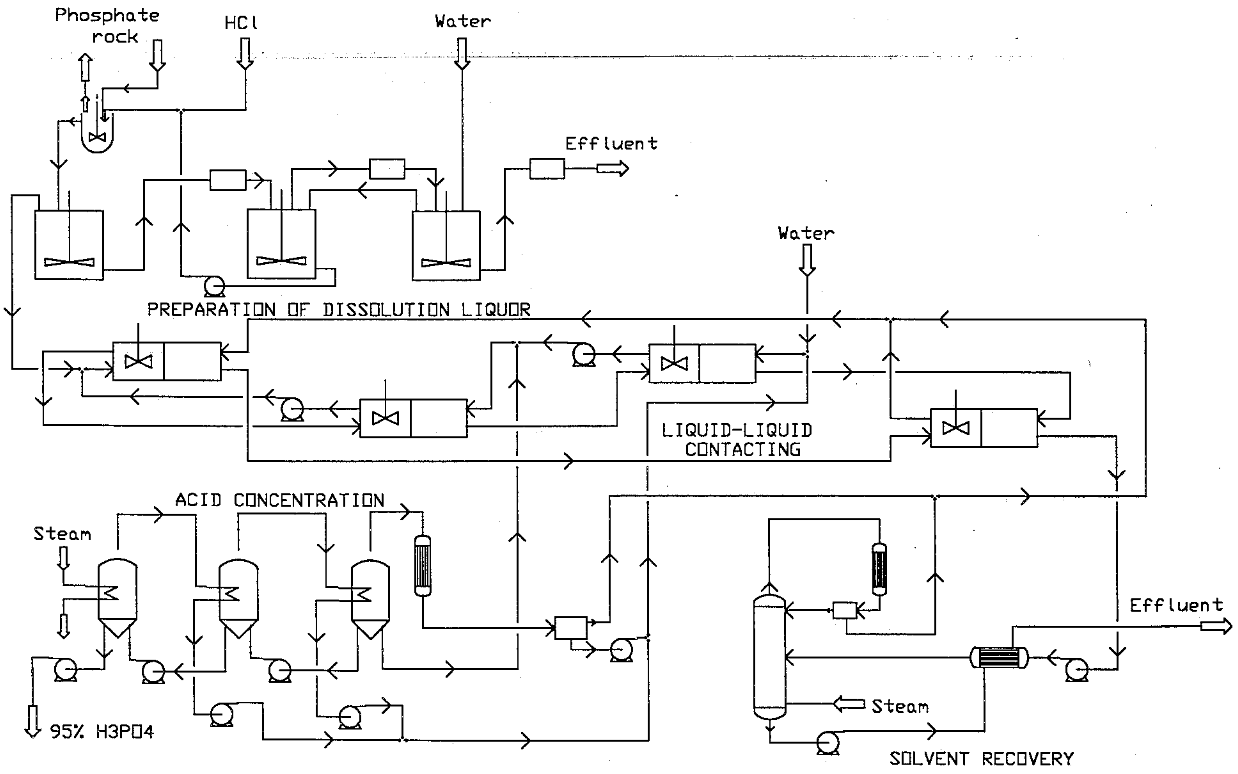


Figure 11.31. Flowsheet of the IMI Phosphoric Acid Process (HCl-Route).

11.9.3 Acid Concentration

The dilute aqueous acid emerging from washing consists of an aqueous solution of H_3PO_4, HCl, and some dissolved solvent. This solution is concentrated to 95% H_3PO_4, which is the end product. The separation of H_3PO_4 from other components of the solution is essentially a distillation operation; this permits a full recovery of the minor quantity of solvent that is dissolved in the aqueous phase on washing and of the HCl, both maintained in closed cycle in the process.

The main requirement of this operation is heat economy, and a multiple-effect evaporator is used to achieve this. The amount of steam used is less than 0.5 tonne/tonne of water evaporated. The complete absence of dissolved solids in the solution being concentrated permits the maintenance of high heat-transfer coefficients. All of the volatile streams from the system are recycled to the previous steps of the process.

11.9.4 Solvent Recovery From Spent Calcium Chloride Brine

The residual brine leaving the stripping stage contains a small amount of dissolved solvent, which must be recovered for economic reasons. The solvents used form an azeotrope with water on rectification so that the simplest system to be applied is steam stripping. The costs of this operation are reduced by the recovery of heat from the brine leaving the system. The recovered solvent is recycled to the liquid-liquid contacting section, and the brine is discarded.

11.9.5 Construction Materials

In those parts of the process where solvent is present, acid-resistant construction materials that are also solvent resistant are required. These parts included the liquid-liquid contacting section and a part of the sections where acid is concentrated and where solvent is recovered from the brine.

Rubber-lined steel is the least expensive material for the dissolution and mechanical separation of insoluble residue. In the liquid-liquid contacting section, rigid polyvinyl chloride (PVC) is very satisfactory. In the parts of the system operating at elevated temperatures, impervious graphite can be used for the heat exchangers. Other construction materials include thermosetting resins and lined steel.

11.9.6 Quality of HCl-Route Phosphoric Acid

HCl-route phosphoric acid is much cleaner than wet-process acid, and its analysis is similar to that of thermal acid (Table 11.30). By making slight adjustments in the process, food-grade acid can be obtained. The composition of wet-process acid is dependent on the rock as raw material; whereas, almost the opposite is true for HCl-route phosphoric acid.

Table 11.30. Comparison of Analysis of HCl-Route Phosphoric Acid and Wet-Process Acid

Components	HCl Route, %	Wet Process, %
H_3PO_4	95	69-77
P_2O_5	69	50-56
Heavy metals as Pb	0.002-0.01	0.5-1.5
CaO	0.008-0.04	0.014-0.35
Fe_2O_3	0.003-0.05	0.86-2.3
Al_2O_3	traces	0.3-2.45
Mg	traces	0.0-0.8
H_2SO_4	traces	1.0-5.6
SiO_2	traces	0.04-0.10
F	traces	0.25-1.10

11.9.7 Capital Investment

The capital investment required for a plant may vary from location to location. However, for comparative purposes, it will be noted that the capital cost for the HCl process is about 35% higher than for the standard (H_2SO_4) wet process when production of the acids is excluded.

If HCl were available as a byproduct from another process, the capital cost would be lower than for a wet-process plant including H_2SO_4 production facilities. However, when using byproduct HCl, the scale of the operation would be limited by the amount of byproduct HCl available.

11.9.8 Process Requirements

Operating costs may be estimated from the process requirements, which are given in Table 11.31 for a plant of 100-tpd capacity.

Table 11.31. Process Requirements for the HCl-Based Process

Inputs	Units/t of P_2O_5	Consumption
Phosphate rock (34% P_2O_5)		3.0
HCl (as 100%)		2.0
Solvent (IAA)	kg	4.0
Steam		4.3
Electric power	kWh	100
Cooling water	m^3	165.5
Process water	m^3	3
Labor	workhours	1.0

If the plant is located adjacent to the sea, disposal of $CaCl_2$ into the sea may be acceptable and economical; for an inland location disposal may be difficult and expensive.

HCl-route phosphoric acid has certain disadvantages as compared with wet-process acid. Its production is economic only in places where HCl is available or where it can be produced at a moderate price. Transport of HCl in the form of an aqueous solution of perhaps 33% HCl is possible only in pipes or railcars lined with rubber, PVC, or similar materials.

However, HCl-route phosphoric acid has some advantages over wet-process acid. Unlike wet-process acid, it contains no scale-forming components, and its composition and quality are practically independent of the type of phosphate rock used. Superphosphoric acid (70%-72% P_2O_5) can easily be produced from HCl-route phosphoric acid.

HCl can be used where it is available as a byproduct. This is important for developing countries producing NaOH, where there is no captive market for the chlorine that is produced simultaneously. Byproduct hydrochloric acid is sometimes available from other sources and may even create disposal problems. In such cases the production of phosphoric acid by the acidulation of phosphate rock with hydrochloric acid can be advantageous if the quantity of the byproduct is adequate for an economical scale of operation and disposal or use of the calcium chloride brine is economically feasible.

An interesting possible source of hydrochloric acid is through calcination and hydrolysis of magnesium chloride according to the following equation:

$$MgCl_2 + H_2O = 2HCl + MgO$$

Magnesium oxide could be useful for production of refractories.

Another possible source of hydrochloric acid is from the production of potassium phosphate from phosphoric acid and potassium chloride, which is described in Chapter 15.

At present the only plants using the HCl process are relatively small ones, and most of the product is used to make industrial phosphates rather than fertilizers.

11.10 Phosphoric Acid Production by the Electric Furnace Process

The first step in the production of furnace acid is to produce elemental phosphorus in an electric furnace (Figure 11.32). Phosphate nodules or other lump

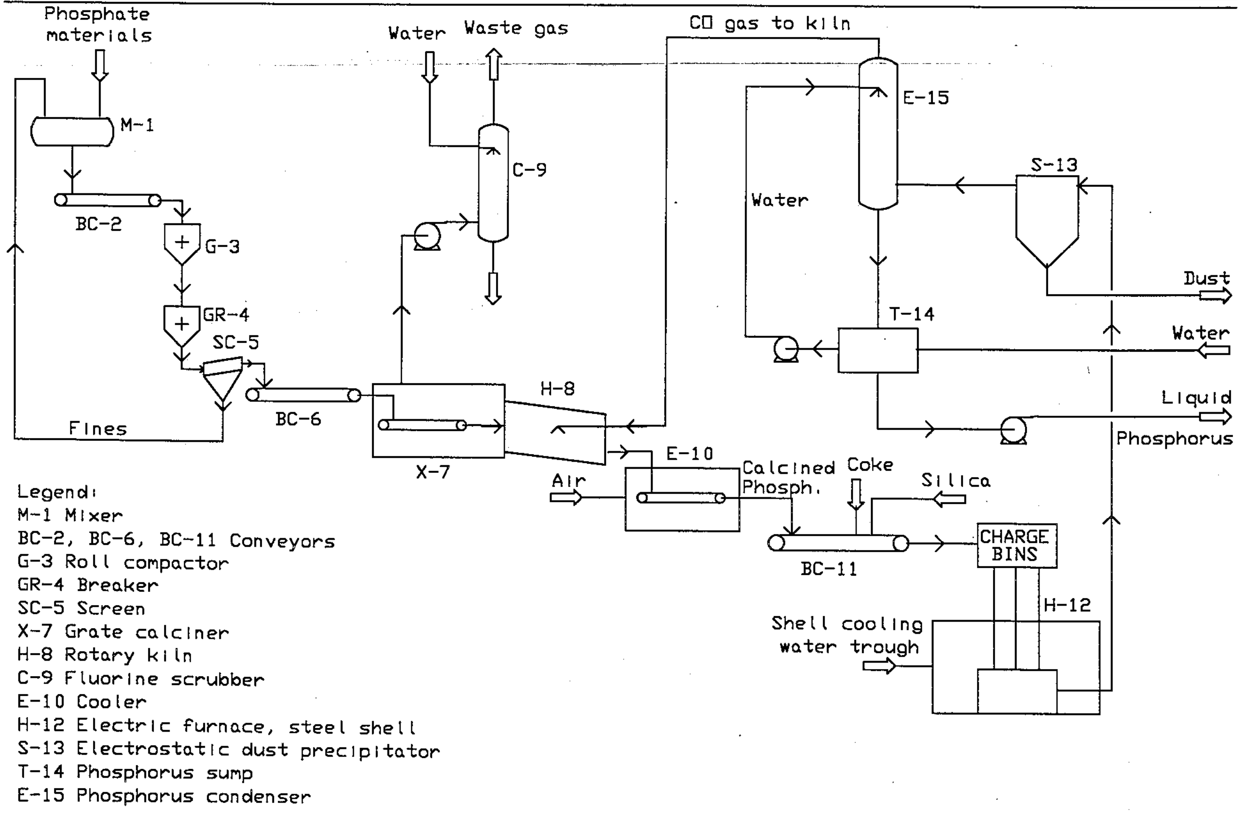


Figure 11.32. Manufacture of Elemental Phosphorus.

phosphate material, silica pebble, and coke are mixed and fed to the furnace. The electric current that is supplied to the furnace through carbon or graphite electrodes fuses the rock and silica, and the carbon in the coke reduces the phosphate. A mixture of phosphorus vapor and carbon monoxide gas is withdrawn continuously from the furnace. The phosphorus is condensed to a liquid that is converted to phosphoric acid in a separate plant, often located far from the phosphorus plant. Molten calcium silicate slag and an iron-phosphorus compound known as ferrophosphorus are tapped from the furnace periodically. The following equation represents the principal reaction in the furnace:

$$Ca_{10}F_2(PO_4)_6 + 15\ C + 6\ SiO_2 \rightarrow 1.5\ P_4 + 15\ CO + 3(3CaO \bullet 2SiO_2) + CaF_2$$

One advantage of the furnace process is its ability to use low-grade phosphate rock provided that the principal impurity is silica. Iron oxide and alumina are much less objectionable in the furnace process than in the wet process. Siliceous phosphate rock containing about 24% P_2O_5 is used in several plants; such rock may be obtained at a very low cost in some locations. Rock containing as much as 7% Al_2O_3 is acceptable.

If lump or pebble rock of suitable size (about 0.6-4.0 cm) that is resistant to decrepitation on heating is available, the cost of agglomerating the charge may be avoided. However, such rock is seldom available; therefore, the rock usually is agglomerated and calcined or sintered before charging it to the furnace. Carbon monoxide gas, which is a byproduct from the furnace, is the usual fuel for the calcination. Even so, this step is expensive.

The recovery of P_2O_5 as elemental phosphorus usually is in the range of 86%-92% of that charged to the furnace. The loss of P_2O_5 in the slag is about 3%. From 2%-8% of the P_2O_5 charged is recovered as ferrophosphorus, which contains about 23% phosphorus, 70% iron, and small amounts of manganese, silicon, and other metallic elements, depending on the charge composition. The amount of ferrophosphorus formed depends on the iron oxide content of the charge. The ferrophosphorus is sold to the steel industry, but the income only partially compensates for the loss of phosphorus production.

Of the phosphorus recovered as elemental phosphorus, about 5% is in the form of sludge, even after a series of settling steps to separate sludge from clean phosphorus. This sludge phosphorus may be recovered by burning it separately to produce impure phosphoric acid, by distillation, or by dewatering and returning it to the furnace.

The main disadvantages of the furnace process are the relatively high capital cost of the plant and the scarcity of locations where low-cost electricity is available. For this reason the electric furnace process is used almost exclusively to produce phosphorus and phosphoric acid for industrial chemicals, insecticides, detergents, and food or animal feed additives.

Production of phosphoric acid from elemental phosphorus is relatively simple. It is carried out by burning liquid elemental phosphorus in air and hydrating the resulting P_2O_5 to H_3PO_4. A diagram of a typical plant is shown in Figure 11.33. All the process equipment is made of stainless steel, usually type 316. The overall reaction is:

$$P_4 + 5\ O_2 + 6\ H_2O \rightarrow 4\ H_3PO_4$$

Typical process requirements per tonne of P_2O_5 produced as phosphoric acid, assuming 86% overall recovery for a plant of about 100,000 tonnes P_2O_5/year capacity, are given in Table 11.32.

Fuel consumption is negligible – about 1.2 million kcal, depending on efficiency of use of byproduct carbon monoxide gas.

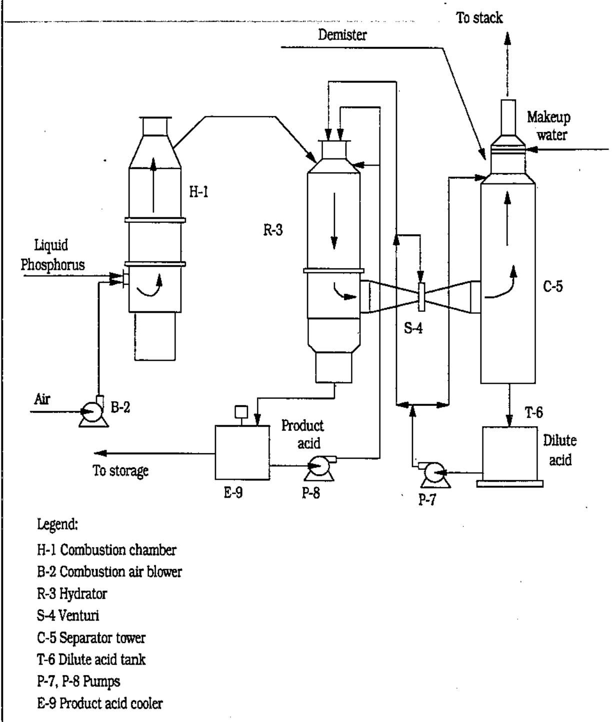


Figure 11.33. Manufacture of Phosphoric Acid From Elemental Phosphorus.

Table 11.32. Consumption Figures for Phosphoric Acid From the Electric Furnace Process

Inputs	Units (per tonne of P_2O_5)	Consumption
Phosphate rock (31.2% P_2O_5)	t/t	3.73
Silica rock, 95% SiO_2	t/t	1.1
Coke, 86% C	t/t	0.6
Carbon/graphite electrodes	kg/t	25
Electric power	MWh/t	6.7
Cooling water	t/t	110
Steam	t/t	1
Labor	workhours/t	4

If phosphate rock is available that is satisfactory for use without agglomeration and calcining, the plant cost would be 25%-30% lower, maintenance and labor costs would also be 25%-30% lower, and fuel requirements would be virtually eliminated. The byproduct carbon monoxide gas from the furnace would be more than sufficient for drying coke, silica, and rock. Some rocks that have been used successfully in electric furnaces without agglomeration, calcining, or sintering are screened Florida pebble (plus 6 mm), Florida hard rock, and Montana hard rock (crushed and screened). Use of uncalcined rock may increase the electric power consumption in the furnace by as much as 10%, depending on the CO_2 and combined water content.

The Tennessee Valley Authority (TVA) began development of the electric-furnace process for producing phosphate fertilizers in 1933 and produced phosphorus and phosphoric acid from 1934 to 1977. At one time five furnaces were in operation. In 1977 operation of all furnaces was discontinued by TVA since the process could no longer compete with the wet process for fertilizer production.

There have been other North American producers of phosphorus: FMC, Monsanto, Occidental Chemical, Stauffer Chemical, and Albright and Wilson. The two largest producers: FMC and Monsanto have had their phosphorus furnace plants in Idaho based on local phosphate rock deposits. For economic reasons Monsanto closed its phosphorus plant in Tennessee in 1986 but has since expanded production in Idaho by debottlenecking. Stauffer Chemical (later Rhone-Poulenc Basic Chemicals) has had phosphorus plants in Tennessee and Montana. Occidental Chemical had a phosphorus furnace plant in Quebec. Almost all the output from these furnaces has been used for production of industrial phosphates (direct derivatives and thermal acid).

11.11 Phosphoric Acid Production by the Blast-Furnace Process

A flow diagram of a TVA pilot plant for producing phosphoric acid by the blast-furnace process is shown in Figure 11.34. The scale of the pilot plant was about 1 tonne of P_2O_5 per day [43].

In general, the blast-furnace process differs from the electric furnace in the following aspects:

a. Coke is used for both fuel and phosphorus reduction. The estimated coke requirement for a large-scale unit is 2.5 tonnes/tonne of P_2O_5 recovered as phosphoric acid (allowing for ferrophosphorus losses). About 0.6 tonne of coke is consumed in reduction of P_2O_5 to phosphorus, and the remainder generates heat by combustion with preheated air to form carbon monoxide.

b. As with the electric furnace, the charge – phosphate rock, coke and silica – must be in lump or agglomerated form, but it is not necessary to calcine or dry the charge since there is sufficient heat for this purpose in the ascending gases in the furnace shaft.

c. The gas from the furnace contains about 37% CO and 1.0%-1.5% P_4 by volume. The remainder is mainly nitrogen. Although recovery of elemental phosphorus by cooling and condensation is feasible, it would be difficult to recover a high percentage because of the low concentration in the gas. In the TVA pilot plant, phosphoric acid was recovered after preferential oxidation of the phosphorus in the gas with air.

d. The gas remaining after phosphoric acid recovery contains about 34% CO, 1%-2% O_2, and the remainder N_2 (dry basis). About 40% of this gas can be used advantageously for preheating the air to the blast furnace. The remainder would be available for other uses.

The blast-furnace process was used commercially to produce phosphoric acid for industrial and chemical products from 1929 to 1938 by the Victor Chemical Works, now Stauffer Chemical Company. The plant was located at Nashville, Tennessee (United States).

The use of the blast furnace to produce phosphoric acid for fertilizer purposes seems unpromising at present due to the high cost of coke. However, with some improvements it might be considered in certain

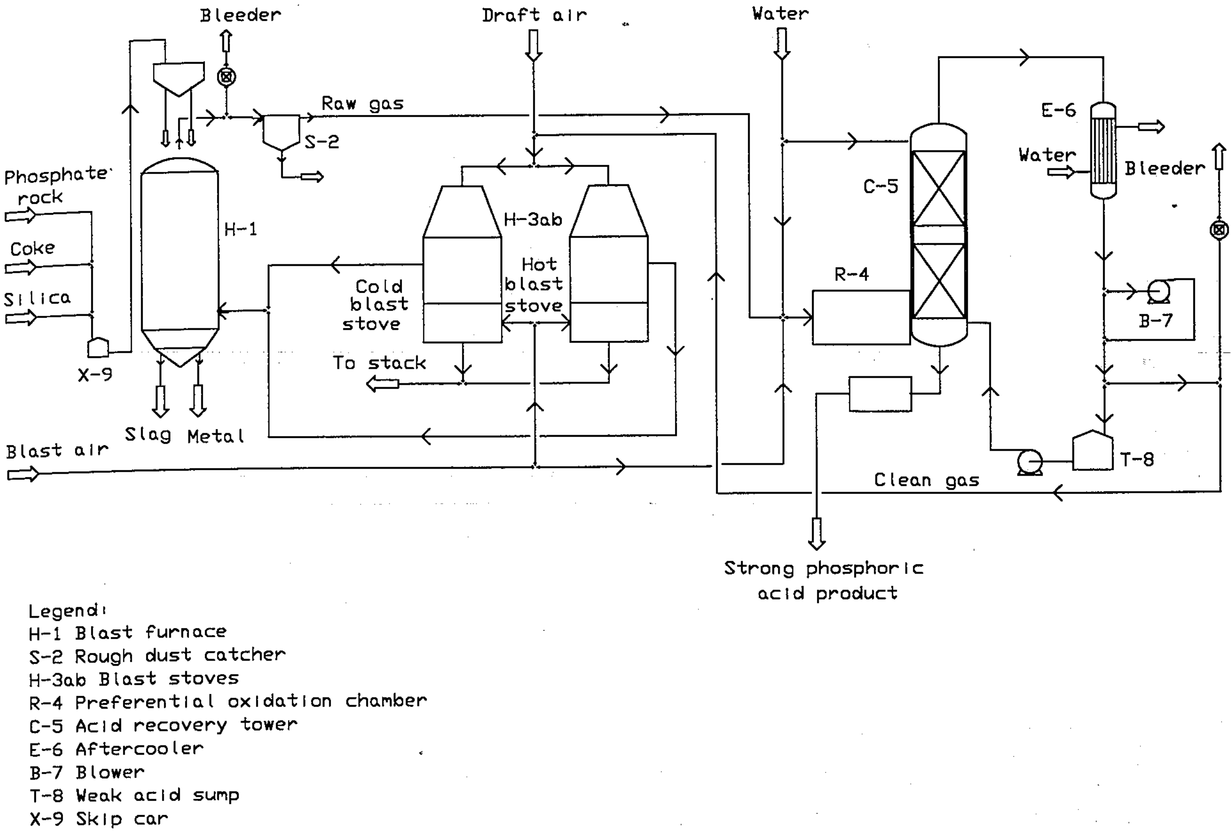


Figure 11.34. TVA Experimental Phosphoric Acid Blast-Furnace Plant.

circumstances [44]. As does the electric furnace it can use low-grade siliceous ore with moderately high alumina and iron oxide content.

11.12 Wet-Process Licensers

The principal licensers of wet processes for phosphoric acid are: Badger/Raytheon, Tampa, USA; BIPROKWAS/ICHN Gliwice, Poland; Davy/Prayon, London, England; Hydro Agri International Licensing (HAIL)/ Norsk Hydro Licensing, Oslo, Norway ; Jacobs/Dorrco, Lakeland, Florida, USA; Prayon Rupel, Engis/Liege, Belgium; Rhone Poulenc, Courbevoie, France; SIAPE, Tunisia.

They offer:

Raytheon	– DH isothermal reactor
BIPROKWAS	– DH monotank reactor
HAIL	– DH, HH, HDH multireactor system
Jacobs	– DH, HH monotank reactor
Prayon	– DH,HH,HDH multicompartment reactor
Speichim-Rhone Poulenc	– DH monotank reactor and DIPLO Process two-reactor system
SIAPE	– DH two-compartment (inner and outer) annular reactor

11.13 References

References to Sulfuric Acid Section

1. Sheldrick, W. F. "World Sulfur Survey," World Bank Technical Paper No. 24, Washington, D.C., U.S.A.
2. Bixby, D. W., D. L. Rucker, and S. L. Tisdale. 1966. "Phosphatic Fertilizers - Properties and Processes," Technical Bulletin No. 8, The Sulphur Institute, Washington, D.C., U.S.A.

3. Duecker and West. 1959. *Manufacture of Sulfuric Acid*. Rheinhold Publishing Company, New York, NY, U.S.A.
4. Ketzien, G. T. 1974. "Modern Sulfuric Acid Practice," *Proceedings of the Fertiliser Society*, (London), No. 140.
5. "Sulphuric Acid Plant Technology." 1985. Chemetics International Company, Toronto, Canada.
6. Bauer, R. A., and B. P. Vidon. 1978. "The Ugine Kuhlmann Pressure Process," *Chemical Engineering Progress*, 74:68-69.
7. Cameron, G. M., P. D. Nolan, and K. R. Shaw. 1978. "The CIL Process for Acid Manufacture," *Chemical Engineering Progress*, September: 74:47-50.
8. McAlister, D. R., A. G. Corey, L. I. Ewing, and S. A. Ziebold. 1986. "Economically Recovering Sulfuric Acid Heat," *Chemical Engineering Progress*, July: 34-38.
9. "Protecting Equipment in Sulphuric Acid Plants." 1988. *Sulphur*.
10. "Sandvik SX - Sulphuric Acid Steel." 1988. EDMESTON Materials System Engineering.
11. "Quantity vs Quality." 1994. *Sulphur*, 231:21-24.
12. Lasaosa, C. M. 1972. "New Techniques in the Use of Spanish Pyritic Ores as Raw Materials," Proceedings of the 1972 ISMA Technical Conference, Seville, Spain.
13. "Process Highlights," *Lurgi Ges.*, C 2123/10,83.
14. Donovan, J. R., and D. R McAlister. 1982. Sulfuric/Phosphoric Acid Plant Operations. AIChE Technical Manual.
15. "Getting Rid of Phosphogypsum, Part II - Portland Cement and Sulfuric Acid." 1977. *Phosphorus and Potassium*, 89:36-44.
16. Ashburner, D. S. 1968. "The Production of Cement and Sulfuric Acid by the Marchon Process," pp. 72-77, *Proceedings of the 18th Annual Meeting of the Fertilizer Round Table*, Washington, D.C., U.S.A.
17. "Clean, White Phosphogypsum and a Way to Use It." 1991. *Phosphorus and Potassium*, 172:28-32.
18. "Phosphogypsum: Liability or Profitable Byproduct." 1993. *Sulphur*, 224:39-44.
19. Ashar, N. G. 1991. "The Recovery of Sulfur from Phosphogypsum Using Biotechnology," Sulphur 91: British Sulphur International Conference, New Orleans, LA, U.S.A.

References to Phosphoric Acid Section

1. Survey of Processed Phosphate Capacities. 1994. International Fertilizer Industry Association (IFA), Paris.
2. *Phosphoric Acid*. 1968. A.V. Slack (Ed.), Marcel Dekker, Inc., New York, NY, U.S.A.
3. Farr, Thad D., and Kelly L. Elmore. 1962. "System $CaO\text{-}P_2O_5\text{-}HF\text{-}H_2O$: Thermodynamic Properties," *Journal of Physical Chemistry*, 66(2):315-318.
4. Rossini, Frederick D., et al. 1952. "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular No. 500, U.S. Department of Commerce, Washington, D.C., U.S.A.
5. Egan, E. P., Jr., and B. B. Luff. 1961. "Heat of Solution of Orthophosphoric Acid," *Journal of Physical Chemistry*, 65(3):523-526.
6. Kelly, K. K. 1934. "Contributions to the Data on Theoretical Metallurgy. II. High-Temperature Specific-Heat Equations for Inorganic Substances," Bureau of Mines Bulletin 371, U.S. Department of Commerce, U.S. Government Printing Office, Washington, D.C., U.S.A.
7. Egan, E. P., Jr., B. B. Luff, and Z. T. Wakefield. 1958. "Heat Capacity of Phosphoric Acid Solutions, 15° to 80°," *Journal of Physical Chemistry*, 62(9):1091-1095.
8. "WPA Production Using Phalaborwa Phosphate Rocks." 1993. *Phosphorus and Potassium*, 184:23-33.
9. "Phosphate Rock Grade and Quality." 1992. *Phosphorus and Potassium*, 178:28-36.
10. "The Acid Test." 1993. *Phosphorus and Potassium*, 188:21-32.
11. Somerville, R. L. 1973. "Fundamentals of Wet Process Phosphoric Acid Plant Design," Paper presented before the American Chemical Society, Division of Fertilizer and Soil Chemistry, Chicago, IL, U.S.A.
12. Houghtaling, S. V. 1973. "DPG-Prayon Modern Dihydrate Process," Paper presented before the American Chemical Society, Division of Fertilizer and Soil Chemistry, Chicago, IL, U.S.A.
13. Shearon, G. B. 1975. "Wet Grinding and Feeding of Phosphate Rock – Plant City Phosphate Complex," IN *Proceedings of the 25th Annual Meeting*

of the Fertilizer Industry Round Table. pp. 164-169, Washington, D.C. (U.S.A.).

14. Lutz, W. A.., and C. J. Pratt. 1968. "Principles of Design and Operation," IN *Phosphoric Acid*, A.V. Slack (Ed.), pp. 159-212, Marcel Dekker, Inc., New York, NY, U.S.A.
15. Stern, S. 1965. "The Use of Calcined Rock in Phosphate Processing," IN *Proceedings* of ISMA Technical Conference, Edinburgh, Scotland.
16. "Phosphoric Acid Plant Revamps." 1990. *Phosphorus and Potassium*, 170:28-32.
17. "Phosphoric Acid Manufacture-Updating Process Technology." 1986. *Phosphorus and Potassium*, 143:25-33.
18. "Reactors, Agitators and Filters for Phosphoric Acid Plants." 1991. *Phosphorus and Potassium*, 174: 23-37.
19. "Effect of Ionic Impurities on Gypsum Filterability." 1990. *Phosphorus and Potassium*, 168:20-21.
20. Moraillon, P., J. F. Gielly, and B. Bigot. 1968. "Principles of Filter Design and Operation," IN *Phosphoric Acid*, A. V. Slack (Ed.), pp. 407-442, Marcel Dekker, Inc., New York, NY, U.S.A.
21. Lehr, J. R. 1968. "Nature of Impurities," IN *Phosphoric Acid*, A.V. Slack (Ed.), pp. 637-686, Marcel Dekker, Inc., New York, NY, U.S.A.
22. "Prayon Displays its Phosphate Technology and Operations." 1991. *Phosphorus and Potassium*, 174:38-43.
23. "Phosphoric Acid Equipment - II." 1991. *Phosphorus and Potassium*, 176:26-40.
24. Processed Phosphate Statistics. 1993. International Fertilizer Industry Association (IFA), Paris.
25. "More Trade, More Ships?" 1989. *Phosphorus and Potassium*, 160:11-14.
26. Charlton, W. T., J. D. Crerar, and R. C. Akroyd. 1973. "The Shipment of Phosphatic Materials—Some Technical and Economic Aspects," *Proceedings of the Fertilizer Society* (London), No. 138.
27. "Getting Rid of Phosphogypsum." 1978. *Phosphorus and Potassium*, Part III, 94:24-29, 32-39; Part IV, 96:30-39.
28. Scaife, C. W., and D. Kitchen. 1968. "As Raw Material for Plaster and Cement—European Practice," IN *Phosphoric Acid*, A.V. Slack (Ed.), pp. 531-540, Marcel Dekker, Inc., New York, NY, U.S.A.
29. Yamaguchi, T. 1972. "Phospho-Gypsum Beneficiation Process," IN *Proceedings of the ISMA Technical Conference*, Seville, Spain.
30. Sanders, M. D. 1968. "Recovery of Fluorides as By-Products," IN *Phosphoric Acid*, A.V. Slack (Ed.), pp. 765-778, Marcel Dekker, Inc., New York, NY, U.S.A.
31. "Production of Synthetic Fluorspar from Waste Fluosilicic Acid." 1976. Paper No. 22. ISMA Technical Conference, The Hague, Netherlands.
32. Kouloheris, A. P. 1979. "Uranium Recovery from Phosphoric Acid (a Process Engineering Review)," Proceedings No. 187. The Fertiliser Society, London, England.
33. Wrobicki, J. 1979. "Assessment of Feasibility of Uranium Extraction from Phosphates in the Middle East," Written submission read in absentia at the British Sulphur Corporation's Third International Conference on Fertilizers, London, England.
34. Hurst, F. J., D. J. Crouse, and K. B. Brown. 1972. "Recovery of Uranium from Wet-Process Phosphoric Acid," *Ind. Eng. Chem. Process Des. Develop.* 11(1):122-128.
35. Hurst, F. J., W. D. Arnold, and A. D. Ryon. 1976. "Progress and Problems of Recovering Uranium from Wet-Process Phosphoric Acid," pp. 100-108, 26th Round Table, Atlanta, GA, U.S.A.
36. "Uranium Recovery: Oak Ridge Laboratory Developing Two Extraction Processes." 1977. *Phosphorus and Potassium*, 88:40-41.
37. Hurst, F. J., and F. A. Posey. 1981. "Uranium from H_3PO_4: A Decade of Change and its Meaning for the Future," AIChE, New Orleans, LA, U.S.A.
38. "Wet Process Acid Cleaning Comes of Age." 1990. *Phosphorus and Potassium*, 170:20-22.
39. "A New Era Dawns." 1990. *Phosphorus and Potassium*, 169:12-15.
40. Lounamaa, N., and L. Niinimaka. 1971. "Typpi Oy's Solvent Extraction Process for Producing Compound Fertilizers," Paper No. ID/WG99/20, Presented at the Second Interregional Fertilizer Symposium (UNIDO), Kiev, U.S.S.R.
41. "Phosphoric Acid Production from Hydrochloric Acid." 1987. Negev Phosphates Ltd. Marketing Division, Israel.
42. "New Process for the Production of Phosphatic Fertilizers Using Hydrochloric Acid." 1969. Fertilizer Industry Series Monograph No 5, UNIDO, Vienna, Austria.
43. Hignett, T. P. 1948. "Development of Blast Furnace Process for Production of Phosphoric Acid," *Chemical Engineering Progress*, 44(10):753-764; 44(11):821-832; and 44(12):895-904.
44. Hignett, T. P. 1968. "Use of the Blast Furnace for Production of Phosphoric Acid," *Phosphorus and Potassium*, 36:20-21,24.

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Chapter 12. Fertilizers Derived From Phosphoric Acid

12.1 Introduction

The production of fertilizers derived from phosphoric acid has increased significantly in the last 50 years because, among other things, these are high-analysis products, thanks to the removal of calcium as byproduct calcium sulfate in phosphoric acid production. Moreover, technical breakthroughs in the field of phosphoric acid and ammonium phosphate manufacture, plus economies of scale, have resulted in high capacity "world size" plants, which produce a limited range of products at very competitive prices.

If we consider the situation from an environmental view, the tendency toward large plants has favorable aspects for several reasons:

- The sulfur used is increasingly a byproduct of oil and natural gas cleaning.
- The calcium sulfate remains near the phosphate mine and in some cases is used to fill it.
- The liquid and gaseous emissions are better controlled and much lower per unit of production than in small local plants.
- Higher analysis products are more efficiently transported.
- Precision blending of high-analysis materials based on soil testing permits lower, more efficient application rates and decreases non-point-source pollution from farming.

Pollution control has been a major objective in the last 15 years. As a result of innovation and development, process improvements have refined scrubbing operations of MAP/DAP/NPK fertilizer plants so that effluents have decreased vastly [1,2]. This has been achieved by improvements in equipment but primarily by careful management of the scrubbing fluids to the extent that scrubbing has almost become a process by itself.

Nearly two-thirds of the P_2O_5 in fertilizers was derived from phosphoric acid in 1988. In fact this figure is around 80% or more in North and Central America, North Africa, and West and South Asia, and around 50%-60% in other areas except Oceania (14%) and China (1%). Moreover, in 1992, 70% of the P_2O_5 in fertilizers worldwide came from phosphoric acid-based products.

With minor exceptions, the commercial fertilizer products are triple superphosphate (TSP), ammonium phosphates, and other compound fertilizers (some of the minor exceptions are potassium phosphates and magnesium ammonium phosphate [$MgNH_4PO_4$]). Use of phosphoric acid in compound fertilizers will be described under subject headings "Compound Fertilizers" (Chapter 16), "Liquid Fertilizers and Nitrogen Solutions" (Chapter 10), and "Nitrophosphate Fertilizers" (Chapter 13). The present chapter will deal mainly with TSP and solid ammonium phosphates.

12.2 Triple Superphosphate

12.2.1 Introduction

In the period 1965-75, TSP supplied approximately 15%-20% of the fertilizer phosphate used worldwide. This declined to 13.3% in 1988 and to 10.7% in 1992, primarily as a result of a continuous increase in the use of ammonium phosphates, mainly diammonium phosphate (DAP).

One of the advantages of TSP is that it is the most highly concentrated straight phosphate fertilizer available, with 44% to 48% available P_2O_5 and 40% to 45% water-soluble P_2O_5. Another advantage is that part of its P_2O_5 content is derived directly from phosphate rock, a relatively low-cost source. The percentage of P_2O_5 in TSP that is derived directly from rock varies from about 25% to 30%, depending on the $CaO{:}P_2O_5$ ratio in the rock, the impurity content of the rock and acid, and other factors. On the other hand, with a given amount of phosphoric acid, a greater amount of fertilizer P_2O_5 can be produced as TSP than as ammonium phosphate.

The manufacture of TSP is quite similar to that of single superphosphate (SSP) and has the same advantages of simplicity, low technical skill requirement, and small capital investment.

TSP has three main disadvantages:

- The total nutrient content is lower than that of ammonium phosphates.
- Its acidic character may cause deterioration of some types of bags (hemp and paper).
- It is not well suited for blending with urea because of reactions that cause deterioration of physical condition.

12.2.2 Fundamentals of TSP Production

The reactivity of phosphate rock is of more importance in TSP production than in phosphoric acid production. Unreactive rocks may require unusually fine grinding or long reaction times or both. Even so, acceptable completion of reaction may be difficult to achieve with some igneous apatites.

Rocks containing carbonates or carbonate substitutions in apatite release CO_2 during reaction. The released gases result in a porous structure of the superphosphate made by den processes. This is considered desirable when the superphosphate is to be used in making compound fertilizers. When the rock contains very little carbonate, the superphosphate may be hard and dense, leading to granulation difficulties and poor ammoniation characteristics.

TSP may be prepared in either granular or nongranular form. The nongranular form is preferred for use as an intermediate for production of compound fertilizer by granulation processes, whereas the granular form is preferred for direct application or for blending. The basic chemical reaction involved in production of TSP is as follows:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + H_2O \rightarrow 3\ Ca(H_2PO_4)_2 \bullet H_2O + 172.58\ \text{kcal}$$

For simplicity, the phosphate source in the reaction is shown as tricalcium phosphate. See Chapter 5 for compositions of carbonate-substituted fluorapatites. In most processes, a large percentage of the fluorine remains in the product, probably as fluosilicates and possibly as calcium fluoride. If some of the calcium is converted to calcium fluoride or fluosilicate, somewhat less phosphoric acid is required than indicated by the equation. However, phosphate rock concentrate usually contains a higher $CaO:P_2O_5$ ratio than does fluorapatite alone. The proportion of acid to rock often is calculated to yield a $P_2O_5:CaO$ mole ratio of 0.95 to 1.0 (weight ratio = 2.41 to 2.54) according to the formula:

$$\frac{\text{Acid } P_2O_5 + \text{Rock } P_2O_5}{\text{Rock CaO}} = 2.41 \text{ to } 2.54 \text{ (weight ratio)}$$

However, various impurities in the acid and rock cause variations in the optimum acid:rock ratio. The product will contain – in addition to monocalcium phosphate – iron, aluminum, and magnesium phosphates; probably a small amount of dicalcium phosphate; unreacted rock; calcium sulfate originating from free sulfuric acid in the phosphoric acid and sometimes from rock impurities; and various other impurity compounds.

The economically optimum acid:rock ratio is best determined by test methods and will depend on whether the commercial value is based on solubility in water, ammonium citrate, or other solvents. When water solubility is the criterion, both the rock and acid should be as low in iron and aluminum as is economically feasible.

The effects of $CaO:P_2O_5$ ratio of the rock and grade of rock on the proportions of rock and phosphoric acid and on the grade of the TSP product are given in Table 12.1. As the $CaO:P_2O_5$ weight ratio increases from 1.35 to 1.70, the percentage of P_2O_5 derived from rock decreases from 30% to 24% while the percentage derived

Table 12.1. Effect of Grade and $CaO:P_2O_5$ Ratio of Rock on Proportions of Rock and Phosphoric Acid

Weight Ratio $CaO:P_2O_5$ in Rock	% Total P_2O_5 in Product From		Grade of Rock, % P_2O_5	Tonnes/Tonne of Product P_2O_5		Grade of Product, % Total P_2O_5[b]
	Rock	Acid		Rock	Acid[a]	
1.70	24.0	76.0	33	0.73	1.40	47.0
1.50	27.0	73.0	33	0.82	1.35	46.1
1.35	30.2	69.8	33	0.92	1.29	45.2
1.50	27.0	73.0	28	0.965	1.35	43.0
1.50	27.0	73.0	38	0.71	1.35	48.5

a. Phosphoric acid containing 54% P_2O_5. Acidulation mole ratio $P_2O_5:CaO$ = 0.97.

b. The grade will be increased by loss of volatile ingredients in the rock and by loss of free moisture; the grade in terms of "available" P_2O_5 will be decreased by citrate-insoluble P_2O_5 in the product. These two factors may approximately offset each other depending on the composition of the phosphate rock and acid.

from acid increases from 70% to 76%; the grade of the product TSP increases from 45% to 47% P_2O_5. As the grade of the rock increases from 28% to 38% P_2O_5 (with the CaO:P_2O_5 weight ratio constant at 1.5), the grade of the product increases from 43.0% to 48.5% P_2O_5. These calculations are based on phosphoric acid of average impurity content and rock with the usual amounts and types of impurities. The calculations are intended only for illustration of general trends; accurate values can be obtained only from experimental data derived during tests with the specific phosphate rock and phosphoric acid in question.

12.2.3 Technology of TSP Production

Powder or Granular TSP by the Den Process – The manufacture of TSP by this route involves the following three (or four) operations:

1. **Reaction** – Very finely ground phosphate rock (95% to 98% < 100 mesh) is mixed with phosphoric acid. With rock of 34% P_2O_5 content, about 2.6 kg of acid P_2O_5 is required per 1 kg of rock P_2O_5. The phosphoric acid used is merchant-grade acid at 52% P_2O_5 concentration. Many plants use the cone-mixer process that was originated by TVA [3,4]. Figure 12.1 shows a flow diagram of the process. A somewhat similar process is known as the Kuhlmann process; in this case, the mixer is a small cylindrical vessel equipped with a high-speed stirrer.
2. **Denning** – The fluid material from the mixer goes to a den where it solidifies. Solidification results from the continued reaction and crystallization of monocalcium phosphate. The process is faster than with SSP, and denning times of 10-30 minutes are suitable for TSP as compared with 30 minutes to 2 hours for SSP. Special belt conveyors are sometimes used for TSP rather than conventional dens. In any case, the belt or den must be enclosed and connected to a fume exhaust system to direct fluorine-containing gases to a scrubber.
3. **Storage/Curing** – The product is removed from the den and conveyed to storage piles for final curing,

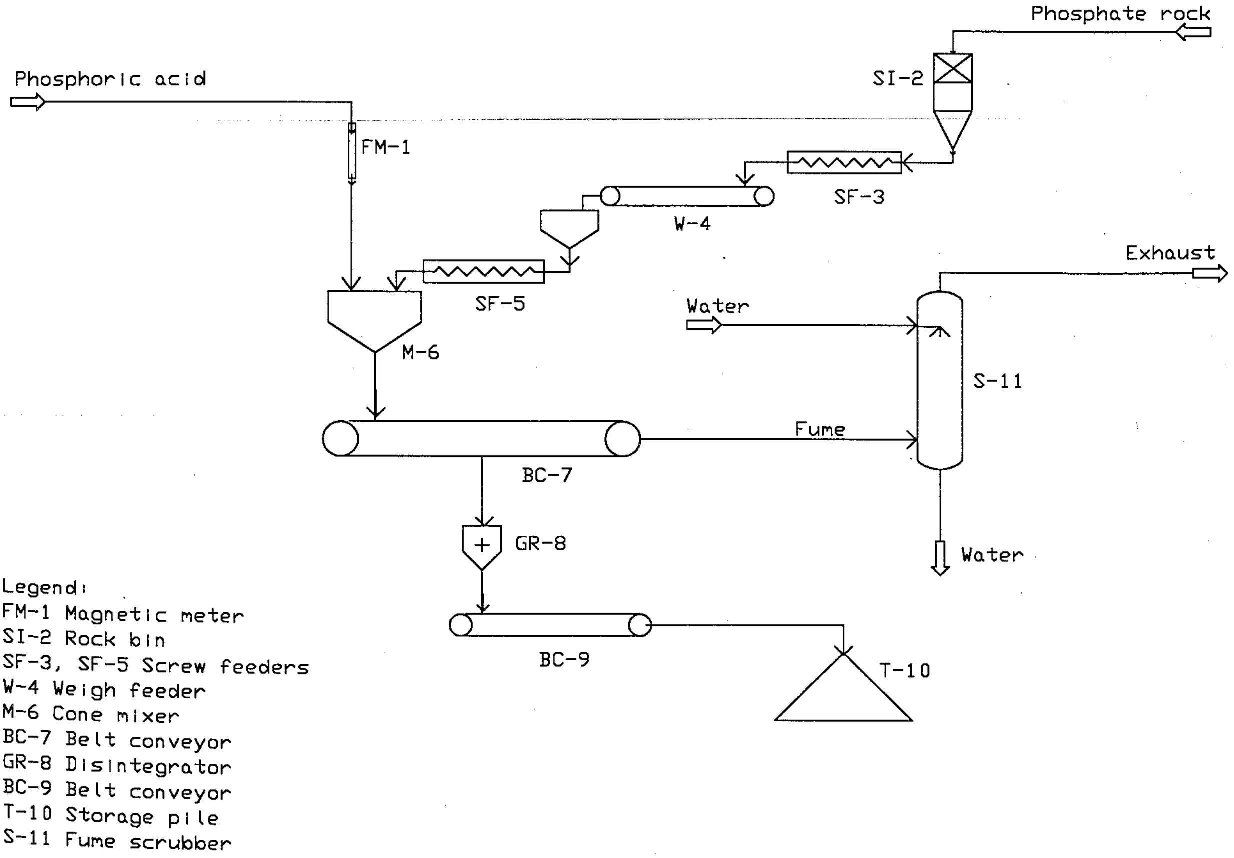

Figure 12.1. Manufacture of Run-of-Pile Triple Superphosphate.

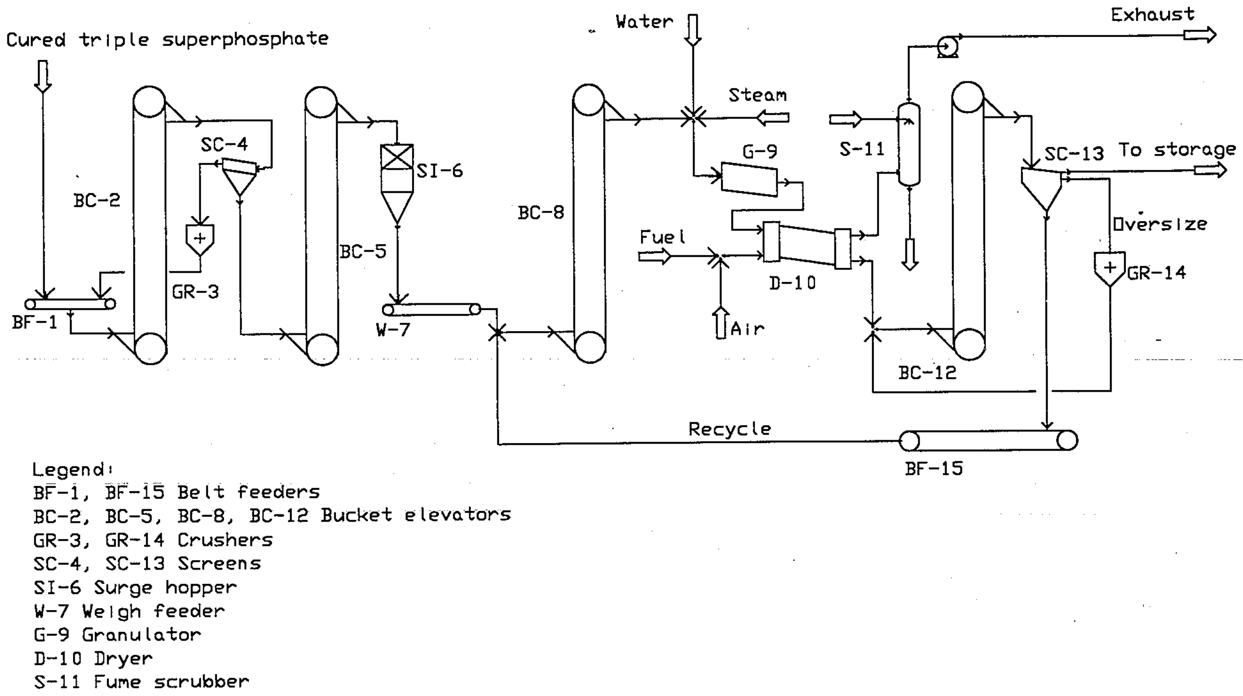

Figure 12.2. Granulation of Cured Run-of-Pile Triple Superphosphate.

which requires 3-6 weeks depending on the nature of the raw materials (more or less soft rock, harmful impurities like Fe_2O_3, Al_2O_3, MgO; useful carbonates). During curing, the reaction approaches completion. The free acid, moisture and unreacted rock contents decrease, and the available and water-soluble P_2O_5 contents increase. Small amounts of fluorine compounds continue to be evolved during storage curing, and good ventilation is needed to remove the fluorine from the working area. Scrubbing of the exhaust gas may be necessary to prevent atmospheric pollution.

After storage curing, the TSP is reclaimed with a power shovel and disintegrated in a cage or chain mill to pass a 6-mesh screen (3.3 mm). The disintegrated TSP (sometimes called run-of-pile TSP or ROP-TSP) may be used for making compound fertilizer by agglomeration granulation, or it may be used as is for direct application. In most countries, farmers prefer a granular form because the TSP is dusty if it is too dry, and it cakes if it is too moist.

Granulation – Granulation of powder or ROP-TSP may take place before or after curing. Cured TSP is granulated by the process shown on Figure 12.2. After milling and screening, the cured powder TSP is conveyed to a rotary drum granulator. Water is sprayed onto the bed of material and steam is sparged underneath the bed to provide wet granular material. The wet granules are discharged to a rotary dryer. The dried granules are screened, and the oversize is milled and returned with the fines to the granulator. Dust and fumes from the dryer are scrubbed in a water scrubber. Alternatively, dust may be removed by a bag filter prior to the wet scrubbing.

In a process variation, phosphate rock and phosphoric acid are fed to the granulator to supply a portion of the phosphates; production cost is lowered and granulation is improved, but greater investment is required.

The typical consumption figures per tonne of product are summarized in Table 12.2.

Table 12.2. TSP Granulation Process Consumption Figures

Inputs	Consumption Per Tonne Product
Cured TSP, tonne	1.02
Steam, kg	75
Cooling water, kg	250
Fuel, GJ	0.67
Electrical energy, kWh	29
Operating labor, workhours	0.3

Ex-Den Granulation – In ex-den granulation, the acidulation and denning steps are similar to those described for producing nongranular TSP except that the rock may be somewhat more finely ground and the den retention time is longer (25-45 minutes vs 10-30 minutes). Also, the product from the den goes directly to a granulator rather than to storage. After granulation, the product is dried, screened, and conveyed to storage. Drying is controlled to yield a product of 4% - 6% moisture. Under these conditions, some further reaction takes place in storage.

The literature [5] describes a plant of this type that is capable of producing 20-35 tph of TSP, SSP, or mixtures of the two. It can also make PK compound fertilizers by the addition of potash at the granulator.

A simplified flow diagram of a typical direct ex-den granulation system is shown in Figure 12.3. Typical data for the production of TSP by ex-den granulation are given in Table 12.3.

Table 12.3. Typical Values for Production of TSP by Ex-Den Granulation Process

Process Data	Units	Value
Phosphoric acid concentration	%	>50
Ratio of recycle	-	1.25-1.0
Moisture content, ex-den	%	10-12
Final moisture content of TSP	%	5-6
Water-soluble P_2O_5	%	>46
– After curing	%	98
– Ex-plant	%	94
Steam consumption	kg/t	50-60
Water consumption	kg/t	60-65
Power consumption[a]	kWh/t	38
Labor required	workhours/t	0.25
Granule size	mm	1.6-4

a. Including rock grinding (10 kWh/t of TSP).

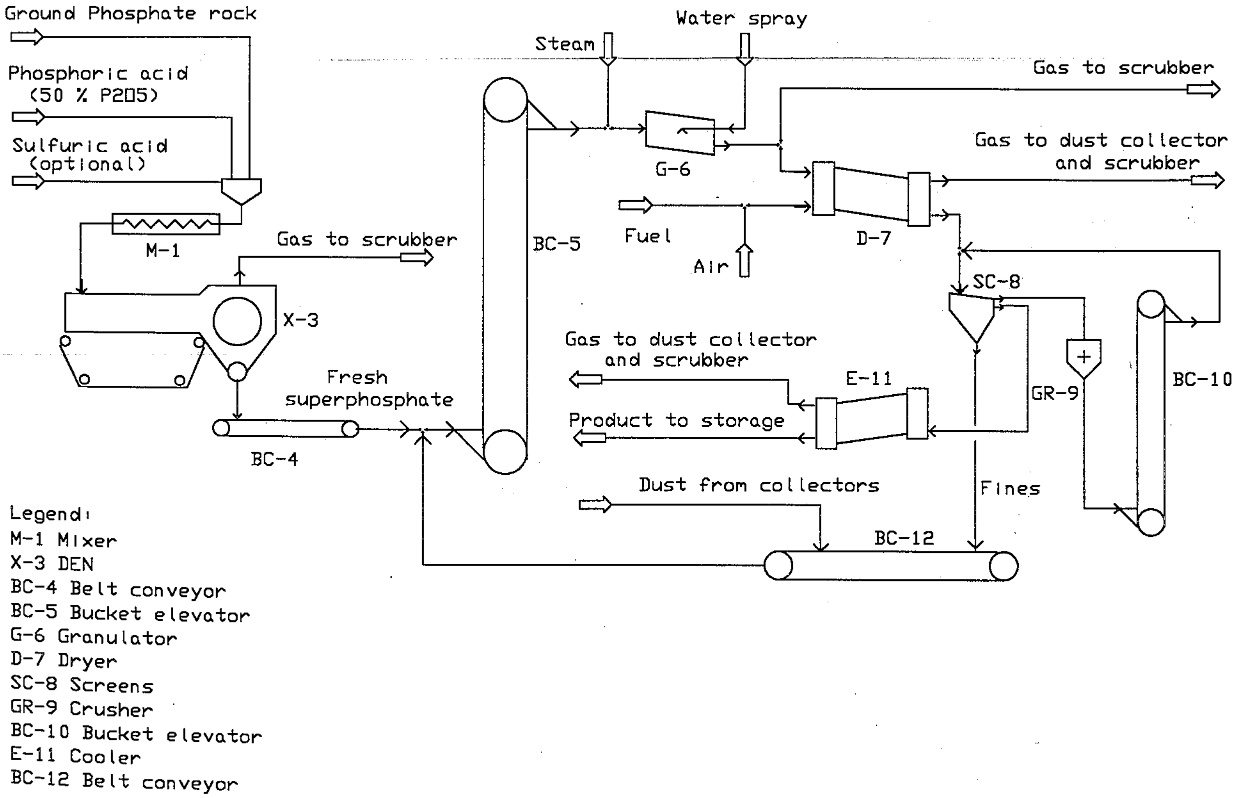

Figure 12.3. Ex-Den Granulation of TSP.

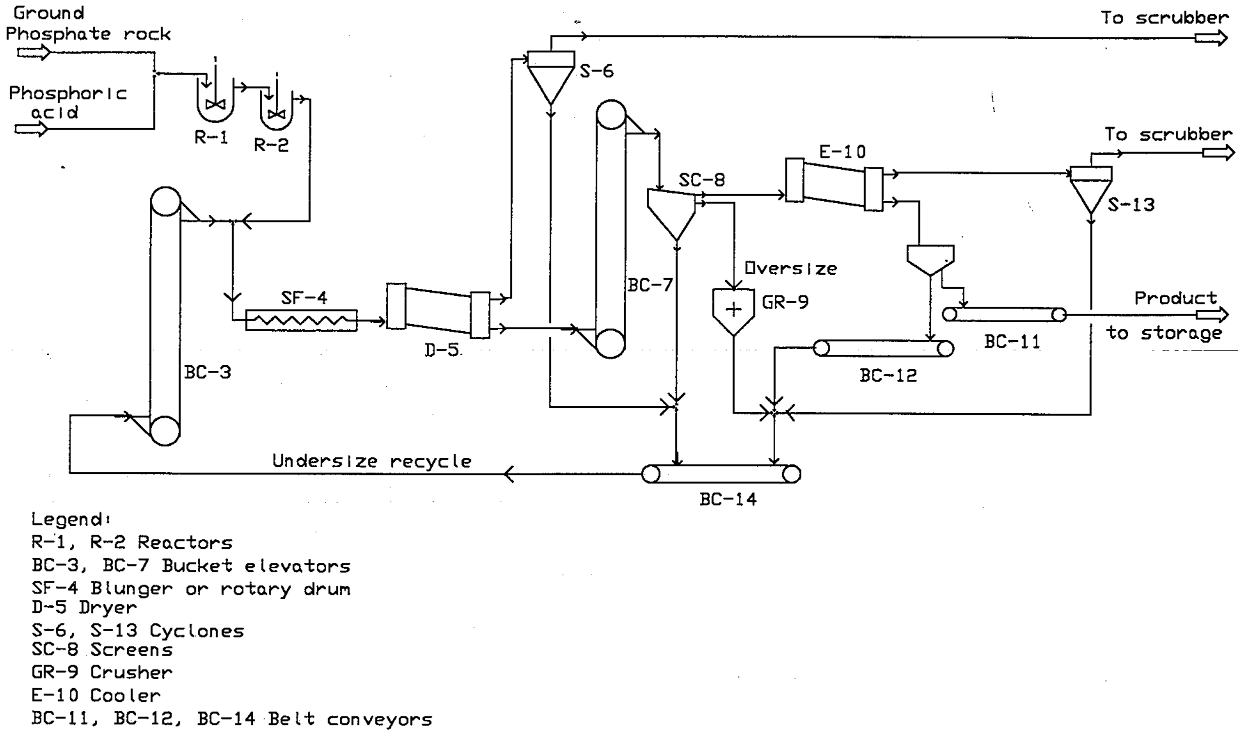

Figure 12.4. Slurry Process for the Manufacture of Granular Triple Superphosphate.

The plasticity and heat content of fresh TSP (or SSP) make it much easier to granulate than cured TSP; less recycle, water, and steam are required. Presumably, less fuel is required for drying. Total electric power consumption is somewhat lower, and labor requirements are only 36% of that required for the "conventional" two-step process. The product is said to be superior in hardness, shape, uniformity, and smoothness.

12.2.4 Direct Slurry Granulation

When granular TSP is the desired end product, it is usually preferable to produce it directly rather than by granulation of powder TSP. Some advantages of direct granulation processes are:

- Cost is usually lower.
- Granules are denser and stronger.
- Granulation equipment can be used interchangeably for producing TSP and ammonium phosphates.

There are two main disadvantages of direct granulation:

- Owing to the limited reaction time, unreactive rocks are poorly suited for use in the direct granulation process.
- Greater losses of soluble P_2O_5 may occur owing to incomplete reaction, or a higher ratio of phosphoric acid to phosphate rock may be needed to prevent this loss.

The first slurry-type granulation process developed was the Jacobs-Dorrco process, formerly known as the Dorr-Oliver process. A simplified flow diagram is shown in Figure 12.4. Ground phosphate rock and phosphoric acid, 38%-40% P_2O_5, are fed to the first of a series of two or three steam-heated, stirred reaction vessels. The overall retention time is about 30 minutes, and the temperature is about 90°C. The thick slurry is fed to a blunger or rotary drum granulator together with a high proportion of recycle. The moist granules are dried and screened, and the product size material is cooled and sent to storage.

Leyshon and Mangat have described some improvements in the process [6]. An "aging conveyor" is used to transport the granules from the granulator to the dryer. A small amount of moisture is evaporated on the conveyor, and moisture is absorbed into the interior of the granule. The result is that the granules are less sticky when they reach the dryer and, hence, less likely to clog feed chutes or cake on the walls of the dryer. Single-deck screens are used; the oversize is separated on one screen, crushed in a chain mill, and recycled. The stream of undersize, including the product size, is split into two streams; one portion is withdrawn for recycle to the granulator, and the other is screened to separate fines, which are recycled, and product size, which is cooled. A final "polishing screen" is used following the cooler for more complete removal of fines and oversize. As with all granulation systems, the dust and fume removal system has been improved to increase efficiency.

Recycle ratios (ratio of recycle:product) are 10-12:1 for blunger granulation and about 8:1 for rotary-drum granulation. The lower ratio for rotary-drum granulation is ascribed to moisture evaporation in the drum granulator enhanced by a countercurrent sweep of air.

The estimated utility requirements per tonne of product are about 40 kWh for electric power (including phosphate rock grinding), about 125,000 kcal of fuel oil for drying, and about 20 kg of steam, mainly for heating the reactors.

Another slurry process reported to have been developed in Europe is similar to the Jacobs-Dorrco process [7]. However, granulation and drying are combined by spraying the slurry onto a cascading curtain of granules at the feed end of a cocurrent rotary dryer.

12.3 Ammonium Phosphates

12.3.1 Fundamentals of Ammonium Phosphates

Ammonium phosphates, particularly DAP, are the most popular phosphate fertilizers worldwide because of their high analysis and good physical properties. The compositions of the pure salts – monoammonium phosphate (MAP) and DAP – are given in Table 12.4.

The standard grade for DAP is 18-46-0. This is the "commodity" grade, and products analyzing lower in N or P_2O_5 may not be sold as DAP. There is no standard grade for MAP; grades range from 11-55-0 to 10-50-0 made from high-sludge acid. A prevalent median grade is 11-52-0. Grades containing both MAP and DAP also are produced; examples are 13-52-0 and 16-48-0.

Table 12.4. Nutrient Content of Pure Ammonium Phosphates

Product	N, %	P_2O_5, %
Monoammonium phosphate (MAP)	12.17	61.71
Diammonium phosphate (DAP)	21.19	53.76

Relatively small amounts of pure DAP and MAP are made by crystallization processes using phosphoric acid made by the electric-furnace process or using wet-process acid purified by any of various processes. The pure, fully soluble ammonium phosphates are used mainly for specialty liquid fertilizers.

Both MAP and DAP usually have very good physical properties when made from wet-process acid. For both, storage properties and ease of granulation depend on the impurity content; a gel-like structure of impurities, mainly aluminum and iron phosphates, promotes granulation and serves as a conditioner to prevent caking, even at a moderately high moisture content (about 3%). On the other hand, pure ammonium phosphates are difficult to granulate and tend to cake badly in storage, even with a very low moisture content, unless coated with a conditioner. It has been demonstrated that the addition of impurities, particularly compounds containing aluminum, can improve granulation and product quality when there are insufficient impurities in the acid for this purpose. Also, the addition of a small proportion of phosphate rock to the phosphoric acid before ammoniation can improve granulation. To determine the influence of acid impurities on ammonium phosphate products, a study was made of carefully "spiked" samples of base merchant-grade acid [8]. The conclusion was that the effects of aluminum, iron, and magnesium were simply cumulative and not multiplicative. Thus, if one impurity is increasing, its effect can be compensated by a decrease of the other impurities. Another finding of this work is that citrate- insoluble P_2O_5 is more influenced by the operating conditions than by iron, aluminum, and magnesium content. Moreover, higher fluorine levels tend to reduce citrate-insoluble P_2O_5 as well as reactor viscosities.

Ammonium phosphates have become the major phosphate fertilizers and in 1988 supplied over 16 million tonnes of P_2O_5 or nearly 40% of the fertilizer P_2O_5 used worldwide; in 1992, these figures became 18.7 million tonnes and nearly 50%.

12.3.2 Early Technology for the Manufacture of MAP/DAP

TVA Basic Process – Granular DAP is commonly produced by a slurry process; the process developed by TVA and illustrated in Figure 12.5 is typical. The average concentration of the wet-process acid is about 40% P_2O_5; however, most plants use part of the acid at 54% P_2O_5 and part at 30% P_2O_5. The acid reacts with ammonia in a preneutralizer where the mole ratio of NH_3:H_3PO_4 is controlled at about 1.4. This ratio corresponds to a point of high solubility (Figure 12.6).

The heat of reaction raises the slurry temperature to the boiling point (about 115°C) and evaporates some

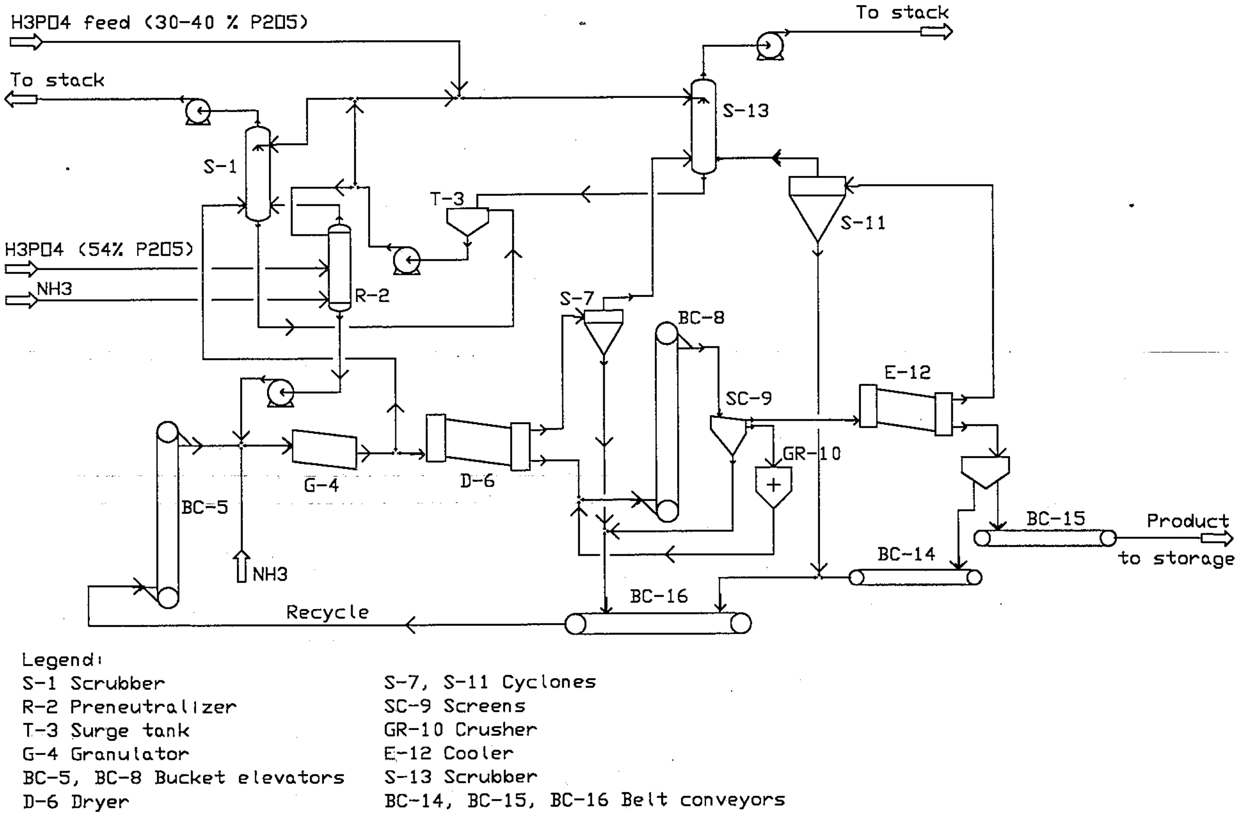

Figure 12.5. TVA DAP Process.

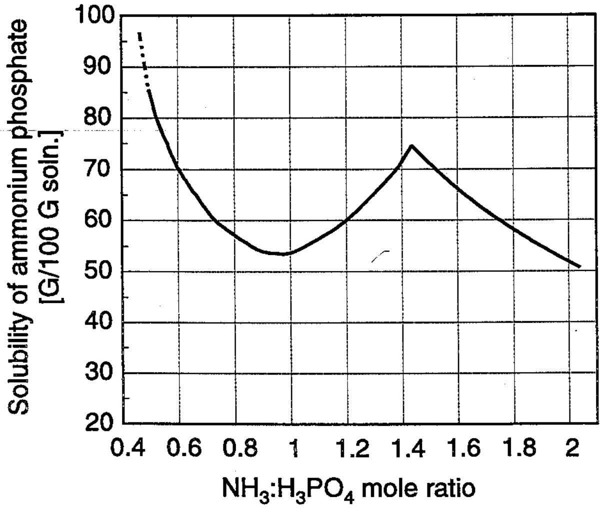

Figure 12.6. Effect of NH_3:H_3PO_4 Mole Ratio on Solubility of Ammonium Phosphate at 75°C.

moisture. The hot slurry containing about 16% - 20% water is pumped to the granulator where more ammonia is added to increase the mole ratio to approximately 2.0. Additional heat is generated, evaporating more moisture. The decreased solubility in going from 1.4 to 2.0 mole ratio assists granulation. The moist granules from the granulator are dried and screened, the product size is cooled, and the undersize and crushed oversize are recycled. The usual ratio of recycle to product is about 5:1. Ammonia escaping from the granulator, dryer, and preneutralizer is recovered by scrubbing with weak acid (30% P_2O_5), and the scrubber solution is added to the preneutralizer.

The same equipment can be used to make MAP by one of two procedures:

- The preneutralizer is operated at an NH_3:H_3PO_4 mole ratio of 0.6 (a point of high solubility) and the balance of ammonia is added in the granulator.
- The preneutralizer is operated at a mole ratio of about 1.4, and phosphoric acid is added in the granulator to decrease the ratio to 1.0.

In producing MAP, ammonia recovery by acid scrubbing is not necessary, but all gaseous effluents are scrubbed to recover dust and fumes.

Other Early Alternatives – An improvement in the TVA-type process for making DAP is to substitute a pipe reactor for the preneutralizer. Ammonia and phosphoric acid react in a pipe which discharges directly into the granulator. Steam generated by the reaction is released in the granulator and swept out with a current of air. This arrangement is simpler and less expensive than the use of a tank preneutralizer. An additional advantage is that it uses more concentrated phosphoric acid; thus, slurry discharged into the granulator contains less water and the recycle ratio is decreased. Fittel and Hollingsworth report that a plant in Australia using the pipe reactor has a recycle ratio of 3:1 (as compared with a 5:1 ratio for tank preneutralization) [9]. A somewhat similar system is used in Spain by the firm of S.A. Cros to produce DAP and other grades of compound fertilizers [10]. The use of pipe reactors in granulation processes will be described further in a later section of this chapter and in the chapter "Compound Fertilizers" (16).

Danos of Jacobs Engineering Group Inc. has described a process for DAP production that involves use of a pipe reactor and eliminates the need for drying [11]. This pipe-reactor process is similar to one demonstrated by TVA in 1978 [12].

12.3.3 Jacobs-Dorrco Industrial Process

The original Dorr-Oliver (now Jacobs) slurry granulation process for DAP production resembled the TVA process with the following exceptions:

- Ammoniation was carried out in reaction vessels. Three vessels were operated with NH_3:PO_4 ratios of 0.6, 1.4, and 1.85.

- Granulation of the slurry with recycle was carried out in a blunger.

The recycle ratio was about 8:1. As in the TVA process, ammonia losses were recovered by acid scrubbing. MAP and grades between MAP and DAP could be produced by adjusting the mole ratio in the reaction vessels. In subsequent modifications, ammonia was added in the blunger, or an ammoniator-granulator drum was substituted for the blunger. Other improvements have been mentioned uin the discussion of TSP and in the description of the Jacobs Engineering pipe-reactor process.

Both the original TVA process and the original Dorr-Oliver process have been modified and improved; in addition, other organizations have developed similar slurry granulation systems using similar basic principles. A basic flowsheet for the improved Jacobs slurry granulation process is shown in Figure 12.7. This and other slurry granulation processes are adaptable to production

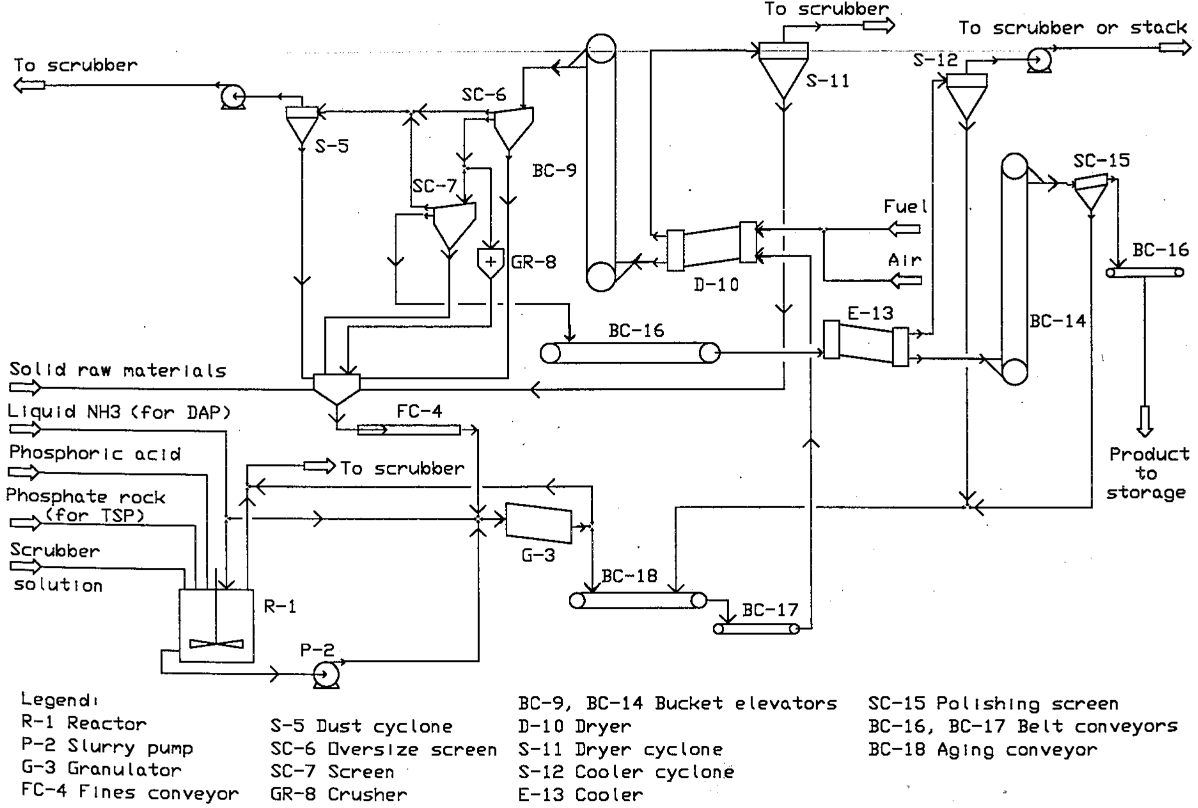

Figure 12.7. Jacobs-Dorrco Slurry Granulation Process.

of a variety of compound fertilizers by the addition of potash salts and urea, ammonium nitrate, or ammonium sulfate. Sulfuric acid can be used in the amount of about 50 kg/tonne in view of adjusting the grade to 18-46-0. Without sulfuric acid, a DAP analysis of 18.4% - 18.8% N and 47.2% - 47.5% available P_2O_5 can be attained using clarified phosphoric acid. However, when unclarified acid from some low-grade rocks is used, it may be difficult to attain a grade as high as 18-46-0 [13].

12.3.4 Subsequent Developments

The efficient use of a pipe reactor, the most significant development in ammonium phosphate and NPK technology of recent years, provides a means of improving the water balance and the energy efficiency as well as eliminating the preneutralizer. The growth of the use of the pipe reactor in both the retrofitting of existing plants and the design of new plants has been rapid [14]. Not that the concept is new – a patent issued to I. G. Farben mentioned the concept in 1927. Widespread use has been limited by concerns about scaling and corrosion, but these have now been almost completely overcome, and the rising cost of energy has increased the interest in optimizing use of the chemical energy of the reaction. The heat of reaction is of the same order as that required to evaporate the water in the phosphoric acid, as can be shown by a simple calculation. If wet-process phosphoric acid is fed at 40% P_2O_5 and 4% H_2SO_4, the reactions will be written:

1. $H_3PO_4 + 2NH_3$ gas → $(NH_4)_2HPO_4$ dry + 46 kcal
2. $H_2SO_4 + 2NH_3$ gas → $(NH_4)_2SO_4$ dry + 46.5 kcal

2,500 grams of phosphoric acid will contain 1,000 grams of P_2O_5 or 14.08 moles of H_3PO_4; 14.08 moles x 46 = 648 kcal of reaction energy; 2,500 grams x 0.04 = 100 g H_2SO_4 = 1.02 moles x 46.5 = 47.4 kcal of reaction energy. At 40% P_2O_5, the acid contains about 36% water or 2,500 x 0.36 = 900 g H_2O, which will require 630 x 0.9 = 567 kcal to evaporate.

The heat requirement to evaporate that amount of water represents:

$$\frac{567}{695.4} = 81.5\% \text{ of the reaction energy}$$

Thus, by providing for energy conservation in the plant design, the process may become autothermal, perhaps with a slight increase in the concentration of the acid used.

A pipe reactor is, literally, just that – a length of pipe into which raw materials are introduced to react. The most common embodiment is the T-reactor, which has a T-shaped mixer at one end. Alternatively, the mixer head may be cross-shaped. In a T-shaped reactor (Figure 12.8), ammonia is introduced to the mixer in the direction of the horizontal axis; the other feed – phosphoric acid and, sometimes, small quantities of sulfuric acid - is added to the mixer head at a right angle to the ammonia.

While in the pipe, ammonia and phosphoric acid react to produce a slurry, which is discharged from the end of the pipe directly into the granulator. Further ammoniation and incorporation of other solid materials, in the case of NPKs particularly, take place in the granulator, which is generally a drum granulator.

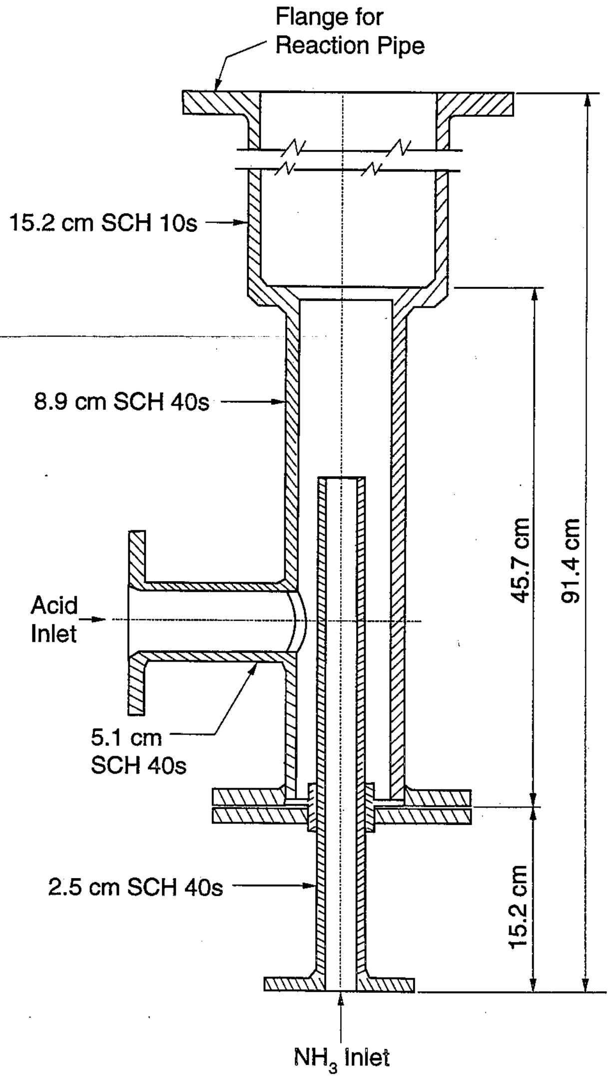

Figure 12.8. T-Shaped Reactor.

The pipe reactor is, in most instances, a replacement for the preneutralizer. It is simpler to operate, avoids the need to pump slurry, and is cheaper too. The main advantage is that the pipe reactor can produce a more concentrated slurry than can a preneutralizer, and thus the specific process water requirement is much less. Consequently, less water needs to be introduced with the raw materials – 54% P_2O_5 phosphoric acid may be used instead of 40%-42% acid – and the recycle ratio can thus be reduced. This, in turn, reduces the size of the materials handling equipment needed or, in an existing plant, permits capacity to be increased.

Because reaction is confined in such a small space, the heat balance of the process is generally improved as well. In that much of the water is vaporized in the reactor itself by the heat of reaction, product leaving the granulator is much drier and energy consumption for drying can be reduced. The main advantages of the pipe-reactor process, compared with the preneutralizer process, can be summarized as follows [14]:

- Lower investment cost:
  - no preneutralizer
  - low recycle ratio
- Lower operating cost:
  - autothermal operation (no heating energy)
  - low electric power consumption
  - lower citrate-insoluble P_2O_5
  - high efficiency in ammonia consumption
- High adaptability concerning feedstocks:
  - suitable for phosphoric acids from various origins; even some sludges may be used
  - can be fed exclusively with merchant-grade acid at 52%-54% P_2O_5 and so is well adapted for plants that import their phosphoric acid
- High operating flexibility and stability:
  - well-proven scrubbing system
  - effective control of granulation conditions
- Wide variety of product formulations:
  - MAP, DAP, or various types of NPK
- Low environmental impact:
  - low emission values in accordance with Environmental Protection Agency (EPA) standards (U.S.A.)

Typical utilities consumptions of the preneutralizer and pipe-reactor processes are given in Table 12.5.

Another point worth noting is that the P_2O_5 in DAP produced by the pipe reactor is almost completely citrate soluble. Much of the early work to use the pipe reactor for ammonium phosphates and NPKs was carried out by TVA, and many processes have been based on this work [15].

Table 12.5. Comparison of Utility Requirements in the Preneutralizer and Pipe-Reactor Processes

Utilities	Preneutralizer	Pipe Reactor
Power, kWh/t	45	35
Fuel, GJ	0.3	0
Process water, kg	135	35

Source: *Phosphorus and Potassium,* No. 144, July-August 1986.

12.3.5 TVA Pipe-Cross Reactor [16]

In the pipe-cross reactor, as in the T-reactor, ammonia enters the pipe along the horizontal axis and phosphoric acid enters at right angles. There is, however, an additional inlet directly opposite the phosphoric acid inlet, through which another feed can be added at a right angle to the ammonia stream. This arrangement was developed to allow sulfuric acid to be added to the reaction mixture.

Typically, pipe-cross reactors are operated at below one atmosphere (gauge) pressure. For the last few years, TVA has been examining the operation of the pipe-cross reactor at pressures of 0.2-0.7 MPa. The following advantages have been noted:

- The slurry has a higher boiling point, which reduces ammonia loss when the material is sprayed into the granulator and, because the slurry is more viscous, improves its uniform distribution (and hence product quality).
- Because the slurry has a low moisture content (4% - 6%), less moisture enters the bed of granulating material, and the recycle rate can be reduced and production rate increased.

The amount of moisture in the bed of material in the granulator is also reduced because there is some flash cooling as the slurry leaves the pipe. The particles that are sprayed from the pipe are small, and there is thus a large surface area for moisture to be disengaged from the slurry.

The overall flow diagram for a process incorporating the pipe-cross reactor (Figure 12.9) is not dissimilar to that of one using a T-reactor, except that slurry from the gas scrubbers can be fed directly to the reactor through the additional inlet. Discharge from the reactor goes directly into an ammoniator-granulator. Partial cooling is recommended before screening, after which final cooling is carried out before storage. Electricity

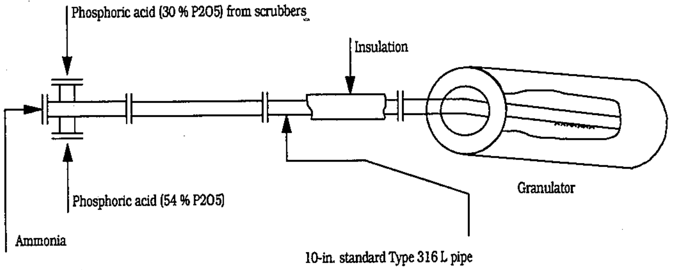

Figure 12.9. TVA Pressure Pipe Reactor for Granulation of MAP/DAP.

consumption in the process is some 90 kWh/tonne, but product drying is not necessary.

The pressure reactor is fabricated from 316 L stainless steel pipe, 25.4 cm in diameter and 13.72 m long. Some 10.36 m of the pipe is outside the granulator and is inclined at an angle of 10 degrees; this section is fully insulated. Gaseous ammonia is fed to the pipe. Slurry discharges from the pipe about 0.92 m above the bed of material in the granulator. TVA recommends that the velocity of the air flow through the granulator be about 1.22 m/second.

12.3.6 Uhde GmbH Process

To provide stable operating conditions in its pipe-reactor process, Uhde of Dortmund developed a computer program, which has shown the following measures to be effective: control of ventilation air in the granulator, a separate liquid circuit for the granulator scrubber, an oversized granulating drum, and use of liquid ammonia in the pipe reactor [17].

The acid from the scrubbing section, together with the main acid stream, is fed to the pipe reactor, to which ammonia and sulfuric acid are added. For a 1,000-tpd DAP plant, two pipe reactors, each capable of producing 25%-60% of the total load, are used (low production loads can be met by one reactor on its own). Slurry from the pipe reactors discharges onto recycle in the granulator. The recycle ratio is commonly 3 - 4, and the granulation temperature is maintained at 100°-110°C by ventilating the granulator with air. Moisture content of the product is typically 2.6% -2.8%.

After leaving the granulator, product is dried and cooled in a countercurrent flow of air at ambient temperature. It is then screened, oversize and fines are recycled, and on-size material is further cooled in a fluidized-bed cooler. Mechanical features of the plant include only one elevator in the granulation loop; no recycle conveyor – the recycle flows by gravity; single-deck screens; and a lump crusher that is outside the main recycle stream and can thus be serviced while the plant is operating.

In essentially the same plant it is possible to produce a wide variety of NPK products simply by adding additional raw materials. Recycle ratios of 1.5 - 2 may be achieved in NPK production. Depending on the product, the additional raw materials may be solid or liquid. For solids, appropriately sized material (< 2 mm) is added to the recycle system; liquid material is fed directly into the granulator.

Typical consumption of raw materials and utilities is given in Table 12.6.

Table 12.6. Raw Materials and Utilities Consumption of the Uhde GmbH Process

Cost Components/Product	DAP[a] 18-46-0	NPK[b] 17-17-17
Raw Materials:		
Phosphoric acid (42% P_2O_5), kg/t	1,035	383
Sulfuric acid (100% H_2SO_4), kg/t	50	36
Ammonia, liquid, kg/t	222	61
Ammonium nitrate (96%), kg/t	0	362
Potassium salt (60% K_2O), kg/t	0	286
Utilities:		
Process water, kg/t	5	144
Steam (LP), kg/t	30	22
Power, kWh/t	35	35
Natural gas, Nm^3/t	–[c]	3.7
Instrument air, Nm^3/h	55	55

a. Nominal capacity 1,000 tpd.
b. Nominal capacity 1,200 tpd.
c. During the startup of the plant: 1,000 Nm^3 total (not per tonne).

Reference plants:
650 tpd plant at BAFGAS, Bandirma (Turkey).
1,000 tpd plant at SASOL, Secunda (South Africa).
500 tpd plant at NCZ, Kafue (Zambia).

Source: [14].

12.3.7 S.A. Cros Technology

The pipe-reactor process developed by Cros S.A., of Barcelona, and licensed by Incro S.A., of Madrid, has been used in a number of plants. For DAP production, the process is essentially that as previously outlined, with the pipe reactor replacing the preneutralizer. Slurry leaving the pipe reactor contains some 4% to 5% moisture (from a preneutralizer, it is typically 12% - 14%). If the water balance is considered on its own, then the recycle ratio would typically be about two. However, although air is drawn through the granulator to reduce the temperature, it is not sufficient to keep the temperature below 90°C, which is necessary for good granulation. Hence, cooled recycle must be used to control temperature, and the recycle ratio is increased [18].

In many ammonium phosphate plants, there must also be the possibility of producing multi-nutrient NPK fertilizers. Although this can be achieved using a standard pipe-reactor process, Cros has developed a mixed process that uses both a pipe reactor and a preneutralizer. Depending on the product and capacity, the pipe reactor and preneutralizer are used together or individually. A 1,200-tpd plant at ENGRAIS DE GABES (Tunisia) uses this process.

12.3.8 ERT – Espindesa Technology

One particular feature of the process developed by ERT - Espindesa, of Madrid, is that, unlike other processes, reaction to MAP or DAP is completed within the pipe reactor and thus further ammoniation is unnecessary (Figure 12.10). Because no additional ammonia is needed, powdered or granular product can generally be made easily. For a powdered product, the pipe is discharged at the top of a tower. A plant of this type has been producing MAP in Spain since 1981. The pipe reactor is located near the top of a 17-m-high tower and fed with phosphoric acid and ammonia. The NH_3:H_3PO_4 molar ratio is adjusted to give that required for the product, and the moisture content of the phosphoric acid is controlled to ensure that the product contains 4% - 6% moisture. Powdered MAP is removed from the bottom of the natural draft-type tower at about 60°C. Production of powdered DAP in a similar system has been carried out in a pilot plant of 400 kg/hour, and the existing commercial powdered MAP plant is now being converted to produce DAP [19].

The process for granular DAP has an unusual feature: all the phosphoric acid feed is used in the two-stage ammonia scrubber, where most of the ammonia lost from the granulator is recovered. The partially neutralized acid from the scrubber has an NH_3:H_3PO_4 molar ratio of about 0.25 and is fed to the pipe reactor where the ratio is raised to 1.9 - 2.05, depending on the impurities present in the acid.

Depending on the impurities in the phosphoric acid, the pipe reactor can be made of 316 L stainless steel or Uranus B6. Pipe diameter and length are variable according to the design rate. For 25 tph of DAP, the

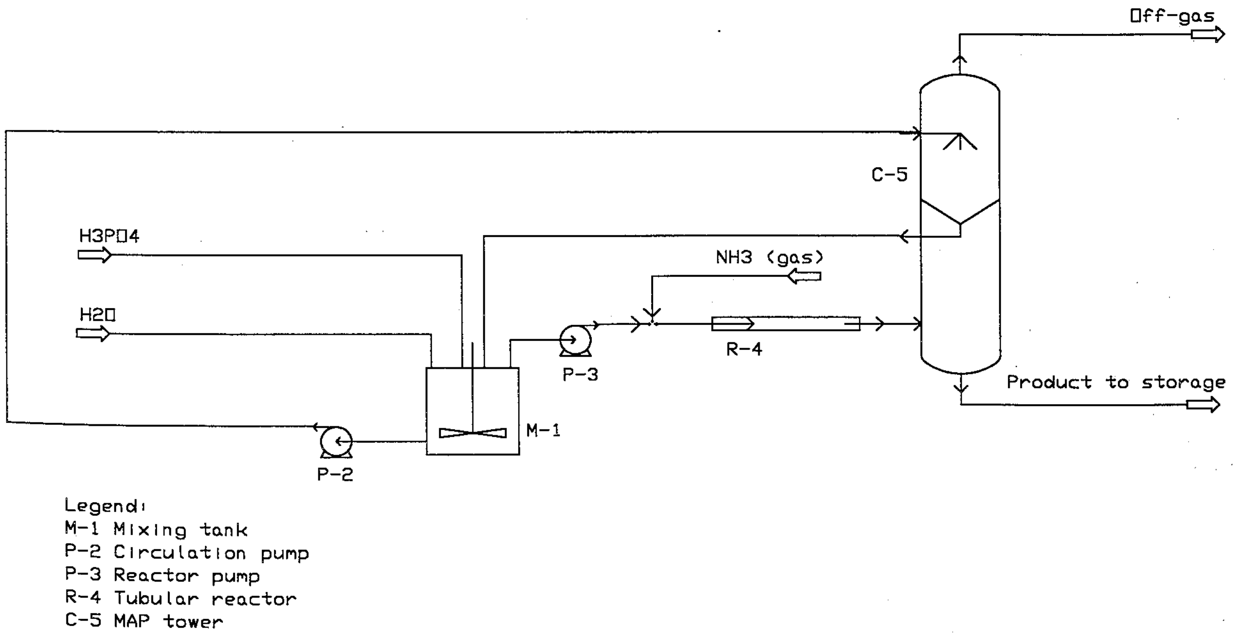

Figure 12.10. ESPINDESA MAP Production Process.

diameter is 10.2 cm and the length is 6.1 m, of which only 1.52 m is inside the granulator.

Discharge from the pipe reactor is fed directly onto recycle in a rotary drum granulator. As indicated, no ammonia is added to the granulator. The recycle ratio can be kept at 2.5 - 3.5, and at the exit of the granulator the moisture content of the DAP is below 3%. Drying is carried out in a rotary dryer, after which the product is screened.

Gas from the granulator is fed through an ammonia scrubber and then a final scrubber before it is vented. Exhaust gas from the dryer also passes through the final scrubber before it is vented to the atmosphere.

Raw materials and utilities consumption per tonne of DAP is given in Table 12.7.

12.3.9 AZF (Now Grande Paroisse) Process

CdF Chimie AZF, of Paris, or, more precisely, one of the group of companies (GESA) that was merged in 1983 to form that organization, has been operating pipe reactors since 1974. Initially, a single pipe reactor discharging into the granulator in a conventional manner was used. For the most part, this arrangement was successful for fertilizers such as 6-15-30 or 16-20-0; however, when higher analysis products were manufactured – for example, 17-17-17, 18-22-12, and 23-23-0, which are based on ammonium phosphate and ammonium nitrate – it was found necessary to have a high recycle rate, perhaps even higher than for a conventional process with preneutralizer. This high recycle was attributed to the introduction of slurry and steam at high temperature into the granulator, which raises the temperature of the granulating material and increases the solubility and liquid phase.

This problem can be overcome by arranging for some of the heat to be released elsewhere. This was accomplished by placing a second pipe reactor in the system. In the AZF dual pipe-reactor process, this second pipe reactor is located in the dryer (Figure 12.11) [20,21, 22,23,24,25].

The pipe reactor in the granulator is designed to receive part of the phosphoric acid feed, part of the ammonia feed (liquid or gaseous), and all the other liquid feeds – sulfuric acid, if required, recycled scrubbing liquor, and, possibly, concentrated solutions of ammonium nitrate or urea, although these can also be added directly to the granulator. The ammoniation rate varies, according to the product, between 0.6 and 1.4. Further ammoniation is carried out in the granulator.

In the dryer, the pipe reactor is fed with ammonia and phosphoric acid only. The N:P ratio is controlled at 1.05, so that essentially MAP is produced. The back pressure fluctuates from 3 to 5 bar.

Gases from the granulator and dryer are scrubbed in venturies with recirculating ammonium phosphate, ammonium sulfate, or ammonium sulfo-phosphate solution. Makeup sulfuric and phosphoric acid are added as necessary, and excess solution is fed to the granulator pipe reactor. Gas is finally vented through a cyclonic column sprinkled with an acidic solution.

When producing DAP, about half the phosphoric acid is fed to the pipe reactor in the dryer. The distribution of raw materials over the process units in the AZF process is given in Table 12.8.

Most of the MAP formed in the dryer pipe reactor crystallizes in the dryer or adheres to the fine particles and is subsequently removed by screening for recycle to the granulator. The DAP is actually formed in the granulator. However, by producing part of the MAP in the dryer, the recycle ratio can be reduced (typically it is about 3) and the heat of reaction and crystallization are used fully in drying the product. The N:P ratio at various positions around the granulation loop is also shown in Figure 12.11.

Raw materials and utilities consumption per tonne of DAP is given in Table 12.9.

Table 12.7. Raw Materials and Utilities Consumption of the ERT-Espindesa Process

Cost Components/Product	Consumption Per Tonne DAP (18-46-0)
Raw Materials:	
Ammonia (100%)	221 kg
Phosphoric acid (as 100% P_2O_5)	463 kg
Utilities:	
Steam	1 kg
Power	25 kWh
Fuel oil	2 kg

Reference plant:

Powder MAP - 500 tpd plant at Huelva (Spain).

Source: *Phosphorus and Potassium*, No. 144, July-August 1986.

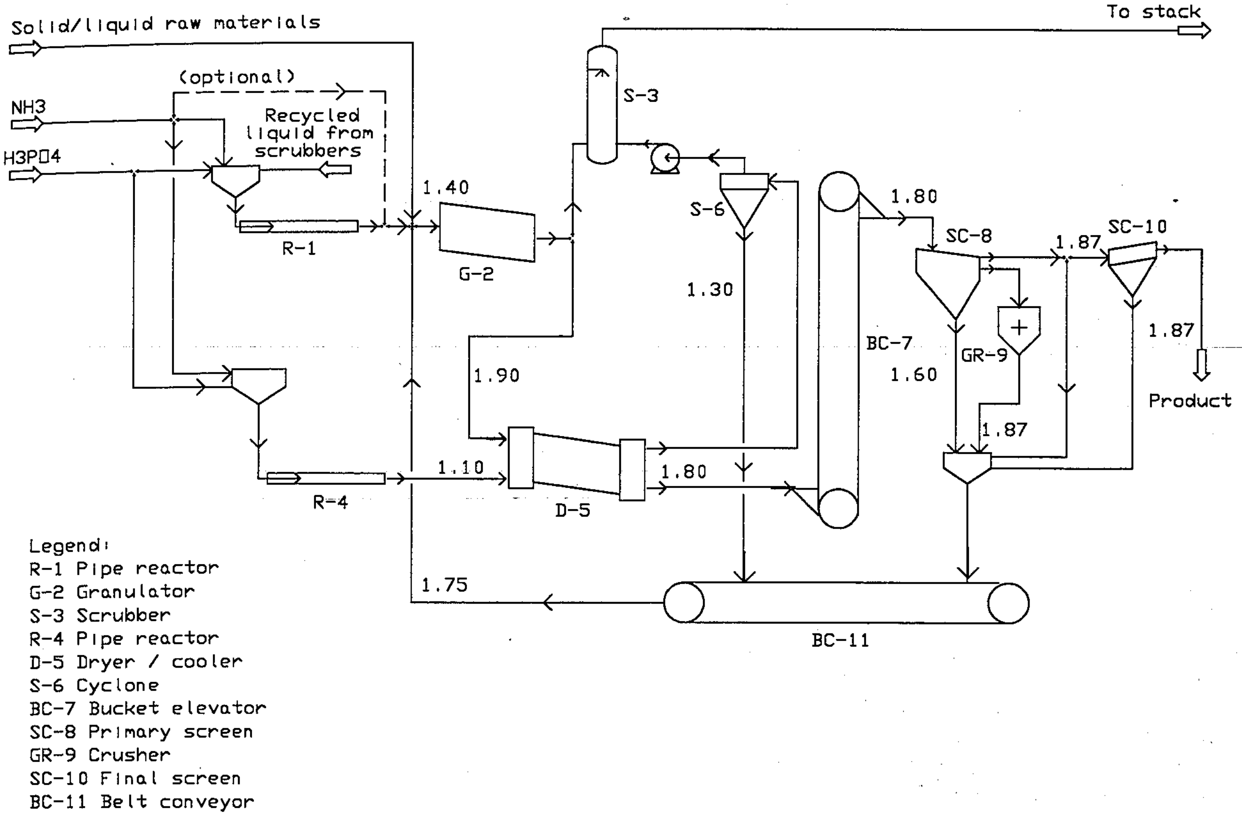

Figure 12.11. AZF DAP/NPK Process.

Table 12.8. Distribution of Raw Materials for DAP Production in the AZF Process

Process Units	Phosphoric Acid (%)	Ammonia (%)
Dryer pipe reactor	50	28
Granulator pipe reactor	37	29
Granulator	–	43
Scrubber	13	(18)[a]

a. Mainly losses from granulator.

Source: [14].

Table 12.9. Raw Materials and Utilities Consumption of the AZF Process

Cost Components	Consumption Per Tonne DAP (18-46-0)
Raw Materials:	
Ammonia (as 100%)	220 kg
Phosphoric acid (as 100% P_2O_5)	468 kg
Sulfuric acid (100%)	5 kg
Utilities:	
Steam	50 kg
Fuel	10 kg

Reference plants:

1,200-tpd plant at Grande Paroisse, Rouen (France).
1,600-tpd plant at Saepa, Gabes (Tunisia).
4- x 1,200-tpd plant at Maroc Phosphore, Jorf/Lasfar (Morocco).

12.3.10 Norsk Hydro Process

Another approach to limit energy consumption is the use of pressure reactors as promoted by Norsk Hydro Fertilizers [26]. They claim the following advantages:

- The solubility of ammonium phosphate increases with temperature.
- The boiling points of solutions increase with increased pressure.

Therefore, by applying pressure to the reaction system, the temperature of the ammonium phosphate solution can be elevated above its atmospheric boiling point. In this way, a pressure reactor can be operated at much lower water contents relative to atmospheric reactors because solubilities can be achieved that are not possible under atmospheric conditions. Figure 12.12 shows the Norsk Hydro fertilizer draft tube reactor used as a pressure reactor in a slurry granulation process for manufacturing a wide range of formulas such as 18-46-0 (DAP); 16-20-0 (MAP + AS); 8-26-26 and 11-33-22 (NPK).

12.3.11 Raytheon Process

This is a typical application of the TVA basic process incorporating many industrially proven developments. Like the basic TVA process, it operates the preneutralizer at a mole ratio of 1.4 and feeds the balance of the ammonia to the granulator to complete the reaction to a 1.95 mole ratio. Some of the developments claimed by Raytheon [27] are as follows:

- A two-stage reactor-granulator scrubbing system to ensure high ammonia recovery and good water balance control and to minimize fluoride emissions.
- A discharge trommel or dryer, which destroys lumps without a lump crusher.
- Improved dryer lifting flight design.
- Improved process screen arrangement that permits higher efficiency.
- Adjustable venturi throats on scrubbers, which can be altered to improve environmental emissions while in operation.
- A simplified and effective dust control system.
- A large sump used to collect wash water for return to the process. It also is used to heat water for total plant wash-down.
- Distributive control system with auto-sequential startup and shutdown feature, including data logging, graphing process variables, and printing periodic production reports.

The following plants use the Raytheon process:

1,300-tpd plant for CHEVRON (U.S.A.)
2 x 900 tpd plant for (formerly) FERTIMEX (Mexico)
2 x 600 tpd plant for Jordan Fertilizer Ind. Co. Ltd. (Jordan)

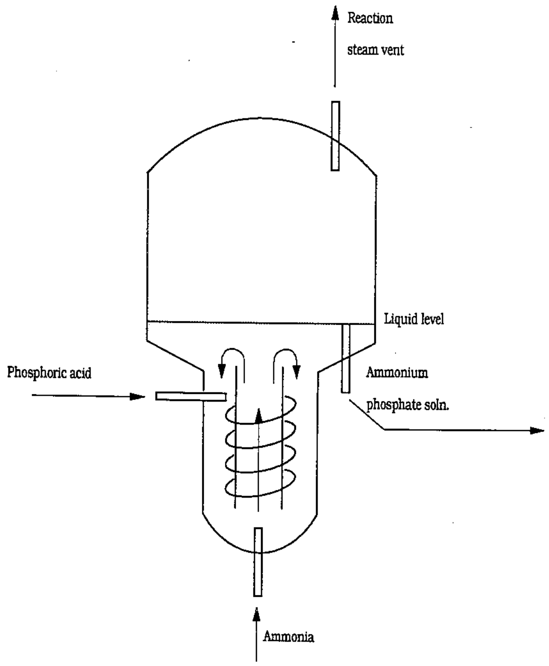

Figure 12.12. Norsk Hydro Fertilizers Draft Tube Reactor.

12.4 Nongranular MAP

Another development has been the production of nongranular MAP for use as an intermediate in producing compound fertilizers. World capacity was estimated at 3.4 million tpy in December 1993, including plants under construction. In most cases, the product is made in large plants located adjacent to phosphoric acid plants. Often the product is shipped to smaller granulation plants for use as raw material to be granulated with others in an agglomeration granulation of compound fertilizers.

Processes for making nongranular MAP have been developed by Scottish Agricultural Industries (SAI), Fison's Ltd., Swift Agricultural Chemicals, Nissan and ERT - Espindesa (described periodically, and in reference 28). In general, all processes aim at a simple, low-cost method by eliminating granulation, recycling, and drying. However, the product should have sufficiently good physical properties to permit storage, handling, and transportation without excessive caking or dust problems.

Although production of powdered MAP is declining, it is still produced in some plants as a cheap and efficient method to solidify sludge phosphoric acid into a fertilizer intermediate or a feed material. MAP is the most concentrated P_2O_5 (52%) product and can be considered as an important component for the production of complex fertilizers in developing countries.

12.4.1 Fisons Process

In the Fisons process (Figure 12.13), phosphoric acid of about 50% P_2O_5 concentration is reacted with gaseous ammonia under 2.1 kg/cm^2 gauge pressure. The heat of reaction drives off part of the water as superheated steam. The remaining slurry contains 9%-10% water, the temperature is 170°C, and the pH is 3.5-4.0. This hot slurry is released into a spray tower through a special spray nozzle. More water is flashed off and evaporates as the droplets cool and solidify by falling through an ascending airstream. The product (trade name – Minifos) contains about 6% moisture; the grade ranges from 10-50-0 to 12-56-0, depending on the impurity content of the acid. The product is in the form of small round particles (microprills) ranging from 0.1 to 1.5 mm.

12.4.2 Swift Process

In the Swift process (Figure 12.14), phosphoric acid (50% P_2O_5) and liquid ammonia react in a two-fluid nozzle, which discharges into a reactor pipe. The mixture of finely divided MAP and steam is injected into a cooling tower where a countercurrent airstream carries away the water vapor formed by the heat of reaction and cools the product. The product moisture content is 3%-5%. The Nissan process is also a spray tower process, in which droplets of phosphoric acid react with ammonia in an ascending airstream.

12.4.3 Scottish Agricultural Industries Process

The Scottish Agricultural Industries (SAI) process (Figure 12.15) consists of a reaction vessel in which phosphoric acid (about 50% P_2O_5) is neutralized with ammonia to a mole ratio of about 1.35, and the resulting hot slurry is mixed with more phosphoric acid in a specially designed twin-shafted mixer somewhat like a pugmill, which disintegrates the mass into small particles releasing water vapor. Water is evaporated in both steps. The product (trade name "PhoSAI") typically contains 6% moisture, 11% N, and 50% water-soluble P_2O_5 [29]. The process can be modified to produce a nongranular diammonium phosphate called "Di-PhoSAI" or an ammonium phosphate-sulfate.

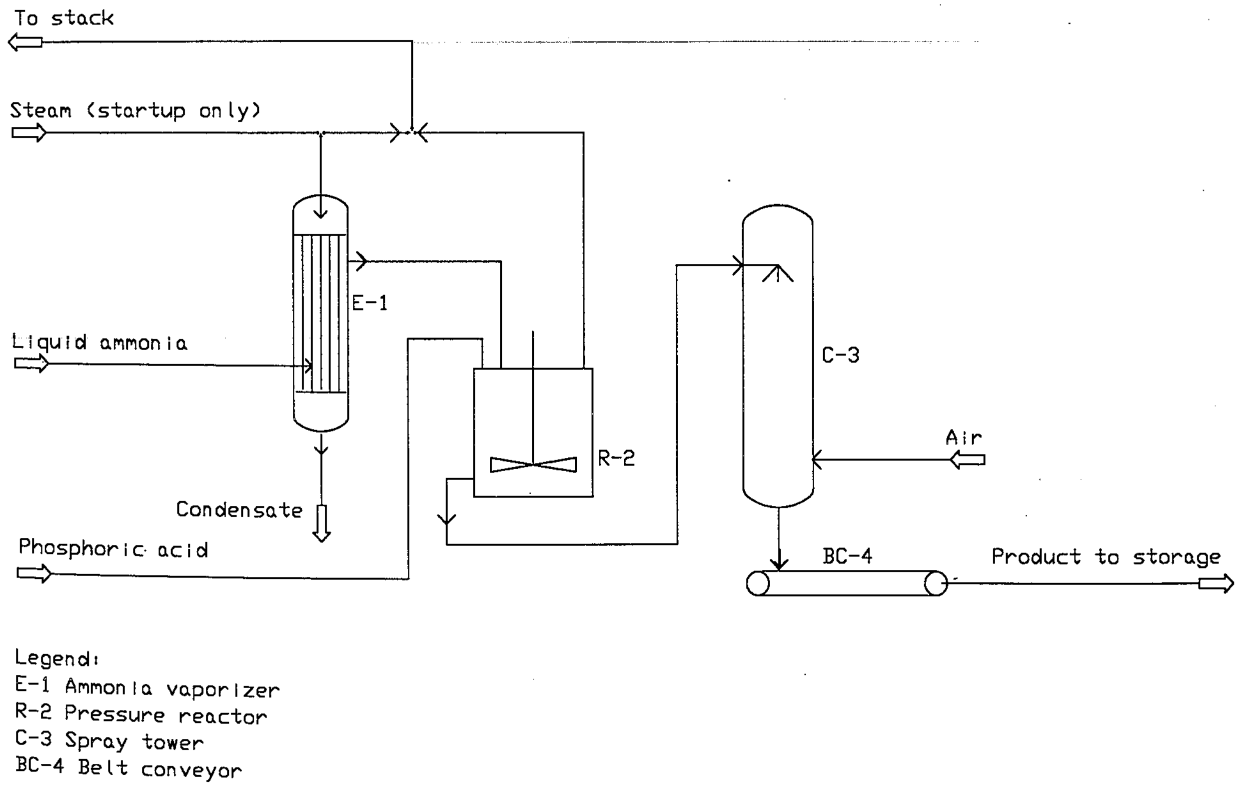

Figure 12.13. Fisons "Minifos" Process.

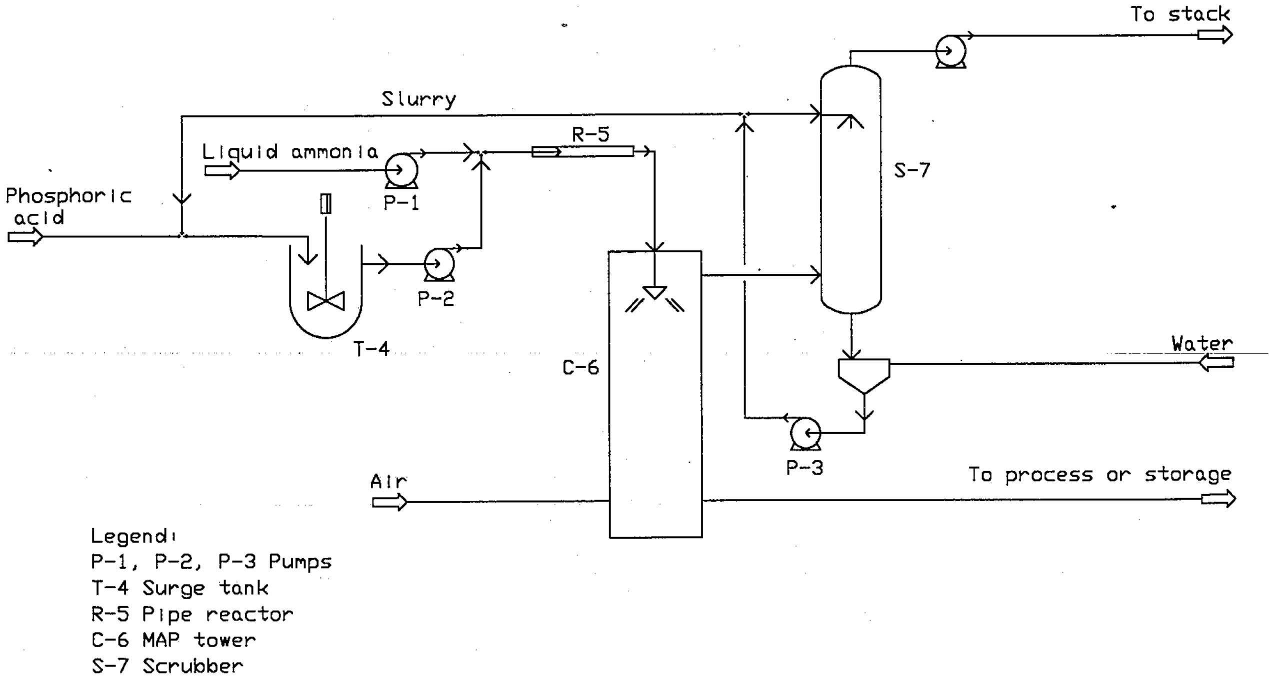

Figure 12.14. Swift Powder MAP Process.

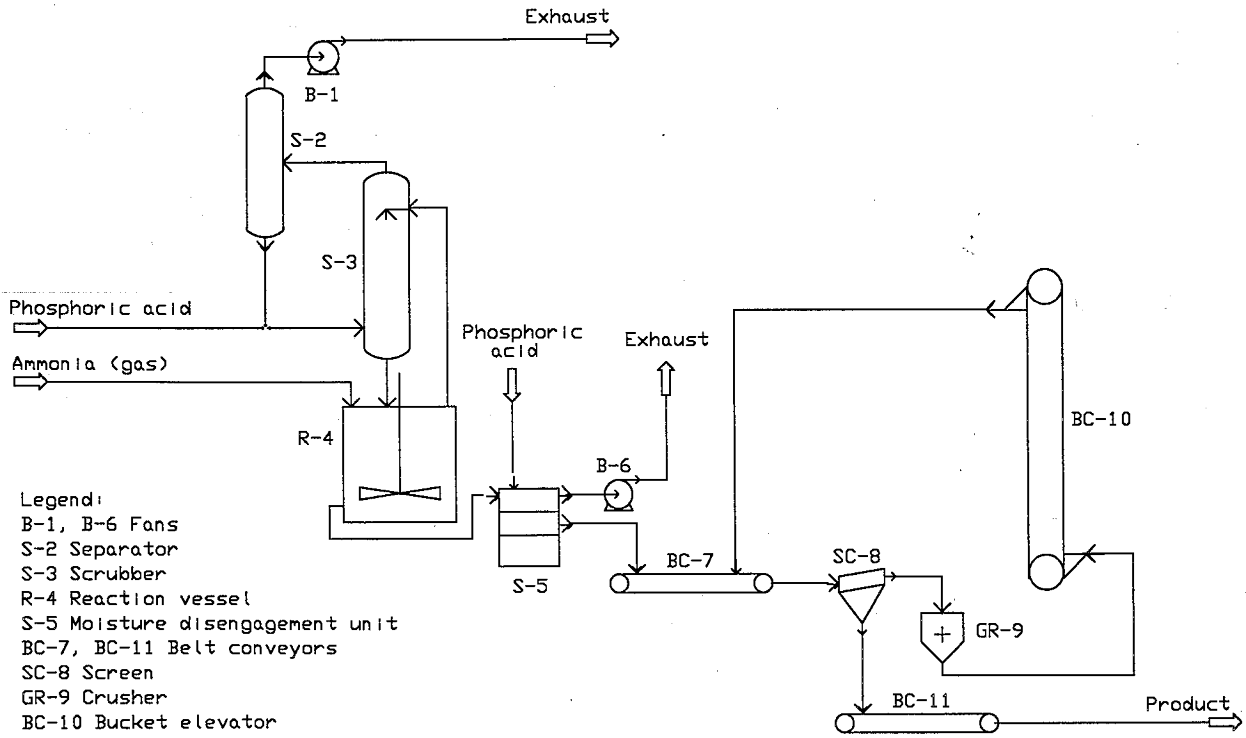

Figure 12.15. SAI Process for Producing Nongranular MAP.

The storage and granulating properties of MAP are affected by the various manufacturing processes used [30,31]. Better properties of the product made by the lower temperature process (SAI process) were attributed to precipitation of impurities in a gelatinous form that coated the MAP crystals.

12.5 Ammonium Polyphosphate

TVA developed a process for producing granular ammonium polyphosphate, and in late 1973 the process was put into operation in a demonstration-scale plant with a capacity of 13-17 tph. The plant produced straight ammonium polyphosphate and urea-ammonium phosphate alternately. A flow diagram is shown in Figure 12.16. The process uses the heat of reaction of phosphoric acid (54% P_2O_5) with gaseous ammonia to evaporate water and dehydrate the ammonium phosphate, thereby forming a melt that can be granulated with or without urea or other additives.

The main reaction takes place in a pipe reactor where the temperature reaches 210° - 230°C. The melt usually contains 15%-25% of the P_2O_5 as polyphosphate, but the polyphosphate content can be increased to almost 50% by preheating the acid and ammonia or by using a more highly concentrated phosphoric acid. The melt was granulated in a pugmill in the demonstration-scale plant, but a rotary granulator was used in later pilot plant tests. The usual grade produced in the demonstration-scale plant was 11-55-0; higher grades (such as 12-57-0) were made in the pilot plant using phosphoric acid with a lower impurity content. By the addition of urea, 28-28-0 and 36-17-0 are produced.

The principal advantage of the process is that products with very low moisture content are made without drying. Elimination of the rotary dryer and its appurtenances

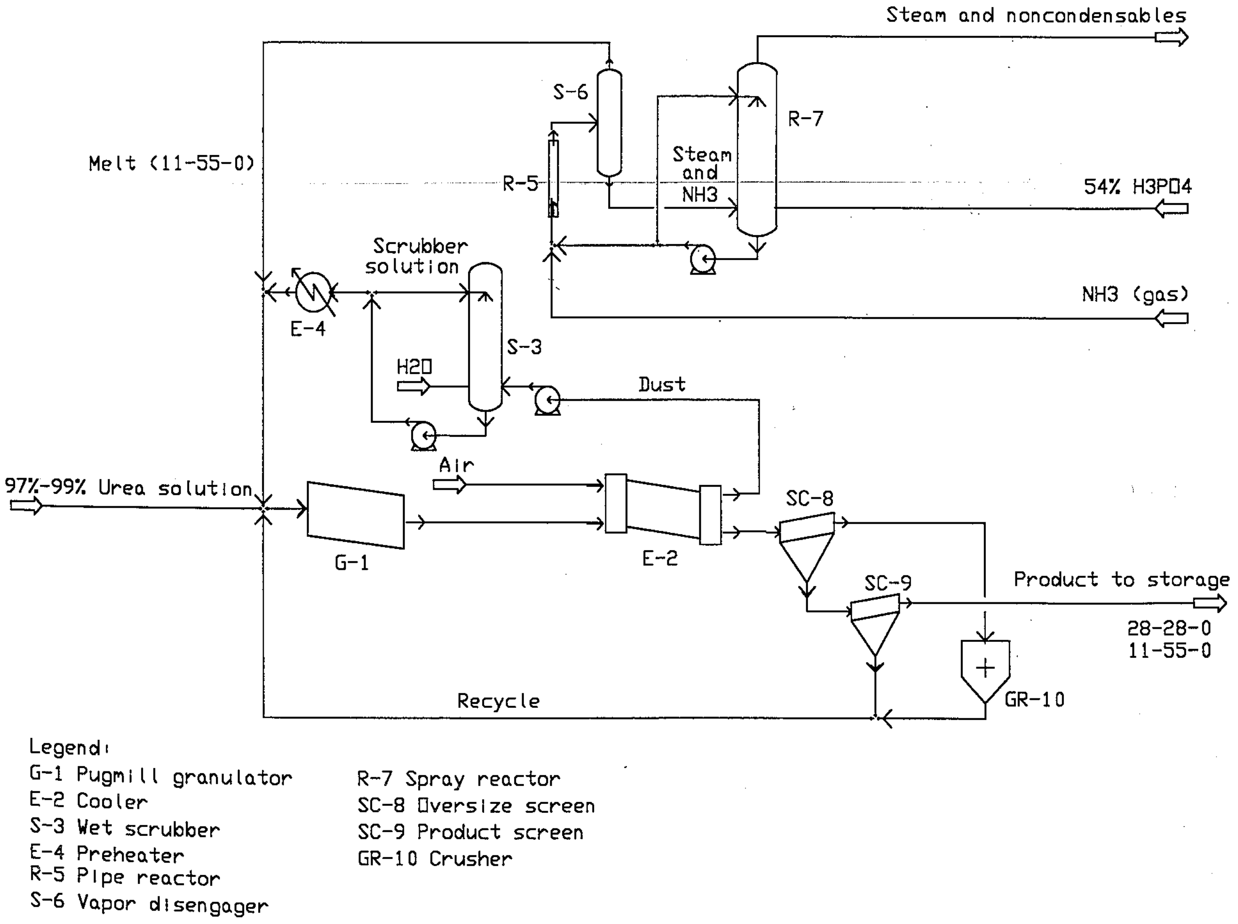

Figure 12.16. TVA Pipe Reactor-Pugmill Process for Production of Ammonium Polyphosphate.

substantially decreases the investment cost and the energy requirement (fuel and electrical energy). Another advantage of the process is that the product has exceptionally good storage properties, which are attributed to the low moisture content and the polyphosphate content of the product.

TVA estimates that the saving in capital cost as compared with a slurry process would be $740,000 for a 30-tph plant or $1,120,000 for a 50-tph plant. This is equivalent to 20%-25% of the battery-limits cost of a granulation plant. The saving in energy cost was estimated at 7 kWh of electrical energy and 140,000 kcal of fuel/tonne of product (11-55-0). The fuel saving would be partially offset by an increased steam requirement for concentrating the phosphoric acid to about 54% P_2O_5 as compared with an average of about 40% for the slurry process.

Norsk Hydro has developed a method for air-prilling MAP melt containing some polyphosphates [32]. The melt is produced in a pipe reactor. The grade is 11%-12% N and 57%-58% P_2O_5 depending on the acid composition.

12.6 Comparative Economics of TSP and DAP

12.6.1 General Comparison

A question often arises regarding the choice of a phosphate product to be produced from phosphoric acid. With established technology, the choice often lies with DAP, TSP, or compound fertilizers based on these products. All of these products can be made in a slurry-type granulation plant; therefore, it is possible to build a single plant that can make the three products alternately although the plant cost would be somewhat higher than that of one designed for a single product. When there is likely to be a market for two or three products, it is probably desirable to have this flexibility, and many plants are so equipped. In large plants there may be two or three granulation lines, but even so it is well to be able to use some lines interchangeably for different products so that the product mix can be altered to suit the market demand.

A given granulation plant will have different capacities for different products. For instance, the production rate may be only 65%-70% as much for TSP as for DAP because of the higher recycle ratio for TSP. Alternatively, a granulation plant for production of TSP by the slurry process should be larger than for DAP if the same output is required.

Because TSP requires finely ground rock, the cost of equipment to grind the rock should be added. If the TSP unit is associated with a wet-process phosphoric acid plant, it is sometimes possible to prepare ground rock for both units in the same equipment. However, phosphoric acid plants often use wet grinding, coarse grinding, or even no grinding, whereas TSP requires dry, finely ground rock. Also, in many plants a higher grade of rock is used for TSP than for acid production. Therefore, separate rock-grinding facilities often are required.

In addition to the factors outlined above, any economic comparison will be influenced by the overall plan, for example, whether there are coexisting phosphoric acid or ammonia production facilities and whether the plant is located adjacent to a phosphate rock mine.

When the net cost of P_2O_5 in ammonium phosphates is compared with that of TSP by crediting the nitrogen cost at the cost of an equivalent amount of urea, it is evident that DAP is the most economical source of P_2O_5. Because of its high concentration of total plant nutrients, DAP provides further savings in storage, bagging, and transportation. These savings are illustrated by Table 12.10, which indicates costs, after leaving the plant production unit, for 1 tonne of DAP as compared with 1 tonne of TSP plus 0.39 tonne of urea. The latter combination provides the same amount of N and P_2O_5 as DAP.

Naturally, the cost of transport will depend on the method and distance, and the cost of bags will depend on the type and size of bags required by the market conditions. However, Table 12.10 shows that a total saving in delivered cost of up to $35/tonne would result under the assumed conditions by producing and marketing 0.18 tonne of N and 0.46 tonne of P_2O_5 in the form of DAP as compared with TSP and urea. The illustration does not assume that TSP and urea are mixed. The mixture (blend) would have poor physical properties because the two materials are incompatible.

12.6.2 Cost Components of the TSP and DAP Processes

The unit costs given in Table 12.11 represent features of the average process. The actual consumption figures and investment cost are functions of the local conditions and the technology selected as well as the engineering company involved. However, the figures presented in Table 12.11 could be used in the early development program and in the decisionmaking process.

12.6.3 Comparison of the Physical Properties of TSP and DAP

The chemical composition and physical properties given in Table 12.12 are for illustration only. In some countries, fertilizer properties have been standardized; however, commerce in fertilizers is organized around

Table 12.10. Cost of Storage, Handling, Bagging and Shipping of DAP Versus TSP Plus Urea[a]

Cost Components	Regional Trade	Regional Trade	Interregional Trade	Interregional Trade
	(US $/t)			
Material	DAP	TSP/urea	DAP	TSP/urea
Storage cost	3.15	4.38	3.15	4.38
Reclaiming from storage, bagging and loading	22.50	31.27	22.50	31.27
Transportation costs	30.00	41.70	30.00	41.70
Port charges, unloading, storage	–	–	20.00	27.80
Reclaiming from storage	–	–	5.00	7.00
Transportation costs to the dealer	–	–	10.00	13.90
Total delivery costs	55.65	77.35	90.65	126.05

a. The costs for 1 tonne of DAP (18-46-0) are compared with costs of 1 tonne of TSP (0-46-0) and 0.39 tonne of urea (46-0-0) handled separately. Comparison is made for bagged products.

Table 12.11. Cost Components of the TSP and DAP Processes

Investment Cost[a]	DAP (18-46-0)	TSP (0-46-0)
Battery limits	US $18.3 million	US $15.5 million
Storage	US $7 million	US $5 million

Consumption of Inputs:

Inputs	Units	DAP	TSP
Ammonia	kg/t	222	–
Phosphate rock (33% P_2O_5)	kg/t	–	400
Phosphoric acid (P_2O_5)	kg/t	467	345
Coating oil	US $/t	1	–
Packaging	US $/t	12	bulk
Electric energy	kWh/t	72	40
Steam	kg/t	–	60
Process water	kg/t	–	65
Fuel	GJ/t	0.38	–
Labor	workhours/t	0.15	0.25

a. Calculations for both products are based on 1,000-tpd capacity and operation time of 90%.

Table 12.12. Basic Properties of DAP and TSP[a]

Properties	TSP	DAP
P_2O_5 content, %	min. 38	46
– limits, %	(44-46)	(45-46)
– solubility, %	min. 93	min. 95
Nitrogen content, %	–	18 (17-20)
Granulation (size), mm	2-4	2-4
Crushing strength, kg/granule	4.5-8[b] 2.5-3[c]	3.0-5.0
Abrasion resistance, % degradation	0-1.0[b] 2.5-3.0[c]	0.5-2.0
Impact resistance, % degradation	0-1.0	0.5-1.5
Flowability, % nonflowable,[d] minutes		
25%	180	70
50%	240	130
75%	300	180
Moisture absorption,[e] mg/cm^2	235	175

a. All physical properties tests are described in Chapter 18.
b. TSP by accretion process.
c. TSP by agglomeration of run-of-pile TSP.
d. At 30°C and 90% RH.
e. At 30°C and 80% RH, for 72 hours.

nutrient content, the physical properties having secondary character. Table 12.12 gives some basic properties of TSP and DAP.

12.7 Other Fertilizers Made From Phosphoric Acid

12.7.1 Ammonium Phosphate-Sulfates

A group of fertilizers known as ammonium phosphate-sulfates has been popular for many years and is still popular in many areas. The best known grade is 16-20-0, which essentially consists of MAP and ammonium sulfate (AS). One reason for its popularity is that it is relatively nonhygroscopic. Hygroscopicity, as measured by the critical relative humidity (CRH) of some phosphate and nitrogen fertilizers and combinations, is discussed in Chapter 18.

It is evident that MAP is one of the least hygroscopic of the phosphate materials and that AS is the least hygroscopic of the straight nitrogen materials. When a fertilizer with a higher $N:P_2O_5$ ratio than that of DAP (0.4:1.0) is needed, the MAP plus AS combination is the least hygroscopic.

Another advantage of ammonium phosphate-sulfate is the sulfur content, which is agronomically useful for many crops and soils. Ammonium phosphate-sulfates have been produced by the Dorr-Oliver slurry process (previously discussed) since 1933 and more recently by other slurry granulation processes like the AZF - Grande Paroisse dual pipe-reactor process. The usual method involves reaction of sulfuric and phosphoric acid with ammonia, although ammonium sulfate from byproduct sources can be used. In addition to 16-20-0 and 11-48-0, several NPK grades are produced such as 14-28-14, 13-36-12, and 13-13-13.

In TVA's pipe-cross reactor system, illustrated in Figure 12.17, most of the reaction of phosphoric and sulfuric acids with ammonia is carried out in a pipe, which discharges a melt into the drum granulator. Steam generated by the heat of reaction is swept out of the granulator by an airstream. One advantage of the process is that the heat of reaction is utilized to dry the product, and thus no dryer is necessary. Another advantage over slurry processes is the comparatively low recycle ratio, in the range of 2-3:1 for 12-48-0 or 1-2:1 for 13-13-13 or 6-24-24.

The process developed by S.A. Cros in Spain is somewhat similar [10]. In both processes, part of the acid is sprayed on the bed of material in the rotary granulator

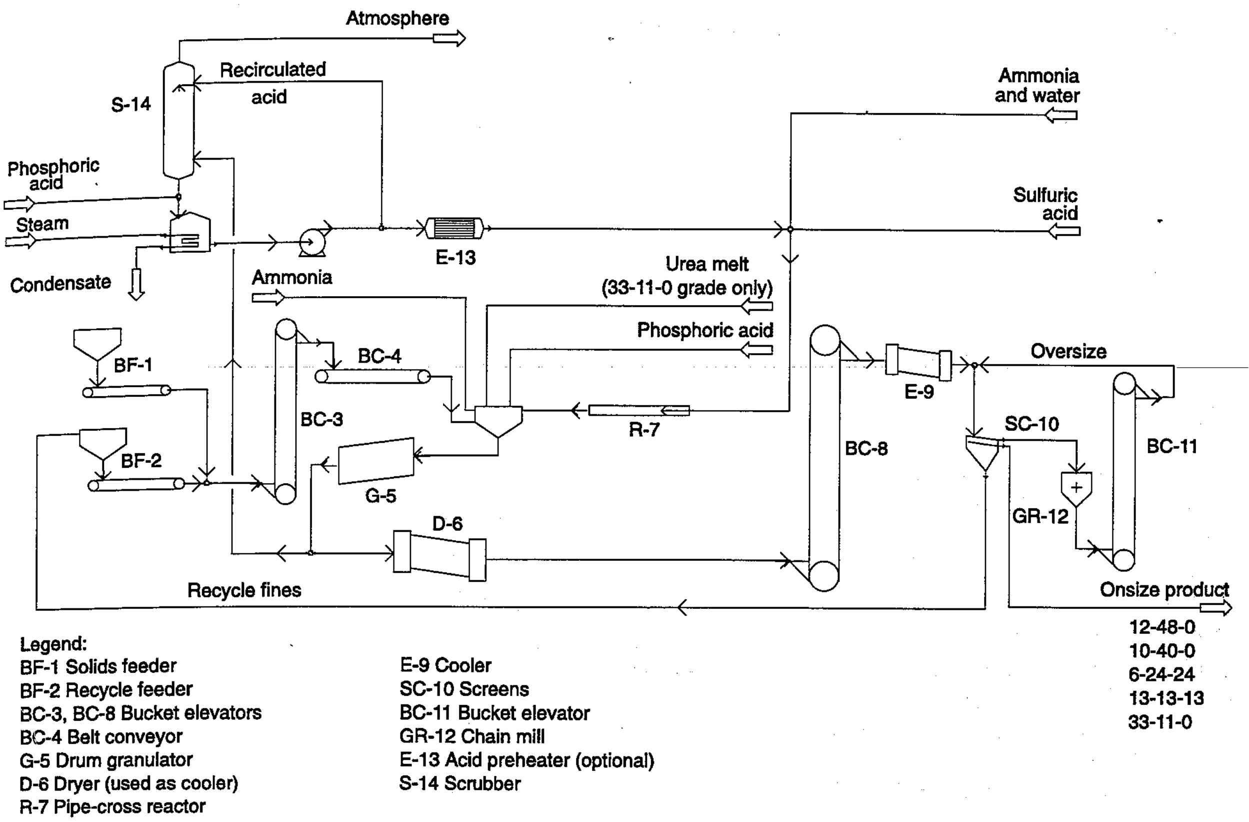

Figure 12.17. The TVA Ammonium Phosphate-Sulfate Process.

and reacted with ammonia that is injected under the bed, thereby promoting granulation and supplying more chemical reaction heat for drying.

12.7.2 Ammonium Phosphate-Chloride

Ammonium chloride is used in Japan and some other countries, both as a straight nitrogen fertilizer and as an ingredient of compound NP, NPK, and PK fertilizers. Ando described the operation briefly [33]. He mentioned that, as compared with ammonium sulfate, ammonium chloride was 10% cheaper per unit of nitrogen (in Japan in 1970) and more concentrated (25% vs 21% N). Filter-grade, wet-process phosphoric acid is ammoniated to form a MAP slurry, which is fed to a pugmill along with ammonium chloride, recycle, potassium chloride (optional), and other fertilizer materials. Ando mentioned that granulation in the pugmill is not as easy as with ammonium sulfate but noted that the difficulty had been overcome. The recycle ratio ranges from 2-4:1. The moisture content of the granulator product ranges from 5% to 6% before drying and 0.5% to 0.8% after drying. The main NP grade is 18-22-0; NPK grades include 14-14-14 and 12-18-14 [34].

12.7.3 Ammonium Phosphate-Nitrate

There are several processes that produce fertilizers containing ammonium phosphate and ammonium nitrate, but most of them are used to produce NPK grades and will be described further under Chapter 16 "Compound Fertilizers."

Leyshon and Bowers, in describing slurry granulation in the blunger in 1967, mentioned a plant in Romania that produced 23-23-0 and several others that produced various NPK grades [35]. The slurry was produced by ammoniation of phosphoric and nitric acids. Detunc described a Pechiney - Saint-Gobain process in which concentrated ammonium nitrate solution (97%) and ammonium phosphate slurry were fed to a rotary-drum granulator [36]. The ammonium phosphate slurry was produced by ammoniating phosphoric acid to an NH_3:PO_4 mole ratio of 0.6 in a preneutralizer; more ammonia was added in the granulator to raise the mole ratio to 1.05. The principal product was 17-17-17. TVA operated a demonstration-scale plant for several years producing 25-25-0 and 30-10-0 ammonium phosphate-nitrate (APN) grades. The slurry or concentrated solution was prepared by reacting ammonia with nitric and phosphoric acid, concentrating the solution to about 5% water by evaporation, and granulating the resulting slurry in a pan granulator.

The production rate was about 20 tph. Mixed phosphoric and nitric acids were neutralized with ammonia in a first stage to a pH of 1.6, then concentrated, and then neutralized in a second stage to a pH of about 5.6 to prepare the hot (170°C) concentrated solution for granulation [37].

The AZF - Grande Paroisse dual pipe-reactor process introduces ammonium nitrate as a solution that is directly sprayed onto the bed of granules in the granulator. SAI has also developed a system for coneutralization of phosphoric and nitric acids to produce a concentrated APN solution, which is granulated with potash in a combination granulator dryer consisting of two concentric drums with internal recycle [38].

APN solutions are readily produced by neutralizing phosphoric acid with ammonia-ammonium nitrate solutions. This method has been used in many small granulation plants in the United States, but the solution is used as supplemental feed for compound fertilizer production. Porter and Sheldrick described Fison's melt granulation process for producing APN such as 24-24-0 [39]. Prilling of APN melts has been carried out by Monsanto Chemical Company Processes for prilling APN melts, with the addition of potash, have been developed by Stamicarbon and Albright and Wilson. APN melts may contain some polyphosphate, which lowers the melting point.

12.7.4 Urea-Ammonium Phosphates

Combinations of urea with ammonium phosphate represent the last step, with available materials, in progress toward higher analysis fertilizers. Fertilizers based primarily on urea and ammonium phosphate have been produced in Japan for many years. Ando described a variety of processes that were in use in 1970 [33]. Ammonium phosphate was supplied either as a slurry produced in the plant by ammoniation of phosphoric acid or in solid form as MAP or DAP. Urea was supplied as a solid (crushed prills or crystals), as a melt, or as a concentrated solution. Several types of granulators were in use; rotary drums were the most common, but pan granulators, pugmills, and other types were used in some plants.

A later paper gave a detailed description of a granulation plant that produces urea-ammonium phosphate (UAP) grades, such as 28-28-0, 22-22-11, 18-18-18, etc. [40]. The main raw materials are crushed urea prills, spray-dried ammonium phosphate (12-50-0), and potash salts. One unusual feature of the plant is a methylene-urea reactor, which is used for production of some NPK grades. Part of the urea is fed into the steam-heated reactor with formaldehyde solution to produce a methylene-urea slurry containing unreacted urea, monomethylene diurea, dimethylene triurea, and trimethylene-tetraurea. The purpose of this step is to facilitate drying, improve the physical properties of the products, and provide some slow-release nitrogen.

Another unusual feature of the plant is a rotary ammoniator-mixer containing roller shafts. Its function is to receive the solid raw materials, the recycled fines, and the methylene-urea slurry (if used) and mix them thoroughly by a kneading action. Ammonia is added in the mixer although, in the example given, the amount of ammonia is small (6 kg/tonne of 18-18-18). From the mixer, the product goes to a rotary granulator and then to a dryer, screening facilities, a cooler, and a coating drum. The moisture content of the granules leaving the granulator typically is about 3%, and this is controlled by the addition of steam and/or water in the granulator or mixer and by the moisture content of the methylene-urea slurry. The temperature in the granulator is about 63°C, and the recycle ratio is 2.0 - 2.5:1. Formulations given in the paper [40] indicate that the methylene-urea reactor is not used for 28-28-0; it is used for several NPK grades in which the mole ratio of urea:formaldehyde is 3.7:1. The paper also mentioned that gypsum may be added as a granulation aid, magnesium or manganese is added to some grades, and nitrification inhibitors are added in some products.

TVA pursued the development of UAP processes for several years. The first approach was to incorporate urea into their DAP slurry granulation process. In pilot-plant tests of this method, UAP grades ranging from 38-13-0 to 21-42-0 were produced. Urea was added in the granulator either as concentrated solution or solids (crystals or prills). This general method has been used in at least two plants in India to make 28-28-0 and other grades using solid urea. Coromandel Fertilizers Limited (CFL) in India implemented the TVA technology using a preneutralizer as well as operation with a pipe reactor [41]. The specification for UAP (28-28-0) produced at CFL is given in Table 12.13.

Table 12.13. Specification of UAP Produced by CFL (India)

Concentration, %	Value
Total nitrogen	28.0
Nitrates	Nil
Ammoniacal N (min.)	9.0
P_2O_5 (min.)	28.0
Water-soluble P_2O_5 (min.)	25.2
Free moisture	1.5

The basic concept of the process is that slurry obtained in the reactor (preneutralizer or pipe reactor), at a NH_3:H_3PO_4 ratio of 1.4-1.45 and water content of 16%-18%, is pumped into the granulator where urea, recycled materials, and ammonia are added. Granules are dried, sieved, and bagged. Unreacted ammonia from the reactor and granulator as well as the fine particles from the dryer and cooler cyclones are recovered in a scrubber by washing with circulated 30% phosphoric acid and water. The continuous stream of weak acid is fed back to the reactor. The parameters of the operation are given in Table 12.14.

The same system has been used to produce NPK 14-35-14. Operating results with the two processes, preneutralizer and pipe reactor, are compared in Table 12.15.

In TVA's production of UAP by a melt granulation process, mentioned previously, ammonium polyphosphate melt and molten urea were cogranulated in a pugmill. The principal grade was 28-28-0, produced at a rate of 16 tph; 35-17-0 was also produced. The production rate was limited by the capacity of the urea synthesis unit. TVA also prilled a molten mixture of UAP in a pilot-plant oil-prilling unit. Norsk Hydro developed a process on a pilot-plant scale for prilling UAP in air with or without potash addition [42]. In the TVA work, ammonium polyphosphate melt was premixed with urea melt immediately before prilling. In one variation of the Norsk Hydro process, preheated solid MAP is premixed with urea melt before prilling; alternatively preheated solid urea is premixed with MAP melt. The prills are relatively large (1.8 mm, average), hard, and dense. Grades of 29-29-0 and 38-16-0 are produced. A diagram of the Norsk Hydro process is shown in Figure 12.18.

The AZF - Grande Paroisse dual pipe-reactor process introduces urea as a solution that is sprayed directly onto the bed of granules in the granulator.

Table 12.14. UAP Process Parameters at CFL Plant

Parameters	Reactor	Scrubber	Granulator	Dryer
Temperature, °C	116-120	50-55	75-79	200-220 75-80
NH_3:P_2O_5 ratio	1.40-1.45	1.1-1.2	1.6	1.6
pH	5.0-5.5		6.5-7	
Specific gravity, t/m^3	1.5-1.55	1.27-1.29		
Free moisture, %	16-18		2.5-3.0	1.7-1.9
Air flow, Nm^3/h			13,600	60,000

Table 12.15. Comparison of the Preneutralizer and Pipe Reactor in UAP Production at CFL (India)

Parameters	Preneutralizer	Pipe Reactor
Slurry temperature entering granulator, °C	116-120	140
Moisture of slurry entering granulator, %	16-18	5
Temperature of granulator bed , °C	75-79	85-90
Temperature of dryer inlet, °C	200-220	110
Consumption of fuel oil, kg/t	10	5
Crushing strength of granule, kg/granule	0.8-1.0	1.2-1.3

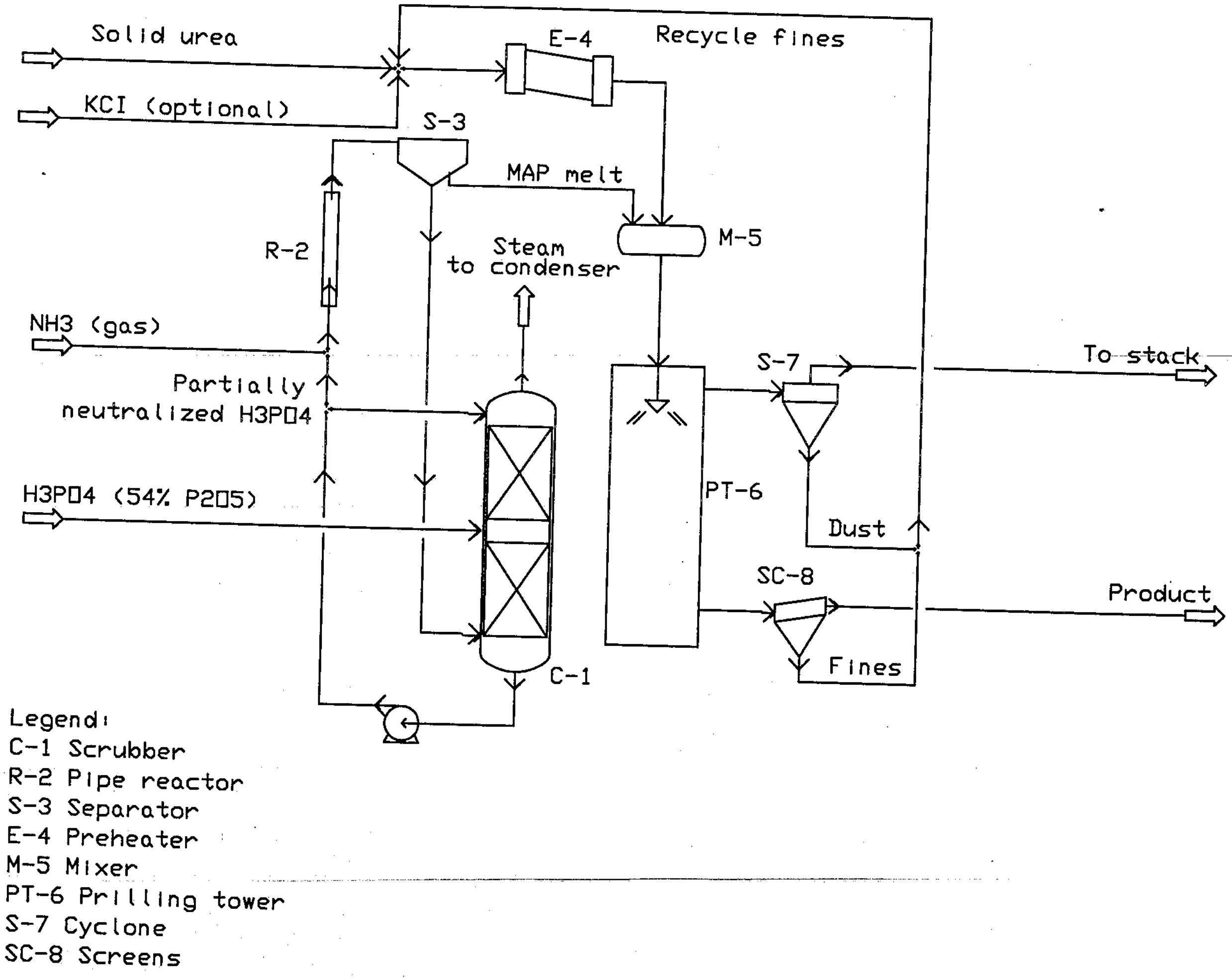

Figure 12.18. Norsk-Hydro UAP Process.

12.7.5 Use of Phosphoric Acid in Granulation Processes

Phosphoric acid often is used in granulating compound fertilizers to supply part of the P_2O_5 in formulations in which the remainder of the P_2O_5 is supplied by single or triple superphosphate or ammonium phosphates. The acid usually is sprayed into the granulator, and ammonia or ammoniating solution is added during granulation to neutralize it. The heat of reaction promotes granulation and moisture evaporation. Both merchant-grade (54% P_2O_5) and superphosphoric acid (69% - 72% P_2O_5) have been used in this way. This approach is described in detail in Chapter 16 "Compound Fertilizers."

12.7.6 Miscellaneous Fertilizer Uses for Phosphoric Acid

A potentially promising use for phosphoric acid is in the production of potassium phosphates. Substantial amounts but relatively small percentages of phosphoric acid are used for direct application to the soil, especially alkaline soils.

Slow-release fertilizers, for example, $MgNH_4PO_4$ and $MgKPO_4$ (or mixtures of the two salts), represent another use. Compounds of the general formula MNH_4PO_4, where M may be a divalent metal ion, such as Fe, Mn, Cu, or Zn, have been tested as slow-release sources of micronutrients. Urea phosphate $CO(NH_2)_2 \bullet H_3PO_4$ is an interesting compound that has been considered for use as a fertilizer. However, a more promising use is as an intermediate for production of high-analysis solid and liquid fertilizers. These possibilities have been studied by TVA and others [12,43].

Other important uses for phosphoric acid are covered in other chapters, i.e., for production of liquid fertilizers (Chapter 10) and for production of mixed-acid nitrophosphates (Chapter 13).

12.8 Process Licensors and Contractors

12.8.1 Process Licensors

The mention of the names of companies does not imply UNIDO/IFDC endorsement for any purpose. The selection is only indicative, and only companies operating worldwide have been mentioned. British Sulphur has developed a list of regional and country licensors [44].

TSP

Amfert, Amsterdam, Netherlands
Grande Paroisse, Paris, France
Hydro Agri Licensing, Brussels, Belgium
Jacobs Engineering, Lakeland, Florida, U.S.A.
Kemira Agro, Helsinki, Finland
Norsk Hydro, Oslo, Norway
Prayon Technologies, Engis, Belgium
Uhde GmbH, Dortmund, Germany

DAP

Cros, Madrid, Spain
Espindesa, Madrid, Spain
Grande Paroisse, Paris, France
Hydro Agri International, Brussels, Belgium
Jacobs Engineering, Lakeland, Florida, U.S.A.
Norsk Hydro, Oslo, Norway
Raytheon Engineers and Constructors, Tampa, Florida, U.S.A.
Uhde GmbH, Dortmund, Germany
Weatherly, Atlanta, Georgia, U.S.A.

Contractors

Most contractors are able to build factories for any of the processes discussed; a few are listed below.

Chiyoda Chemical Engineering and Construction, Tokyo, Japan
Coppee - Lavalin, Brussels, Belgium
Jacobs Engineering, Lakeland, Florida, U.S.A.
John Brown Engineers and Constructors Ltd, London, U.K. including Davy Powergas Ltd, London, U.K. and John Brown Deutsche Engineering GmbH, Essen, Germany
Krebs, Montigny-le-Bretonneux, France
Lurgi Chemie und Huettentechnik, Frankfurt-am Main, Germany
Mitsui and Co Ltd, Tokyo, Japan
Raytheon Engineers and Constructors, Tampa, Florida, U.S.A.
Snamprogetti s.p.a., Milan, Italy
Technip - Speichim, Cergy-Pontoise, France
Uhde GmbH, Dortmund, Germany

12.9 References

1. Benes, J. A., and H. Franzrahe. 1994. "Modifying Existing DAP/NPK Fertilizer Plants to Comply With New Environmental Regulations," IFA Technical Conference Proceedings, Amman, Jordan.
2. Houghtaling, J., and V. J. Margiotti, Jr. 1994. "Advanced Ammonia Phosphate Scrubbing With Minimum Water Discharge," IFA Technical Conference Proceedings, Amman, Jordan.
3. Bridger, G. L., R. A. Wilson, and R. B. Burt. 1947. "Continuous Mixing Process for the Manufacture of Concentrated Superphosphate," *Industrial Engineering Chemistry*, 39:1265-1269.
4. Bridger, G. L. 1949. "Development of Processes for Production of Concentrated Superphosphate," *Chemical Engineering Report 5*, TVA, Muscle Shoals, AL, U.S.A.
5. Sinte Maartensdijk, A. 1976. "Direct Production of Granulated Superphosphates and PK Compounds From Sulphuric Acid, Phosphoric Acid, Rock Phosphate and Potash," ISMA 1976 Technical Conference Proceedings, The Hague, Netherlands.
6. Leyshon, D. W., and I. S. Mangat. "Innovations in Slurry Granulation Plants," *Ibid.*
7. "Superphosphate: Its History, Chemistry and Manufacture." 1964. U.S. Department of Agriculture and TVA, pp. 105-106.

8. Handley, M. M. 1984. "Effects of Impurities on Production of Diammonium Phosphate," IFA Technical Conference Proceedings, Paris, France.

9. Fittel, R. S., and L. A. Hollingsworth. 1977. "Manufacture of Ammonium Phosphates Using a Pipe Reactor Process," Proceedings of the 27th Meeting of the Fertilizer Industry Round Table, pp. 70-80.

10. "The Cros Fertilizer Granulation Process." 1977. *Phosphorus and Potassium*, 87:33-36.

11. Danos, R. J. 1978. "Pipe Reactor Making Diammonium Phosphate Now," *Chemical Engineering*, 85, N22, 81-83.

12. TVA. 1978. "New Development in Fertilizer Technology," Bulletin 136:52-55, TVA, Muscle Shoals, AL, U.S.A.

13. "Predicament Posed by Poor Quality Phosphate Rock." 1978. *Chemical Engineering* 85, N22, 67-69.

14. "Improved Techniques for Ammonium Phosphate Production." 1986. *Phosphorus and Potassium*, 144 (July-August):27-33.

15. Achorn, F. P., and D. G. Salladay. 1982. "Optimizing Use of Energy in the Production of Granular Ammonium Phosphate Fertilizer," IFA Conference Proceedings, Kallithea, Greece.

16. Salladay, D. G., and W. H. Paulson. 1984. "Development of TVA Pressure Reactor for Production of Ammonium Phosphate," Proceedings of the 34th Annual Fertilizer Round Table Meeting, Baltimore, MD, U.S.A.

17. Uhde GmbH. 1985. "Diammonium Phosphate and Compound Fertilizer Plants: The Uhde Pipe Reactor Concept," Uhde GmbH, Dortmund.

18. Loste, R., and J. L. Toral. 1983. "Improvements in the S.A. Cros Pipe Reactor Technology," British Sulphur International Conference Fertilizer '83, November.

19. Marzo, L. M., and J. L. Lopez-Ninio. 1986. "Powdered or Granular DAP," IN New Diammonium Phosphate Technology Proceedings N245, The Fertilizer Society, London.

20. Moraillon, P. H., and Y. Cotonea. 1984. "Energy Conservation in Fertilizers Granulation," IFA Technical Conference Proceedings, Kallithea, Greece.

21. Chinal, P., Y. Cotonea, and C. Debayeux. 1984. Proceedings of AIChE Meeting, Clearwater, FL, U.S.A.

22. Chinal, P., and Y. Cotonea. 1984. "New Development in the Dual Pipe Reactor Process," IFA Technical Conference Proceedings, Paris, France.

23. Sundaravadivelu, M. 1985. Communication to the Fertiliser Association of India, New Delhi, India.

24. Chinal, P., et al. 1985. "AZF Process for the Manufacture of Granular Fertilizers Using Two Tubular Reactors," United Nations Seminar, Istanbul.

25. Chinal, P., et al. 1986. "Dual Pipe Reactor Process for DAP, NP, NPK Production," IN *New Diammonium Phosphate Technology, Proceedings* N245, The Fertilizer Society, London.

26. Ivell, D. M., and N. D. Ward. 1984. "The Use of a Pressure Neutralizer for Slurry Granulation," IFA Technical Conference Proceedings, Paris, France.

27. Raytheon Engineers and Constructors, Tampa, FL, U.S.A. 1994. Private communication.

28. Lopez-Ninio, J. L., and L. M. Marzo. 1986. "Nongranular or Granular MAP and DAP Through a Pipe Reactor," IFA Technical Meeting Proceedings, Port El Kantaoui, Tunisia.

29. Brownlie, I. A., E. Davidson, and T. R. Dick. 1977. "Developments in Ammonium Phosphate Technology," Proceedings N162, The Fertilizer Society, London.

30. Kolmeyer, N. W., and P. H. Anderton. 1976. "Powder Monoammonium Phosphate Production at Resources Tunisie S.A.," *Phosphorus and Potassium* 86:39-43.

31. "Caking in Powder Monoammonium Phosphate." 1976. *Phosphorus and Potassium*, 86:45-47.

32. Freng, T., and O. H. Lie. 1974. "Urea Based NP/NPK Fertilizers by Air Prilling," American Chemical Society Meeting Proceedings, Atlantic City, NJ, U.S.A.

33. Ando, J. 1970. "Development in Granulation of Mixed Fertilizers in Japan," Fertilizer Industry Round Table Proceedings, Tokyo, Japan, 85-92.

34. UNIDO. 1969. "The Ammonium Chloride and Soda Ash Dual Manufacturing Process in Japan," Fertilizer Industry Series Monograph N4, UNIDO, Vienna, Austria.

35. Leyshon, D. W., and Q. D. Bowers. 1967. "Concepts of Ammoniation and Granulation in the Blunger," Fertilizer Industry Round Table, 17th Annual Meeting Proceedings, 39-44.

36. Detunc, Y. "Manufacture of 17-17-17 High Analysis Fertilizers." *Ibid.*

37. Meline, R. S., T. W. McCamy, J. L. Graham, and T. S. Sloan. 1968. "Plant-Scale Production of Fertilizers in a Pan Granulator," *Journal of Agricultural and Food Chemistry*, 16:235-240.

38. Whyte, G. B. 1972. "Low Recycle NPK Granulation Design and Practical Aspects," Proceedings N127, The Fertilizer Society, London.

39. Porter, S. J., and W. F. Sheldrick. 1966. "Fisons' Melt Process for Manufacture of Concentrated Granular Fertilizers," Fertilizer Industry Round Table, 16th Annual Meeting Proceedings, 104.

40. Kuwabara, M., S. Hayamizu, and A. Hatekeyama. 1977. "Trends in Urea-Based Granular Compound Fertilizer Technology," IN *Granular Fertilizers and Their Production*, pp. 125-147, British Sulphur Corporation, London, England.

41. Ramadurai, S. 1990. "Operational Experiences With NP/NPK Granulation at Coromandel Fertilisers Limited – India," IN J. J. Schultz and G. Hoffmeister (Eds.), Urea-Based NPK Plant Design and Operating Alternatives, Workshop Proceedings, pp. 21-26, SP-15, IFDC, Muscle Shoals, AL, U.S.A.

42. "Urea Based NP and NPK Fertilizers." 1975. *Phosphorous and Potassium*, 76:48-54.

43. TVA. 1974. "New Developments in Fertilizer Technology," 10th demonstration Bulletin Y-81, TVA, Muscle Shoals, AL, U.S.A.

44. British Sulphur. 1992. List of licensing and contracting companies in the field of fertilizers technology.

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Chapter 13. Nitrophosphate Fertilizers

13.1 Introduction

"Nitrophosphate" is the generally accepted term for any fertilizer that is produced by a process involving treatment of phosphate rock with nitric acid. The nitrophosphate process was originally developed in Norway by Erling Johnsen as a means of avoiding the diluting effect of the sulfate ion in superphosphate. The process was named for the town of Odda, where it was developed, and that is still the generic name of certain nitrophosphate processes that embody its central principle.

After the invention of this principle in 1928, Erling Johnsen transferred his patent to Norsk Hydro A.S., which developed it in the 1930s and introduced its own technology in 1938. Norsk Hydro was among the first to produce multinutrient fertilizers – NPs and NPKs – via the nitrophosphate route.

Nevertheless, the beginnings were quite slow, and it was not until the sulfur shortage of the early 1950s that nitrophosphates became the focus of widespread interest and a number of variants of the process were developed. The principal steps of the nitrophosphate process are compared with the sulfuric acid-based process in Figure 13.1.

13.2 Fundamentals of Nitrophosphates

The basic (and simplified) acidulation reaction can be represented by the following reaction equations:

$$Ca_3(PO_4)_2 + 4\ HNO_3 \rightarrow 2\ Ca(NO_3)_2 + Ca(H_2PO_4)_2 + 20.2\ \text{kcal} \quad (1)$$

$$Ca(H_2PO_4)_2 + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + 2\ H_3PO_4 + 2.05\ \text{kcal} \quad (2)$$

overall

$$Ca_3(PO_4)_2 + 6\ HNO_3 \rightarrow 3\ Ca(NO_3)_2 + 2\ H_3PO_4 + 22.25\ \text{kcal} \quad (3)$$

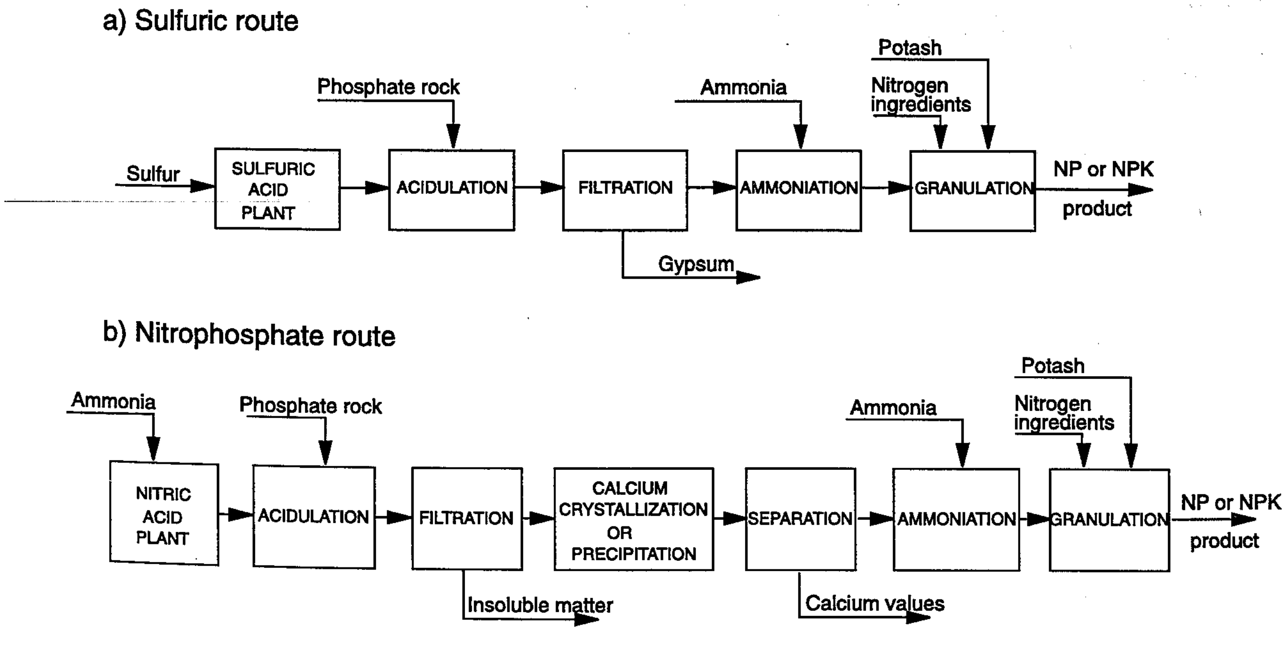

Figure 13.1. Comparison of NP/NPK Production by Sulfuric and Nitrophosphate Routes.

After separation of the insoluble material, phosphoric acid is neutralized with ammonia to produce a fertilizer. If the calcium nitrate is left in the solution, it reverts to dicalcium phosphate upon ammoniation following the reaction:

$$2H_3PO_4 + Ca(NO_3)_2 + 4NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4 + 2NH_4NO_3 + 66.67 \text{ kcal} \quad (4)$$

Dicalcium phosphate is insoluble in water but soluble in ammonium citrate solution and is therefore regarded as a source of "available" P_2O_5, at least in the United States. However, fertilizer specifications often require high water solubility, and this type of product is limited to 50% water solubility of the P_2O_5.

Furthermore, the calcium is non-nutrient in terms of N, P, and K and is therefore seen as a diluent. For these reasons alone, it is desirable to remove calcium from the solution. But there is another, more important reason. If the calcium nitrate is left in the solution, when it is neutralized the N:P ratio will be fixed. To produce grades with lower N:P ratios, it is necessary to remove calcium nitrate, whereas if higher nitrogen grades are required, the removed calcium nitrate can be converted to ammonium nitrate and returned to the solution. Therefore, most nitrophosphate processes include some means of removing calcium nitrate from the solution. With maximum calcium nitrate removal, it is possible to produce grades with N:P ratios ranging from about 0.6:1 (when none of the nitrate is returned) to about 2:1 (when all the calcium nitrate is converted to ammonium nitrate and returned).

This is possible with the Odda-type processes, in which the solution is cooled so that most of the calcium nitrate crystallizes. About 60% of the calcium is removed from the solution at 20°C and 85%-90% at –5°C.

Alternatively, the calcium can be precipitated chemically by adding ammonium sulfate to the solution. In this case only calcium rather than nitrate is removed; therefore, the range of grades that can be produced is restricted to the higher end of the N:P range.

It is also possible to precipitate only the calcium using carbon dioxide.

$$Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ NH_4NO_3 + 39.88 \text{ kcal} \quad (5)$$

In this case, care has to be taken to suppress reversion to tricalcium phosphate, which is citrate-insoluble and water-insoluble.

$$2\ CaHPO_4 + CaCO_3 \rightarrow Ca_3(PO_4)_2 + H_2O + CO_2 + 9.03 \text{ kcal} \quad (6)$$

Other ways to influence the $N{:}P_2O_5$ ratio are to use a mixture of nitric and sulfuric or phosphoric acids or to remove the calcium by ion exchange. These alternatives will be discussed later.

13.3. Nitrophosphate Processes

13.3.1 Selection of Phosphate Rock

In general, reactivity of the phosphate rock is no problem; even igneous apatites dissolve readily in nitric acid. The rock need not be finely ground; rock finer than 1 mm is satisfactory, and some operators even accept particles up to 4 mm. In general, the rock need only be fine enough to prevent rapid settling in stirred reaction vessels. High-silica rock can be used if the equipment is designed for that purpose. Most nitrophosphate plants include a silica removal step. Coarse silica particles can be very abrasive to pumps and piping, and this fact should be considered in plant design.

It is desirable that the $CaO{:}P_2O_5$ ratio in the rock should be as low as economically feasible to minimize the amount of calcium that must be removed or offset (in mixed-acid processes). While additional calcium requires more nitric acid, it does not necessarily involve a direct economic penalty because the nitrate is subsequently converted to ammonium nitrate either in the nitrophosphate product or in a coproduct.

Carbonates in phosphate rock cause foaming, which is usually dealt with by using mechanical foam breakers. However, foaming can be a difficult problem with some rocks.

Organic matter is undesirable in nitric phosphate processes; it reacts with nitric acid with emission of nitrogen as NO_2 or other nitrogen oxides.

Iron and aluminum oxides present no special problem within the range of occurrence in commercial phosphate rocks; these oxides usually are dissolved in nitric acid and reprecipitated during ammoniation as citrate-soluble phosphates. TVA tested "leached-zone" Florida phosphate containing a high percentage of aluminum phosphate minerals in a special nitrophosphate process [1].

Chloride is generally limited to 300 ppmw to prevent pitting corrosion, but phosphate concentrates with about 500 ppmw chloride have been used [2].

13.3.2 Process Alternatives

The two commercially important nitrophosphate processes differ in the way they solve the problem of phosphate water solubility caused by the presence of calcium nitrate in the slurry resulting from the reaction of phosphate rock with nitric acid. The first process, historically, is the Odda process wherein calcium nitrate is precipitated and separated. The "mixed acid" process does not separate the calcium nitrate; the phosphate water solubility is increased by adding phosphoric acid to decrease the CaO:P_2O_5 ratio.

13.4 Odda Process With Calcium Precipitation

The principal developers of the Odda process (Figure 13.2) have been BASF and Norsk Hydro. In the following account of the Odda process, the descriptions of the dissolving and crystallization sections were originally written for the BASF process [3]. The BASF and Norsk Hydro processes, however, are similar in these two sections.

13.4.1 Dissolving Section

In the dissolving section phosphate rock and nitric acid are mixed together in the dissolving reactors. Nitric acid of about 60% concentration is used in slight stoichiometric excess. The temperature in the reactors is kept constant at 60°-70°C by cooling or heating nitric acid. In addition to fresh nitric acid, wash acid from the inerts filter and from the calcium nitrate tetrahydrate (CNTH) filter is fed to the reactors.

The dissolving solution contains suspended solids, mostly quartz, originating from the rock. Quantity and size of the solids vary with the source of rock. Inerts act as an undesirable diluent of the nutrients in the final product and can cause damage to equipment and piping by erosion.

Inerts are separated from the dissolving solution by gravity in lamella separators; the clear solution overflows

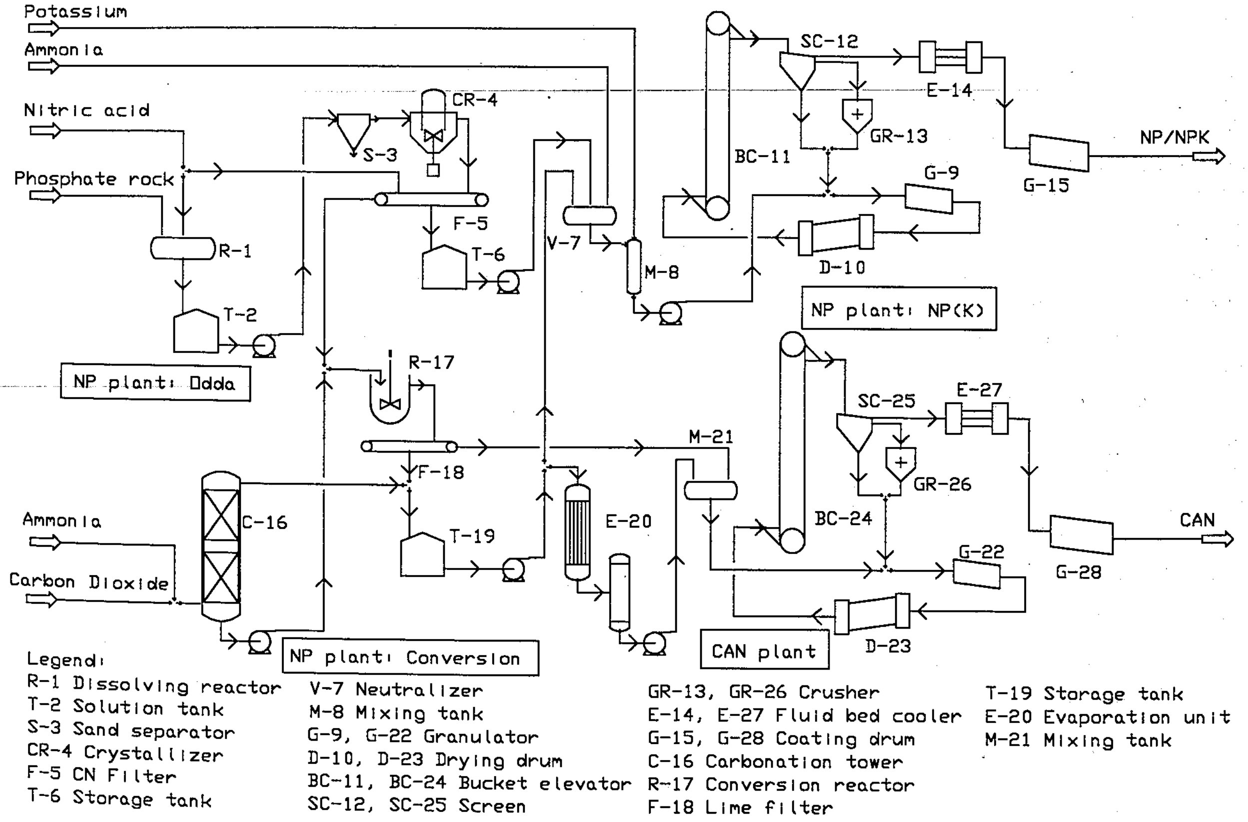

Figure 13.2. Simplified Nitrophosphate Process Concept.

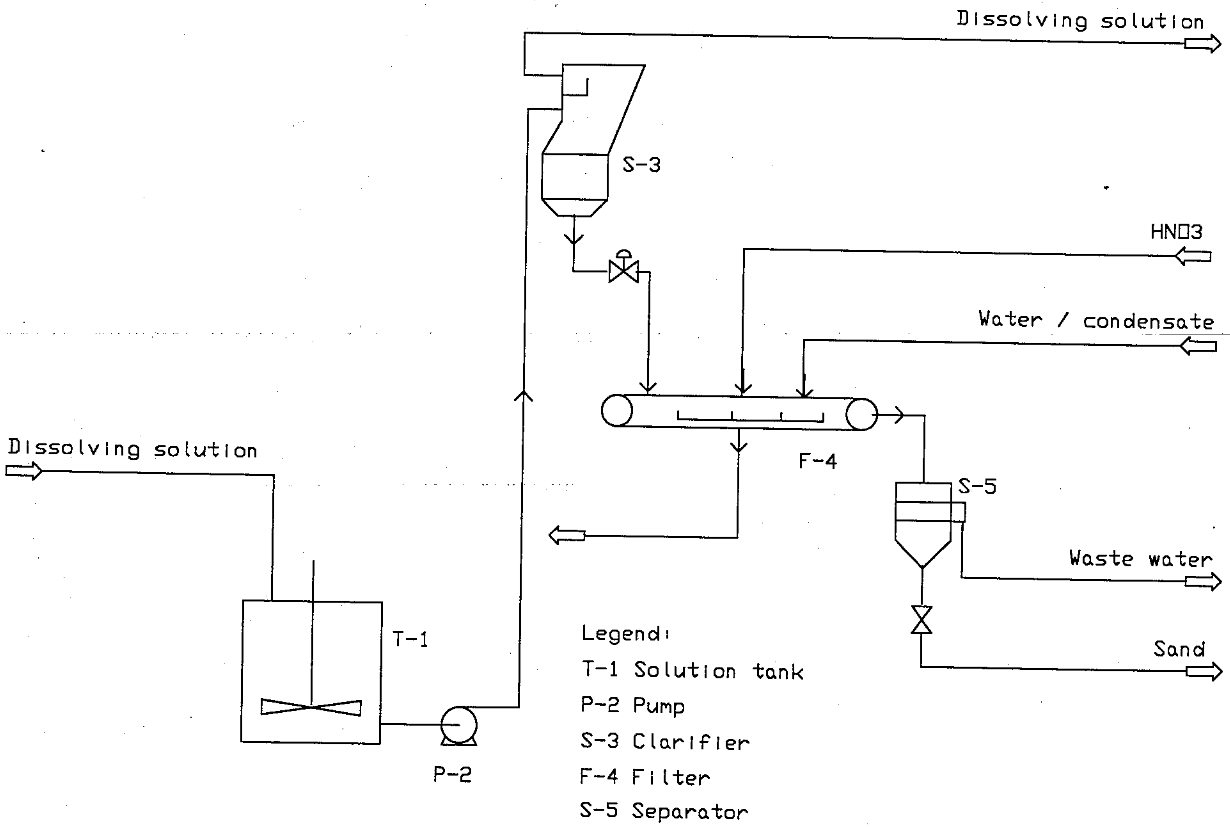

Figure 13.3. Inert Removal in BASF Odda Process.

into the dissolving solution storage tank, and a thickened inerts slurry is washed out to a belt filter or to hydroclones. Sand is washed with nitric acid and a small amount of water, and, if necessary, washed to neutral in a batch washing tank. The liquid effluent from this washing tank is sent to the effluent treatment plant. Inerts are sold, e.g., to the building industry (Figure 13.3).

The submerged part of the reactor may be made of low-grade stainless steel. The top part of the reactor, which is in contact with reaction gases that contain NO_x and fluorine compounds, must be made of appropriate more resistant material.

13.4.2 Crystallization Section

Dissolving solution (NP solution) is fed intermittently to a number of batch-operated standard crystallizers. Cooling for crystallization is obtained by evaporating ammonia for the NP solution neutralization and calcium nitrate (CN)-conversion sections. The balance is supplied by a refrigeration system, if required.

The crystallization process is entirely computer-controlled. The coldest crystallizer, having obtained the required final temperature, discharges to the filter head tank. The final temperature is fixed, e.g., –2° to –5°C when about 80% water-solubility is required, or +2°C when about 70% water-solubility is sufficient. Separation of crystals is done on a belt filter using several washing zones or with drum filters in series. Cold nitric acid and CN-solution are used as washing liquid. NP acid, the product from the filter, is stored in the NP acid storage tank. To fine tune the NP-acid quality (CaO/P_2O_5-ratio), dissolving solution is passed over the crystals. The separated CNTH crystals are dissolved in dilute ammonium nitrate solution to form the CN solution.

13.4.3 Neutralization Section

In the neutralization section, the nitrogen and phosphorus elements in the NP solution are converted to the form they will have in the product. Correct operation of this section is important because the $N:P_2O_5$ ratio of the final product is controlled here. This control is achieved by mixing NP acid obtained from the CNTH-filters with ammonium nitrate solution and with an original dissolving solution. Neutralization by gaseous ammonia occurs in a pressurized reactor at 1.5-2.5 bar and a temperature of 150°-180°C or in forced-circulation neutralizers. Because of the heat of reaction, water and ammonia are evolved during neutralization; this decreases the water content of the slurry which is then further concentrated in a series of circulating evaporators.

The neutralization and evaporation operations have their own scrubber system for off-gases. The scrubbing liquor is composed mainly of ammonium nitrate solution, which is later recycled to the neutralization section for nutrient recovery.

13.4.4 Finishing (Forming or Particulation) Section

The final slurry after ammoniation and evaporation is formed into granules, with or without addition of potash salts, by a variety of methods including:

- Granulation in a pugmill or blunger.
- Ammoniation and granulation in a rotary drum.
- Granulation and drying in a Spherodizer®.
- Granulation and drying in a spouted bed system .
- Prilling of a melt.

These granulation methods will be described in more detail under granulation of compound fertilizers in Chapter 16. However, it may be useful to mention a few characteristics guiding the choice of the techniques for the granulation of nitrophosphates.

Drum Granulation and Pugmill – The advantage of rotary drum and pugmill granulators is that ammoniation may be carried out in the bed. The heat of reaction may cause some water evaporation in the granulator and provide a hotter feed to the dryer. The pugmill requires considerably more electrical power than the drum, and the ammonia sparger must be more strongly mounted in the pugmill.

Spherodizer® Granulation – The Spherodizer®, which was developed as a proprietary granulator by C & I Girdler, is a spray drum granulator in which granulation and drying are combined. It can be operated as a "cold sphero," when it is swept by a current of cold air in the case of melt granulation or as a "hot sphero," when hot air is used for its drying effect in the case of slurry granulation. Large capacities require very large or multiple units, but the capacity of the Spherodizer® to produce onsize granules (up to 75% between 2 and 4 mm) and to dry them during granulation allows it to operate with low recycle rates. Hence, the capacity of a unit 4.5 m in diameter by 12.0 m long can reach 600 tpd [4].

Spouted Bed Granulation – The spouted bed system represented in Figure 13.4 consists of injecting the slurry to be granulated upward into a "spouted bed" conical granulator concurrently with a stream of hot gas. At the center of the bed, where the gas velocity is highest, the granules travel upward; at the periphery of the bed they travel downward, thus producing a circulating action. Each passage through the spray area adds a thin coating to the granules. This process has been reported by Arzani (Montecatini) and Berquin (PEC) [5,6,7]. More recently, Agrimont claimed economically competitive results for this process as long as it is applied to pumpable slurries [8] stating:

> One may definitely conclude that the spouted bed process is perfectly fitted to nitrophosphates with a N:P_2O_5 ratio varying between 2:1 and 1:1.
>
> For products with a higher P_2O_5 content (MAP, DAP), the process seems less advantageous because it is necessary to operate with diluted slurries at the highest degree of ammoniation. In such a case, the process is only competitive if you start operation with weak phosphoric acid.

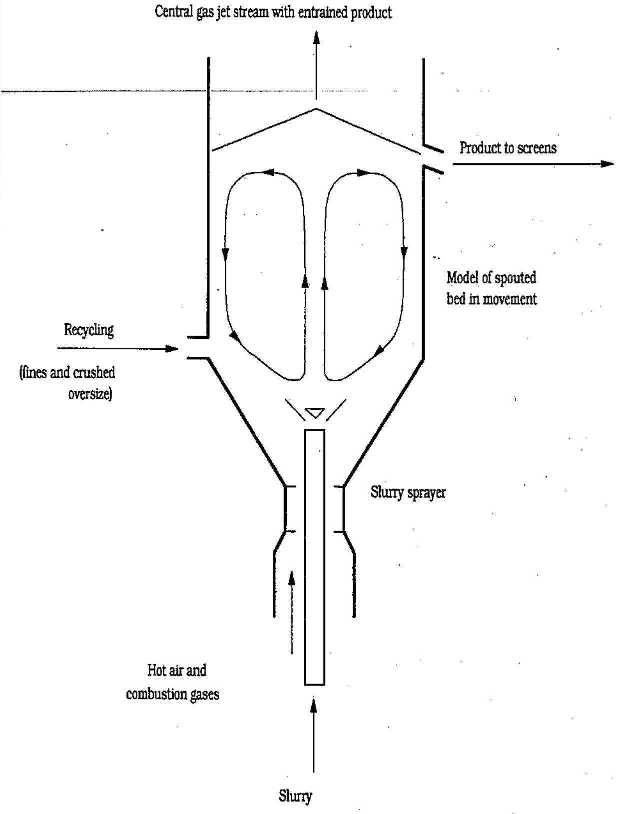

Figure 13.4. Operating Principle of a Spouted Bed Granulator.

13.4.5 Prilling of Melt

This process is used by Norsk Hydro, which cites the following advantages:

- Very high single-train capacities possible (up to 4,500 tpd).
- Good properties of the prills (smoothness, low dusting during handling).
- Advantageous granulometry of the prills (90% between 2 and 4 mm with an average diameter of 3 mm).

The spreading characteristics of this product are stated to be at least as good as those of a granulated product.

The prilling head is of the spinning bucket type. The offsize amounts to only 10% of the prills leaving the tower. The dust content of the exhaust air is less than 5 mg/m^3, which is low enough to require no cleaning before discharge [9,10] because the total dust emission is less than 5 kg/h for a 4,000-tpd plant (Figure 13.5).

Some details of the preceding description are part of the BASF technology. The Norsk Hydro process differs in that it uses [9]:

- Hydrocyclones to remove the insolubles.
- Drum filters to remove the CNTH.
- Addition of urea to suppress NO_x formation.
- A prilling tower rather than a Spherodizer®.

13.4.6 Process Requirements of the Odda Process

Several process and equipment alternatives are used in practice of the Odda process; Table 13.1 gives the unit process consumption values for an average Odda nitrophosphate plant.

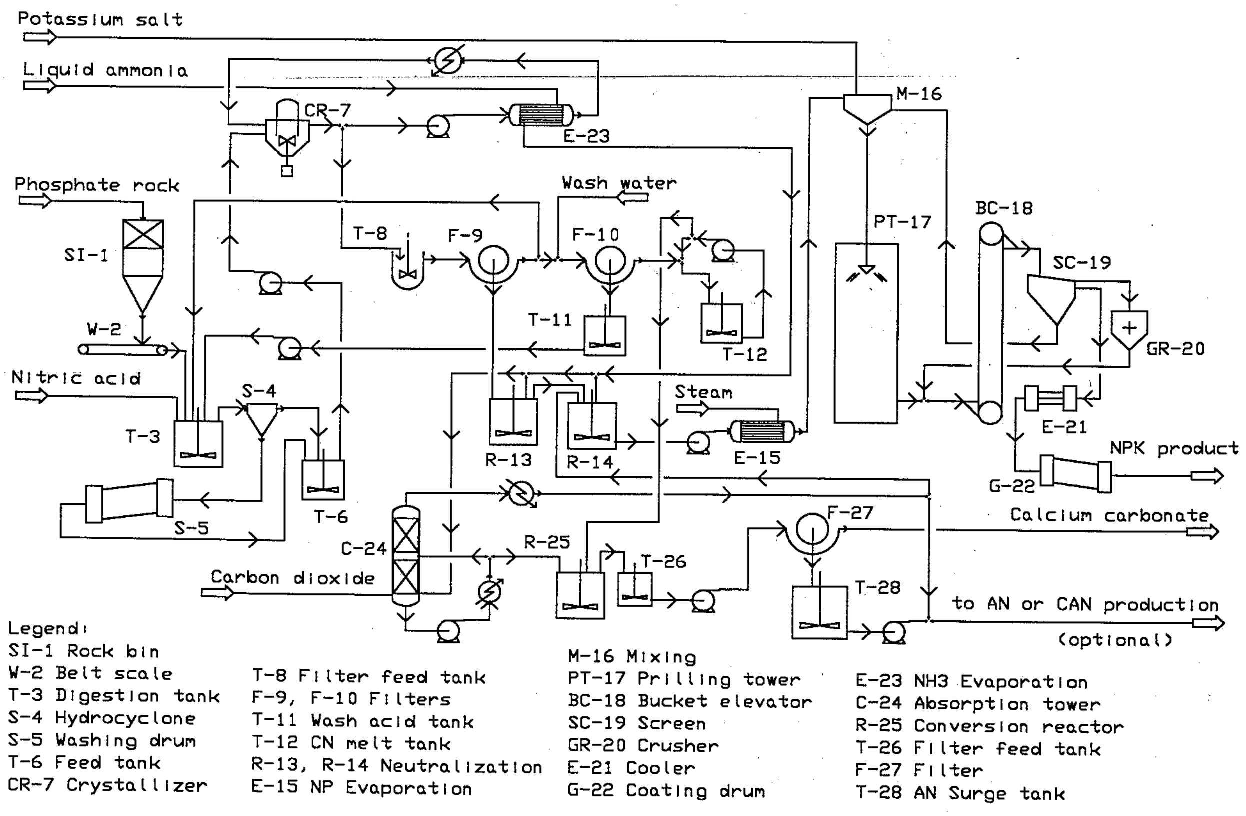

Figure 13.5. The Norsk Hydro Process.

Table 13.1. Process Requirements of the Odda Nitrophosphate Process

Parameters	Units	Value
Product NPK	1	16-16-16
Capacity	tpd	1,250
Annual operation time	h	7,200
Investment cost (battery limits)	US $ million	35[a]
Cost Components	Units	Unit/t
Raw Materials:		
Ammonia	t	0.224
Nitric acid	t	0.696
Carbon dioxide	t	0.189
Phosphate rock (P_2O_5)	t	0.495
Potash	t	0.268
Coating agent	kg	3-4
Byproducts:		
Ammonium nitrate	t	0.491
Calcium carbonate	t	0.365
Energy		
Electrical energy	kWh	140
Steam	kg	270
Process water	m^3	3.0
Fuel	GJ	0.16
Disposal:		
Off-gases	Nm^3	3,500

a. Does not include the ammonia and nitric acid plants.

13.4.7 Calcium Nitrate Conversion and Calcium Ammonium Nitrate (CAN) Unit

The CN-conversion and CAN units contain the following sections:

- CN Conversion Unit
  - Ammonium carbonate preparation section
  - CN-conversion section
  - Lime separation section
- CAN Unit
  - AN concentration section
  - Additives preparation section
  - Mixing, granulation (or prilling), and drying section
  - Cooling, screening, and coating section
  - Off-gas treatment section

As shown in Figure 13.6, the CN-conversion section begins with the preparation of ammonium carbonate solution in a dilute ammonium nitrate solution in a packed carbonation tower with external circulation. Heat exchangers are used to control the temperature gradient over the tower. Raw materials are carbon dioxide and gaseous ammonia evaporated in the refrigeration section. The required ammonium carbonate solution is taken from the circulation loop and sent to the conversion reactor with the corresponding quantity of CN solution. A lime settler and a vacuum filter separate the reaction products, dilute ammonium nitrate solution, and calcium carbonate (lime). The AN-solution obtained here requires a second filtration step on precoat filters before AN-concentration. The precoat is established with the product lime itself. After this second filtration step the remaining ammonium nitrate is stored in the AN-solution tank; from there it is pumped to the AN evaporation

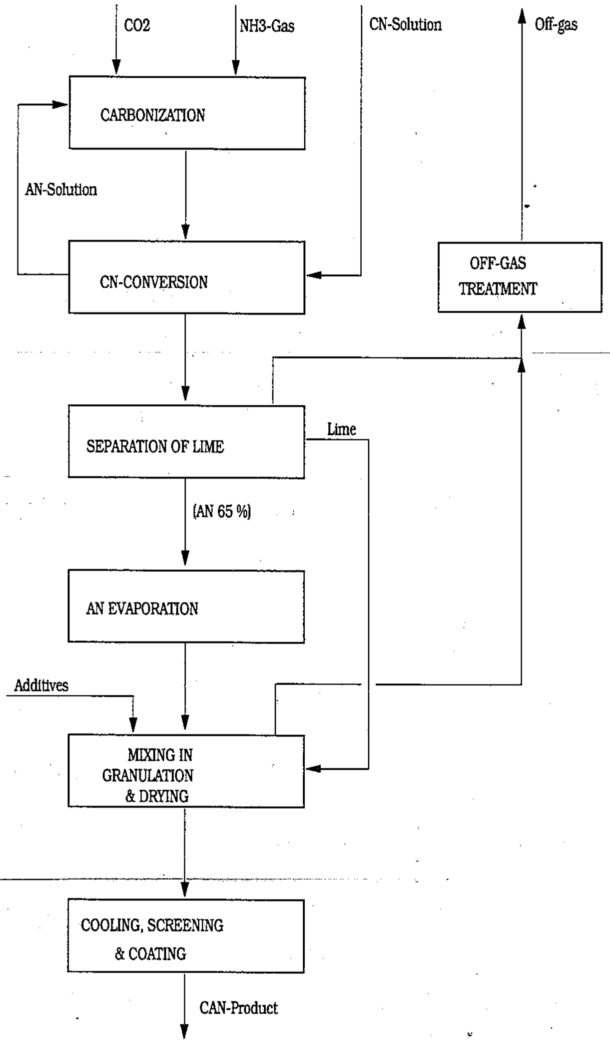

Figure 13.6. Odda-Process CN-Conversion/ CAN-Granulation Sequence.

section and to the CNTH-filter to dissolve fresh calcium nitrate tetrahydrate crystals.

The CN-conversion section has its own packed off-gas scrubber with external circulation. The scrubber liquid is an acidified dilute AN-solution, which is returned to the process.

The AN-evaporation section consists of several falling film evaporators in series. The first part of this section produces a concentrated AN-solution of 93-94 wt % AN. Depending on the capacity and cost of energy, this step may consist of double- or triple-effect evaporation. Each falling film evaporator set consists of a preheater, heater/evaporator, vapor separator and transfer pump. A two-stage water ring vacuum pump provides the necessary vacuum, and a steam saturator, operating at 0.9 MPa absolute (175°C condensing temperature), provides the necessary energy for the concentration unit.

The ammonium nitrate solution at 93-94 wt % is stored and pumped to the second part of the evaporation unit and/or to the NP-unit. This second part is composed of one falling film evaporator with the separator operating at 0.3 bar (absolute) and concentrating up to the required concentration of about 98 wt %. Steam is removed from a separate steam saturator at 9 bar (absolute). The vacuum system of this section can be combined with that of the first part.

CAN-slurry is produced in a mixing section, which consists of dissolving vessels for additives and feeding equipment for gypsum, which is added to the lime. Dissolved additives, lime/gypsum mixture and concentrated AN-melt are delivered to a mixing vessel with an agitator. From there it flows into a second vessel and is then circulated back to the mixing vessel. CAN-slurry for granulation is taken from this circulation loop.

The CAN granulation section uses a granulation drum with internals to produce a screen of falling materials, on which the concentrated CAN slurry is sprayed. The granules that are produced fall by gravity into a countercurrently operated drying drum. The drying drum is operated autothermally, which means that no external heat source is required to preheat the drying air. Off-gas from the dryer and granulator is first dedusted in cyclones, and then sent to the same gas scrubber used for scrubbing the off-gas from the CN-conversion section.

Dry granules are screened over double-deck screens. Fines, crushed oversize, and part of the onsize are returned to the granulator. A two-stage fluidized bed cooler, of which the second stage is operated with chilled and conditioned air, cools the product to the desired final temperature. The waste air from the fluidized bed cooler must be treated to remove dust.

Coating takes place in a rotating coating drum to improve product characteristics during storage. From the coating drum, product is sent to storage.

The BASF granulation process for CAN can use either "AN-wet" lime – lime from the lime filter, which is washed with AN solution, or dry lime, which is water-washed lime. For either alternative the residual water content of the AN-melt must be adjusted.

The advantage of using "AN-wet" lime is that a considerable amount of energy and capital is saved. A saving of energy occurs because no dilution of AN-solution with wash-water occurs and no lime drying takes place. Investment is reduced because lime drying equipment is not required.

In prilling CAN, the AN solution is premixed with dry lime immediately before prilling. A rotating, perforated bucket is the preferred type of drop-forming apparatus. Prill towers for both CAN and AN commonly are 46-56 m high although shorter ones are also used. For high-density prilling using 99.7% solution, prilling towers that are 15-30 m tall may be used. Cooling may be conducted in a rotary cooler or in a fluidized bed either in the bottom of the prill tower or in a separate unit.

13.5 The Mixed-Acid Process

This process is very flexible and is able to produce various grades of fertilizers with a varying degree of phosphate water solubility. The Kemira Oy process is described below [11,12]. This nitrophosphate slurry-based process uses mixed acids. The general flowsheet of the process is given in Figure 13.7.

13.5.1 Phosphate Rock Digestion and Ammoniation

The first step of the process is the digestion of phosphate rock with nitric acid, which results in a solution of phosphoric acid and calcium nitrate (first reactor).

$$Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 3Ca(NO_3)_2 + 2H_3PO_4 + 22.25\ \text{kcal} \qquad (7)$$

Depending on the type of phosphate rock, formation of acid gases containing, for example, nitrogen oxides and compounds of fluorine takes place during the digestion. In the second reactor the overflow from the first reactor is ammoniated, and scrubber liquor is added.

The acid slurry is ammoniated with gaseous ammonia along the following reactions.

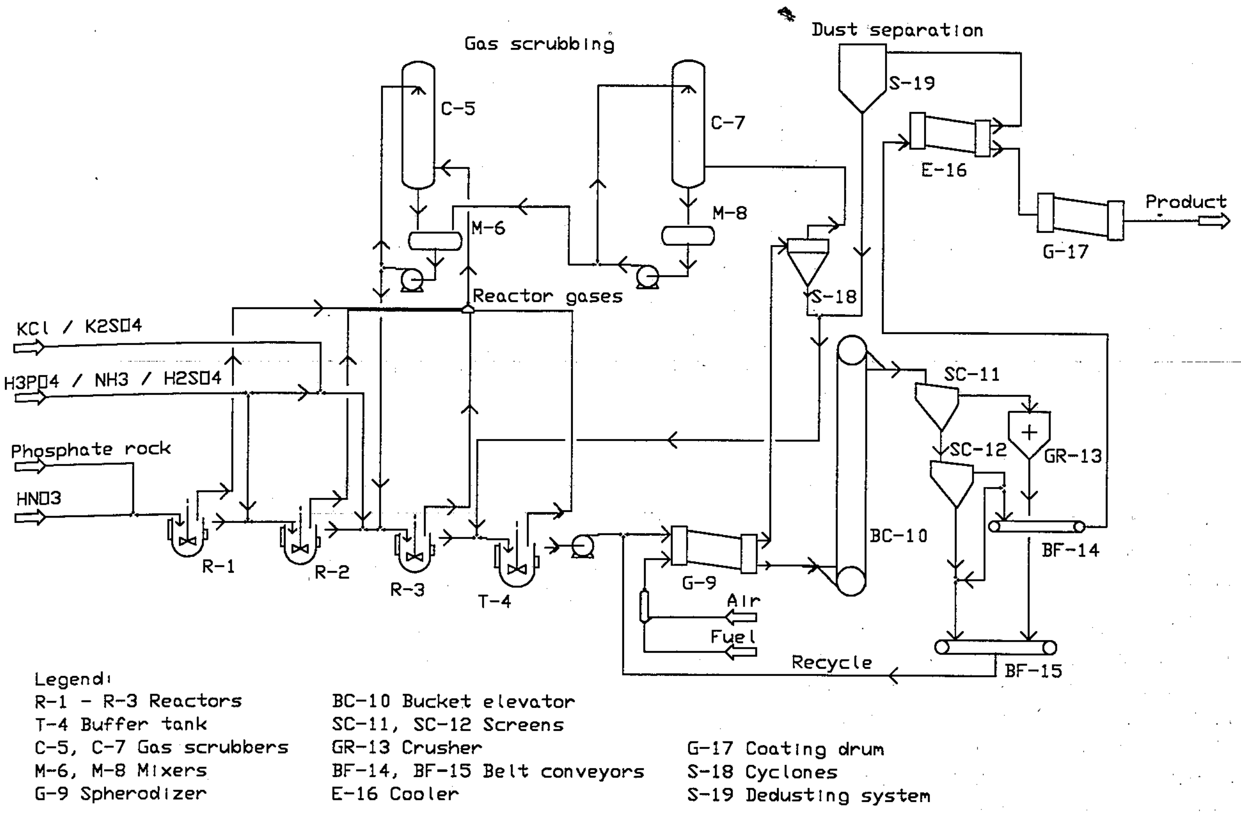

Figure 13.7. Mixed Acidulation Nitrophosphate Process.

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 + 22.27\ \text{kcal} \qquad (8)$$

$$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4 + 33.52\ \text{kcal} \qquad (9)$$

$$2H_3PO_4 + Ca(NO_3)_2 + 4NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4 + 2NH_4NO_3 + 66.67\ \text{kcal} \qquad (4)$$

The third reactor provides for final ammoniation of overflow from the second reactor. Phosphoric and sulfuric acids are added and the KCl dissolved (when NPK is produced).

If sulfuric acid is introduced, the sulfate ions induce the precipitation of calcium sulfate following the reaction:

$$Ca(NO_3)_2 + H_2SO_4 \rightarrow 2HNO_3 + CaSO_4 + 9.37\ \text{kcal} \qquad (10)$$

This calcium sulfate can be removed by filtration, but generally it is left in the slurry where it may be considered as a diluent that supplies two secondary nutrients: calcium and sulfur.

Any micronutrients to be incorporated in the formulation are added at this point. A buffer tank is used as a liquor feed tank for the Spherodizer® and as a receptacle for recovering fertilizer dust from the bag filters and cyclones.

The water solubility of P_2O_5 in the product can be adjusted by varying the phosphoric acid/phosphate rock ratio in the formulation. A wide range of grades may be produced; these grades include: for minimum nitrogen content, 8-24-14 grade; and for maximum nitrogen content, 30-10-0 grade. Standard grades such as 17-17-17 and 23-23-0 may be produced.

After neutralization other components, e.g., ammonium phosphates, superphosphates, ammonium sulfate and compounds containing potassium and magnesium, may be added. Most of these materials may also be added before or during neutralization, but if the raw material contains chloride, the pH-value of the slurry should be 5-6 to avoid development of hydrogen chloride.

The design of the reactor battery can vary from a few large reactors to many small reactors, but at present the three-reactor system is considered optimal. A common feature for all the designs is that the row of reactors ends with a buffer tank. Depending on the type of raw material, the amount of gas scrubber liquid to be recycled, and the degree of ammoniation, the water content of the slurry in the buffer tank can vary between 5% and 30% and the temperature from 100°C to 140°C.

13.5.2 Further Processing

Granulation and Drying – The slurry in the buffer tank typically contains about 10% of water and the temperature is about 140°C. Granulation and drying occur simultaneously in a combined granulator-dryer called a Spherodizer®. The principle of Spherodizer® operation was described previously. To improve fuel economy, the hot exhaust gas is recycled to the dryer inlet via a bag filter.

Screening, Crushing, and Recycle Handling – Product sized 2-4 mm is separated from the granulator discharge by screens. The oversize material is crushed and recycled with undersize to the granulator. Part of the product-size material is also recycled to keep the recycle rate constant. The product that is not recycled goes to the cooler. The cooler is often a fluidized-bed cooler rather than a rotary-type cooling drum. The fluidized-bed cooler has higher operating costs; however, it has a lower investment cost and requires less area in the plant. The product from the cooler is coated with anticaking additives in a small rotating drum.

Nutrient Recovery From Gas Streams – A multistage scrubbing system captures fumes from the reactors and any dust that escapes the cyclones. The nutrient content of the scrubber liquor increases as it moves countercurrently through the reactor gas scrubbing system to the granulator exhaust gas scrubber. Nutrient salts in scrubber liquor are recycled to the reactors. There are no liquid effluents from the plant.

Process Requirements – Raw material and utility requirements for the mixed-acid process are given in Table 13.2.

Table 13.2. Process Requirements of the Phosphonitric Process

Parameters	Units	Value
Product NPK	1	-15-15-15
Capacity	tpd	1,700
Annual operation time	h	7,900
Investment cost (battery limits)	US $ million	35

Cost Components	Units	Unit/t
Raw Materials:		
Ammonia	t	0.108
Nitric acid	t	0.285
Phosphoric acid (P_2O_5	t	0.037
Phosphate rock (P_2O_5)	t	0.055
Sulfuric acid	t	0.015
Potash	t	0.251
Coating agent	t	0.007
Others	t	0.025
Energy:		
Electrical energy	kWh	70
Steam	kg	20
Process water	m^3	0.5
Fuel	GJ	0.38
Disposal:		
Off-gases	Nm^3	3,500

13.5.3 Product Quality

The nitrophosphates – obtained by either the Odda route or the mixed-acid route – cover a range of formulations with $N:P_2O_5$ ratios ranging from 0.5 to 2.0; moreover, the P_2O_5 water solubility can be controlled – although at increasing costs – from 30% to 90%.

The most popular are the following grades:

NP: 20-20-0 to 25-25-0; 28-14-0; 20-30-0
NPK: 15-15-15 to 17-17-17
20-10-10; 10-20-20; 15-20-15; 12-24-12

Note that the mixed-acid route allows $N:P_2O_5$ ratios smaller than 0.5 such as 8-24-14 grade. The European Council Directive 76/116/EEC defines the quality requirements as summarized in Table 13.3.

The nitrophosphates are exclusively manufactured in granular form (size 2-4 mm) for direct application by the farmer or use in bulk-blending operations. Because of the hygroscopic nature of the ammonium nitrate that is always present in the nitrophosphate, storage must be protected from moisture. The very presence of ammonium nitrate imposes its manufacturing, handling, and storing conditions that are summarized in the booklets edited in 1992 by IFA and EFMA [13,14].

The nitrophosphates are generally packed in watertight bags for delivery to the farmers. These are generally plastic bags that can keep the product in good condition even if stored for a period of time in the open air.

Table 13.3. European Union Nitrophosphate Quality Requirements

(a) NPK fertilizer is a product obtained chemically or by blending without addition of organic nutrients of animal or vegetable origin:

	Total	N	P_2O_5	K_2O
	(% by weight)			
Minimum content of nutrient	20	3	5	5

(b) Declared forms and nutrient content required:

Nitrogen	P_2O_5	K_2O
Total nitrogen	Water soluble	Water soluble
Nitrate nitrogen	Ammonium citrate soluble	
Ammoniacal nitrogen	Mineral acids soluble	
Ureic nitrogen	Alkaline ammonium citrate soluble	
Cyanamide nitrogen	2% citric acid soluble	
	Minimum 75% soluble in 2% citric acid	

(c) Identification data (declaration obligatory):

Nitrogen	P_2O_5	K_2O
Total nitrogen	All under 2% solubility	Water solubility
Any amount of	in ammonium citrate	Chlorine content
nitrogen over 1%	Water solubility	Low chlorine means less than 2% Cl

13.6 Other Processes

Some processes that have been developed and commercially operated remove the calcium from solution in a different way. These routes have not been as successful, however, as those described previously.

13.6.1 Removal of Calcium by Sulfate Addition

The solution obtained by reaction of nitric acid with phosphate rock can be treated by the addition of a soluble sulfate to precipitate part or nearly all of the calcium as calcium sulfate (gypsum or hemihydrate). In commercial processes, ammonium sulfate, potassium sulfate, and sulfuric acid have been used. Langbeinite ($K_2SO_4 \bullet 2MgSO_4$) has been used experimentally. The calcium sulfate may be separated by filtration or allowed to remain in the product. In most plants, the calcium sulfate is removed to produce a higher grade product. Chemical reactions are:

$$(NH_4)_2 SO_4 + Ca (NO_3)_2 \rightarrow 2 NH_4 NO_3 + CaSO_4 + 11.90 \text{ kcal} \quad (11)$$

$$K_2 SO_4 + Ca (NO_3)_2 \rightarrow 2 KNO_3 + Ca SO_4 + 11.37 \text{ kcal} \quad (12)$$

The reaction using sulfuric acid is shown in equation 10.

Potassium sulfate and ammonium sulfate solution obtained as a byproduct from caprolactam production are used industrially. In the Veba phosphoric acid process (Figure 13.8), phosphate rock is reacted with a mixture of sulfuric and nitric acids under conditions that form calcium sulfate in the hemihydrate form, which is removed by filtration [15]. In this process, part of the sulfuric acid may be replaced by ammonium sulfate.

When ammonium sulfate is used to precipitate calcium as gypsum, the gypsum can be treated with ammonia and carbon dioxide to regenerate ammonium sulfate, which is recycled, and to convert the calcium to calcium carbonate:

$$CaSO_4 \bullet 2H_2O + 2NH_3 + CO_2 \rightarrow CaCO_3 + (NH_4)_2 SO_4 + H_2O + 24.51 \text{ kcal} \quad (13)$$

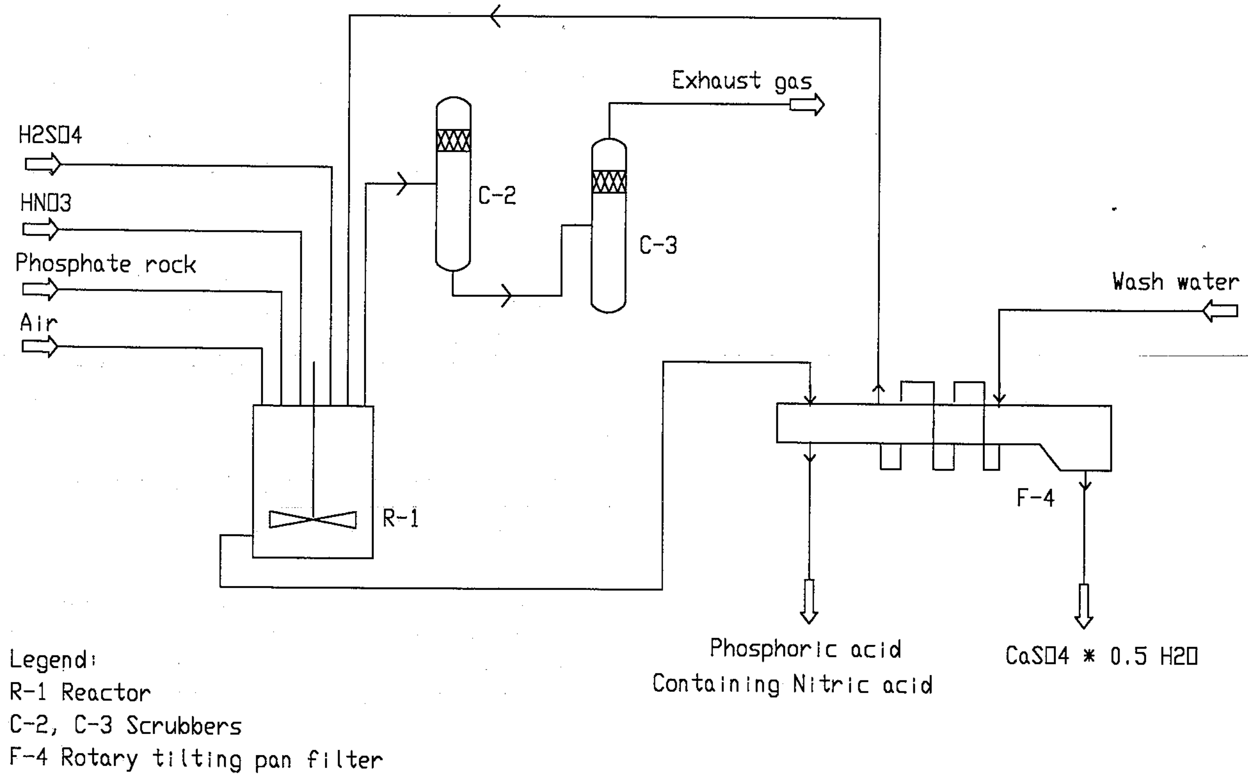

Figure 13.8. The Veba Phosphoric Acid Process.

This is the basis for the "sulfate recycle process," which was developed by TVA on a pilot-plant scale [16]. One disadvantage of this process is that the N:P_2O_5 ratio in the product is fixed at about 2:1 (28-14-0 grade).

13.6.2 Removal of Calcium by Carbon Dioxide Addition

A process known as the "carbonitric process" has been used commercially but has not gained much success, mainly because of the relatively low analysis and the absence of water soluble P_2O_5 in the end product. Nevertheless, CO_2 is primarily the cheapest precipitant for calcium. The process consists of four steps:

1. Dissolving phosphate rock in nitric acid.
2. Ammoniating the solution from the first step to precipitate essentially all of the P_2O_5 as dicalcium phosphate; the remainder of the calcium remains in solution as calcium nitrate.
3. Adding ammonia and carbon dioxide to convert the calcium nitrate to ammonium nitrate and calcium carbonate.
4. Granulating and drying.

The final product consists of a mixture of dicalcium phosphate, ammonium nitrate, and calcium carbonate. The grade is about 16-14-0. None of the P_2O_5 is water soluble, but nearly all of it is citrate soluble.

13.6.3 Removal of Calcium by Ion Exchange

The firm Superfos (now KEMIRA-Denmark) has developed an ion-exchange process for calcium removal [17]. The phosphoric acid-calcium nitrate solution is passed through a potassium-loaded resin that absorbs calcium and releases potassium. The resin is regenerated by a potassium chloride solution; calcium chloride is discharged to waste. A simplified flow diagram of the process is shown in Figure 13.9.

The process can be represented by the following reactions.

$$\text{Digestion: } Ca_3(PO_4)_2 + 6\,HNO_3 \rightarrow 3\,Ca(NO_3)_2 + 2\,H_3PO_4 + 22.25\text{ kcal} \qquad (3)$$

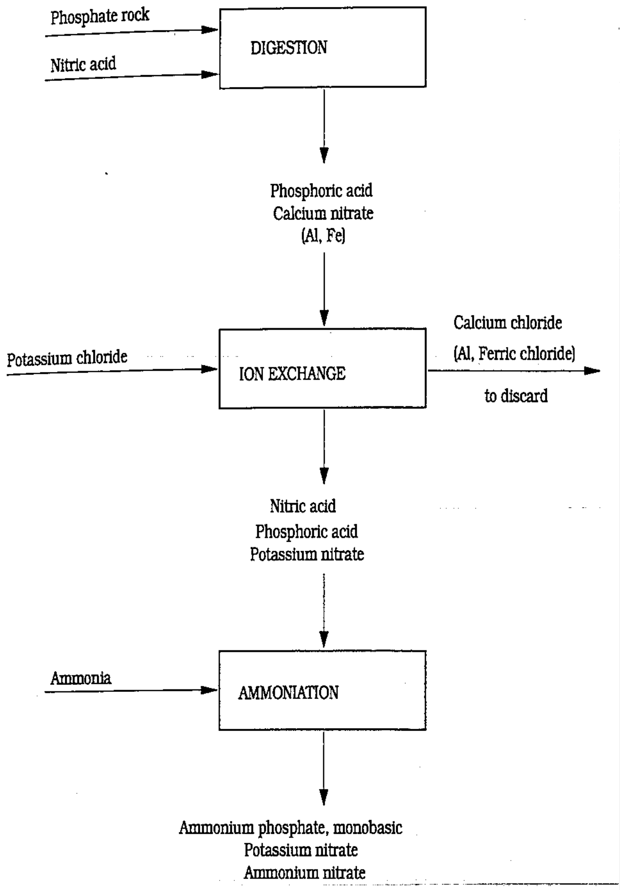

Figure 13.9. Superfos Ion Exchange Nitrophosphate Process Used in Denmark.

Ion exchange: $2\ KCl + Ca(NO_3)_2 \rightarrow 2\ KNO_3 + CaCl_2 + 13.10\ kcal$ (14)

Ammonination: $H_3PO_4 + 2\ NH_3 \rightarrow (NH_4)_2\,HPO_4 + 33.52\ kcal$ (9)

$HNO_3 + NH_3 \rightarrow NH_4NO_3 + 22.70\ kcal$ (8)

If the rock contains cationic impurities other than calcium, such as iron and aluminum, these elements may also be removed by the ion-exchange process. After ion exchange the solution, which contains phosphoric acid, potassium nitrate, some excess nitric acid, and perhaps some residual calcium nitrate, is ammoniated, dried, and granulated. Grades ranging from 21-9-12 to 17-17-17 are produced.

The solution leaving the ion-exchange unit has a $K_2O:P_2O_5$ weight ratio of about 1.8:1.0. When lower ratios are desired in the final product, the current practice is to add phosphoric acid from another plant unit before ammoniating. An alternative is to remove part of the potassium nitrate by cooling the solution to crystallize KNO_3, which can be marketed as a separate product.

One advantage of the process is the production of low-chloride fertilizers (less than 0.6% Cl). Such products are agronomically desirable for some crops and soils. Another potential advantage is the ability to use phosphate rocks of high iron and aluminum content.

13.7 Advantages and Disadvantages of the Nitrophosphate Route

The relative economics of fertilizer production by the nitrophosphate and sulfuric routes have been a matter of discussion for many years, especially at times of sulfur shortage when prices tend to be high. The balance swung sharply away from nitrophosphates and in favor of the sulfuric route for most of the 1960s and 1970s. The reason for this change was first, because sulfur prices declined and then remained stable at a low level for several years; the second reason was because of the sharp rises in energy and ammonia feedstock prices (which directly affect nitric acid production costs) from about 1974 onward. Interest revived considerably when a sulfur shortage caused prices to increase very sharply. Although the acute phase of the shortage proved to be shortlived, sulfur prices have settled to a level that is fairly high in comparison with their 1970s levels; on the other hand, energy and feedstock prices have declined considerably from their peak. In the mid-1990s, sulfur prices declined, but energy prices remained stable, thus creating a more balanced competition. Under these conditions, several other factors besides mere process economics can influence the ultimate choice of the nitrophosphate route; just recently it has been evident that this has been happening in some cases.

Prominent among the other factors are the comparative logistics and security of sulfur and ammonia feedstock supplies and the difficulty and cost of disposing the phosphogypsum byproduct. The former was important in the choice of the process for large fertilizer complexes in Central Europe and the Indian subcontinent in the 1960s and 1970s. The latter is assuming greater importance today in many areas as a result of environmental regulations.

As a result of developments in recent years, the nitrophosphate process of today is more economically and environmentally competitive. It claims advantages such as raw material flexibility and efficiency, adaptation to increasingly stricter environmental requirements, and avoidance of byproduct disposal problems.

However, the process has its limitations in that it combines phosphate and nitrogen processing. The advantage of being sulfur independent is counterbalanced by the need for carbon dioxide, which is normally obtained from an ammonia plant.

The summary of advantages and disadvantages is given in Table 13.4.

13.8 Development in Quantities and Market Share

World consumption of nitrophosphates increased from 3.46 million tonnes of P_2O_5 in 1975 to 3.9 million tonnes in 1988; this represents an increase of 13% in 13 years, and nitrophosphates supplied less than 10% of world fertilizer P_2O_5 in 1988 [18].

Changes in the relationship between the prices of sulfur and costs of feedstock and energy, which occurred in the mid-1980s, reactivated interest in nitrophosphates.

Even though the process was not successful in America, BASF and Norsk Hydro promoted it in Western Europe. Plants were operating in several countries of Western and Eastern Europe before 1980. Since 1980, licenses have been granted for factories in Russia, China, and India [9,19].

Under these influences, world consumption of nitrophosphates increased to 4.33 million tonnes of P_2O_5 in 1990; this represented 10.5% of world fertilizer P_2O_5. These figures decreased to 3.2 million tonnes P_2O_5 and 8.5% of the world production in 1992.

With a reduction of 26%, nitrophosphates were more severely affected by the crisis than the average of fertilizers. The reason for this seems to be that their main market was in Europe, where the fertilizer market decreased more than the world average under the combined influences of fertilizer use restrictions in Western Europe and farm economy disturbances in Eastern Europe and Russia.

13.9 References

1. Hignett, T. P., M. R. Siegel, T. M. Kelso, and R. S. Meline. 1957. "Phosphate Ore: Fertilizer from Leached - Zone Ore," *Journal of Agricultural and Food Chemistry*, 5(8):587-591.
2. Richmann, R. 1993. "The BASF Nitrophosphate Process," IN *Nitric Acid-Based Fertilizers and the Environment*, International Workshop Proceedings, pp. 203-210, R. G. Lee (Ed.), SP-21, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
3. UHDE G.m.b.h. 1994. *Nitrophosphate - UHDE Technology Based on the BASF Process."*
4. Berquin, Y. F., and J. Burks. 1974. "Hot Spherodizer Processes and Complex Fertilizers," *Proceedings of the Fertilizer Industry Round Table*, pp. 110-115.
5. Berquin, Y. F. 1961. "Nouveau Procédé de Granulation et son Application dans le Domaine de la Fabrication des Engrais," *Génie Chimique*, p. 45.

Table 13.4. Advantages and Disadvantages of the Nitrophosphate Route [11]

Advantages of DAP	Advantages of Nitrophosphate
Higher product nutrient content	Independence of sulfur
Higher location flexibility (all raw materials may be delivered from outside)	Higher energy efficiency
Higher flexibility of nutrient content	No byproducts disposal problem
	All commercial grades of phosphate rock are acceptable Large size rock particles are acceptable CAN granulation is an autothermal process

5. Swanstrom, S. 1986. "The Kemira NPK Process," IN *Phosphorus and Potassium*, No. 145.

6. Arzani, A. "New Developments in Fluid Bed Granulation of High Analysis Fertilizers," Paper presented at the 158th National Meeting of the American Chemical Society, New York, NY, U.S.A.

7. Berquin, Y. F. 1977. "Prospects for Full-Scale Development of Spouting Beds in Fertilizer Granulation," IN *Granular Fertilizers and their Production*, pp. 296-303, British Sulphur Corporation, London, England.

8. Brusasco, G., R. Monaldi, V. De Lucia, and A. Barbera. 1986. "Production of NPK Fertilizers With a Spouted Bed Granulator Dryer," Proceedings of IFA Technical Meeting held in Port El Kantaoui, Tunisia.

9. Conradsen, A., and G. Kongshaug. 1993. "Nitrophosphate Technology and the Environment. An Overview of Potential Sources of Pollution From an Integrated Nitrophosphate Fertilizer Production Complex," IN *Nitric Acid-Based Fertilizers and the Environment*, International Workshop Proceedings, pp. 135-151, R. G. Lee (Ed.), SP-21, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

10. "Fertilizers by the Nitrophosphate Route." 1988. IN *Phosphorus and Potassium*, No. 155.

11. E. Aasum. 1988. "Nitrophosphates Versus Ammonium Phosphates," IN *NPK Fertilizer Production Alternatives*, International Workshop Proceedings, pp. 29-40, J. J. Schultz and E. D. Frederick (Eds.), SP-9, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

12. Kemira Engineering Oy. 1994. "Private Communication," Helsinki, Finland.

13. IFA and EFMA. 1992. "Handbook for the Safe Storage of Ammonium Nitrate-Based Fertilizers," Paris, France.

14. IFA and EFMA. 1992. "Selected Tests Concerning the Safety Aspects of Fertilizers," Paris, France.

15. Kurandt, K. 1976. "The VEBA Phosphoric Acid Process," Paper presented at ISMA Technical Conference, The Hague, Netherlands.

16. Meline, R. S., H. L. Faucett, C. H. Davis, and A. R. Shirley, Jr. 1971. "Pilot Plant Development of the Sulfate Recycle Nitric Phosphate Process," *Journal of Industrial and Engineering Chemistry, Process Design Development*, 10:257-264.

17. Knudsen, K. 1977. "The Case for Chloride - Free Fertilizer Materials," IN *Granular Fertilizers and Their Production*, British Sulphur Corporation, London, England.

18. Schultz, J. J., D. I. Gregory, and O. P. Engelstad. 1992. *Phosphate Fertilizers and the Environment – A Discussion Paper*, P-16, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

19. Diehl, L. 1988. "Ateliers de nitrophosphate. Concept de recyclage pour minimiser la pollution de l'air et de l'eau," Paper presented at the IFA Technical Meeting, Edmonton, Alberta, Canada.

Other Sources:

Diehl, L., K. F. Kummer, and H. Oertel. 1986. "Nitrophosphates With Variable Water Solubility: Preparation and Properties," Fertiliser Society Proceedings, No. 243.

Durocher, A. H., L. Diehl, and H. J. Eisen. 1984. "Product Grade vs. Variable Manufacturing Cost," Presented at the IFA Technical Meeting, Paris, France.

Chapter 14. Other Phosphate Fertilizers

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Chapter 14. Other Phosphate Fertilizers

14.1 Single Superphosphate (SSP)

14.1.1 Fundamentals of SSP

Single superphosphate (SSP), also called normal or ordinary superphosphate, has been the principal phosphate fertilizer for more than a century and supplied over 60% of the world's phosphate as late as 1955. Since then its relative importance has declined steadily. In 1975, it supplied only 20% of the phosphate fertilizer, and this figure fell to 17% in 1988. The decline in actual tonnage has been small, but most of the new facilities have been built to produce other, higher analysis products. For the world as a whole, TVA estimated 1972 SSP production at 7.87 million tonnes of P_2O_5, and IFDC mentions a figure of 7.083 million tonnes in 1988, which means a decrease of 10% over 16 years [1].

Another decrease of 10% reduced the production to 6.3 million tonnes in 1992, which was about 16% of the 38.6 million tonnes of P_2O_5 produced in 1991/92. Thus, SSP is still an important phosphate fertilizer and is likely to remain so even though its relative importance will decrease.

The advantages of SSP are:

1. The process is simple, requiring little technical skill and small capital investment.
2. The economies of scale are minor; thus, small plants can be economical.
3. Since the process is not capital intensive, there is little advantage of a high percentage utilization of capacity. In fact, many SSP plants operate on a planned seasonal schedule.
4. The fertilizer effectiveness of SSP is unquestioned. In fact, it is a standard of comparison for other phosphate fertilizers.
5. SSP supplies two secondary elements, sulfur and calcium, which are sometimes deficient in the soil.

Despite these impressive advantages, the disadvantage of low analysis, 16% - 22% P_2O_5, and consequent high distribution costs have caused declining interest in its production because the delivered cost at the farm level is usually higher per unit of P_2O_5 than that of TSP or ammonium phosphates.

SSP will still be a logical choice in several situations such as:

1. Where both P_2O_5 and sulfur are deficient, SSP may be the most economical product to meet these needs. This is the case in much of Australia and New Zealand, some parts of the United States, and Brazil. It is likely that more locations where sulfur is deficient will be identified.
2. In small countries or remote regions where demand is insufficient to justify an economical scale of production of concentrated phosphate fertilizers and where importation is expensive, SSP can be the most economical means of supplying local needs.
3. In many cases, SSP can be an attractive way to use byproduct sulfuric acid that cannot be used to produce more concentrated products because the quality or quantity of the acid is unsuitable. Likewise, SSP can use deposits of phosphate rock that are too small to justify a more expensive plant.

14.1.2 Suitability of Phosphate Rocks

Since the grade of the rock determines the grade of the product SSP, a high-grade rock is desirable. Reactivity is also important; unreactive rocks must be ground more finely. It is extremely difficult to produce SSP from some igneous apatites. Iron and aluminum compounds can be tolerated up to a point although they decrease the P_2O_5 water solubility. Silica has no adverse effect other than decrease in grade. An increase in $CaO : P_2O_5$ ratio raises the sulfuric acid consumption per unit of P_2O_5 and decreases the grade. High-chloride rocks (up to 0.5% Cl and perhaps higher) can be used without serious disadvantage since corrosion is not a serious problem in SSP production.

14.1.3 Chemistry of SSP

The main overall chemical reaction that occurs when finely ground phosphate rock is mixed with sulfuric acid in the manufacture of SSP may be represented by the following equation.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + H_2O \rightarrow Ca(H_2PO_4)_2 \bullet H_2O + 2CaSO_4 + 108.44 \text{ kcal}$$

It is generally agreed that the reaction proceeds in two stages: (1) the sulfuric acid reacts with part of the rock, forming phosphoric acid and calcium sulfate and (2) the phosphoric acid formed in the first step reacts with more phosphate rock, forming monocalcium phosphate. The two reactions take place concurrently, but the first stage is completed rapidly while the second stage continues for several days or weeks.

The calcium sulfate is mainly in the anhydrous form. Most of the phosphate in the rock is fluorapatite, and the fluorine reacts with the sulfuric acid to form hydrogen fluoride. The hydrogen fluoride reacts with silica in most rocks, and part of it is volatilized, usually as SiF_4. The remainder may form fluosilicates or other compounds in the SSP. Usually 25% or more of the fluorine is volatilized and must be recovered to prevent atmospheric pollution. In some cases recovery as salable fluorine compounds is feasible, but more often the scrubber liquor is disposed in a pond by neutralizing it with lime or limestone. A technical curiosity among SSPs is the "Kotka superphosphate." "Kotka superphosphate" is a mixture of superphosphate and phosphate rock. It is named for the city of Kotka, Finland, where it was originally made. It has the advantage that little curing is needed, and the free acid content is low. Its effectiveness generally is equal to that of equivalent amounts of fully acidulated superphosphate plus raw phosphate rock applied separately. Kotka superphosphate is essentially the same as partially acidulated phosphate rock, which is discussed later in this chapter.

Table 14.1 shows the chemical composition of one sample of Kotka superphosphate and five typical samples of SSP. SSP usually contains 6% - 10% moisture; therefore, its grade could be increased by drying, but this would be too expensive compared with the value of the SSP.

Another specialty is a "serpentine superphosphate." "Serpentine superphosphate" has been produced in New Zealand by mixing serpentine (a mineral consisting of hydrous magnesium silicate) with SSP. The usual proportion is one part of serpentine to four parts of SSP. The serpentine improves the physical properties of SSP by reacting with the free acid, and it supplies magnesium to crops. Various other minerals or chemical compounds sometimes are added to supply magnesium or micronutrients that may be needed locally.

14.1.4 Production Methods

The manufacture of superphosphate involves the following three (or four) operations.

1. Finely ground phosphate rock (90% < 100-mesh) is mixed with sulfuric acid. With rock of 34% P_2O_5 content, about 0.58 kg of sulfuric acid (100% basis) is required per kilogram of rock. Sulfuric acid is available commercially in concentrations ranging from 77% to 98% H_2SO_4. The acid usually is diluted to 68% - 75% H_2SO_4 before it is mixed with the rock, or in the case of the cone mixer, the water may be added separately to the mixer. When concentrated sulfuric acid is diluted, much heat is generated; many plants cool the acid in heat exchangers to about 70°C before use.
2. The fluid material from the mixer goes to a den where it solidifies. Solidification results from continued reaction and crystallization of monocalcium phosphate. The superphosphate is excavated from the den after

Table 14.1. Composition of Single Superphosphates

	Source of Rock					
Composition	Florida (granular)	Florida	Morocco	Morocco	Ocean Island	Morocco and Kotka[a]
	(% by weight)					
P_2O_5, total	19.9	21.5	19.8	21.4	22.8	22.8
P_2O_5, available	19.6	20.7		20.2		14.6[b]
P_2O_5, water soluble	17.5	17.4	18.8		20.8	14.5
Free acid	2.4	0.6	2.0	1.7	4.6	1.3
Water	5.9	1.1	8.4	9.8	10.6	8.9
CaO	27.1	30.5				
SO_3	28.4	30.7				
N_2O_3	1.3	2.3				
F		1.6				

a. Superphosphate plus additional phosphate rock.
b. Alkaline citrate soluble.

0.5 - 4.0 hours. At this time it is still somewhat plastic, and its temperature is about 100°C.

3. The product is removed from the den and conveyed to storage piles for final curing, which requires 2 - 6 weeks, depending on the nature and proportions of the raw materials and the conditions of manufacture. During curing, the reaction approaches completion. The free acid, moisture, and unreacted rock contents decrease, and the available and water-soluble P_2O_5 contents increase. The material hardens and cools. After curing, the product from storage is fed to a disintegrator, usually of the hammer mill or cage mill type. The product from the mill is discharged onto an inclined screen of about 6-mesh size. The material that fails to pass the screen is returned to the mill for further grinding.

4. If granular superphosphate is desired, the product is granulated either before or after it is cured. Granulation before curing has the advantage that less water or steam is required. After granulation, the product is dried in a direct contact dryer and screened; the fines are returned to the granulation unit.

For many years SSP was produced only by batch mixing methods; however, most modern plants use continuous mixing and denning processes. There is a wide variety of both batch and continuous mixers and dens; no attempt will be made to describe them all. More detail may be found in the book, *Superphosphate: Its History, Chemistry and Manufacture* [2].

One popular batch system is shown in Figure 14.1. The rock and acid are weighed and discharged into a pan mixer, which may have a capacity of 1 - 2 tonnes per batch. After mixing about 2 minutes, the fluid mix is discharged into a box den, which may hold 10 - 40 tonnes. When the den is filled, one side is removed and the den is advanced slowly on a track to a mechanical cutter, which shaves thin slices of superphosphate from the block and discharges them to a conveyor or elevator.

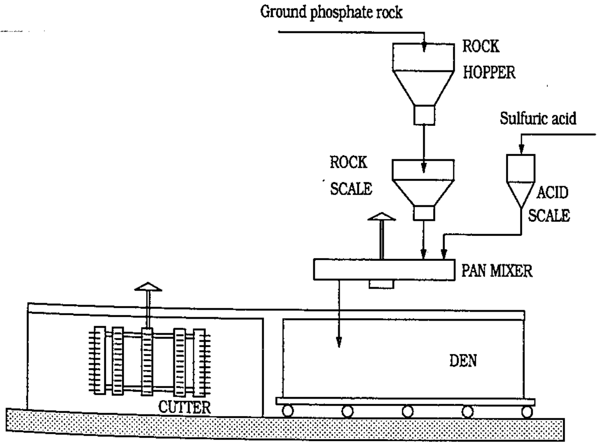

Figure 14.1. Batch Manufacture of Single Superphosphate.

With automated weighing and pan discharge, a 3 - minute mixing cycle is feasible; with a 2-tonne mixer a 40-tonne den can be filled in 1 hour. Some plants have two dens so that one is being filled while the other is being emptied. This arrangement gives a production rate of 40 tph.

Batch mixing has practically disappeared in favor of continuous mixing, but there are two cases where it remains very competitive. They are as follows:

1. When the only rock available is igneous rock, the batch mixing and associated denning system are preferred because they allow precise control of the mixing conditions and because the den can be made tight enough to contain the very fluid slurry delivered by the mixer.

2. When the purpose is to develop a small phosphate resource in a remote country, the batch process can be built at low cost and is easy to operate; these two qualities will make it a good choice in that case.

Figure 14.2 shows a flow diagram of a popular type of continuous den; the Broadfield den is a well-known example. The mixer may be a cone mixer, as shown, a paddle mixer (pugmill), or sometimes a cone mixer with a mixing impeller. Retention time in such dens usually ranges from 30 minutes to 1 hour and can be varied by changing the speed of the slat conveyor. This type of den is also suitable for making triple or enriched superphosphate.

The production of 1 tonne of SSP of 20% available P_2O_5 content would require 626 kg of ground phosphate rock (34% P_2O_5), 390 kg of sulfuric acid (93% H_2SO_4), and 90 kg of water. The reaction generates considerable heat. Approximately 8%-10% of the weight of the ingredients (water vapor and volatiles) is lost in the manufacturing and curing steps.

A typical continuous mixer plant to produce 20 tonnes of nongranular superphosphate per hour would have a 60-kW electrical load. One operator, two laborers, and a part-time supervisor per 8-hour shift would be required to operate the plant. By applying prevailing unit costs, a rough approximation of the direct cost of producing superphosphate in a specific location can be obtained. The operating requirements per tonne of superphosphate are given in Tables 14.2 and 14.3.

The capital cost for SSP production will vary widely depending on the battery limits adopted. The cost is

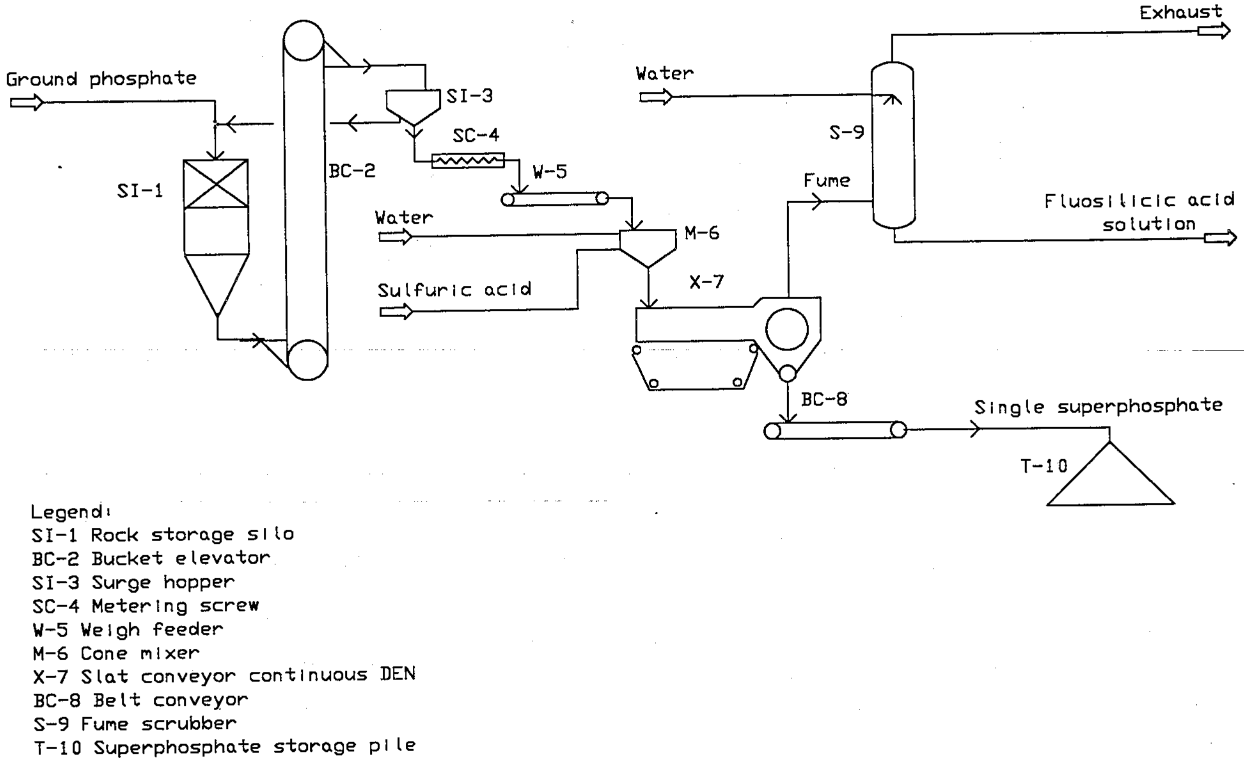

Figure 14.2. Continuous Manufacture of Single Superphosphate.

Table 14.2. Process Requirements for Powdered SSP

Parameters	Units	Value
Product SSP	1	0-18-0
Capacity	tpd	800
Annual operation time	h	7200
Investment cost (battery limits)	US $ (million)	10

Cost Components	Units	Unit/t
Raw Materials		
Phosphate rock (33% P_2O_5)	kg	626
Sulfuric acid (96%)	kg	390
Energy		
Electrical energy	kWh	19
Process water	m^3	0.1
Disposal		
Off-gases	Nm^3	350

Table 14.3. Process Requirements for Granular SSP

Parameters	Units	Value
Product SSP	1	0-18-0
Capacity	tpd	800
Annual operation time	h	7200
Investment cost (battery limits)	US $ (million)	20

Cost Components	Units	Unit/t
Raw Materials		
Phosphate rock (33% P_2O_5)	kg	626
Sulfuric acid (96%)	kg	390
Energy		
Electrical energy	kWh	34
Process water	m^3	2
Steam	kg	55
Fuel	kcal	62
Disposal		
Off-gases	Nm^3	350

much greater if the battery limits include the investment for sulfuric acid manufacture; in fact SSP plants often use byproduct sulfuric acid derived from a plant that is not a part of the SSP plant. Also, small SSP plants may purchase sulfuric acid from a larger plant that supplies several customers or use byproduct sulfuric acid from other industries (e.g., metal industry, or organic industry).

When several SSP plants are planned or in use, the phosphate rock may be ground at the mine or at a port and shipped to individual plants to take advantage of economies of scale in grinding. When in-plant rock grinding facilities are necessary, the cost depends on the initial size and hardness of the rock.

Storage curing costs will partially depend on the extent of fluorine emission control that is required.

Whether the SSP should be granulated depends on local preference. In some countries nongranular SSP is acceptable. Also, in many cases the SSP will be used as an ingredient for producing granular compound fertilizer.

When granular SSP is desired, the ex-den granulation system described in Chapter 12 is suitable. According to Sinte Maartensdijk, the recycle ratio in this plant was 0.63:1.0 [3].

The SSP bulk production cost, by the P_2O_5 content, is equivalent to the cost of P_2O_5 in TSP. The bulk cost equivalence is quickly eroded by the cost of bagging, transportation, and storage because the mass of SSP required is more than twice that of TSP. Thus, it may be concluded that large-scale production and distribution of SSP is seldom economical in comparison with TSP or DAP, unless there are special circumstances such as an agronomic requirement for sulfur that would render the SSP more valuable.

On the other hand, small SSP plants to serve small local markets can be economical where suitable raw materials are available and where the alternative of importing more concentrated materials is very expensive.

14.1.5 Product Properties

The European Council Directive 76 / 116 / EEC indicates that single superphosphate must contain at least 16% of P_2O_5 soluble in neutral ammonium citrate of which at least 93% is water soluble. SSP may be either powder form for use as a raw material in the manufacture of compound fertilizers or for application by the farmer, or granular (2 - 4 mm) for use as a raw material in a bulk-blending operation or for application. SSP may be shipped in bulk and in bags, provided it is protected from moisture.

14.1.6 Licensers and Contractors

The mention of the names of companies does not mean endorsement by UNIDO or IFDC. The companies that are listed have cooperated with UNIDO on technical assistance and project implementation and have contributed directly or indirectly to the manual.

- **Licensers**

  Amfert, Amsterdam, Netherlands
  Grande Paroisse, Paris, France
  Hydro Agri Licensing, Brussels, Belgium
  Jacobs Engineering, Lakeland, Florida, U.S.A.
  Kemira Agro, Helsinki, Finland
  Prayon Technologies, Engis, Belgium

- **Contractors**

  Coppée - Lavalin, Brussels, Belgium
  Jacobs Engineering, Lakeland, Florida, U.S.A.
  John Brown Engineers and Constructors Ltd., London, U.K.,
  - including Davy Powergas, Ltd., London, U.K. and John Brown Deutsche Engineering G.m.b.h., Essen, Germany

  Kemira Oy, Helsinki, Finland
  Krebs, Montigny-le-Bretonneux, France
  Lurgie Chemie und Hüttentechnik, Frankfurt-am-Main, Germany
  Mitsui and Co, Tokyo, Japan
  Uhde G.m.b.h., Dortmund, Germany.

14.1.7 Enriched Superphosphate

"Enriched" superphosphate is essentially a mixture of SSP and TSP, usually made by acidulation of phosphate rock with a mixture of sulfuric and phosphoric acids. Theoretically, any grade between SSP and TSP can be produced, but the usual range is 25%-35% P_2O_5. Processes and equipment are about the same as for SSP [4].

Enriched superphosphate may be a useful product for application in sulfur-deficient areas where SSP would supply more sulfur than necessary. One advantage is that mixed acid of the proper concentration can be obtained by mixing concentrated sulfuric acid (93% or 98% H_2SO_4) with dilute phosphoric acid (30% P_2O_5), thereby avoiding the need for concentrating the latter.

14.2 Phosphate Rock as a Fertilizer

14.2.1 Ground Phosphate Rock

Ground phosphate rock is not classified as a fertilizer in most countries and is not included in fertilizer consumption statistics reported by most countries. However, FAO reports consumption of ground rock phosphate separately; in 1976 reported consumption was equivalent to 1.2 million tonnes of P_2O_5, about 5% of phosphate fertilizer consumption.

It is likely that actual consumption of phosphate rock for direct application is substantially higher than reported due to unreported consumption or, in some countries, inclusion with fertilizer use.

Considerable difference of opinion exists as to the merits of ground rock phosphate as a fertilizer. In some countries, the chemical phosphate fertilizer industry perceives ground rock as a threat to its prosperity and has urged government restrictions of its use. In other cases, industry or government authorities have promoted its use.

The main purpose of the latter policy is to enable much less costly sources of phosphate rock to be brought into use. This plays an important role in countries with large reserves of phosphate rock, but with inadequate financial resources to invest in industrial production of phosphoric acid, TSP, and ammonium phosphates.

Some of the factors that contribute to the difficulty of making an impartial appraisal of the merits of direct application of ground rock phosphate are:

1. Phosphate rocks vary widely in their reactivity hence their agronomic value varies.
2. The agronomic response to phosphate rock strongly depends on the type of soil and, to some extent, on the crop and climatic factors.
3. The response depends on timing, method of application, and particle size.
4. The residual value of a single application or cumulative value of repeated applications is important with all phosphate fertilizers, but this is not easily evaluated. Ground phosphate rock often has a more favorable long-term than short-term effect.
5. Agronomic and economic studies of long-term use on food crops are generally lacking.

The principal advantage of ground phosphate rock is its low cost. When both must be imported, ground rock may cost about one-half as much as TSP; when indigenous rock is available, the cost differential may be greater. Other advantages are:

1. A very low capital investment is required for processing.
2. No particular technical skills are required.
3. The energy requirement is small.
4. There is little or no loss in processing.
5. Rocks unsuitable for chemical processing are in some cases suitable for direct application.
6. The delay involved in building chemical processing plants can be avoided.
7. Economy of scale is relatively unimportant.
8. Ground phosphate rock has a liming value on acid soils.

The main disadvantages are uncertainty as to agronomic value, inconvenience of handling and applying the fine, dusty material, and relatively low P_2O_5 content compared with TSP or ammonium phosphates.

It is generally agreed that ground phosphate rock is effective only on acid soils (pH 6 or less). This statement applies to apatitic rocks, not to calcined aluminum phosphate ores that are effective on neutral or calcareous soils.

Phosphate rocks are also more effective in warmer climates, in moist soils, and on crops that have fairly long-term growing patterns. They are less effective for short-season crops grown under cool soil temperatures, particularly in the first year of application.

It is generally agreed that the rock should be finely ground and well mixed with the soil. However, there is some difference of opinion as to the usefulness of very fine grinding. The majority opinion seems to be that there is little to be gained by grinding finer than about 90% through 100-mesh (0.147 mm), although there are some who claim that very fine grinding such as 80% through 320-mesh (0.043 mm) is worthwhile.

Ground rock that has been granulated after grinding has given rather poor first-crop results even when the granules disintegrate in the soil, presumably because granulation reduces the area of contact with the soil. However, in most of the tests, the granules have been in the range of 1-4 mm.

While it is generally agreed that reactivity is important, there is some disagreement as to how important it is and how to measure it. Chemical methods for evaluating reactivity are discussed later. The importance of reactivity is greatest for the first crop or season; the long-term or residual effectiveness does not seem to be closely related to reactivity. Rocks of relatively low reactivity have shown good long-term effectiveness.

Some investigators have attributed the response to phosphate rock to annual rainfall; better results were obtained on well-watered soils.

In the early part of the 20th century, several long-term experiments were conducted in the United States with ground phosphate rocks in Tennessee, which is one of the less reactive sedimentary rocks. Hopkins has reported results from experiments in four states of the United States that show the increased value of crops grown in a rotation with phosphate rock added exceeded the cost of the phosphate rock by factors ranging from about 5:1 to 10:1.

When superphosphate was used, the ratio of the value of increased yield to cost was much lower, primarily because the superphosphate cost was about four times as much per tonne of P_2O_5 as the cost of ground phosphate rock.

As a result of these tests, use of ground phosphate rock increased in the United States to a maximum of more than 1 million tpy in 1953. However, more recently use has decreased sharply, and in 1976 consumption amounted to only about 37,000 tonnes, including "colloidal phosphate," a fine material recovered from Florida waste ponds.

The decreased use is attributed to two factors. First, large-scale production of high-analysis phosphates (TSP and DAP) has brought the delivered cost of these materials down to the point that ground phosphate rock has little cost advantage, particularly when transported over long distances. Secondly, the granular phosphates are much easier to handle and apply to the soil than the finely ground phosphate rock.

Ground phosphate rock has been advocated and used for reclaiming low-phosphorus soils of abandoned farms or of new (previously uncultivated) land of low native phosphorus fertility. For this purpose a heavy application is recommended, such as 1-3 tonnes/ha, which may be repeated at 5- to 10-year intervals. Also, phosphate rock is used in Europe as a replacement for basic slag to maintain soil fertility, usually by relatively large applications at intervals of several years. In either case there may be supplemental application of soluble phosphate fertilizers, depending on crop needs.

In tests with single-season crop results, the most reactive phosphate rocks have shown effectiveness nearly equal to superphosphate with some crops and soils.

In the past few years a considerable amount of research has been done to evaluate the agronomic effects of Latin American phosphate rocks. The results indicate that it is feasible to apply ground phosphate rocks directly, especially on permanently cropped acidic soils that predominate in tropical zones.

14.2.2 Calcined Aluminum Phosphate

Ores consisting mainly of hydrated aluminum phosphate minerals are useful for direct application after being calcined at a controlled temperature. The calcining may be done in a rotary kiln or in a fluidized bed calciner. Calcining removes the combined water and thereby enhances the grade and destroys the crystallinity of the phosphate minerals, thereby improving the reactivity of the phosphate.

At present, only two aluminum phosphate ores are known to be used for direct application after calcining. One of these occurs in Senegal near Thies. The ore, as mined, contains about 29% P_2O_5 on a dry basis; after calcination it contains over 34% P_2O_5. A partial analysis of the calcined product is given in Table 14.4.

Table 14.4. Chemical Analysis of Calcined Product

Components	% Weight
P_2O_5	34.6
Al_2O_3	35.9
CaO	10.9
Fe_2O_3	9.1
SiO_2	2.9
TiO_2	1.9
MgO	0.3

After calcination, the ore is ground to about 95% minus 100-mesh and marketed for direct application under the trade name "Phosphal." About 75% of the P_2O_5 is soluble in alkaline ammonium citrate. Field tests showed that fertilizer effectiveness of the product was approximately equal to that of superphosphate on calcareous, neutral, and acid soils. Superphosphate was marginally better immediately after application while Phosphal was better in long-term tests. The product is used mainly in France, Senegal, and some nearby countries.

A similar ore occurs in the upper stratum ("C-grade") of the phosphate deposit on Christmas Island. The C-grade ore contains about 25% P_2O_5 dry basis; the composition range of this ore after calcination is given in Table 14.5.

Table 14.5. Composition of Calcined "C-Grade" Phosphate

Components	% Weight
P_2O_5	29-33
Al_2O_3	29-34
CaO	15-21
Fe_2O_3	11-19
CO_2	0.9-1.0
F	0.6-0.8

It is composed almost completely of iron and aluminum phosphates (mostly crandallite, Ca (Fe, Al)$_3$ (PO$_5$)$_2$ (OH)$_5$•3H$_2$O, and millisite Ca (Na,K) (Fe, Al)$_6$ (PO$_5$)$_2$ (OH)$_5$•3H$_2$O) and is altogether unsuitable for conventional phosphoric acid/soluble phosphates production. All the accessible reserves of phosphate rocks on Christmas Island have been significantly depleted and will suffice for 16 to 17 years at most.

Calcination is carried out in a fluidized bed. Experiments showed that maximum citrate solubility was obtained in the range of 400°-600°C. The maximum solubility in alkaline ammonium citrate solution was about 70%; the solubility in 2% citric acid solution is much lower, about 20%-30% [5]. The product is used for direct application after being ground to pass a 100-mesh (0.15 mm) screen.

Both the "Phosphal" from Senegal and the Christmas Island product may be shipped in bulk after calcination to be ground in the importing country.

Some of the ground product is used in mixtures with other fertilizer materials. However, if the mixture is granulated to the usual size (1-4 mm), the agronomic effectiveness is lower, at least for the first season after application.

TVA conducted experiments with Florida "leached-zone" ore, which also contains a high percentage of aluminum phosphate minerals–millisite, crandallite, and wavelite. It was found that maximum P_2O_5 citrate solubility of 70%-79% was obtained by calcining at 500°-600°C. However, the leached zone material is low grade and variable in composition and hence poorly suited for commercial use.

14.2.3 Defluorinated Phosphate Rock

There is a substantial production of defluorinated phosphate rock for fertilizer usage in Japan (about 100,000 tpy). Ground, high-grade rock is mixed with small proportions of sodium carbonate or sulfate and wet-process acid. The mixture is calcined at a temperature of 1350°C in an oil-fired rotary kiln 45.0 m in length and 2.7 m in diameter. The product contains 38%-42% P_2O_5 of which more than 90% is soluble in neutral ammonium citrate solution. Substantially all of the fluorine is driven off. Sodium bifluoride ($NaHF_2$) is recovered as a byproduct. A similar product is made in the United States, but it is mainly used for animal feed supplement. The principal phosphate compound in the product is tricalcium phosphate.

Requirements per tonne of product containing 41%-42% total P_2O_5 are:

Phosphate rock (37% P_2O_5), kg	900
Wet-process acid, kg (as P_2O_5)	95
Sodium carbonate, kg	120
Heavy fuel oil, liters	200

The product is said to be an effective fertilizer when applied in finely ground form on acid soils.

TVA has studied defluorination of lower grade phosphate rock through fusion processes. Ten pilot plants and two demonstration-scale plants were built and operated. The more successful plant operated for 10 years (1945-55) and produced about 170,000 tonnes of product containing 28% P_2O_5 from low-grade Tennessee rock. The results of the studies have been published [6].

14.2.4 Partially Acidulated Phosphate Rock

In some instances, an indigenous phosphate rock may prove unsuitable for direct application and require the addition of a more soluble form of phosphate. An alternative is partial acidulation to render its P_2O_5 more available. This option is of particular interest since the crop response is often similar to that obtained when using fully acidulated products such as SSP or TSP. In this situation, less acid is used, and production capacity may be increased.

The partially acidulated phosphate rock (PAPR) process depends on treating ground phosphate rock with only a portion of the stoichiometric value of acid, for example 50% PAPR. The amount of water-soluble phosphate in PAPR varies according to the degree of acidulation.

Sulfuric and phosphoric acids are the most common acids used for partial acidulation. Possibilities exist for using three processes: a conventional run-of-pile process followed by granulation; single-step acidulation and granulation; and a slurry granulation triple superphosphate-type process.

For reasons of economics, the use of sulfuric acid for acidulation and a run-of-pile process (Figure 14.1) are the most common choices.

14.3 Basic Slag

Basic slag, also called Thomas slag, is a byproduct of the steel industry. Iron made from high-phosphorus ore is converted to steel in a Thomas converter by oxidation in contact with a basic (high CaO) slag. The usual range of P_2O_5 content in slag that is used for phosphate fertilization is 10%-20%. Sometimes phosphate rock is deliberately added to the blast furnace charge to increase the phosphorus content of the iron and thereby increase the P_2O_5 content of the slag.

Basic open-hearth slag also may contain P_2O_5 up to 10%-12%, and it is used in agriculture in some countries, both for liming and phosphorus supply.

Since most of the high-phosphorus iron ores occur in Western Europe, most of the basic slag is produced and used there. A typical range of composition for high-grade basic slag is given in Table 14.6.

Table 14.6. Composition of Basic Slag

Components	% Weight
P_2O_5	15-20
Al_2O_3	0.5-2.5
CaO	42-50
Fe_2O_3	9-13
SiO_2	4-6
MnO	3-6
MgO	2-4

The P_2O_5 in basic slag is mainly present as calcium silicophosphates – silicocarnotite ($5CaO \cdot P_2O_5 \cdot SiO_2$) and nagelschmitite ($7CaO \cdot P_2O_5 \cdot SiO_2$). Small amounts of fluorspar (CaF_2) may be added to slags to decrease their viscosity during the steel-refining process. Such slags contain fluorapatite and are likely to be less suitable for fertilizer use.

The Wagner test, which measures the solubility of P_2O_5 in 2% citric acid, is widely accepted for evaluating the suitability of basic slag for fertilizer use. P_2O_5 solubility in this reagent ranges from 85% to 98% for English basic slags [7]. The consumption of agricultural-grade basic slag was equivalent to 1.2 million tonnes of P_2O_5 in 1973 and varied only slightly from this level for many years. However, the available supply later decreased because of changes in steel-making processes and importation of low-phosphorus iron ore. In 1977 world production was about 572,000 tonnes of P_2O_5, less than half of the 1960-65 average [8]. More recently, in 1988 this figure dropped another 65% to 205,000 tonnes or 0.5% of the P_2O_5 in fertilizers [1]. In 1992 the figures were 175,000 tonnes and 0.46%. Slag is regarded as a good phosphate fertilizer on acid soils and is also valued for its liming effect and micronutrient content. It is usually applied in a finely ground state although granulation with potash has been practiced to some extent.

14.4 Potassium Phosphates

Potassium phosphates are excellent fertilizers, and their very high analysis is an advantage that has stimulated much research in an effort to find an economical production process. However, no process has been developed that is economical enough to result in widespread production; therefore, present use is limited to special purposes for which the high cost can be justified.

At present, most of the potassium phosphates used in fertilizers are produced from potassium hydroxide or carbonate and phosphoric acid and are used in liquids for foliar application or other specialty uses.

Some of the alternative salts of potassium phosphates are given in Table 14.7.

Table 14.7. Phosphate Potassium Salts

Compound	Formula	Grade
Monopotassium phosphate	KH_2PO_4	0-52-35
Dipotassium phosphate	K_2HPO_4	0-40-54
Tetra potassium pyrophosphate	$K_4P_2O_7$	0-43-57
Potassium metaphosphate	KPO_3	0-60-40

In addition, a potassium polyphosphate solution of 0-26-27 grade has been produced from superphosphoric acid and potassium hydroxide; it contains a mixture of ortho, pyro, and higher polyphosphates.

TVA, SAI, and others have produced potassium metaphosphate in pilot plants by high-temperature reaction of KCl and phosphoric acid. The pure material, KPO_3, has a grade of about 0-60-40 and, thus, a 100% nutrient content (on an oxide basis).

In a process developed jointly by Goulding (Ireland) and Pennzoil (United States), potassium chloride is treated with concentrated sulfuric acid to produce potassium bisulfate [9,10]:

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCL$$

After removal of hydrogen chloride as a dry gas, the potassium bisulfate is reacted with more sulfuric acid and phosphate rock to produce a mixture of monopotassium phosphate and phosphoric acid. The latter can be ammoniated to obtain a chloride-free NPK fertilizer, such as 8-48-16, or monopotassium phosphate can be separated from the phosphoric acid by precipitation in methanol solution and marketed separately.

The metaphosphate and Pennzoil processes are not in commercial use.

14.5 Bone Meal

A relatively small amount of bone meal is used as fertilizer mainly by home gardeners. It is much too expensive for farm use. Most bone meal is marketed for use in animal feeds.

14.6 Fused Calcium Magnesium Phosphate

In a TVA-developed process, a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace [11]. The molten product is quenched with water and used in a finely divided state as a fertilizer. The product, a calcium magnesium phosphate (CMP) glass, contains about 20% P_2O_5 and 15% MgO. Over 90% of the product is soluble in citric acid.

CMP is produced in several plants in Japan where the annual production is about 500,000 tonnes. It is also produced in Korea, Taiwan, China, Brazil, and South Africa. Either electric or fuel-fired furnaces are used.

The theoretical compositions of some magnesium-containing minerals that can be used to produce CMP are:

Olivine	$(Mg, Fe)_2 SiO_4$
Serpentine	$Mg_3H_4Si_2O_9$
Garnierite	$(Mg, Ni) H_2SiO_4$
Magnesite	$MgCO_3$

The minerals are variable in composition; iron, nickel, and sometimes manganese may substitute for magnesium. A sample of Japanese serpentine contained 38% MgO, 38% SiO_2, 8% Fe_2O_3, and 14% ignition loss [12]. Magnesium oxide, obtained by calcining magnesite or extracting it from sea water, can be used in the process; in this case, silica must be added in sufficient quantity to result in 20%-30% SiO_2 in the product. Huang reported that ratios of serpentine to phosphate rock in the range of 6:10 to 8:10 gave the highest P_2O_5 solubility in citric acid, using phosphate rock from Christmas Island (39% P_2O_5) or Lao Kay (33% P_2O_5) [12]. Moulton reported using ratios of olivine to phosphate rock of 1 : 2 with Montana phosphate rock (30%-32% P_2O_5) [13]. Walthall and Bridger recommended a ratio of olivine to phosphate rock of 0.46:1.00 using Tennessee phosphate rock (33% P_2O_5) and North Carolina olivine (45% MgO and 44% SiO_2) [11]. About 30% of the fluorine was volatilized, but the product P_2O_5 solubility was not related to its fluorine content. In tests in which magnesia and silica were supplied separately, it was found that 0.24 kg of MgO and 0.25 kg of SiO_2/kg of phosphate rock gave a product P_2O_5 solubility of 96% (in citrated ammonium nitrate solution). Also, 0.28 kg of MgO and 0.21 kg of SiO_2 gave essentially complete solubility. In Japan, CMP is produced in electric-arc furnaces of the type used for the manufacture of calcium carbide. The furnace charge is prepared by crushing and mixing phosphate rock and serpentine or olivine. About 850 kWh/tonne of product is required for the fusion process. It is essential to quench the molten material rapidly, and this is usually accomplished in a trough provided with high-velocity jets of water. Approximately 10 tonnes of quench water, which may be recycled, is required per tonne of product. The quenched material is allowed to drain and is then dried and ground. The specified fineness is at least 70% through a 100-mesh screen.

Ando reported tests in which charges of garnierite, phosphate rock, gypsum, and coke were fused in a blast furnace or electric furnace to produce CMP and nickel matte, a mixture of sulfides of nickel and iron containing 20%-25% Ni, 60%-66% Fe, and 14% -17% S [14]. The nickel matte was processed further to recover the nickel. The coke reduced the gypsum and the iron and nickel oxides to form the sulfides. When the process was carried out in the blast furnace, combustion of additional coke supplied the necessary heat for the fusion process. A blast-furnace process is used in China also to produce CMP with separate recovery of iron and nickel.

Greenhouse tests made by the U.S. Department of Agriculture showed that the product is, on the average, more effective than superphosphate when used on acid soils. Field tests in Japan have given favorable results on many different crops and soils. The product has a liming value equivalent to 0.5 - 0.7 tonne of calcium carbonate per tonne of material. The magnesium oxide content is available to growing plants. In some situations, the soil-soluble silica may be an advantage.

14.7 Rhenania Phosphate

Rhenania phosphate is another thermally produced phosphate fertilizer. It is made by calcining a mixture of phosphate rock, sodium carbonate, and silica in a rotary kiln at 1250°C [15]. Enough sodium carbonate is used to form the compound $CaNaPO_4$ and enough silica to form Ca_2SiO_4 with the excess calcium. Typical charge proportions are one part of sodium carbonate to three parts of phosphate rock and enough silica to raise the SiO_2 content of the product to about 10%. The product contains 28%-30% P_2O_5, which is nearly all soluble in neutral or alkaline ammonium citrate solution even though much of the fluorine remains in the product. It is applied to the soil in pulverized form or granulated in small granules with potash salts. Some grades are produced containing magnesium or boron, which are added during granulation as kieserite or borax, respectively. A substantial quantity is produced in European countries, particularly West Germany.

A somewhat similar product, Roechling phosphate, uses a soda slag that is a byproduct from the steel industry as the source of sodium. Also, the naturally occurring minerals, trona (sodium sesquicarbonate) or natron (sodium carbonate), may be used. Experiments have shown that a similar product can be made by sintering potassium carbonate with phosphate rock and silica to produce a product grade of 0-25-25. The phosphate compound in this product is presumed to be $CaKPO_4$.

The overall reaction in producing Rhenania phosphate is assumed to be:

$$Ca_{10}F_2(PO_4)_6 + 4Na_2CO_3 + 2SiO_2 \rightarrow$$
$$6CaNaPO_4 + 2Ca_2SiO_4 + 2NaF + 4CO_2$$

Any grade of phosphate rock can be used, but since the grade of the product is determined by the grade of the rock, a high grade is preferred.

Estimated consumption figures using an igneous apatite are given in Table 14.8.

The product has been reported to be substantially more effective than superphosphate on several acid tropical soils in Costa Rica, Liberia, Congo, Zaïre, Ghana, and Malawi perhaps because of its alkalinity and resistance to fixation by the soil [16]. In some crops or soils the sodium or soil-soluble silica may be beneficial.

Table 14.8. Process Requirements for Rhenania Phosphate 0-29-0 Grade

Raw Material/Utility	Units	Unit/Tonne
Phosphate rock (38.7%)	kg	749
Soda ash (100% Na_2CO_3)	kg	289
Sand (97% SiO_2)	kg	77
Electrical energy	kWh	36
Steam	kg	10
Fuel oil	GJ	2.4

14.8 Calcium Metaphosphate

For several years TVA produced calcium metaphosphate, $Ca(PO_3)_2$, in a demonstration-scale plant. The process consisted of burning elemental phosphorus and reacting the resulting P_2O_5 vapor with phosphate rock. The molten product was tapped out of the furnace and solidified on a water-cooled steel drum [17]. The resulting vitreous flakes were cooled further and crushed to pass a 10-mesh screen (about 1.6 mm). Development of a process for production of calcium metaphosphate involved three pilot plants and three demonstration-scale plants and a considerable amount of laboratory- and bench-scale work [18]. The third demonstration-scale plant was technically successful and operated about 16 years, starting in 1949. A total of nearly 1 million tonnes was produced, including relatively small amounts from the first and second demonstration-scale plants. The process was economically competitive with TSP when both products were based on elemental phosphorus made by the electric-furnace process.

Pure calcium metaphosphate contains 71.7% P_2O_5; the TVA product contained about 65% P_2O_5 because of impurities in the rock. The material was not water soluble but hydrolyzed slowly in water or moist soil, forming water-soluble compounds [19]. About 98% or more of the P_2O_5 was soluble in neutral ammonium citrate.

The main disadvantage of the process was its dependence on elemental phosphorus, which has become too expensive for fertilizer use in most situations. Also its agronomic effect depends on the rate of hydrolysis in the soil, which may be too slow for short-season crops.

Calcium metaphosphate glass may also be produced by heating TSP to fusion; crystalline structures, which are not citrate soluble, are formed at lower temperatures.

14.9 Dicalcium Phosphate

Dicalcium phosphate is a common constituent of nitrophosphate fertilizers and of compound fertilizers formed by ammoniation of superphosphates. There is a relatively small but substantial production of straight dicalcium phosphate in Europe, which is based on use of byproduct hydrochloric acid. The process consists of dissolving phosphate rock in hydrochloric acid and then precipitating dicalcium phosphate by stepwise addition of limestone and slaked lime. The product is recovered by filtration and washing, and the remaining solution of calcium chloride may be used or discarded.

Various other methods for producing dicalcium phosphate are known, but none are known to be used commercially for fertilizer production. Direct neutralization of pure or defluorinated phosphoric acid with lime or limestone is used to produce feed- or food-grade dicalcium phosphate.

14.10 Magnesium Phosphates

Monomagnesium, dimagnesium, and trimagnesium phosphates are known to be effective fertilizers, but there is no known commercial production of these materials for fertilizer use. No doubt small percentages of these compounds are formed in processing phosphate rock containing magnesium.

14.11 Urea Superphosphate (USP)

14.11.1 Introduction

A newcomer in this field is the USP process disclosed by AZF GRANDE PAROISSE at the IFA technical meeting in Amman [20] in 1994.

Even though mixing urea and superphosphate is not recommended because the products react to form lumps and a sticky mixture, GRANDE PAROISSE and their partner ARMINES found that as early as 1934 Dalman [21] had reported that urea and sulfuric acid form the following complexes:

$CO(NH_2)_2 \bullet H_2SO_4$ and $2CO(NH_2)_2 \bullet H_2SO_4$

There are two eutectics E1 and E2 (Figure 14.3) that correspond respectively to 3.6 moles of urea to 1 mole of H_2SO_4 and 1.8 mole of urea to 1 mole of acid. While the melting point of urea is 132.7°C, both eutectics have a melting point of about 10°C.

The preparation of the mixtures of urea, sulfuric acid, and water at the mole ratios, 3.6:1 and 1.8:1, is exothermic in both cases. Heat release with the first ratio is lower than with the second one and allows the preparation of the mixture under stable and reliable conditions at an equilibrium temperature of 60°-70°C, which is ideal to acidulate phosphate rock.

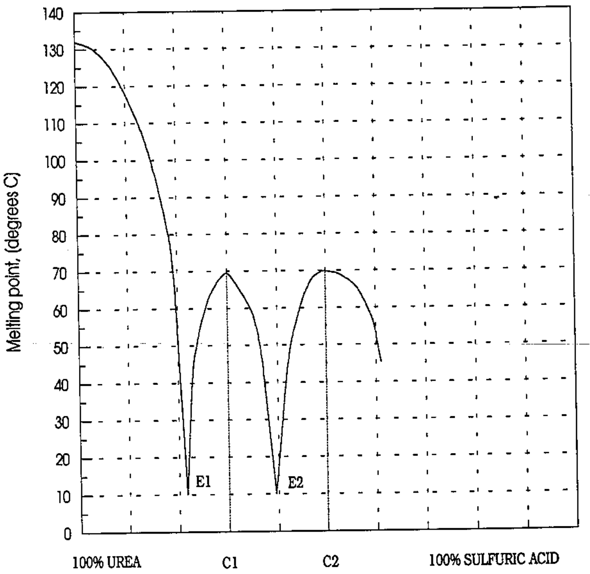

Figure 14.3. Urea/Sulfuric Acid Eutectics.

In the manufacture of USP, the reaction of acidulation may be written as follows.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + (8a + 2f)\ CO(NH_2)_2 + (e + 2bx)\ H_2O \rightarrow 2a\ [CaSO_4 \bullet 4CO(NH_2)_2] + 2b(CaSO_4 \bullet xH_2O) + eCa(H_2PO_4)_2 \bullet H_2O + f[Ca(H_2PO_4)_2 \bullet 2CO(NH_2)]$$

with a + b = 1, and e + f = 1.

It will be noticed that urea is associated with calcium sulfate rather than water of hydration [22]. But the sulfuric acid to rock ratio has not changed.

14.11.2 Identification of the Reaction Products

X-ray analysis of the product showed that:

- There is no more free urea.
- There is a substantial amount of tetra urea calcium sulfate.
- P_2O_5 as monocalcium phosphate may be linked to two ureas.

14.11.3 Development of the Process

The process was studied on laboratory scale and further developed in a pilot plant with a capacity of 100 kg USP per hour. It was also demonstrated in an industrial plant at the rate of 15 tph. The superphosphate plant used for this demonstration was equipped with a paddle mixer and a drum den (Figure 14.4).

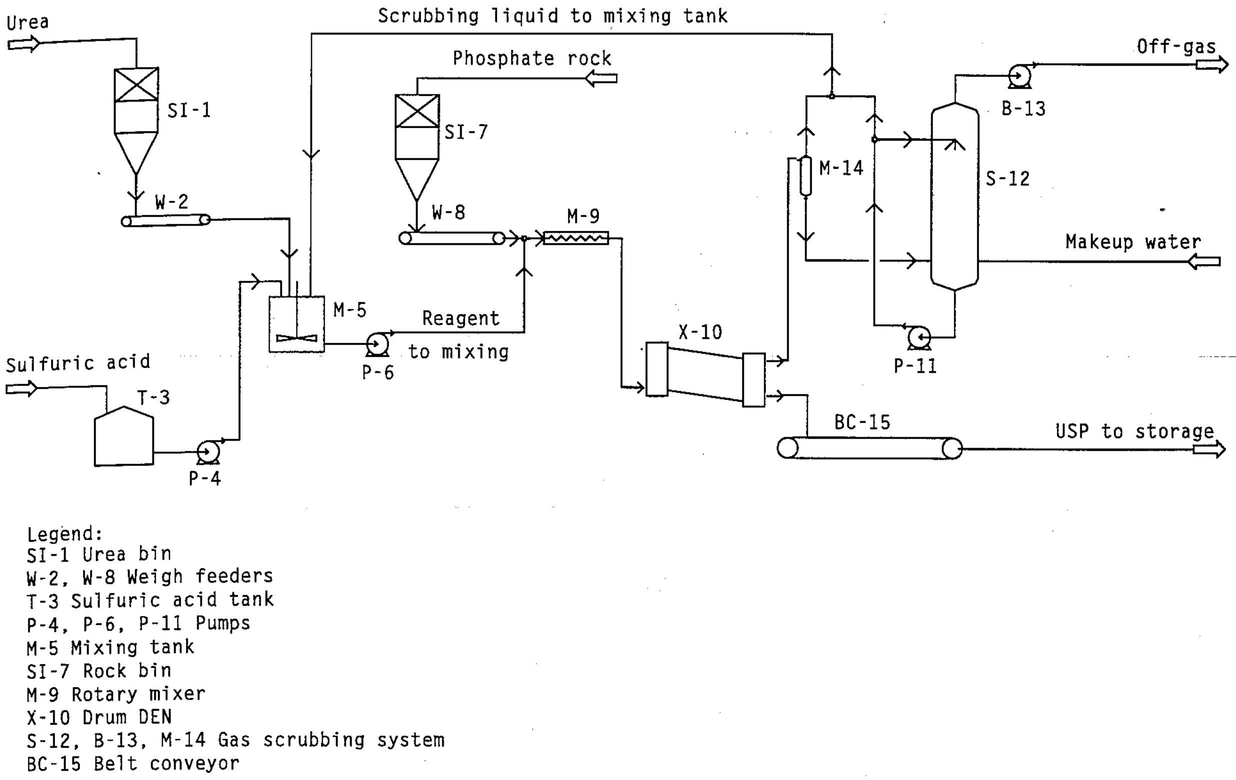

Figure 14.4. USP Pilot-Plant Technological Process.

It was necessary to add only a 12 m^3, 316L stainless steel agitated tank, into which 94% sulfuric acid and urea were introduced. Operating conditions were the same as those of the pilot plant. The residence time was about 1 hour. No evolution of gas was detected, and this observation was confirmed by fluorine determinations. The fluorine contained in the rock was entirely recovered in the powdered product.

After delumping, powdered USP was fed to a granulation loop. It has been granulated alone and with addition of other materials such as phosphoric and/or sulfuric acids, ammonia, potassium salts (any fertilizer except nitrated salts), fillers such as gypsum and sand, and micronutrients. The following compound fertilizers were produced: 14-14-14; 14-7-14; 9-17-24; 8-18-26; 8-15-22. The recycle rate was 2.5 to 4, depending on the formulation used.

14.11.4 Qualities of the Product: 20-10-0 USP

USP simultaneously supplies urea nitrogen, sulfur, calcium, and phosphate; 95% of the citrate soluble phosphate is soluble in water. A typical analysis of the product after granulation is given in Table 14.9.

Table 14.9. Properties of USP 20-10-0

Properties	% Weight
Total nitrogen	20.9
Urea nitrogen	19.3
Ammoniacal nitrogen	1.6
Total P_2O_5	10.2
Citrate-soluble P_2O_5	9.7
Water-soluble P_2O_5	9.2
SO_3	16.1
H_2O	1.0

14.11.5 Storage Properties

USP can be used as produced, i.e., in powdered form, or as a granular material. In the latter case, its physical properties are quite similar to those of urea-based NP and NPK grades. The product stores well. Its critical relative humidity is 65%-70% at 20°C; consequently, it is suitable for bulk storage.

14.11.6 Agronomic Interest

To determine whether this new fertilizer with urea in the molecular structure has agronomic properties typical of traditional fertilizers, agronomic tests were done with maize and rice (Figures 14.5 and 14.6).

USP was tested in comparison with the same quantities of nitrogen and phosphate supplied by DAP and urea. In both cases the same input of potassium was supplied by potassium chloride (KCl) containing 60% K_2O. Tests were carried out in five different combinations of clay, silt, sand, and loam soils.

An increase in yield was found at the optimum nitrogen input. Thus, for a yield of 11,500 kg/ha of maize, the fertilization rate can be reduced by 40 kg/ha of nitrogen when using USP.

USP of the 20-10-0 grade with 60% K_2O potassium chloride was compared with a mixture comprising ammonium sulfate, TSP, and potassium chloride. Only one type of soil was used for this comparison: a loam soil composed of clay, sand and silt. With the same fertilization rate of 140 kg/ha nitrogen, the yield was increased by 10%. The tests also showed that splitting the application of nitrogen, which was advisable in traditional fertilization, was no longer necessary with USP.

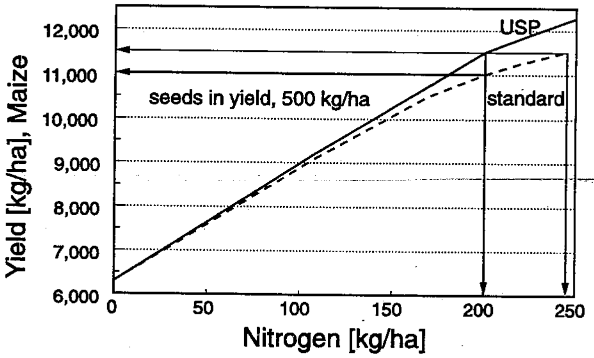

Figure 14.5. Maize Fertilization With USP.

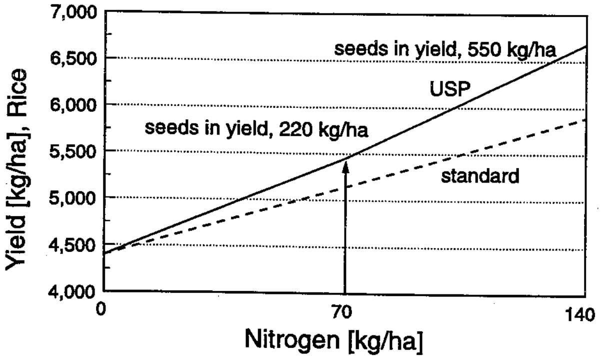

Figure 14.6. Rice Fertilization With USP.

The tests have shown that USP affects maize and rice fertilization very positively. At constant yield the consumption of nitrogen can be cut by at least 10%.

14.11.7 Advantages of the Process

- Zero liquid effluents, near zero fluorine emission.

  Because the fluorine in the phosphate rock is entirely recovered in the USP, a single-stage scrubbing unit satisfies the most stringent standards while SSP requires three or four stages. Moreover, the scrubbing liquor is recycled into the preparation of the urea-sulfuric acid mixture.

- The phosphoric acid route is avoided.

  This is one of the rare processes that allow for the production of a urea-based compound fertilizer without using phosphoric acid, thus avoiding its costs and nuisances.

- Granulation plants can be retrofitted to operate the USP process.

- The USP process is cost effective.

  USP is cost effective because it uses the lowest cost raw materials based on concentrated sulfuric acid, it produces a drier product that requires no additional drying when used in powdered form or saves 40% of the drying energy when it is granulated. The production technology is simple and requires limited capital cost.

- It can be produced in SSP or TSP plants after an easy and cheap revamping.

14.12 References

1. Schultz, J. J., D. I. Gregory, and O. P. Engelstad. 1992. *Phosphate Fertilizers and the Environment–A Discussion Paper*, P-16, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
2. U.S. Department of Agriculture and Tennessee Valley Authority. 1964. *Superphosphate: Its History, Chemistry, and Manufacture*, U.S. Government Printing Office, Washington, D.C., U.S.A.
3. Sinte Maartensdijk, A. 1977. "Direct Production of Granular Superphosphates and PK Compounds

from Sulfuric Acid, Phosphoric Acid, Rock Phosphate, and Potash," *Proceedings of 1976 ISMA Technical Conference*, The Hague, Netherlands.

4. Yates, L. D., F. T. Nielsson, E. J. Fox, and R. M. Magness. 1953. "Enriched and Concentrated Superphosphate," *Industrial and Engineering Chemistry*, 45(3):681-690.

5. Doak, B. W., P. J. Gallaher, L. Evans, and F. B. Muller. 1965. "Low-Temperature Calcination of C-Grade Phosphate From Christmas Island," *N. Z. Agric.*, 8:15-29.

6. Brosheer, J. C., and T. P. Hignett. 1953. "Development of Processes for Production of Fused Tricalcium Phosphate," TVA Chemical Engineering Report No. 7, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.

7. Brown, G. G., and K. F. Thatcher. 1967. "The Production and Properties of Basic Slag," *Proceedings of the Fertiliser Society* (London), No. 96.

8. ISMA. "Phosphate Fertilizer Statistics, 1978," ISMA Economics Committee, Paris, France.

9. Thompson, W. H. 1971. "New Route Cuts Costs for Potassium Orthophosphates," *Chemical Engineering,* 78(8):83-85.

10. Drechsel, E. K. 1973. "Potassium Phosphates: The New Generation of SUPER Phosphates," Paper presented to the American Chemical Society, Division of Fertilizer and Soil Chemistry, Chicago, IL, U.S.A.

11. Walthall, J. H., and G. L. Bridger. 1943. "Fertilizer by Fusion of Rock Phosphate with Olivine," *Industrial and Engineering Chemistry,* 35(7):744-777.

12. Huang, T. H. 1953. "Serpentine Fused Phosphate," *Journal of Agricultural and Food Chemistry,* 1(1):62-67.

13. Moulton, R. W. 1949. "Electric Furnace Fertilizer – Ca - Mg - Phosphate," *Chemical Engineering,* 56(7):102-104.

14. Ando, J. 1959. "Simultaneous Production of Nickel Matte and Calcium Magnesium Phosphate," *Industrial and Engineering Chemistry,* 51(10):1267-1270.

15. Werner, W. 1967. "*Die Rhenania-Dunger,*" Verlag M & H Schaper, Hannover, West Germany.

16. Werner, W. 1969. "Die Bedeutung Kalk-und Silikathaltiger Phosphatdunger for die Dungung von Latosolen," *Der Tropenlandwirt*, 57-81.

17. Yates, L. D., L. F. Roy, and R. S. Meline. 1951. "Improved Fertilizer Plant Design," *Chemical Engineering,* 58(6):435-437.

18. Brosheer, J. C. 1953. "Development of Processes for Production of Calcium Metaphosphate," TVA Chemical Engineering Report No. 6, Tennessee Valley Authority, Muscle Shoals, AL, U.S.A.

19. Brown, E. H., J. R. Lehr, J. P. Smith, W. E. Brown, and A. W. Frazier. 1957. "Crystalline Intermediates in the Hydrolytic Degradation of Calcium Polyphosphate," *Journal of Physical Chemistry,* 61(12):1669 - 1670.

20. Limousin, L., B. Neveu, and J. B. Peudpiece, P. Achard, and Y. Schwob. 1994. "A New Way to Produce Urea-Superphosphate Fertilizers: The AZF USP Process," pp. 172-186, Proceedings of IFA Technical Conference, Amman, Jordan.

21. Dalman, L. H. 1934. "Ternary Systems of Urea and Acids," JACS, 56:549-553.

22. Frazier, A. W., J. R. Lehr, and J. P. Smith. 1967. "Urea-Monocalcium Phosphate, a Component of Mixed Fertilizers," *J. Agr. Food Chem.,* 15(2):345-347.

Chapter 15. Potash Fertilizers

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Chapter 15. Potash Fertilizers

15.1 Introduction

The term "potash" generally refers to potassium chloride, but it is also loosely applied to other potassium compounds that may be differentiated by the words muriate of potash, sulfate of potash, etc. Also, when referring to ores, or in geology, all of the naturally occurring potassium salts are called "potash ores." This confusion began early since "potash" originally only referred to crude potassium carbonate, which was recovered by the leaching of near-seacoast wood ashes in large pots. The ashes of inland plants were generally higher in sodium carbonate, which gave rise to the Arabic word for soda ash, al kali. The term was then carried over after potassium was discovered to form the Latin word for it, "kalium." The recovery of potash from ashes became a thriving small cottage industry throughout the world's coastal areas, and people of developing economies, such as the early settlers in the United States, were able to generate much-needed income from its recovery and sale.

This industry was rapidly phased out with the advent of the LeBlanc process for producing soda ash in 1792, and the discovery about the same time of the massive sodium-potassium nitrate deposits in the Atacama Desert of Chile. During the 1800s many "officinas" were established throughout the deposit to produce crude potassium nitrate, which became the world's source of potash for industrial, agricultural, and most of all, gun powder needs. This remained the case until the large buried carnallite ($KCl \bullet MgCl_2 \bullet 6H_2O$) deposits were found by drilling in the Stassfurt, Germany, area. Afterward, buried deposits and brines became the world's dominant potash sources. With the rapidly expanding world population and subsequently more intensive farming, the need for potash has rapidly increased, and an ever-increasing number of potash deposits have been discovered and exploited, which gives rise to the very large industry that exists today. Potash has become one of the world's largest tonnage chemicals.

The size and economic attractiveness of the world's commercial potash operations vary considerably, and their pattern of development and continued production have often been only partially based upon true economic merit. This has led to considerable overcapacity in the industry, primarily because the industry is dominated by nationalistic considerations of jobs, foreign exchange, etc. A second distinguishing feature of the potash industry is that the generally poor economics and similarity of mining and processing do not allow for much R&D; therefore, cost reduction and efficiency changes have been comparatively infrequent. Finally, increasing maintenance costs and usually much higher mining costs are incurred as potash operations age and face dwindling reserves, declining ore grade, longer mining distances, and often thinner or deeper ore. The purpose of this chapter is to review the role of potash as a fertilizer and production in different chemical and physical commercial forms. The potash mineralogy, description of deposits, and the potash ore beneficiation are given in Chapter 5.

15.2 Potash in Agriculture

By far most of the world's potash production is used in agriculture [1]. Over 95%-97% of it is sold to improve the world's food, fiber, and other farm output. Potassium is one of the three major plant nutrients and as such must be added to all intensive farming soils as it becomes depleted. Some potassium-containing minerals such as clay, feldspar, and mica are found naturally in soils, and the potassium slowly becomes available with weathering. It then goes into solution or is in an ion exchangeable form, both of which are available to the plants. The potassium from fertilizers may also become ion exchanged with clays or organic matter (Table 15.1) near the surface and thus not be very mobile; therefore, the placement is important in many soils. Finally, the function of potassium in plant metabolism is different

Table 15.1. Cation Exchange Capacities of Clays and Organic Matter Found in Soils (Munson, 1980)

Material	Cation Exchange Capacity (meq/100 g)
Clay Mineral	
Vermiculite	150
Montmorillonite (Smectite)	100
Biotite	40
Muscovite	20
Kaolinite	5
Soil Organic Matter	50-250

from that of the other major nutrients. The other nutrients become part of the plant structure, but potassium largely remains as an ion in the cells and sap. The function of potassium is to help control the plant's water intake and metabolism. Potash is as vital to the plant as the other fertilizers and is removed from the soil in the same manner, even though its action in the plant is different. For these reasons fertilization with potash is somewhat more complex than with the other nutrients [2].

Some of the specific effects of potash are to increase root growth; improve drought resistance by reducing water loss, wilting, and respiration (maintaining "turgor"); and also lower the plant's energy losses. Potash helps form cellulose and reduce lodging, enhances many enzyme actions, aids in photosynthesis and food formation, helps in the translocation of sugars and starch, helps increase the starch and/or protein content of plants, and helps retard crop diseases. It is sometimes called the "quality" nutrient because of these many beneficial functions. To attain maximum effectiveness, primary nutrients must be supplied to crops in essentially the same proportions as they exist in most plant life, where the ratio of nitrogen to potassium is about 2:1. Thus, among the commercial fertilizers, about one-half as much potash is used as nitrogen, except when soil is capable of supplying potash. Thus, the ever-increasing use of nitrogen fertilizer necessitates the proportional application of potash.

15.3 Potash Production, Consumption, and Price

Table 15.2 lists the potash production from the major producing countries [3]. World production has declined with the economic transformation occurring in Central and Eastern Europe and the Commonwealth of Independent states (CIS) as a result of less consumption by those countries and production problems with Russia and East Germany. By 1994 the trend toward a higher percentage of total production from Canada and less from Russia and Germany had considerably increased. The consumption of potash, as indicated by Table 15.3, is dominated by Western Europe, Russia, Asia, and North America. Data on both imports and exports are listed in Table 15.4. The latter two areas represent the largest import markets; Europe and Russia are primarily supplied by their own production. The U.S. price of granular potash is shown in Figure 15.1, (f.o.b. Saskatchewan), and it was fairly stable until Canada and Russia entered the market with large plants. Since then the oversupply has made the price quite erratic, but at least it had risen by 1994 to a point where most of the operators could make a profit.

Projections for the short-term consumption (Table 15.5) are from a World Bank publication summarizing the joint FAO/UNIDO/World Bank Working Group results [4].

Table 15.2. Estimated World Potash Production in '000 t K_2O

Country	1986	1987	1988	1989	1990	1991	1992
Brazil	10	37	56	109	68	102	100
Canada	6,697	7,266	8,327	7,360	7,002	7,398	7,327
Chile	20	20	20	20	20	20	20
China	24	39	62	56	47	98	25
England	390	428	460	463	488	494	450
France	1,620	1,539	1,502	1,191	1,300	1,200	1,130
Germany	5,646	5,730	5,801	4,384	4,850	3,902	3,427
Israel	1,250	1,252	1,245	1,273	1,311	1,270	1,300
Italy	109	122	125	152	68	32	100
Jordan	661	722	766	742	686	585	600
Russia	10,220	10,888	11,300	10,233	9,037	8,562	7,300
Spain	702	739	766	742	686	585	600
United States	1,172	1,218	1,461	1,580	1,654	1,692	1,705
Total	**28,507**	**29,964**	**31,891**	**29,335**	**27,354**	**26,153**	**24,327**

Table 15.3. Consumption of Potash in % of the Total

Region	1973	1991
Western Europe	24.32	20.42
North America	21.9	21.62
Russia	16.28	20.73
Asia	9.78	24.24
Others	15.74	12.99

Projection of a given country's consumption can be made on the basis of projections of the nitrogen consumption. For a diversified crop mix one can expect that consumption of K_2O should be 50% of nitrogen consumption.

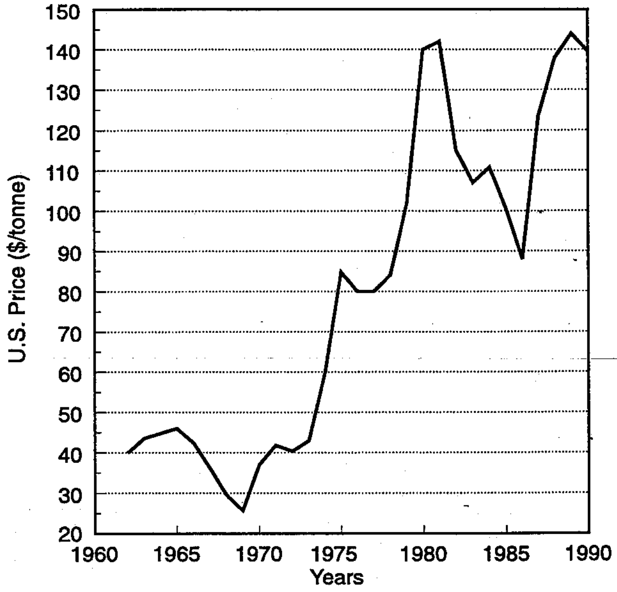


Figure 15.1. Granular Potash U.S. Prices.

Table 15.4. Trade in Potash Worldwide

	1991		1988		1984	
	Imports	Exports	Imports	Exports	Imports	Exports
	('000 t of K_2O/year)					
Canada	21	6,153	16	6,281	20	6,841
England	298	350	365	296	367	104
France	915	236	798	393	752	347
Germany, East	210	3,010	5	2,829	0	2,860
Germany, West			396	1,368	298	1,571
Italy	387	33	530	148	472	120
Russia	0	2,708	10	3,558	13	3,156
Spain	115	323	75	428	3	372
United States	3,663	647	4,160	466	4,933	552

	1978		1975		1972	
	Imports	Exports	Imports	Exports	Imports	Exports
	('000 t of K_2O/year)					
Canada	31	6,268	21	4,277	62	4,200
England	445	106	410	45	512	16
France	338	323	401	662	479	695
Germany, East	0	2,734	0	2,252	0	1,820
Germany, West	267	1,583	129	918	57	1,304
Italy	348	109	197	46	210	29
Russia	0	2,401	0	2,493	0	1,706
Spain	3	332	7	143	3	230
United States	4,703	774	3,584	823	4,891	482

Table 15.5. Short-Term Potash Consumption Projections

	1991/92			1994/95			1997/98		
Region	S	C	B	S	C	B	S	C	B
	--- (million tonnes K_2O)---			--- (million tonnes K_2O)---			--- (million tonnes K_2O)---		
World	27.8	23.5	+4.3	26.9	21.3	+5.6	27.3	23.4	+3.9
Africa	0	0.5	−0.5	0	0.6	−0.6	0	0.6	−0.6
America	11.2	6.7	+4.5	11.2	6.8	+4.3	11.5	7.2	+4.3
Asia	2.1	5.8	−3.7	2.2	5.6	−3.4	2.3	6.4	−4.1
Europe	5.3	1.8	+3.5	6.2	4.8	+1.4	5.7	4.9	+0.8
CIS	7.4	5.0	+2.4	7.2	3.1	+4.1	7.7	4.0	+3.7
Oceania	0	0.3	−0.3	0	0.3	−0.3	0	0.3	−0.3

S – supply potential.
C – consumption.
B – balance.

15.4 Product Quality

15.4.1 Nongranular Materials

During much of the history of potash production from the 19th century to the early 1950s, particle size was of little consequence. The material called "standard" had an average size of 0.8 mm. In the 1960s when bulk blending was increasing in the United States, producers developed "coarse" material with a typical size range of 0.8-2.0 mm. Introduction of granular fertilizers for bulk blending required an increase in the size of potash particles. The "coarse" material was hardly compatible with other fertilizers. The adequacy of the sizes is shown in Figure 15.2.

Obviously the quality and size of particles depend on the flotation and purification methods. Crystallization is the dominant method in Germany because of the quality of the raw material. Recent crystallization technology allows production of rounded grains of about 1-mm size, which is suitable for compaction.

Most potash is sold without detailed "quality" specifications as to either purity or particle size. Potassium chloride is guaranteed to have at least 60% K_2O (and potassium sulfate 50% K_2O), but this is only a 95%-96% purity. The impurity is primarily assumed to be NaCl, but there are no specifications for it. With the technical (industrial) grades, however, the specifications for various uses can be very demanding; for example, limits on heavy metals in KCl that is sold to KOH producers, KCl in low-sodium food use, etc.

Table 15.6 [13] lists general K_2O limits and typical U.S. customer expectations on particle size ranges for the most common fertilizer grades. Obviously, there is

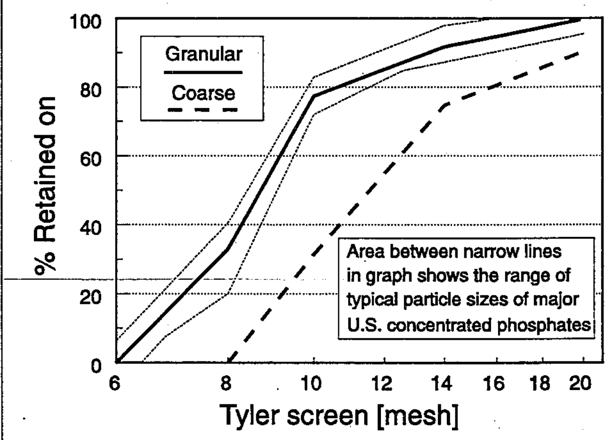


Figure 15.2. Comparison of Sizes of Fertilizer Granular Material With "Coarse" and Granular Potash.

Table 15.6. Nominal U.S. Potash Specifications (Searls 1991)

Name	Nominal Particle, Mesh	Size Range, mm	% K_2O
Blend	6-14	1.19-3.36	60
Granular	6-20	0.841-3.36	60
Coarse	8-28	0.595-2.38	60
Standard	14-65	0.210-1.19	60
Special standard	35-150	0.105-0.420	60
Soluble/suspension	35-150	0.105-0.420	62
Chemical	–	–	63

still an unusually large overlap in the particle sizes of the various grades, which is a carryover from the days when run-of-the-plant K_2O content (i.e., in Germany it was commonly 50%) and screen size (such as 16-150 mesh) were all that was available. This will probably change in time because of the competitive advantages of purer and more closely sized potash grades and the comparative ease in obtaining them.

An undesirable aspect of product quality is that potash tends to cake, and there is also some unavoidable crystal breakage with shipping and handling, which generally results in a dust problem. An interesting effect from the strong adsorption of amine groups to potash is the fact that the flotation reagents used are also effective anticaking agents. However, to enhance the effect most companies include amounts of amines in the different grades of product before shipment and an oil to help reduce dust problems (Table 15.7) [5]. For those special grades in which such impurities are not allowed, a more closely sized and drier product is shipped.

15.4.2 Granular Potash Materials

Compaction/granulation is now an important stage in the overall potassium chloride production/beneficiation process. Compaction implies the agglomeration of particles under force to produce a densified and coherent sheetlike material referred to as flake. In this case, granulation refers to the dry milling of flake into a prescribed size distribution employing a screening step. Compaction/granulation of potash began in the 1950s as an economic alternative to the thermal processes (sintering, melting). Currently, about 40% of the total world capacity of potash production is compacted; this amounts to about 5% of total world capacity of granular fertilizers.

The general flowsheet of potash compaction/granulation is shown in Figure 15.3 [6]. The system is composed of four groups of equipment for the following process steps [7], [8]:

- Storage and feeding.
- Compaction.
- Size reduction and classification.
- Finishing.

Storage and Feeding – The section usually includes:

- Material storage hopper allowing the undersize material from the granulation section to be recycled.
- Feeding hopper system, possibly with magnet and rough screening system.
- Control feeding system.

Compaction – The section usually includes:

- Feeder.
- Compacting rolls.
- Flake breaker.

There are two types of feeders: gravity and force-type feeders.

A gravity system is composed of a slightly diverging chute located above the rolls and an adjustable vertical feed control tongue to keep the level constant.

The force feeders are equipped with single or multiple screws. These screws may be positioned vertically, at an angle, or horizontally. Tapered screws deaerate and

Table 15.7. Anticaking Additives

Anticaking Reagent	Armeen C	75% Armeen C in Glycol[a]	Armeen HT Flake	Amine in Oil
Quantity	g/t	g/t	g/t	g/t
Granular product	108	225	100	73[c]
Coarse product	108	225	100	73[c]
Standard	108	320	100	140[d]
Special standard	108	320	100	140[d]
Soluble	227[b]	400	100	–
Antidusting reagent	oil	oil	No. 2 fuel oil	oil
Quantity, g/t	–	1.2	1.3	0.45-1.0

a. Plus 10% HCl for soluble product.
b. Plus 900 g/t glycol.
c. 8% amine in oil.
d. 25% amine in oil.

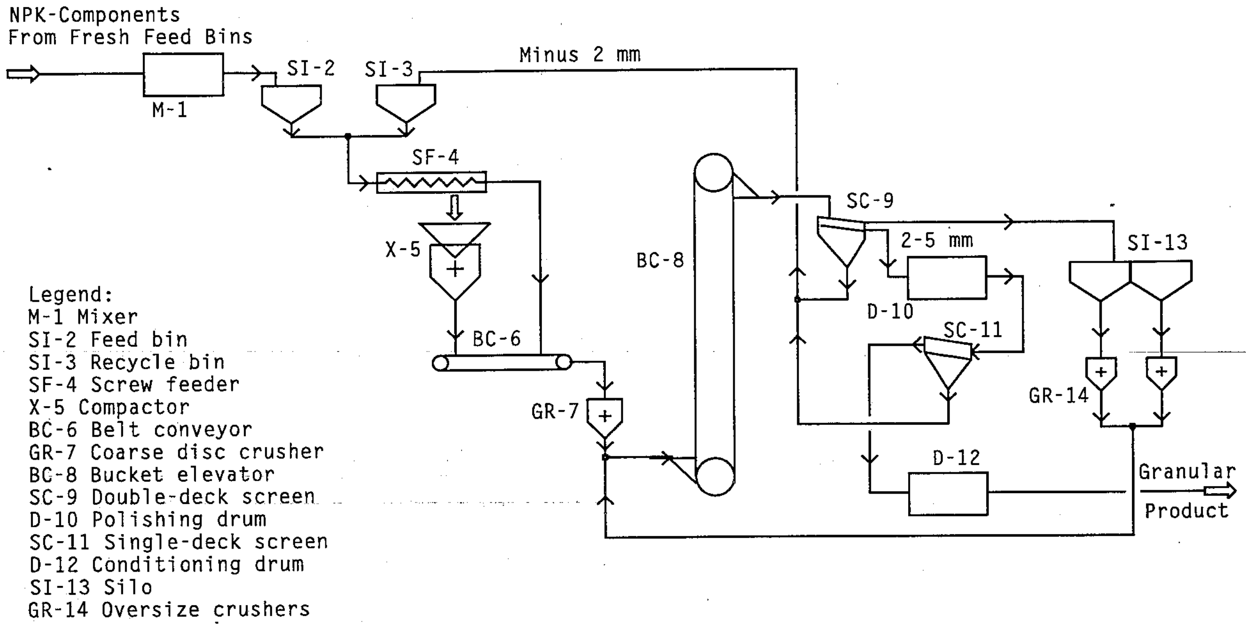


Figure 15.3. General Flowsheet for Potash Compaction/Granulation Plant.

predensify the feed to the compactor. Force feeders facilitate automation of the process by regulating of the speed of the screw. Both gravity and force feeders are deaerated through ports connected to the dust system.

The amount of the air removed depends on the size of material and compression ratio. In case of compacting potash from specific gravity of 1 g/cm^3 to 2 g/cm^3, the amount of air is about 0.5 Nm^3/t of product.

The compactors are two counterrotating rolls. One roller is located in a set of fixed bearings; the other is a floating-bearing unit. The feed passed between the two rollers is progressively transformed from a loose to a dense state. The rolls can be smooth or corrugated, waffled, or have pocketed surfaces. The chevroned surfaces increase flake production and allow the nip angles to be increased. The nip angle also establishes the compression ratio. Compression ratios range between 1.5 and 3. Table 15.8 gives ranges of compaction parameters [8].

The selection of equipment depends on the material and its properties [6], including particle shape, size, size distribution, and compaction force needed. For compaction the general rule is that the larger particles should be accompanied by fines to fill in the larger pores or open space. The van der Waals attraction forces are often not sufficient to produce flake with adequate strength. Sometimes binders are added, or creation of crystalline bridges is used.

The temperature of potash feed determines its plasticity. In comparison with colder feed the warmer feed may require less pressure to obtain product with a given strength and density, or, at the same energy input, produce material with greater strength and density. Elevated temperatures are beneficial for the formation of crystal bridges.

In general compaction is defined as a dry agglomeration process. Sometimes the addition of water may be beneficial; however, it is rare to observe compaction of material with a water content of more than 2%. The compaction of KCl is accomplished essentially in a dry

Table 15.8 Variations in Compaction Parameters

Parameters	Units	Maximum	Minimum
Roller diameter	m	1.2	0.6
Roller width	m	0.8	0.2
Compaction pressure	kN/cm	120	30
Roller speed	rpm	22	10
Flake thickness	mm	25	2
Capacity	tph	100	10
Drive power	kW	750	55
Recycle ratio	1	3.5	2.5
Flake density	g/cm^3	2.5	0.8

state. Table 15.9 gives the compaction parameters for potassium salts [9].

The product from the compaction process is the flake. The thickness of the potash flake varies from plant to plant but on average is about 20 mm. After compaction the flake is cured in the conveying system. For potash the normal design of the plant provides about 3 minutes of curing time. The flake is broken into smaller pieces immediately below the roller. Pin-type breakers and coarse tooth roll crushers are used to break the flakes.

Table 15.9. Compaction of the Potassium Salts

Product	Temperature (°C)	Pressing Force (kN/cm)	Moisture Particle (%)	Feed (mm)
Potassium chloride, 60% K_2O	120-140	50	dry	<1
	90	60	dry	<1
	20	70	dry	<1
Potassium sulfate	70-100	70	1	<0.5
Potassium nitrate	20	100	0.5-1.0	<1

Granulation – The granulation section is essentially composed of crushing and screening equipment. Potash granulation mainly consists of primary and secondary crushers in closed circuit with a multi-deck screening system. Two-stage milling decreases the recycle ratio. The primary crusher grinds large materials from the compactor, and the secondary crusher is fed with oversize from the screen. Hammer mills, cage mills, or chain mills are used as the primary crushers. Roll crushers with toothed rolls are often used as secondary crushers.

The roll crusher parameters are important, in particular the rotational speed, size, and shape of the crusher teeth. Usually the mills are fitted with variable speed drives. The discharge from the compression (roll) crusher is controlled by the gap setting. Evaluation of circuits using roll crushers indicates higher yields than from those equipped with impact crushers.

Finishing Section – This section includes:

- Polishing unit.
- Coating unit.
- Final product storage.

The particles after granulation have sharp edges and are of irregular shape. To diminish the crushing of the material during further handling and dust creation the potash particles are quenched, dried, and passed through the polishing screen. Quenching consists of wetting particles with water or brine by direct spraying on the conveyer or mixing in screw conveyers (maximum 5% but usually about 1%). During the quenching stage the sharper corners of the particle break off and a shell of dissolved salt envelops the particles. After wetting the product is dried in a rotary drum or fluid bed dryer at a temperature as high as 200°C. Dry product is passed over a polishing screen to remove the fines.

In the final steps the product is cooled and coated in a rotary drum with anticaking agents (amines and oils). Amines depress the caking tendency of potash during transportation, and oils prevent the formation of dust clouds at the handling points.

Dust Collection System – Major dust sources are the hopper in which the payloader dumps the raw material, the crushers, the transfer points, the mixer, and the screens. The amount of air needed in the dust collection system depends on the number and types of collection points. The system consists of a fan, cyclones, and filter bags connected by air ducts.

The velocity of the air in the ducts must be kept high, a minimum of about 1,000 m/min. The fan is sized on the basis of the volume of air required and the pressure drop through the system. The fan is installed on the clean air side of the cyclone or filter bags.

Process Requirements – Process unit requirements for a large potash compaction plant are given in Table 15.10.

Table 15.10. Process Requirements of the TIMAC Compaction/Granulation Plant, Saint-Malo, France [8]

Parameters	Units	Value
Product:		
Granular potash	1	0-0-60
Capacity	tpd	1,250
Annual operation time	h	7,200
Investment cost (battery limits)	US $ million	4.8

Cost Components	Units	Unit/t
Raw materials		
Potash (60% K_2O)	kg	1,001
Energy		
Electrical energy	kWh	35
Process water	kg	10
Fuel	GJ	0.06

15.5 Other Potassium Fertilizers

15.5.1 Potassium Sulfate

Potassium sulfate is the second largest tonnage potassium compound, and it is also used primarily as a fertilizer. The sulfate or other nonchloride forms of potassium are preferred for certain crops that do not tolerate the chloride ion well, e.g., tobacco and some fruits and vegetables. Nonchloride potash sources are also needed in areas where chloride accumulation in the soil is a problem. This is important in arid areas where chloride salts from irrigation water accumulate or in areas of very intensive agriculture, e.g., in the Netherlands. Potassium sulfate may be preferred because of its sulfur content where soils are deficient in both potassium and sulfur.

15.5.2 Potassium Sulfate Production

15.5.2.1 Mannheim Process – Historically potassium sulfate has been made primarily from KCl and sulfuric acid (and a small amount from KCl and SO_2) when the byproduct HCl was the dominant product. However, over the years the HCl market has had more competition, and "natural" K_2SO_4 with lower capital and operating costs has begun to dominate its production in some countries with natural complex salts.

The Mannheim process was originally developed from sodium sulfate production by reacting NaCl with sulfuric acid. Replacing NaCl with KCl produces potassium sulfate. The reaction is two-stage:

a. Exothermic reaction

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$

b. Endothermic reaction

$$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$$

The potassium chloride reacts during slow mixing in the heated Mannheim furnace with sulfuric acid, producing gaseous HCl and K_2SO_4. The furnace is heated by natural gas or fuel oil. The product K_2SO_4 is cooled in a cooling drum. Lump material from the cooler is crushed and finished or can be compacted and granulated as with KCl. Although the price of agricultural grade potassium sulfate is twice as high as potassium muriate, granulation would add about 18 US $18/tonne to the processing costs. However, considering the difference of 25% between prices of coarse and granulated material, the process seems to be feasible.

The HCl gas is cooled in a graphite heat exchanger and absorbed in water in two stages to produce 33% hydrochloric acid as a byproduct. The process gives an excellent quality that contains over 50% K_2O and less than 1% chlorine. Emissions are well controlled and the process is computerized. The process as operated by Kemira Oy [10] is shown in Figure 15.4. Process requirements for the Kemira Oy plant are given in Table 15.11.

15.5.2.2 Recovery of Potassium Sulfate From Natural Complex Salts – The chief natural complex salts that are the source of the potassium sulfate are:

- Kainite ($KCl \bullet MgSO_4 \bullet 3H_2O$)
- Langbeinite ($K_2SO_4 \bullet 2MgSO_4$)
- Carpathian polymineral ores

The natural process [11] involves the initial conversion with recycled K_2SO_4 end liquor of "mined" kainite (from the solar evaporation of Great Salt Lake brines, or deposits in Sicily, and Carpathia), or langbeinite (from Carlsbad) to form an intermediate product, schoenite (or leonite if done hot). All processes are based on intercrystalline reactions of ion exchange.

The basic reactions leading to potassium sulfate from kainite by transformation of the kainite into schoenite and later water leaching are:

$$2KCl \bullet MgSO_4 \bullet 3H_2O \rightarrow K_2SO_4 \bullet MgSO_4 \bullet 6H_2O + MgCl_2$$

$$K_2SO_4 \bullet MgSO_4 \bullet 6H_2O \rightarrow K_2SO_4 + MgSO_4 + 6H_2O$$

The Italkali's Pasquasia potassium sulfate process based on the latter alternative in Figure 15.5 [12] The process comprises four basic units:

- Preparation of the ore and flotation;
- Production of schoenite and its recovery;
- Leaching of the schoenite to potassium sulfate;
- Liquor treatment.

The kainite is repulped with recycled brine, screened, and directed to ball mills and hydroclassifiers. Overflows go to a thickener and main filter and underflows to flotation and filtration. Float material, after filtration, is combined with the solid fraction from the main filter and directed to the schoenite reactors and separating cyclones. After a two-step hydroseparation, centrifugation, and filtration, schoenite is directed to the leaching reactors. After decomposition of the schoenite, product is directed to a thickener. The underflow solids are sent directly to final centrifuges and a dryer; the overflows are cooled and crystallized. After additional thickening, the product is centrifuged and dried. The product specification ensures that the K_2O content is not lower than 50% and the chlorine content is less than 1%.

In the recovery unit, Italkali forms syngenite [$K_2Ca(SO_4)_2 \bullet H_2O$] to moderately increase the recovery

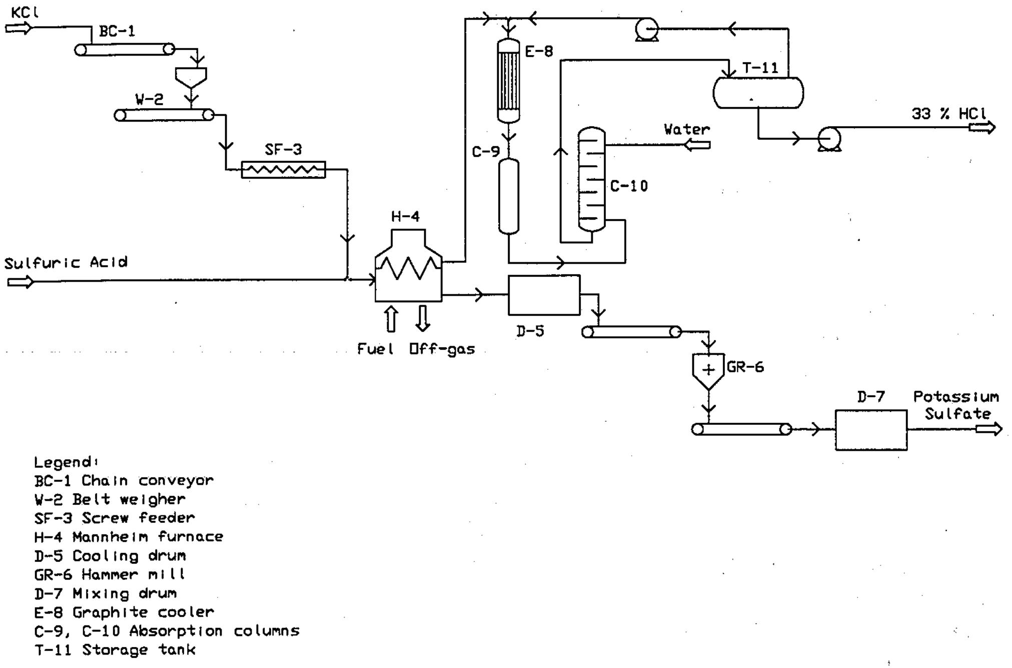


Figure 15.4. Kemira Oy Potassium Sulfate Process [10].

Table 15.11. Process Requirements of the Kemira Oy Potassium Sulfate Plant [10]

Parameters	Units	Value
Product:		
Potassium sulfate	1	0-0-50
Capacity per unit	tpd	30
Annual operation time	h	7,900
Investment cost (battery limits) per line	US $ million	1.5

Cost Components	Units	Unit/t
Raw materials		
Potash (60% K_2O)	kg	850
Energy		
Electrical energy	kWh	45
Cooling water	m^3	60
Process water	kg	77
Fuel	GJ	4.1

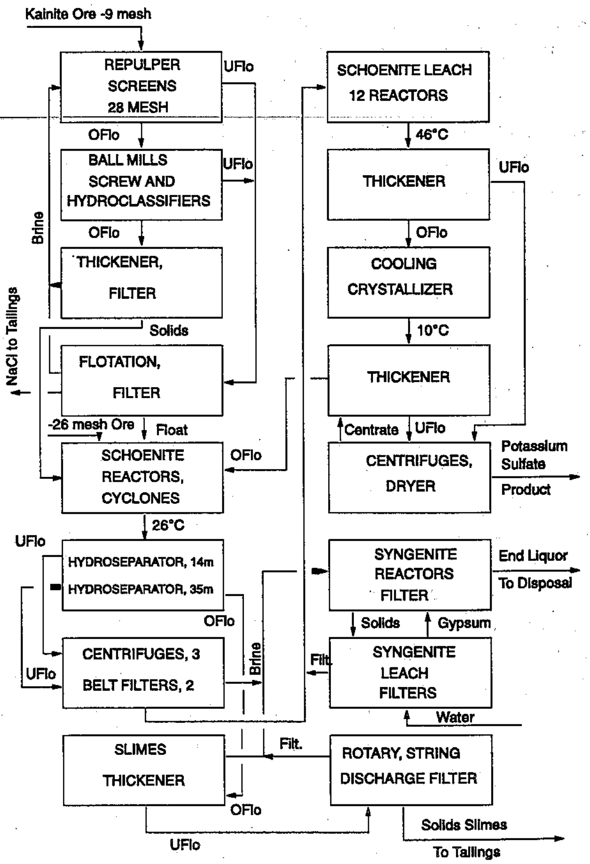


Figure 15.5. Potassium Sulfate Recovery From Kainite.

of schoenite from the plant's end liquor. The brine from the schoenite filter is reacted with recycling gypsum. The schoenite formed is combined with main flow to the leaching reactors.

Other processes involve adding sylvite to kainite, langbeinite, kieserite, etc. The schoenite intermediate can be formed by reacting KCl with mined kieserite ($MgSO_4 \bullet H_2O$) or with epsomite. A similar intermediate, glaserite, is formed from the reaction of KCl with salt cake or glauber salt, $Na_2(SO_4) \bullet 10H_2O$ (Searles Lake, Spain, Canada). Either double salt can be transformed into pure K_2SO_4 by a partial leach or in greater yield by reacting it with additional KCl. Where solar or plant evaporation can be done economically, the yields can be further improved by evaporating the schoenite or glaserite end liquor and recycling the salts.

The reactions are as follows:

a. by mixing kainite and sylvite

$$KCl + KCl \bullet MgSO_4 \bullet 3H_2O \rightarrow K_2SO_4 + MgCl_2 + 3H_2O$$

b. by mixing sylvite with kieserite and other magnesium salts to give kainite

$$KCl + MgSO_4 \bullet H_2O + 2H_2O \rightarrow KCl \bullet MgSO_4 \bullet 3H_2O$$

A complex process for production of potassium sulfate from potash ores has been implemented on an industrial scale in Russia in the Kalush plant [14]. The natural ores are composed of calcium sulfate anhydrite, epsomite, halite, kainite, kieserite, langbeinite, polyhalite, sylvite, and clay. The treatment of such an ore requires permanent analytical services and the development of a large number of formulations for different compositions of the raw material and for the kind of salts intended to be produced. Additional sylvite must be added in varying amounts to maintain the right proportions for crystal formation. The basic process concept is to produce schoenite from all available salts. The remaining products or processes are subjugated to this basic process. The process is shown in the flowsheet, Figure 15.6.

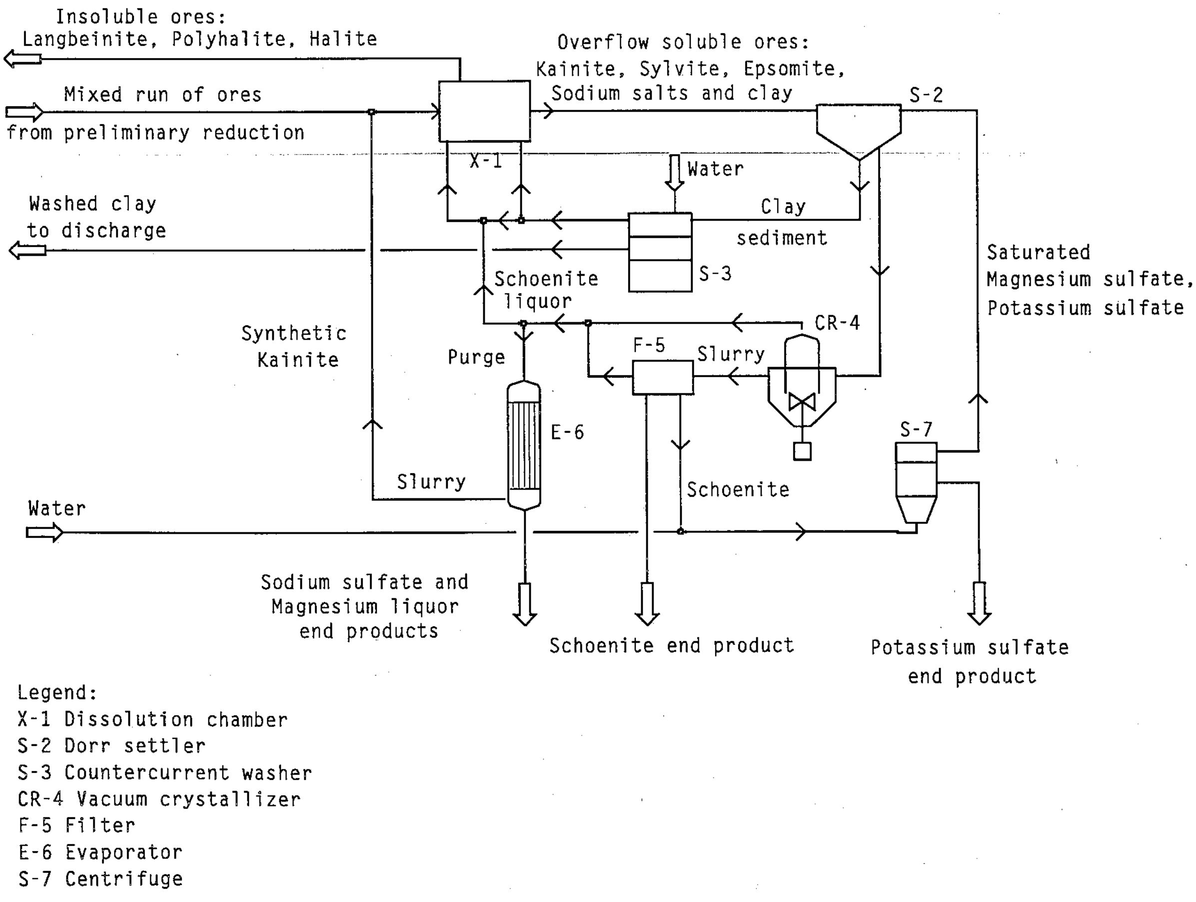


Figure 15.6. Flowsheet of Carpathian Ore Treatment [14].

The Carpathian ore contains about 9% potassium and 15% clay. The ore is leached with hot "synthetic kainite" solution in a dissolution chamber. The langbeinite, polyhalite, and halite remain undissolved and are discarded. The overflow from the dissolution chamber containing salts and clay is directed to a Dorr-Oliver settler where clay is settled and directed to a washer and discarded. The solution is crystallized at the proper cation and anion proportions to produce crystalline schoenite. To avoid crystallization of potassium chloride and sodium chloride, the saturated solution of potassium and magnesium sulfates is added to the Dorr-Oliver settler. The slurry of schoenite is filtered, and crystals are leached with water to produce K_2SO_4 crystals, which are centrifuged and recycled, and a liquor of potassium and magnesium sulfates. Also, liquid phase from filter is recycled and added to the schoenite liquor from vacuum crystallization. Part of the schoenite liquor is evaporated to produce crystalline sodium sulfate and discard the magnesium chloride liquid end products. The slurry from the evaporation unit is recycled as "synthetic kainite." This process permits the use of the Carpathian ores to produce several commercially valuable products such as potassium sulfate, potassium-magnesium sulfate, potassium chloride, sodium sulfate, and magnesium chloride liquors. Neither the economic evaluation of the process nor any of the consumption figures have been published.

The production of potassium sulfate from langbeinite is possible with a large amount of muriate of potash by mixing langbeinite and sylvite:

$$4KCl + K_2SO_4{\bullet}2MgSO_4 \rightarrow 3K_2SO_4 + 2MgCl_2$$

$$2KCl + 2(K_2SO_4{\bullet}2MgSO_4) \rightarrow 3(K_2SO_4{\bullet}MgSO_4) + MgCl_2$$

The Bureau of Mines (U.S.A.) developed the process [13]. The principles of the process are given in the block flowsheet shown in Figure 15.7.

The langbeinite ore is separated from sylvite and halite by selective washing, froth flotation, or heavy media separation. The commercial langbeinite used in the process must be pulverized in ball mills, and fine powder is mixed with a solution of the muriate of potash. The muriate of potash is dissolved and clarified in a separate unit. The reaction in the presence of water yields potassium sulfate in a crystalline form and brine. Crystals are centrifuged or filtered, dried in a rotary dryer, sized, and finished. The finishing methods either produce coarse material or granulated product. The brine is evaporated, crystallized, and filtered. The mixed salts are added to the sulfate reactor. The liquor is discarded as a waste.

Raw material consumption at 80% conversion per tonne of potassium sulfate is given in Table 15.12. Consumption of utilities and capital costs has not been published.

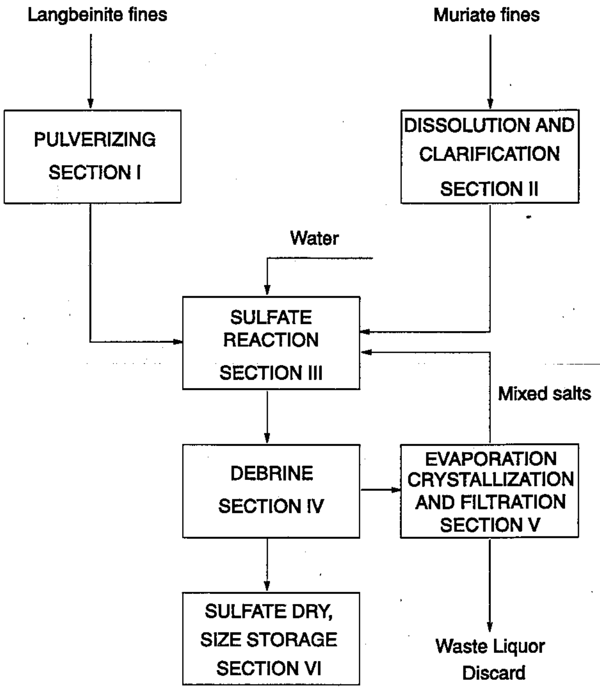


Figure 15.7. Potassium Sulfate Process From Langbeinite.

Table 15.12. Raw Materials Required for the Bureau of Mines Process

Raw Material	Units	Theoretical Consumption	Estimated Consumption
Langbeinite (96%)	kg/t	0.788	1.056
Sylvite (60% K_2O)	kg/t	0.568	0.780

15.5.3 Potassium Nitrate

The third most widely used potassium salt in agriculture is potassium nitrate. An ore containing sodium nitrate, potassium nitrate, some chlorides, and sulfates is mined in Chile; KNO_3 is produced by the process shown in Figure 15.8 [15]. The ore is leached and part of the sodium nitrate is crystallized and removed. Potassium chloride is added to the brine, and the resulting sodium chloride is separated. Cooling to 5°C crystallizes the potassium nitrate, which is then recovered with centrifuges. Residual brine is concentrated by solar evaporation to remove salt and sodium sulfate, more KCl is added, and KNO_3 is again crystallized. KCl or K_2SO_4 may also be used in fractional crystallization processes with NH_4NO_3 or $Ca(NO_3)_2$ to produce potassium nitrate.

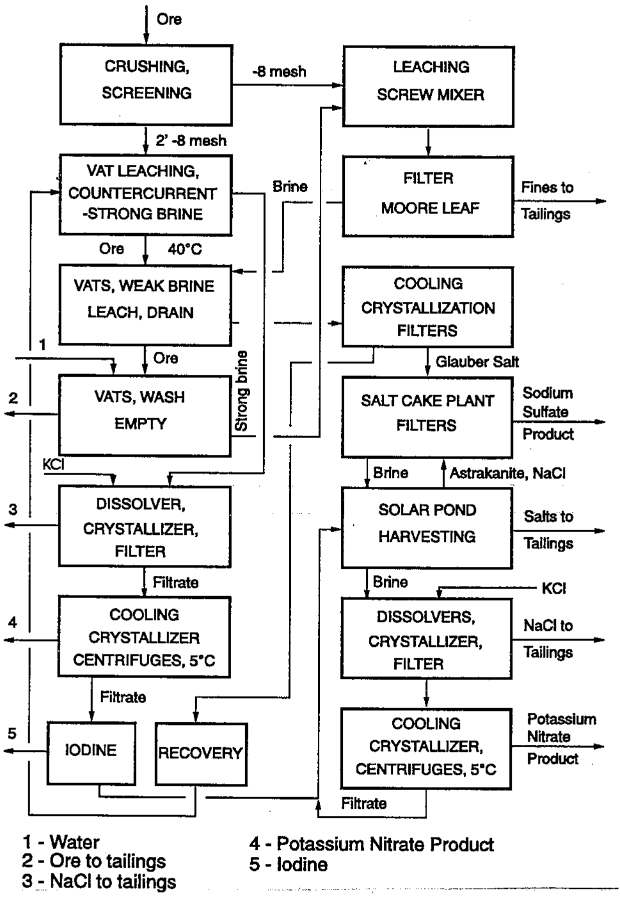


Figure 15.8. Recovery of Potassium Nitrate From Natural Salts Deposits.

Potassium nitrate is made synthetically in Israel by Israel Mining Industries (IMI) by low temperature reaction of potash with nitric acid with solvent extraction of the coproduct hydrochloric acid [16]. The HCl is re-extracted from the solvent with water and then distilled as about a 20% HCl solution. The solvent is recycled to the first extraction stage (Figure 15.9).

Nitric acid reacts with potassium chloride at low temperature according to the equation:

$$KCl + HNO_3 \rightarrow KNO_3 + HCl$$

Potassium chloride and a stoichiometric quantity of chilled 60%-70% nitric acid are fed into the first reactor at 5°-10°C. Recycled brine and solvent are added to the reactor. In the presence of the solvent, the reaction goes almost to completion. During the process potassium nitrate crystallizes from solution. Solid product is separated in a decanter and directed to a centrifuge and dryer. It can be sold in the powder form or melted and prilled.

The hydrochloric acid and the unreacted nitric acid are dissolved in the liquid phase. Obviously both nitric acid and hydrochloric acid are soluble in the solvent, but distribution coefficients differ sufficiently for the hydrochloric acid to be removed in a countercurrent liquid extraction system by water. The extraction is carried out in the mixer-settler extraction system vessels. The remaining nitric acid and solvent are recycled through a refrigeration unit to the first reactor. The water is stripped from the solvent, which is also recycled. The low concentration hydrochloric acid is evaporated in a multiple effect evaporator to a concentration of 22%. This acid is used in another plant to produce phosphoric acid by a hydrochloric acid attack. The latter process is described in Chapter 11.

The raw materials consumption figures, utilities, and investment costs have not been published.

In another process [17], [18] the same reactants are used, except at a higher temperature to take advantage of the oxidizing power of nitric acid. In a complex process with exotic corrosion-resistant equipment, chlorine is produced as a byproduct with the potassium nitrate. The process flowsheet is given in Figure 15.10.

Potassium chloride is slurried with 65% nitric acid, which has been previously chilled to prevent a reaction occurring before the slurry is fed into the reactor. In the reactor, which operates at about 0.18 MPa, the slurry is heated with nitric acid vapor to about 75°C, whereupon the reaction takes place, according to the following equation:

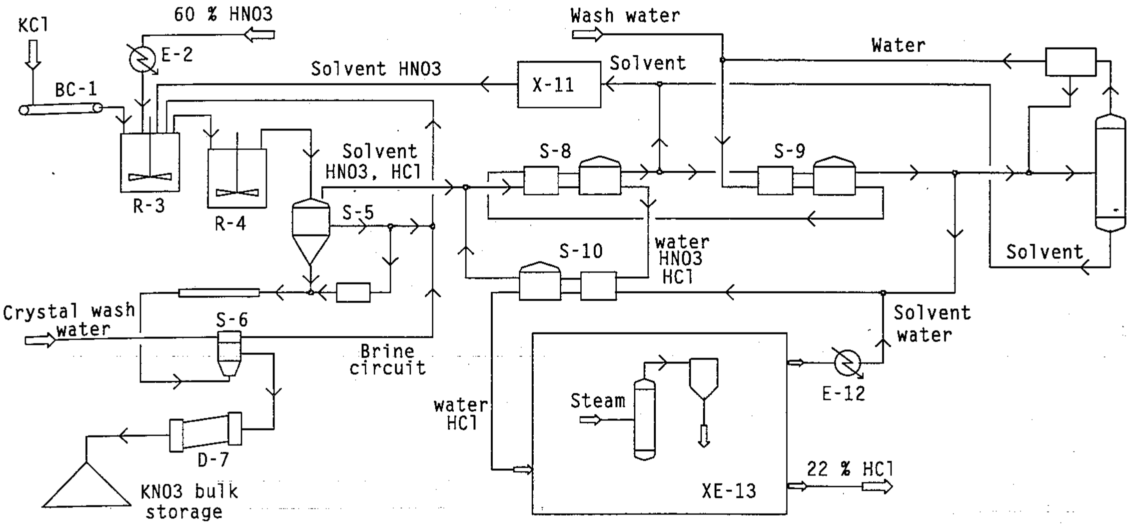
$$3KCl + 4HNO_3 \rightarrow 3KNO_3 + Cl_2 + NOCl + 2H_2O$$

Approximately 90% of the chlorine is removed in gaseous form. Because of the extreme corrosiveness prevailing in the reactor, this vessel, which is in fact an agitated autoclave, has to be fabricated from titanium and lined with acid-resistant brick.

The solution from the reactor flows to the chloride-stripping column where it is heated with more nitric acid vapor to its boiling point of about 150°C. This treatment takes the reaction to completion and gives rise to a stripped solution containing less than 10 ppmw of chlorine. If this degree of completion is to be obtained, it is necessary to maintain an excess of nitric acid corresponding to a concentration of 55% in the solution.

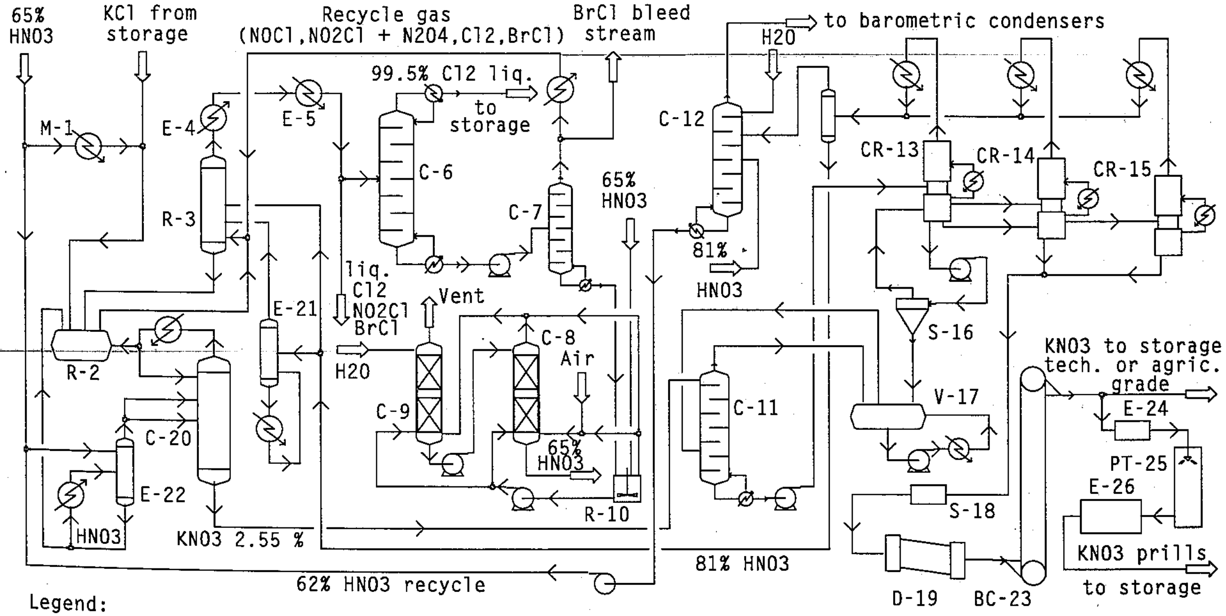
The gaseous mixture, containing nitrosyl chloride and chlorine from the agitated reactor, is oxidized in the gas reactor by using hot nitric acid at a concentration of at least 80% at 150°C. The reaction that occurs yields nitrogen dioxide and more chlorine as follows:

$$NOCl + 2HNO_3 \rightarrow 1/2\ Cl_2 + 3NO_2 + H_2O$$



Legend:
BC-1 Belt conveyor
E-2 Chiller
R-3, R-4 Conversion reactors
S-5 Decanter
S-6 Centrifuge
D-7 Dryer
S-8 Extraction mixer-settlers
S-9 Washing mixer-settlers
S-10 Stripping mixer-settlers
X-11 Refrigeration unit
E-12 Cooler
XE-13 Multiple-effect evaporator

Figure 15.9. IMI Potassium Nitrate Production Process.



Legend:
M-1 Mixer
R-2 Agitated primary reactor
R-3 Gas reactor
E-4 Reflux condenser
E-5 Total condenser
C-6 1-st Fractionating column
C-7 2-nd Fractionating column
C-8, C-9 HNO3 Absorption towers
R-10 Agitated reaction tank
C-11 Acid distillation column I
C-12 Acid distillation column II
CR-13 - CR-15 Vacuum crystallizers
S-16 Cyclone thickener
V-17 Saturator
S-18 KNO3 Centrifuge
D-19 Direct-fired dryer
C-20 Chloride stripping column
E-21 HNO3 vaporizer
E-22 HNO3 Melter & vaporizer
BC-23 Bucket elevator
E-24 Melter
PT-25 Prilling tower
E-26 Rotary cooler

Figure 15.10. High Temperature Potassium Nitrate Process.

Water formed in the oxidation is condensed and fed to the primary reactor. The chlorine and nitrogen dioxide are separated into liquid products; the chlorine is fed to storage while the nitrogen dioxide is oxidized with air and absorbed in water to produce 65% nitric acid. This oxidation step is characterized by the following chemical equation:

$$2NO_2 + H_2O + 1/2O_2 \rightarrow 2HNO_3$$

The overall reaction through the process is given by:

$$2KCl + 2HNO_3 + 1/2O_2 \rightarrow 2KNO_3 + Cl_2 + H_2O$$

In the gas section of the process, two distillation columns are used to separate the pure chlorine from pure nitrogen dioxide. Chlorine is removed from the top of the first column and nitrogen dioxide from the bottom of the second column while in the wet section the potassium nitrate-nitric acid solution is concentrated in the acid distillation column. It has been practical to concentrate the solution up to 81% nitric acid; the weak acid vapors in the overhead fraction are subsequently concentrated to about 62% HNO_3 in a second distillation column. Bottoms from the first acid distillation column are fed to a battery of vacuum crystallizers where potassium nitrate is precipitated and separated by a centrifuge. The product is dried and may be stored directly or melted and prilled at 340°-350°C in a 35-ft (10.7-m) tower. Either technical grade (99.3%) or agricultural grade (99%) potassium nitrate may be produced.

15.5.4 Compound Fertilizers

Potash is often applied in mixtures with other nutrients to provide the specific fertilizers needed by crops or soil and to allow placement in one application. To meet this need most fertilizer dealers have modest blending equipment, but to prevent segregation the fertilizers must be in the granular or coarse form. Some fertilizer manufacturers make certain blends such as the German combination of potash with kieserite when both are produced at the same mine. In the United States two operators also sell naturally occurring langbeinite as a similar mixture. The langbeinite ore is separated from its companion salts by either dissolving the others (with only a 10%-15% langbeinite loss) or by heavy media separation of the langbeinite.

15.6 Chemical-Grade Potash

About 4%-5% of potash production is used in industrial applications. The industrial potash (chemical grade) has a different purity from fertilizer-grade potash. The composition of chemical-grade potash is given in Table 15.13 [5].

Table 15.13. Chemical Grade Potash Analysis

Component	Unit	Standard Content
KCl	%	>99.90
K_2O	%	>63.12
H_2O (at 105°C)	%	<0.07
H_2O (at 700°C)	%	<0.67
Water insolubles	ppmw	<75
Acid insolubles	ppmw	<75
Sodium	ppmw	<150
Bromine	ppmw	<700
Sulfate (SO_4)	ppmw	<10
Calcium	ppmw	<10
Calcium and magnesium	ppmw	<30
Iron	ppmw	<5
Lead	ppmw	<3
Copper	ppmw	<0.5
Nickel	ppmw	<0.5
Chromium	ppmw	<0.1
Molybdenum	ppmw	<0.1
Vanadium	ppmw	<0.1
Titanium	ppmw	nil

Product is shipped in bags or in bulk form in modified hopper cars called spargers (in slurry form) or solution cars (in liquid form).

Chemical-grade potash has the following consumption pattern:

Detergents and soaps	35%-30%
Glass and ceramics	25%-28%
Textiles and dyes	20%-22%
Chemicals and drugs	13%-15%
Other	7%-5%

Most of the chemical-grade potash is used for production of potassium hydroxide. Potassium hydroxide (KOH) and its derivative potassium carbonate are the next largest industrial potassium compounds. The KOH is made by the electrolysis of KCl in installations similar to caustic soda/chlorine production. The main use of caustic potash is in the manufacture of liquid soaps; textile operations; production of grease, catalysts, alkaline batteries, electropolishing, and rubber production.

Several other potassium compounds have a limited use in agriculture but much wider use in industrial or commercial applications. Potassium phosphate, for instance, is used in some high-analysis, low-salt content fertilizer mixtures. It is not yet a large tonnage fertilizer, but several companies over the years have announced plans to produce it for that purpose. Potash is reacted with sulfuric acid, and the HCl is removed at the $KHSO_4$ stage. This salt is then reacted with more H_2SO_4 and phosphate rock $[Ca_3(PO_4)_2]$ usually to produce the more easily crystallized monopotassium phosphate (KH_2PO_4). However, the yields are low because of K losses with many of the impurities in the rock, and the process is corrosive and complex. By far the widest use of potassium phosphates has been as an additive to heavy-duty detergents, predominantly as low molecular weight polymers created by fusing various KOH and H_3PO_4 mixtures.

Potassium carbonate is used primarily in the glass manufacture, e.g., of televisions and similar display tubes. Potassium carbonate solution (0-0-30 grade) is marketed in the United States as a specialty liquid fertilizer. Potassium carbonate is produced by carbonating KOH with CO_2. Some potassium carbonate is further carbonated to produce $KHCO_3$ (potassium bicarbonate), which is used largely in the food and pharmaceutical industries.

15.7 References

1. Munson, R. D. 1980. "Potassium Availability and Uptake," *Potassium in Agriculture*, Potash and Phosphate Institute, pp. 67-108.
2. Garrett, D. E. 1995. *Potash: Deposits, Processing, Properties and Uses*, Chapmen & Hall, New York.
3. "Statistical Supplement," *Phosphorus and Potassium*, 1986-1992, British Sulphur Corp., London, England.
4. IBRD. 1993. "World and Regional Supply and Demand Balances for Nitrogen, Phosphate, and Potash for 1991/1992-1997/1998," World Bank Technical Paper N 206.
5. Potash Corp. of Saskatchewan. 1991. "Product Specifications," PCS Sales, Canada.
6. Zisselmar, R. 1988. "Compacting/Granulation of Fertilizers," IN *NPK Fertilizer Production Alternative*, Proceedings of an international workshop, pp. 46-56, SP-9, Madras/Bombay, India, International Fertilizer Development Center, Muscle Shoals AL, U.S.A.
7. Pietsch, W. 1990. "Granulation of Fertilizers by Compaction," IN *Urea-Based NPK Plant Design and Operating Alternatives*, Proceedings of international workshop, pp. 89-98, J. J. Schultz and G. Hoffmeister (Eds.), SP-15, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
8. Fayard, C., and P. Hervieu. 1990. "Compaction/Granulation of Fertilizers," IN *Urea-Based NPK Plant Design and Operating Alternatives*, Proceedings of international workshop, pp. 99-108, J. J. Schultz and G. Hoffmeister (Eds.), SP-15, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
9. Klein, M.O. 1990. "The Manufacture of Fertilizers by Compaction/Granulation," IN *Urea-Based NPK Plant Design and Operating Alternatives*, Proceedings of international workshop, pp. 119-132, J. J. Schultz and G. Hoffmeister (Eds.), SP-15, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
10. Swanstroem, S. 1994. "Private Communication," Kemira Oy.
11. Cormode, G. A. 1992. "Personal Communication," Cominco Fertilizers.
12. Carcara, D. 1992. "Personal Communication," Italkali, Pasquasia.
13. Searls, J. P. 1991. "Potash," Mineral Industry Surveys, Bureau of Mines, U.S. Department of Interior, Washington, D.C., U.S.A.
14. "Technical Advances by the U.S.S.R. Potash Industry." 1972. *Phosphorus and Potassium*, 59:41-45.
15. Crozier, R. D. 1981. "Chilean Nitrate Mining," *Mining Magazine*, September, pp. 160-173.
16. Anonymous. 1991. "SOQUIMICH Increases its Potassium Nitrate Capacity," *Phosphorus and Potassium*, 173:37-40.
17. Anonymous. 1971. "Routes to Potassium Nitrate: Parts 1 and 2," *Phosphorus and Potassium*, 51:50-57.
18. Araten, I. Y., A. Baniel, and R. Blumberg. 1967. "Potassium Nitrate," The Fertiliser Society Proceedings, London, England.
19. Medemblik, L. 1992. "Personal Communication," Mines de Potasse d'Alsace.
20. Mireau, R. M. 1992. "Personal Communication," Cominco Fertilizers.

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Chapter 16. Compound Fertilizers

16.1 Introduction

The total annual worldwide production of all fertilizer materials amounts to about 350 million tonnes (1995), containing about 125 million tonnes of nutrients ($N + P_2O_5 + K_2O$) [1]. Of this total, compound fertilizers, excluding physical mixtures (bulk blends), account for about 14%, or about 50 million tonnes of product annually. The production and marketing of compound fertilizers are unique compared with commodity-type fertilizers such as urea, ammonium phosphates, and potash. Unlike commodity-type fertilizers, compound fertilizers are usually manufactured (formulated) to meet local or regional crop requirements. Often, in addition to containing various ratios of the primary nutrients ($N + P_2O_5 + K_2O$), they contain certain secondary and micronutrients specific to the crop needs in a particular agroclimatic region.

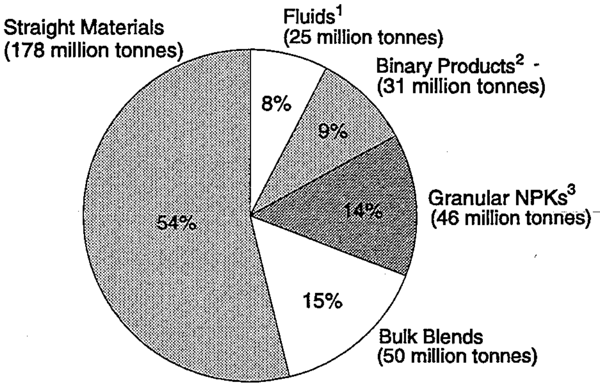
16.2 Trends in Supply and Demand for Compound Fertilizers

Supply/demand data on compound fertilizers are not routinely or uniformly reported. Therefore, such data must be obtained through ad-hoc surveys and informal sources.

IFDC surveys conducted in 1990 and 1995 indicated that compound fertilizer production (exclusive of dry mixed blends) occurred in at least 50 countries, and the total production during the 1990-94 period amounted to about 45-50 million tonnes of product annually. These results are generally corroborated by other surveys conducted by various producers and industry associations [2].

Based on the IFDC surveys, it is estimated that dry mixed compound fertilizers (bulk blends) account for an additional 40-50 million tonnes of product annually to bring the total production of all types of compound fertilizers to about 100 million tonnes annually (Figure 16.1).

Growth in the NPK granulation industry has been stagnant-to-declining during the past decade while the bulk blending of NPKs has increased significantly, particularly in Asia, Europe, and Latin America. The total number of granular compound fertilizer plants currently operating throughout the world is estimated at about 300 excluding numerous, perhaps as many as 1,000, very small village level-type units reportedly operating in China. The combined annual production of these small Chinese units may be as much as 1 million tonnes.



World Total: 330 million tonnes product (1994)[4]

1. Single and multiple nutrient fluids, including anhydrous ammonia.
2. Ammonium phosphate products.
3. Steam/water, chemical, and compacted granular products.
4. Nutrient production (1993/94 reporting year) amounted to 131.5 million tonnes ($N + P_2O_5 + K_2O$).

Source: IFDC data file.

Figure 16.1. Estimated World Production of Fertilizers by Product Type.

16.3 Role of Compound Fertilizers

The decision to use compound fertilizers is usually driven by one or more of the following factors:

1. Convenience.
2. Crop nutrient needs.
3. Government policy objectives.
4. Economics.

16.3.1 Convenience

Compound fertilizers are frequently used because it is more convenient to purchase, transport, store, and apply one product than several as is the case if one chooses to use individual nutrient sources such as urea, ammonium nitrate, ammonium phosphate, and potash. However, in many instances a single dose of a compound fertilizer will not meet the nutrient needs of the crop over the entire growing season.

16.3.2 Crop Nutrient Requirements

Compound fertilizers are often a good choice for providing a basal application of nutrients, including secondary and micronutrients, prior to or at planting time. However, because most crops benefit from higher doses of nitrogen than other nutrients, the basal dose of compound fertilizer often needs to be followed by subsequent doses of nitrogen timed to meet the nitrogen requirements of the crop. Additionally, compound fertilizers, especially the homogeneous granulated products as opposed to dry mixed (blended) compounds, provide a means for uniformly distributing a basal dose of relatively small quantities of secondary and micronutrients in the soil without the risk of segregation, which could be detrimental to the crop.

16.3.3 Government Policy Objectives

In some cases, compound fertilizers are specified under subsidized pricing programs as a means for achieving an approximation of balanced nutrition in cases where farmer education and extension are lacking or where the cost of single-nutrient products (for example, urea, ammonium phosphate, and potash) varies widely. A wide variation in the farm-level cost of individual nutrients often leads to the excessive and unwarranted use of the least cost nutrient. Thus, the required use of compound fertilizers in a government-controlled market provides a means for avoiding such price-driven distortions in fertilizer use. The current global trend toward free and competitive markets is expected to diminish the influence of government policy as it relates to the choice of a particular fertilizer product.

16.3.4 Economics

The simplicity of purchasing, transporting, storing, and applying a single compound product compared with several single- or double-nutrient materials clearly has economic merit. However, it is important to note that compound fertilizers, on a nutrient basis, are almost always more expensive than single-nutrient products. Furthermore, the economics of fertilizer use must be viewed in a holistic way; not only the cost of the fertilizer but also the cost of labor, fuel, water, pest control, and, of course, the price received for the crop (refer to Chapter 2) must be considered. Therefore, the increased cost of compound fertilizers compared with the usually less costly single- or double-nutrient products may not be of overriding significance.

Finally, compound fertilizers are uniquely suited for the fertilization of plantation crops (for example, oil palm and rubber) and forests using aerial application techniques. Large, free-flowing granules of homogeneous compound fertilizer facilitate uniform distribution and penetration of the plantation or forest canopy. Aerial application, and therefore the increased need for homogeneous compound fertilizers, is expected to increase in the plantation sector as the cost of labor and conventional application of single nutrient materials continue to increase.

16.4 Compound Fertilizer Production Technology

The method used for granule formation has a pronounced impact on the design and operation of the granulation process equipment. Therefore, a good knowledge of the primary mechanisms of granule formation, growth, and consolidation is essential in determining the design features of the granulation process. The following is a brief description of the two major granule formation mechanisms encountered in most fertilizer granulation processes. Granulation by drop formation (prilling) and pressure roll compaction is treated separately (refer to sections 16.6.3 and 16.6.4).

16.4.1 Agglomeration-Type Processes

With most granular NPK products (excluding the slurry-based nitrophosphate-type processes), agglomeration is the principal mechanism responsible for initial granule formation and subsequent growth (Figure 16.2). In most agglomeration-type NPK formulations, 50%-75% of the raw materials are fed as "dry" solids. These solid particles are assembled and joined into agglomerates (granules) by a combination of mechanical interlocking and cementing – much as a stonemason fashions a stone wall by using stones of various sizes and shapes and mortar as the cementing agent. The cementing medium for fertilizer granules is derived from salt solutions, for example, a preneutralized ammonium phosphate slurry and/or the dissolution of salts on the moist surface of the soluble solid particles. The size, shape, surface texture, strength, and solubility of the solid particles vary widely (Figure 16.3) and have a profound influence on the granulation characteristics of the mixture.

16.4.2 Accretion-Type Processes

Accretion refers to the process in which layer upon layer of a fluid material (for example, an ammonium phosphate slurry) is applied to a solid particle causing it to grow in size. The slurry-type granulation processes used to produce DAP, MAP, TSP, and some nitrophosphate compounds are examples of accretion-type granulation processes. The accretion process is quite different from the agglomeration process with respect to the mechanism of granule formation and growth. As a result, the required process parameters for optimum operation of these slurry-type accretion granulation processes are often quite different from those used in agglomeration processes. With a slurry-type granulation process, a relatively thin film of moist slurry, or a nearly anhydrous melt, is repeatedly applied, dried, and hardened to a relatively firm substrate consisting of granules that are often product size or nearly product size. In this process, layer upon layer of new material is applied to a particle, giving the final granule an "onion-skin"-like structure (Figure 16.2). In the process, of course, some

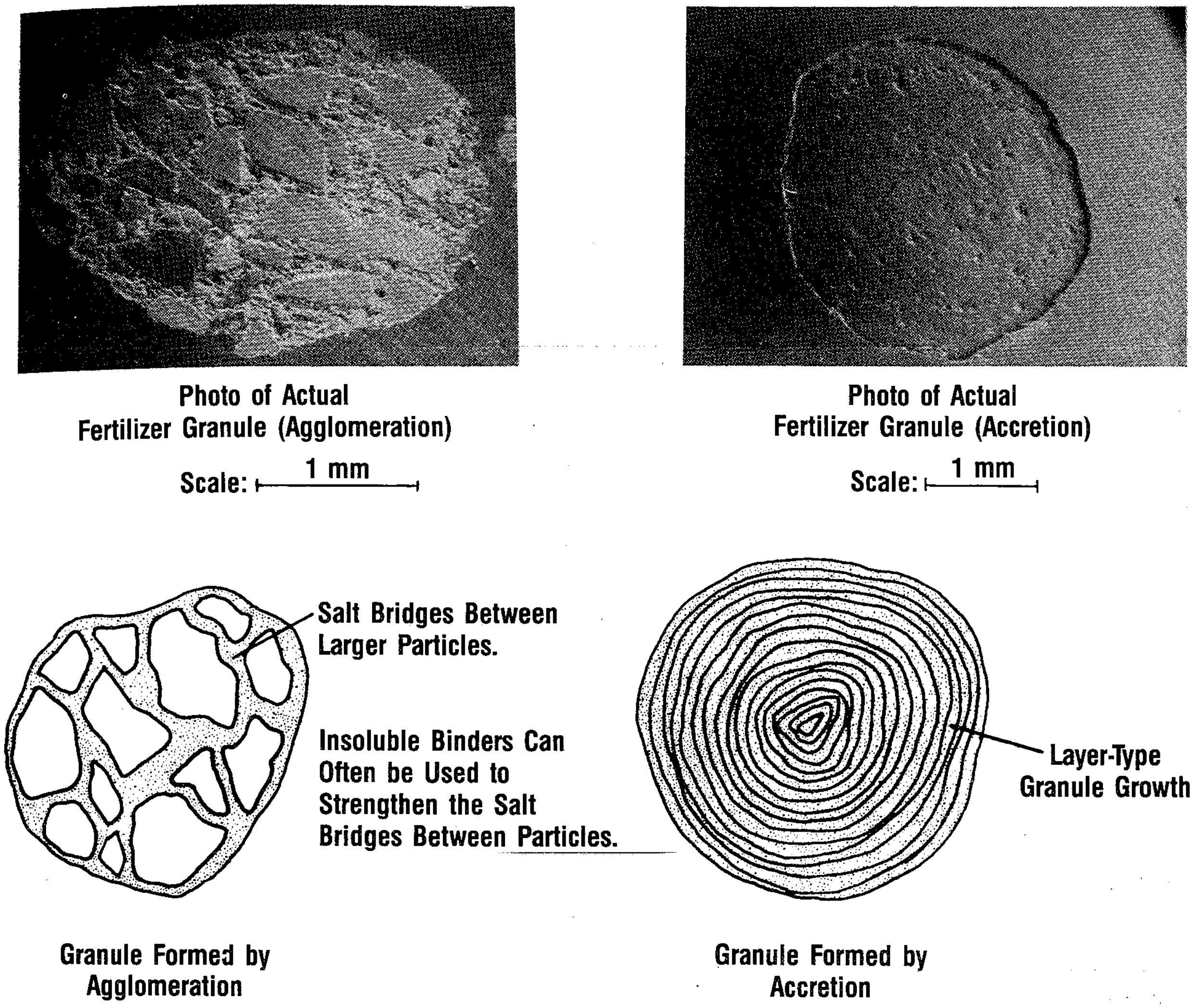


Photo of Actual Fertilizer Granule (Agglomeration)

Scale: 1 mm

Photo of Actual Fertilizer Granule (Accretion)

Scale: 1 mm

Granule Formed by Agglomeration

Granule Formed by Accretion

Figure 16.2. Principal Mechanisms for Granule Formation.

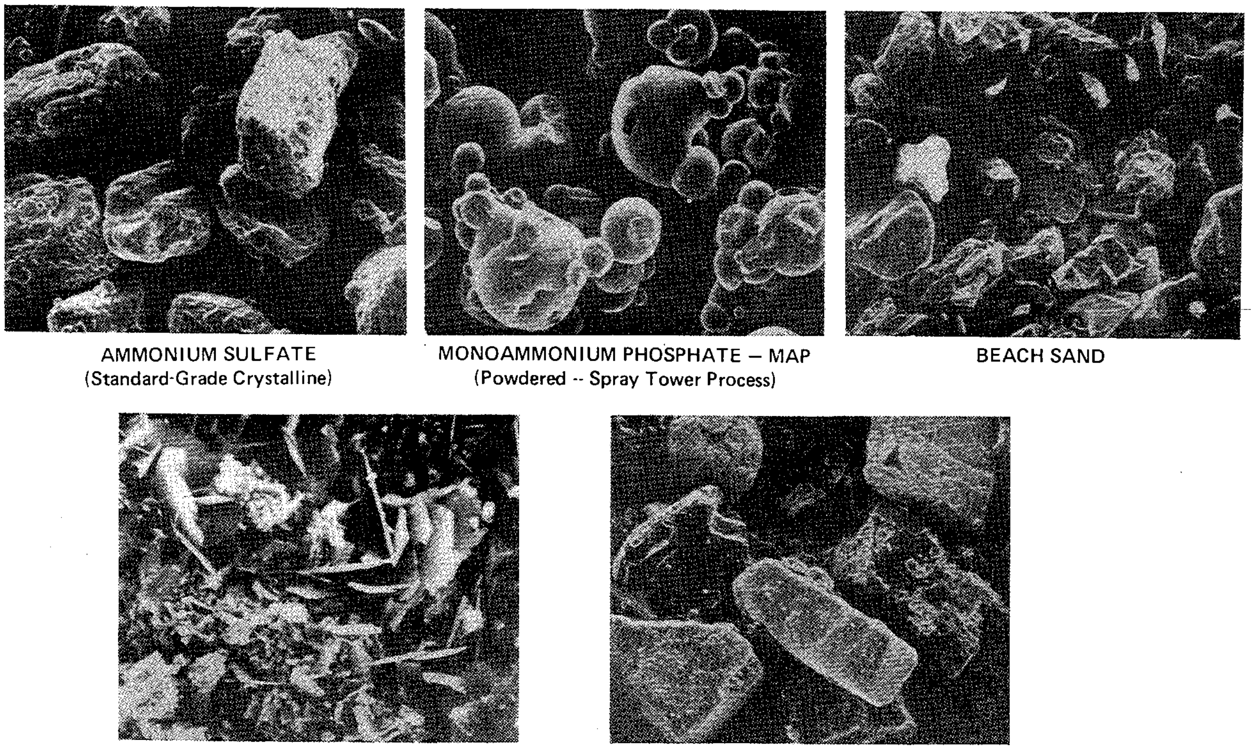
agglomeration of particles also occurs, but this is not the predominant granule formation mechanism.

The recycle-to-product ratio required for accretion-type granulation is normally higher than that required for agglomeration-type processes. Accordingly, for a given production rate, the material handling capacity of the process equipment must be larger for accretion-type granulation plants than for most agglomeration-type plants. However, because of particular temperature- and relative humidity-related processing requirements for some agglomerated NPKs, certain equipment, especially the dryer and process cooler, may actually be larger in some agglomeration-type plants to achieve the same production rate as in the accretion-type processes (refer to section 16.7).

Granules formed by accretion are almost always harder, more spherical, and more durable than those formed by agglomeration. For example, a typical well-formed NPK, DAP, or TSP granule produced by accretion-type granulation may have a crushing strength of about 4-8 kg, whereas the crushing strength of an agglomerated granule may not only be less (often less than 3 kg) but also more variable depending upon its raw material composition and a number of specific factors related to granule formation. Some examples of the variability in granule strength for a number of fertilizers are shown in Table 16.1.

16.5 Physical and Chemical Parameters for Producing Agglomerated NPKs

A discussion of the key physical and chemical parameters required for the production of agglomerated NPK products follows. Refer to section 16.7 for parameters specific to the production of most urea-based NPKs and



AMMONIUM SULFATE
(Standard-Grade Crystalline)

MONOAMMONIUM PHOSPHATE – MAP
(Powdered -- Spray Tower Process)

BEACH SAND

SINGLE SUPERPHOSPHATE
(Run-of-Pile)

POTASSIUM CHLORIDE – KCl
(Standard-Grade Crystalline)

Magnification Approximately 15X.

Figure 16.3. Surface Texture of Materials Commonly Used in NPK Granulation Formulas.

other NPKs that exhibit similar high solubility, temperature sensitivity, and low critical relative humidity (CRH) characteristics. CRH is the ambient relative humidity below which a material loses moisture to the atmosphere and above which the material absorbs moisture from the atmosphere. The CRH of a material varies with temperature.

16.5.1 Raw Material Particle Size and Surface Characteristics

Because much of the initial (in-process) and final mechanical strength of the agglomerated NPK granule is obtained by the mechanical interlocking or fitting of the individual particles, the particle size, size distribution, and surface characteristics of the solid raw materials are very important. If the final product is in the size range of 2-5 mm, then the raw materials should be quite widely distributed within a range of about 0.2-3 mm. An example of the particle size distribution of solid materials frequently used in agglomeration-type NPK granulation plants without further size reduction (crushing) is shown in Table 16.2.

16.5.2 Liquid Phase

Although mechanical interlocking of the particles within the granule structure must be optimized through selection and/or processing (crushing) of the raw materials (and sometimes recycled material), cementing is also needed to permanently bond the particles into strong agglomerates (granules). The liquid phase is derived from (1) soluble-salt solutions added to the granulator, for example, an ammonium phosphate slurry and/or a solution of urea or ammonium nitrate and (2) dissolution of a small portion of material on the moist surface of the soluble raw material and recycle particles. This dissolution is caused by the combination of heat and water contained in the above solutions or by steam or water fed to the granulator. Solubility data for some of the more common fertilizer salts are given in Table 16.3. Liquid phase control is the key to achieving the desired level of granulation efficiency and product quality. Ideally, after drying, the liquid phase (salt solution) forms strong crystal bonds (salt bridges) between the particles of the agglomerate that are mechanically well-fitted and interlocked – again, the concept of a stone wall.

Table 16.1. Typical Granule Strength Data for Various Granular Fertilizers[a]

Granular Fertilizer	Principal Method of Granular Formation	Typical Crushing Strength (kg/granule)
Diammonium phosphate (DAP)	Accretion	3.4-4.9
Triple superphosphate (TSP)	Accretion	4.6-8.1
10-30-10[b]	Accretion	5.0-5.5
10-20-20[b]	Accretion	4.8-5.2
Triple superphosphate (TSP)	Agglomeration of run-of-pile TSP	2.4-2.9
Single superphosphate (SSP)	Agglomeration of run-of-pile SSP	2.0-3.2
15-15-15	Agglomeration	1.5-2.9
17-17-17	Agglomeration	2.0-3.0
14-6-21-4 MgO	Agglomeration	2.0-4.0
12-19-9	Agglomeration	2.5-3.0

a. Typical values for commercial materials tested by the International Fertilizer Development Center (IFDC) according to IFDC Test Method S-115 (2.36- to 2.80-mm granule size). These values are shown as examples only; crushing strength can vary considerably depending on moisture content, degree of aging, granule shape, porosity, composition, and other specific factors.

b. Produced using slurry (accretion) process; could also be produced by agglomeration.

Table 16.2. Typical Particle Size Data for Commercially Available Materials Frequently Used to Produce Granular NPKs

Material	Percent Retained on Indicated Mesh[a]					
	4 (4.75)	8 (2.36)	16 (1.00)	28 (0.60)	48(0.30)	100 (0.15)
Ammonium sulfate (crystalline)	0	0	1	7	75	98
Diammonium phosphate[b] (granular)	0	22	98	100	100	100
Monoammonium phosphate (nongranular)	0	1	7	30	65	90
Potassium chloride (standard)	0	0	6	55	90	99
Potassium chloride (special standard)	0	0	0	5	35	90
Potassium sulfate (standard)	0	0	15	75	95	100
Single superphosphate (run-of-pile)	3	11	25	36	52	76
Triple superphosphate (run-of-pile)	7	14	19	26	51	80
Urea (prilled)[b]	0	15	92	95	100	100

a. Tyler mesh, opening size in mm indicated in parentheses.

b. Crushing of these materials is preferred to obtain a more uniform (homogeneous) NPK product.

Table 16.3. Solubility of Common Fertilizer Salts in Water[a]

Fertilizer Salt	Approximate Concentration of Saturated Solution at Indicated Temperature 0°C	20°C	100°C
	(%)		
Ammonium nitrate	54	66	90
Ammonium sulfate	41	43	51
Diammonium phosphate	30	41	58
Monoammonium phosphate	18	27	63
Potassium chloride	22	25	36
Potassium nitrate	12	24	71
Potassium sulfate	6	10	19
Urea	41	52	88

a. Values indicated are for pure salts.

16.5.2.1 Estimating Liquid Phase Values – Experience has shown that there are considerable differences in the amount of liquid phase generated by the various materials normally used in the production of agglomerated NPKs. Several years ago (during the 1960s), the Tennessee Valley Authority (TVA) examined a wide variety of NPK production formulations that were known to granulate quite well and devised a numerical value to express empirically the "apparent" liquid phase contribution that could be expected from a number of materials commonly used to produce NPKs. These "liquid phase factors" are shown in Table 16.4. Experience has shown that, when these values are used as a guide, a liquid phase of about 300 kg/tonne of product is about optimal for most agglomeration-type NPK formulations. Of course, it should be appreciated that liquid phase, while important in granule formation, is only one of the criteria that must be carefully evaluated when the granulation characteristics of a particular formulation are estimated.

16.5.3 Heat of Chemical Reaction

The level of liquid phase is also closely linked with another criterion, i.e., the expected amount of heat created by various chemical reactions that occur during the granulation of a given NPK formulation. The amount of heat generated, particularly within the granulator, can have a marked effect on the solubility of the fertilizer materials and the amount of liquid phase formed and, therefore, the resulting granulation characteristics of the mixture. In general, to achieve optimum granulation, the calculated total liquid phase for a formulation, using the data in Table 16.4, should be lowered if the formulation produces a large amount of chemical heat of reaction in the granulator. However, the optimum relationship between liquid phase and heat of reaction for a specific formulation must be learned from actual operating experience.

Table 16.4. Liquid Phase Factors for Selected Materials Frequently Used in NPK Granulation (Agglomeration) Formulas

Material	Liquid Phase Factor (kg/kg)
Anhydrous ammonia	0.50
Ammonia/ammonium nitrate solutions (various compositions)	1.00
Ammonium nitrate (prills)	0.30
Wet-process phosphoric acid	1.00
Sulfuric acid	1.00
Superphosphoric acid	1.00
Water or steam	2.00
Ammonium sulfate (crystalline)	0.10
Single superphosphate (run-of-pile)	0.10
Triple superphosphate (run-of-pile)	0.20
Potassium chloride (coarse or granular)	0.30
Potassium chloride (standard)	0.00
Diammonium phosphate (granular)	0.25
Monoammonium phosphate (nongranular)	0.20
Urea (prilled)	0.30

To obtain the total weight of the liquid phase in a formulation, multiply the weight of each raw material in the formula (kg) by the appropriate liquid phase factor. A total liquid phase weight value of about 300 kg/tonne is considered optimal in many cases.

The most important heat-generating chemical reaction in most NPK granulation plants is the neutralization of acidic materials with ammonia inside the granulator. The approximate net amount of heat released when ammonia reacts with some common acids and other fertilizer materials is shown in Table 16.5. As with liquid phase, experience has shown that if the amount of heat released in the granulator is equivalent to about 45,000-50,000 kcal/tonne of product (not including recycle), conditions are generally favorable for obtaining optimum granulation. Of course, as with liquid phase, the proper level of heat is just another one of the many critical criteria that must be determined by experience and that must be met to obtain optimum granulation efficiency.

16.5.4 Insoluble Binders

In some cases, the mechanical and crystal (salt bridge) bonding of particles can be greatly improved by adding

Table 16.5. Approximate Net Amount of Heat Released When Ammonia Reacts With Various Materials Commonly Used to Produce Granular NPKs

Material Reacted With Ammonia	Reaction Product (Solid)	Heat Released (Net)	
		NH_3 Gas	NH_3 Liquid
		- - (kcal/kg NH_3 reacted)- -	
Wet-process phosphoric acid (54% P_2O_5)	Monoammonium phosphate (MAP)	1,890	1,370
Wet-process phosphoric acid (54% P_2O_5)	Diammonium phosphate (DAP)	1,510	990
Monoammonium phosphate (MAP)	Diammonium phosphate (DAP)	1,130	610
Triple superphosphate (TSP)	Ammoniated TSP	1,580	1,060
Single superphosphate (SSP)	Ammoniated SSP	1,460	940
Sulfuric acid (100%)	Ammonium sulfate	2,165	1,645

a small amount of a finely divided insoluble binder powder, for example, kaolin or attapulgite clay or finely ground phosphate rock, to the granulating mixture. The binder powder helps to fill the many small voids between the fertilizer particles and acts as a saturated wick in helping to join the particles (Figure 16.2). This concept works particularly well with NPKs that contain large amounts of crystalline ammonium sulfate, potassium chloride, potassium sulfate, and/or kieserite (magnesium sulfate monohydrate) and relatively low levels of highly soluble salts or solid binders such as ammonium phosphate slurry or superphosphate, respectively. Depending upon the characteristics of the binder and the materials being granulated, the amount of binder used may need to be approximately 2%-15% of the total formula weight to be effective. It is important to note, however, that some insoluble binders (some clays, for example) have the capacity to retain moisture and thus make subsequent drying more difficult. Finely ground phosphate rock that contains high levels of iron and aluminum impurities is a very effective binder that also adds a primary nutrient, albeit slowly available, to the product.

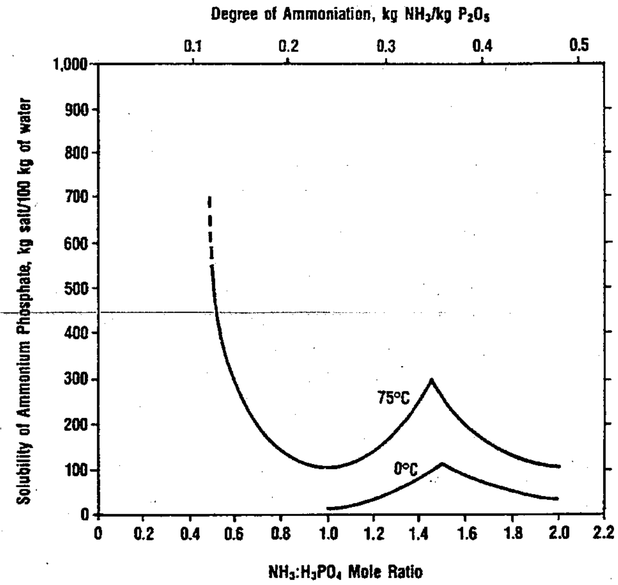


Figure 16.4. Effect of Mole Ratio on Solubility of Ammonium Phosphate.

16.5.5 Liquid Phase Control

In all NPK granulation formulations, most of the liquid phase is obtained from materials that are introduced to the process at a fixed rate to achieve a final product with the desired chemical analysis. The resulting liquid phase can, of course, be adjusted within rather specific limits through the selection of raw materials or by controlling the free water content and/or chemical composition of the slurry (for example, the NH_3:H_3PO_4 mole ratio as shown in Figure 16.4). However, once this is established (optimized), the flow rates of the liquids must remain constant to ensure the correct analysis of the final product. For this reason, all agglomeration-type formulations should allow for a moderate degree of liquid phase "tuning" performed by the operator using steam and/or water fed directly to the granulator. The discretionary use of a small amount of steam and/or water by the operator helps to compensate for variations in granulation efficiency caused by changes in the temperature of the materials, quantity and particle size of the recycled material, and minor (but normal) upsets within the overall processing system. This fine tuning of the process by the operator is the basis for the observation: "NPK granulation by agglomeration is more of an art than a science." The unique skill of an experienced granulator operator often greatly overrides the effectiveness of the most costly and sophisticated process design and engineering skills.

16.5.6 Acid/Ammonia Neutralization Methods

As indicated earlier, the acid/ammonia neutralization reactions create heat that contributes to the overall liquid phase conditions in the granulator and therefore greatly influences the efficiency of the granulation process. The method used for neutralization (reacting ammonia) can significantly influence the overall performance of the granulation process. A brief discussion of the most common methods used for neutralization in agglomeration-type NPK granulation plants follows.

16.5.6.1 Direct Neutralization in Granulator – This was one of the most common methods used for reacting ammonia in the many NPK granulation plants that were operated in the United States and elsewhere during the 1960s and early 1970s. Direct neutralization in the granulator is particularly well suited for NPK grades containing large amounts of superphosphate (SSP or TSP) and a relatively low level of nitrogen. With direct neutralization, optimum operation is usually obtained if the amount of ammonia reacted in the granulator does not exceed the equivalent of about 50 kg/tonne of product.

In the direct neutralization process, ammonia is distributed using a perforated pipe (sparger) positioned beneath the bed of material in the granulator. If sulfuric acid is used, it too is usually distributed through a sparger beneath the bed of material whereas the phosphoric acid, if used, is most often sprayed or dribbled on top of the bed of material. When sulfuric acid is used, precautions should be taken to ensure that the acid is added at a particular location with respect to the ammonia to ensure quick and uniform neutralization and thus minimize the unwanted reaction of sulfuric acid with muriate of potash (MOP) that is usually present in most NPK formulations. This acid/MOP reaction causes the formation of very corrosive hydrochloric acid, which reacts rapidly with ammonia to form a dense fume of ammonium chloride that is very difficult and costly to collect in the plant's emission control (scrubbing) system.

Rotary drum-type granulators are best suited for direct neutralization because the submerged spargers can be more easily positioned beneath the bed of material and the reactions contained within the relatively deep bed of material. When using a pugmill- or pan-type granulator, the positioning and effectiveness of submerged spargers are often less than optimum because of the mechanical configuration of the equipment and the relatively shallow bed of material.

16.5.6.2 Tank-Type Neutralizers – The use of an atmospheric or pressurized tank-type neutralizer offers maximum flexibility in managing the acid/ammonia reactions and obtaining the critical heat/liquid phase criteria needed for good granulation when producing a wide variety of granular NPK grades. Because the acid/ammonia reactions are most often only partially completed in these tank-type neutralizers, they are often referred to as "preneutralizers." Such preneutralizers are commonly used in most of today's ammonium phosphate plants and in many NPK plants.

When a preneutralizer is used, large amounts of acid can be partially reacted with ammonia. The degree of reaction performed in the preneutralizer is determined by a number of factors; however, the most important criterion is the production of a fluid slurry that is easy to transport (pump) to the granulator and uniformly distribute onto the rolling bed of material in the granulator. The fluidity of the preneutralized slurry is maintained through careful control of the NH_3:H_3PO_4 mole ratio (Figure 16.4), temperature, and free water content of the reacted slurry. The neutralization reactions that are only partially completed in the preneutralizer are completed in the granulator where additional ammonia is added beneath the rolling bed of material. In some cases, phosphoric acid may be added to the granulator to adjust the NH_3:H_3PO_4 mole ratio to achieve optimum granulation.

When sulfuric acid is reacted in combination with phosphoric acid in the preneutralizer, special precautions must be taken to select construction materials that will resist the more corrosive environment caused by the presence of sulfuric acid. Type 316L stainless steel (SS) is not a suitable construction material if sulfuric acid is neutralized in combination with phosphoric acid; a more noble alloy is required. The selection of construction materials for the preneutralizer system should be made only after careful testing of possible construction materials under actual operating conditions. Also, at the higher mole ratio and pH when sulfuric acid is present (for example, about 1.5 and 6.8, respectively), the presence of ammonium sulfate crystals tends to thicken the slurry and make pumping difficult; thus, operation at a lower NH_3:H_3PO_4 mole ratio and pH (about 0.4 and 2.0, respectively) is often preferred, when sulfuric acid is fed to the preneutralizer.

16.5.6.3 Pipe-Type Reactors – In the early 1970s, TVA demonstrated the feasibility of replacing a conventional tank-type preneutralizer with a novel device referred to as a pipe or "tee" reactor [3]. This type of reactor was a radical departure from the conventional tank-type preneutralizer normally used to react large amounts of ammonia with phosphoric acid. The pipe reactor consists basically of a length of corrosion-resistant pipe (about 5-15 m long) to which phosphoric acid, ammonia, and often water are simultaneously added to one end through a piping configuration resembling a tee, thus the name "tee reactor." The acid and ammonia react quite violently, pressurizing the unit and causing the superheated mixture of ammonium phosphate slurry ("melt") and water vapor to forcefully discharge from the opposite end of the pipe that is positioned inside the granulator. Uniform distribution of the "melt" on top of the rolling bed of material in the granulator is achieved by varying the configuration and orientation of the discharge opening(s) of the pipe. A primary advantage of the pipe reactor over conventional preneutralizers is that the preneutralized slurry pump and piping system is eliminated and a much more concentrated slurry can be delivered directly to the granulator. Thus the chemical heat of reaction is more effectively used to evaporate unwanted water from the process compared with the operation of a conventional preneutralizer. The tee reactor was modified by TVA to also accept an additional flow of sulfuric acid through another pipe inlet located opposite the phosphoric acid inlet, giving the unit a "cross" configuration and thus the name "pipe-cross reactor" (PCR) [4,5].

Use of the PCR makes it possible to react a wide variety of phosphoric/sulfuric acid mixtures with ammonia. This capability is particularly useful in NPK granulation plants and allows a greater choice in the selection of raw materials to improve granulation and optimize the overall cost of production. In addition, the problem of ammonium chloride fumes is eliminated because the sulfuric acid does not come in direct contact with the MOP that may be in the formulation.

In general, the mixture discharged from the PCR does not require further reaction with ammonia in the granulator. In some cases, however, the level of reaction in the PCR may be altered (decreased) to minimize the escape of ammonia or to obtain improved granulation characteristics of the "melt" when it is combined with the solids in the granulator.

Several variations of pipe-type reactors (and materials of construction) are currently used in NPK, DAP, and MAP plants; sometimes the pipe-type reactor is used in combination with a conventional tank-type preneutralizer. Perhaps one of the greatest advantages offered by the use of pipe reactor technology in the NPK industry is that it provides an opportunity to effectively use a greater variety of raw materials including, for example, larger quantities of dilute acids and scrubber liquor. This added flexibility in raw material choices can often result in more favorable production costs and at the same time provide a method for disposing of certain "problem materials" such as excess scrubber liquor. It should be noted, however, that the technology does not fit all situations equally well. Therefore, its potential should be carefully examined with regard to the particular circumstances.

16.5.7 Preparing the Production Formula

According to the foregoing discussion, a large number of raw material and process variables must be considered when developing NPK production formulations that result in good granulation characteristics. As with the operation of an NPK granulation plant, formulation too, requires a considerable amount of skill and an element of "art" to ensure that the particular formulation will yield the desired results in a specific situation.

A given NPK fertilizer can be formulated in many ways depending on the available raw materials and specific equipment system. Table 16.6 shows some examples of NPK production formulations that have been successfully used in commercial practice. Because the performance of these formulations will depend heavily upon a number of factors as described herein, these examples are offered only to illustrate the variability that should be considered in the planning and design of an NPK fertilizer granulation plant.

16.6 Processes for Manufacturing Compound Fertilizers

16.6.1 Steam/Water Granulation

In the steam/water granulation process (Figure 16.5), granules are formed by agglomeration. The solid raw materials are proportioned (weighed) and usually premixed before being fed to the granulator where agglomeration is initiated. In some plants, the raw materials are crushed either before or after weighing to obtain a more uniform particle size distribution. In the granulator (usually a rotary drum or a pug mill) steam and/or water or scrubber liquor is added to provide sufficient liquid phase and plasticity to cause the dry raw materials to agglomerate into product-size granules. In some processes, a pugmill may be used to premix the solids and liquids prior to granulation in a rotary drum unit. In other cases a small amount of ammonia may also be added during granulation to react with superphosphate to promote granulation and improve product quality by decreasing the acidity and increasing the CRH. The moist and plastic granules are dried, usually in a rotary drum-type, fuel-fired dryer, and screened to remove the product-size fraction. The oversize material is crushed and recycled to the granulator along with the undersize fraction. To ensure a uniform particle size distribution of the material returned to the granulator, it is best to return the crushed oversize material to the screening unit so that only material passing the product screen is recycled to the granulator. In some cases it is necessary to cool the material before screening depending on the fertilizer grade and local conditions. If cooling is required, it is usually performed in a rotary drum-type unit that is very similar to the rotary dryer. Fluid bed-type coolers may be used to cool product-size material, but they are

Table 16.6. Examples of Typical Commercially Proven NPK Production Formulas in Which Agglomeration is the Principal Mechanism for Granule Formation and Growth[a]

Material as Fed to Process[c]	Direct Ammoniation in Granulator			Pipe-Cross Reactor (PCR)[b]		Tank-Type Preneutralizer (PN)[b]		Urea Solution/Steam (No Chemical Reaction)		
	3-9-18	5-20-20	13-13-13	8-24-24	13-13-13	15-15-15	17-17-17	12-12-17-1.2Mg	14-6-21-2.4Mg	16-0-30
	---- (kg/tonne finished product)[d] ----			(kg/tonne finished product)[d]		---- (kg/tonne finished product)[d] ----		------ (kg/tonne finished product)[d] -----		
Anhydrous ammonia — 82% N	37	52	-	66 (90% to PCR)	85 (100% to PCR)	127 (75%-80% to PN)	82 (65%-70% to PN)	-	-	-
	-	-	-							
Ammonia/ammonium nitrate solution — 46% N	-	-	145	-	-	-	-	-	-	-
Urea (prills) — 46% N	-	-	-	-	-	105	231	115	153	240
Urea solution — 35% N	-	-	-	-	-	-	-	155	204	156
Ammonium sulfate (crystalline) — 21% N, 24% S	-	50	205	121	300	-	-	-	-	-
Sulfuric acid — variable % H_2SO_4	63 (93% H_2SO_4)	-	64 (78% H_2SO_4)	40 (78% H_2SO_4) (100% to PCR)	192 (78% H_2SO_4) (100% to PCR)	261 (96% H_2SO_4) (100% to PN)	108 (96% H_2SO_4) (100% to PN)	-	-	-
Wet process phosphoric acid — 54% P_2O_5	-	170	63	443 (90% to PCR)	250 (85% to PCR)	292[e]	330[e]	-	-	-
			-	-	-					
Single superphosphate (ROP) — 18% P_2O_5, 12% S	508	332	216	-	-	-	-	-	-	-
Triple superphosphate (ROP) — 46% P_2O_5	-	124	-	-	-	-	-	-	-	-
Monoammonium phosphate (powdered) — 10% N, 50% P_2O_5	-	-	-	11	-	-	-	-	-	-
Diammonium phosphate (crushed granules) – 18% N, 46% P_2O_5	-	-	130	-	-	-	-	87	-	-
Phosphate rock (ground) — 32% P_2O_5	-	-	-	-	-	-	-	247	191	-
Potassium chloride (standard) — 60% K_2O	-	342	221	402	223	255	289	276	353	500
Potassium sulfate (standard) — 50% K_2O, 18% S	320	-	-	-	-	-	-	-	-	-
Sulfate of potash-magnesium (standard) — 22% K_2O, 11% Mg, 22% S	110	-	-	-	-	-	-	-	-	-
Magnesium sulfate (kieserite) — 16% Mg, 22% S	-	-	-	-	-	-	-	-	150	-
Magnesium oxide — 50% Mg	-	-	-	-	-	-	-	25	-	-
Insoluble binder	-	-	-	-	-	-	-	110	-	130
Micronutrient mix (various elements as required)	10	-	-	-	30	-	-	10	-	-
Conditioning agent (coating on product)	-	-	10	-	10	15	15	15	10	15
Subtotal	1,048	1,070	1,054	1,083	1,090	1,055	1,055	1,040	1,061	1,041
Evaporation	-48	-70	-54	-83	-90	-55	-55	-40	-61	-41
Total (product basis)	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000

a. Examples intended to partially illustrate large number of formulation possibilities depending upon specific process equipment system, available raw materials, agronomic requirements, product composition guarantees, and other local factors.
b. Flows of acid and ammonia to PCR and PN may vary; indicated flows typical for commercial practice. The addition of steam and/or water to the granulator is generally required to optimize granulation efficiency.
c. All materials are fed directly to granulator unless otherwise noted. Indicated composition is typical of industry practice.
d. Values rounded for simplicity.
e. Phosphoric acid is first fed to fume scrubbing system and then onward to PN.

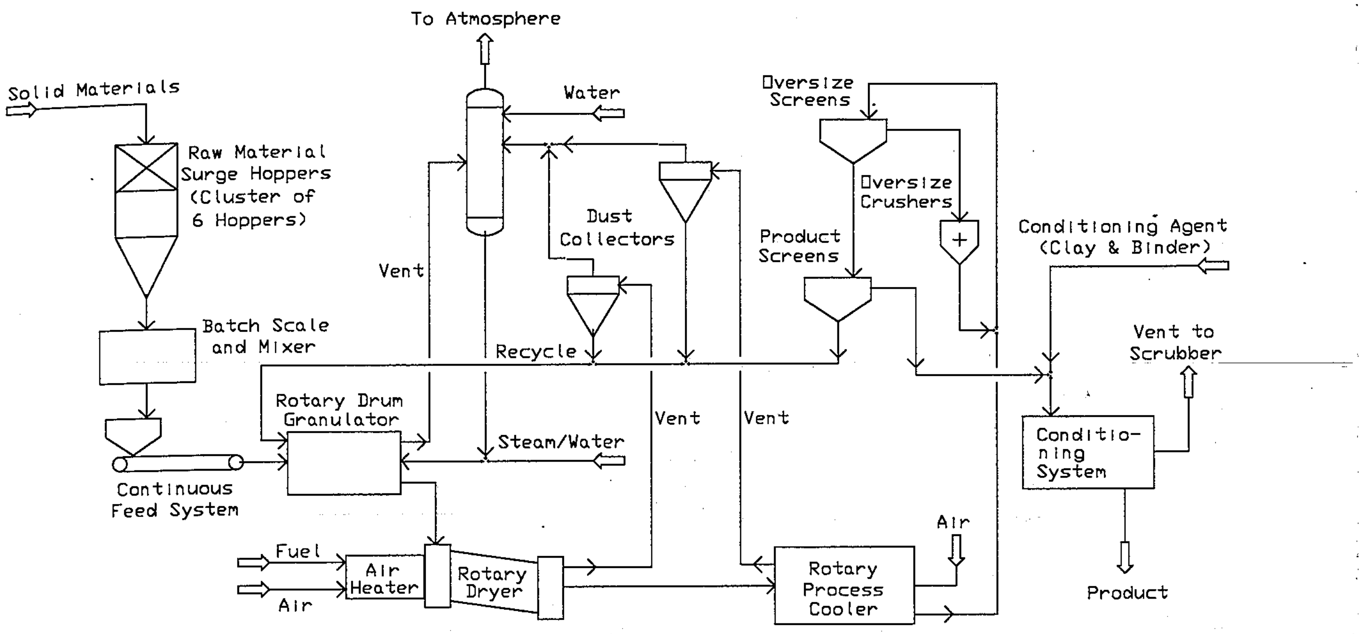


Figure 16.5. Typical NPK Fertilizer Granulation Plant Using Steam and/or Water.

not recommended for cooling material having a wide particle size range.

16.6.2 Chemical Granulation

Chemical granulation is the most complex method for preparing granular NPKs (Figure 16.6). The chemical granulation process is very similar to the previously described steam/water granulation process except that most of the liquid phase required to achieve granulation is obtained by reacting ammonia with phosphoric, sulfuric, and/or nitric acid. In some cases, a concentrated solution of urea or ammonium nitrate may also be used (refer to 16.7). Some processes also involve a significant reaction between ammonia and single or triple superphosphate (SSP or TSP). Much of the ammonia-acid reaction is often performed outside the granulator either in a tank-type preneutralizer or in a pipe-type reactor. In many cases steam, water, scrubber liquor, and/or additional ammonia and acid are also fed to the granulator to optimize the granulation characteristics of each particular formulation. In most NPK chemical granulation plants, a significant amount of solid raw materials is also used; therefore, the granules are formed primarily by agglomeration. The relationship between the consumption of solid and liquid raw materials is determined by a number of variables, including (1) required nutrient ratio (fertilizer grade) and nutrient solubility requirements, (2) liquid phase requirements, (3) heat of reaction and temperature limitations, and (4) process plant equipment capacity and operating features. The granulation process shown in Figure 16.6 also incorporates the design features recommended for the production of NPKs containing relatively large amounts of urea or other very soluble and hygroscopic materials.

In some chemical granulation processes, the solid raw materials, for example MOP, are partially dissolved in an ammonium phosphate and/or ammonium nitrate slurry and the mixture is then sprayed onto a bed or curtain of material in the granulator which is usually a heated rotary drum, for example, a Spherodizer®. In this process, granules are formed primarily by accretion (refer to Chapter 13).

16.6.3 Drop Formation (Prilling)

The formation of NPK granules by prilling using nitrophosphate-type processing is practiced quite widely in Europe (refer to Chapter 13). In this process the NPK mixture (solution) is concentrated to approximately 96%-98% solids before it is introduced to the top of the prilling tower through either a nozzle assembly or a perforated vessel referred to as a "prilling bucket." The nozzle or prilling bucket assemblies are designed to produce droplets of the "molten" fertilizer mixture that, upon solidification, will yield the desired granule (prill) size. NPKs produced by the prilling process are very homogeneous with respect to nutrient content. However, due to the practical limitations of the drop formation and solidification process, prilled NPK products usually exhibit a smaller particle (granule) size, typically 1.3 mm-

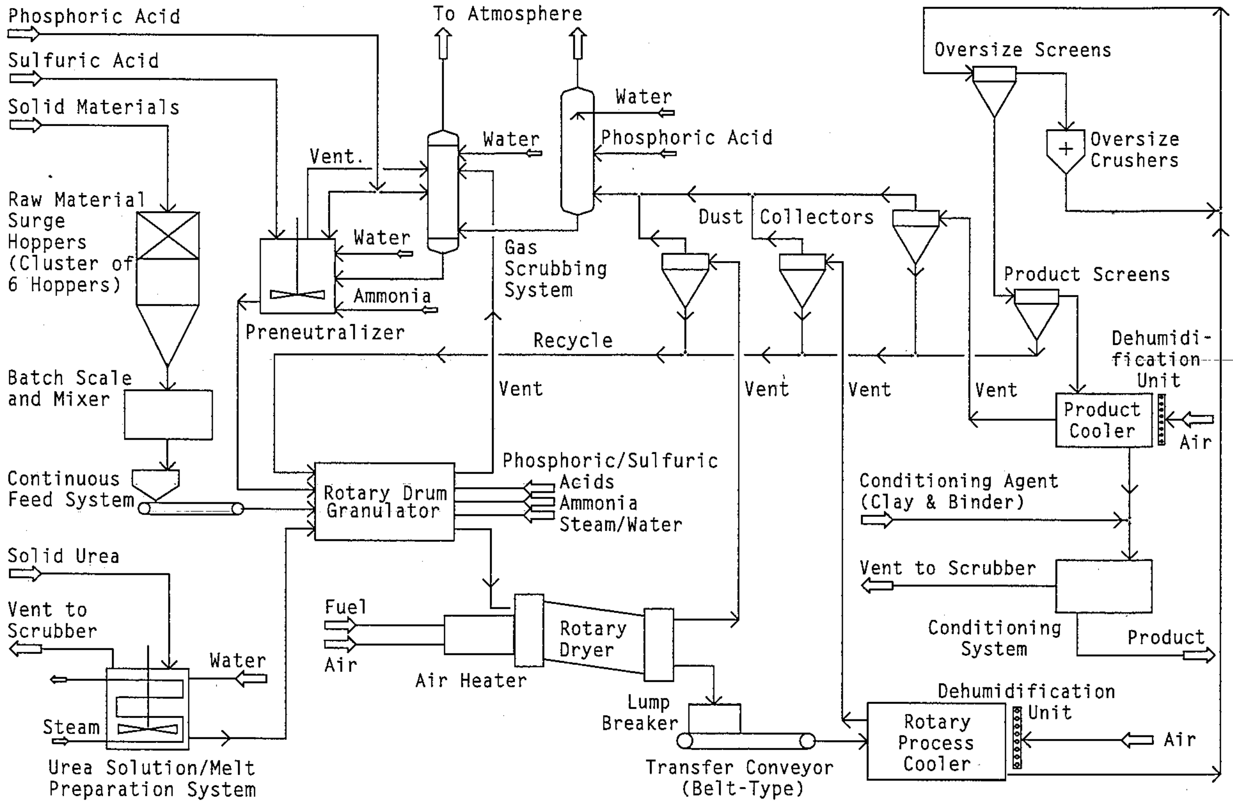


Figure 16.6. NPK Fertilizer Granulation Plant Designed for Maximum Flexibility in the Use of Raw Materials, Including Urea.

3.0 mm in diameter, than do NPKs produced by other granulation processes.

16.6.4 Compaction Granulation

In this process (Figure 16.7) mechanical force is used to form dense particles (granules) from finely divided (nongranular) solid raw materials. With compaction granulation the dry materials are first proportioned and thoroughly mixed (blended) to achieve the desired nutrient ratio (fertilizer grade). This step of the process is identical to that normally used in the steam/water granulation process. The mixture is then continuously fed to a pressure-roll compaction machine that forms the powdered mixture into a dense, hard sheet of material usually about 2-3 cm thick and 60-100 cm wide. The compaction machine consists of two horizontally opposed rollers that turn inward toward each other. The rollers may be as much as 100 cm wide and about the same diameter. The shaft of one roller has a stationary shaft while the other is movable. Pressure is applied by a hydraulic system to the movable roller shaft and bearing assemblies, which in turn determines the pressing force applied to the fertilizer material fed to the machine. The compacted sheet of material is crushed in a controlled manner to form smaller particles. The crushed material is screened to obtain the desired product-size fraction. The oversize material is crushed and recycled to the screens and the undersize material is returned (recycled) to the compaction machine after first being thoroughly mixed with the fresh raw material feed. No chemical reaction is required for the process although the raw material properties (especially chemical compatibility, thermal characteristics, and plasticity) have a major influence on the performance of the process. The pressing force of the compaction rollers required to produce an acceptable granular product is measured in terms of tonnes of force per centimeter of roller width. Refer to Table 16.7 for typical pressing forces required for various fertilizer materials and mixtures.

Granular fertilizers prepared by compaction have a more irregular particle shape as compared with the more smooth and rounded (spherical) granules produced by other granulation processes. The irregular particle surface and shape characteristics of compacted products may promote caking during storage because of the

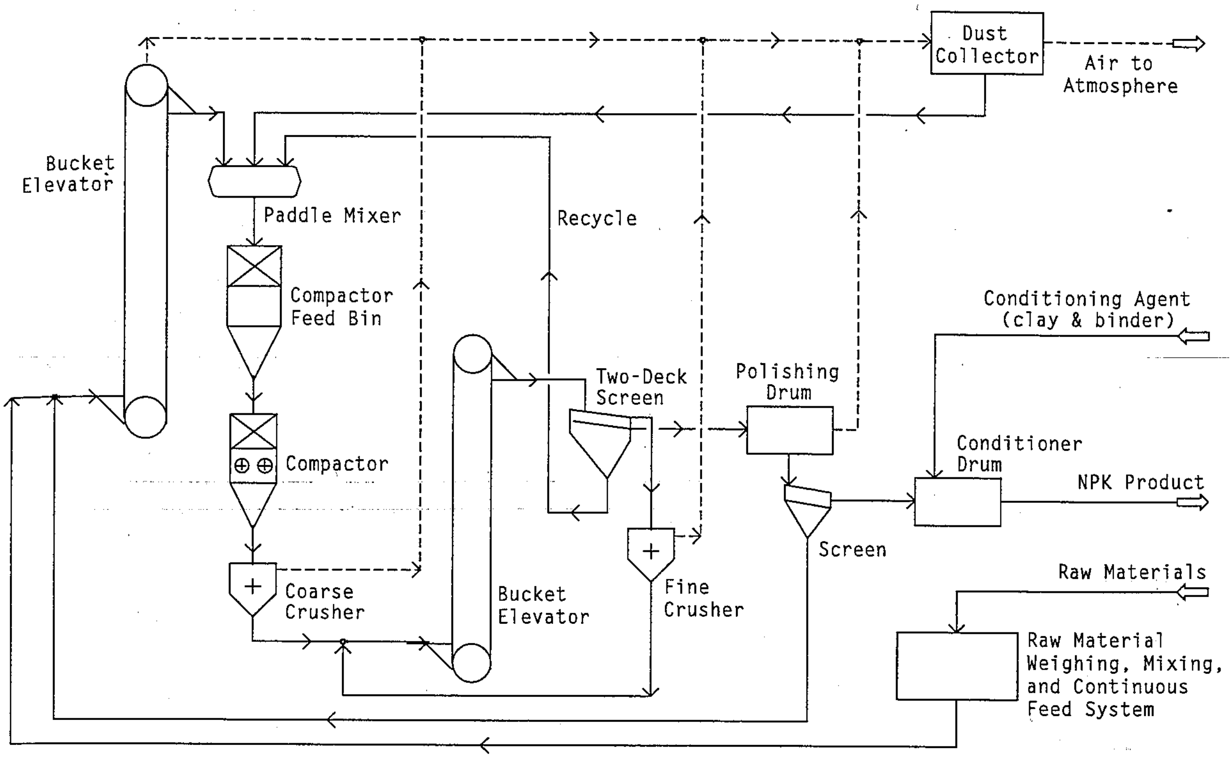


Figure 16.7. Typical NPK Fertilizer Compaction Granulation Plant.

Table 16.7. Typical Pressing Forces for Fertilizer Compaction

Feed Material	Pressing Force[a] (kN/cm)[b]	Water Content (%)	Feed Particle Size (mm)
Ammonium sulfate	100-120	0.5-1.0	<1.0
Potassium chloride			
Feed temperature >120°C	45-50	nil	<1.0, with max. of 3% <0.06[c]
Feed temperature 20°C	70	nil	
Potassium sulfate			
Feed temperature >70°C	70	1.0	<0.5
Potassium nitrate	100	0.5-1.0	<1.0
Calcium nitrate	60	nil	<1.0
Urea	30-40	nil	1-3
Compound fertilizer containing			
– No raw phosphate rock	30-80	<1.0	<1.0
– Raw phosphate rock	>80	<1.0	<1.0
– Urea	30-40	<1.0	<1.0

a. Indicated pressing force is for machine having 1.0-m diameter rollers.
b. 1 kN/cm = approximately 0.1 tonne/cm.
c. Size criteria applies to material feed temperature as indicated.

Source: Koppern Equipment, Inc., U.S.A.

generation of fines during handling and because of the increased surface area of the irregular particles compared with the more rounded granules produced by other granulation processes. The irregular shape of compacted fertilizer granules may cause some resistance among users who are accustomed to the more traditional spherical fertilizer granules. However, experience has shown that market resistance to compacted products can be largely overcome through refinements in the process, for example, tumbling/abrasion, to round the rough edges and produce more spherical granules and through promotion and customer education.

16.6.5 Dry Mixing (Blending)

This technology refers to the physical mixing (blending) of dry fertilizer materials without the deliberate introduction of chemical reactions or the enlargement of the material particle (granule) size. The blending of solid and liquid fertilizer materials is also practiced in some instances to produce fluid multinutrient products. However, the production and marketing of fluid fertilizers are beyond the scope of this examination (refer to Chapter 10).

16.6.5.1 Producing High-Quality Blends – The materials used to prepare dry solid blends (often referred to as bulk blends) are usually granular in form and are also often sold as finished or "straight" products, for example, urea, DAP, and MOP. In some instances, nongranular or semigranular materials are used to prepare blends; however, this practice usually leads to a lower quality product. In the context of this discussion, a distinction is also made between "prilled" and "granular" materials such as urea, ammonium nitrate, and potassium nitrate. While technically speaking prilled materials are granular, the particle size of most prilled products is too small (often less than 1.5 mm) to remain homogeneously mixed with other common granular materials such as DAP and MOP, which are significantly larger in particle size (usually in the range of 2 to 5 mm).

Because of the importance that particle (granule) size plays in the preparation of high quality, homogeneous blends needed for balanced plant nutrition, many material suppliers provide the customer with very specific particle size data to help the blender closely match the various materials used to prepare a blended NPK product. The Size Guide Number (SGN) is one such type of particle size information widely used in the industry. The SGN, developed in Canada, refers to the particle size of a material expressed in millimeters multiplied by 100, which divides a sample of material into two equal halves on a weight basis [6]. For example, if the mid-point or average particle size (weight basis) of a sample of material is 2.50 mm, the SGN would be expressed as 250. In this example, the blender would try to select all other ingredients in the blend with an SGN as close to 250 as possible. In practice, a variation of about 25 points from the desired SGN will usually result in an acceptable blend; for example, if an SGN of 250 is ideal an SGN of 225-275 will be acceptable.

Another indicator to assist in the selection of materials for the preparation of high-quality blends is the Uniformity Index (UI), also developed in Canada [7]. A UI of 100 would indicate that all particles in a sample are the same size. In practice a UI of about 50 is typical. A UI of 50 means that the size (diameter) of the smallest particles in the sample is one-half (50%) the size (diameter) of the largest particles in the sample. Typical UIs in commercial practice range from 35 to 60.

16.6.5.2 Blending Plant Technology – Blending, particularly in the United States, Central and South America, and Asia, is normally done on a batch basis with batch sizes varying from 1 to 5 tonnes (Figure 16.8). However, continuous blending is becoming quite popular, especially in Europe (Figure 16.9). Continuous blending units usually have a capacity in the range of 30-60 tph. A third alternative is on-farm manual or hand blending. This practice is often appropriate in cases where labor is abundant and the quantity of material to be blended is small.

Because of the simplicity of the blending process and its relatively low investment and operating cost, blending plants are often located in the immediate area they serve. For example, in the United States approximately 5,000 blending plants are in operation, serving the needs of some 2 million farms, including about 400 million ha (about 1.0×10^9 acres) of land. In the United States scenario, on average, a blender rarely serves a farmer more distant than 40 km from the blending plant site. This micromarketing approach to blending results in very prompt and personalized service. The importance of timely service tailored to the customer's needs cannot be overemphasized regardless of the country location or farming practice. The fertilizer blender is often engaged in providing a broad range of products and integrated services to the farmer in addition to fertilizers. In the United States, for example, these products and services often include the supply and application of plant protection chemicals, seeds, machinery repair parts and service, soil testing, and crop advisory services. Thus, the custom blending of fertilizers to meet specific crop/soil needs may be more appropriately viewed as a customer service rather than a production technology.

In some settings, large centralized blending plants are most appropriate. For example, in Ireland nine relatively large blending plants, each with an annual production ranging from 50,000 to 250,000 tonnes, supply about 50%-55% of the total Irish fertilizer market [8].

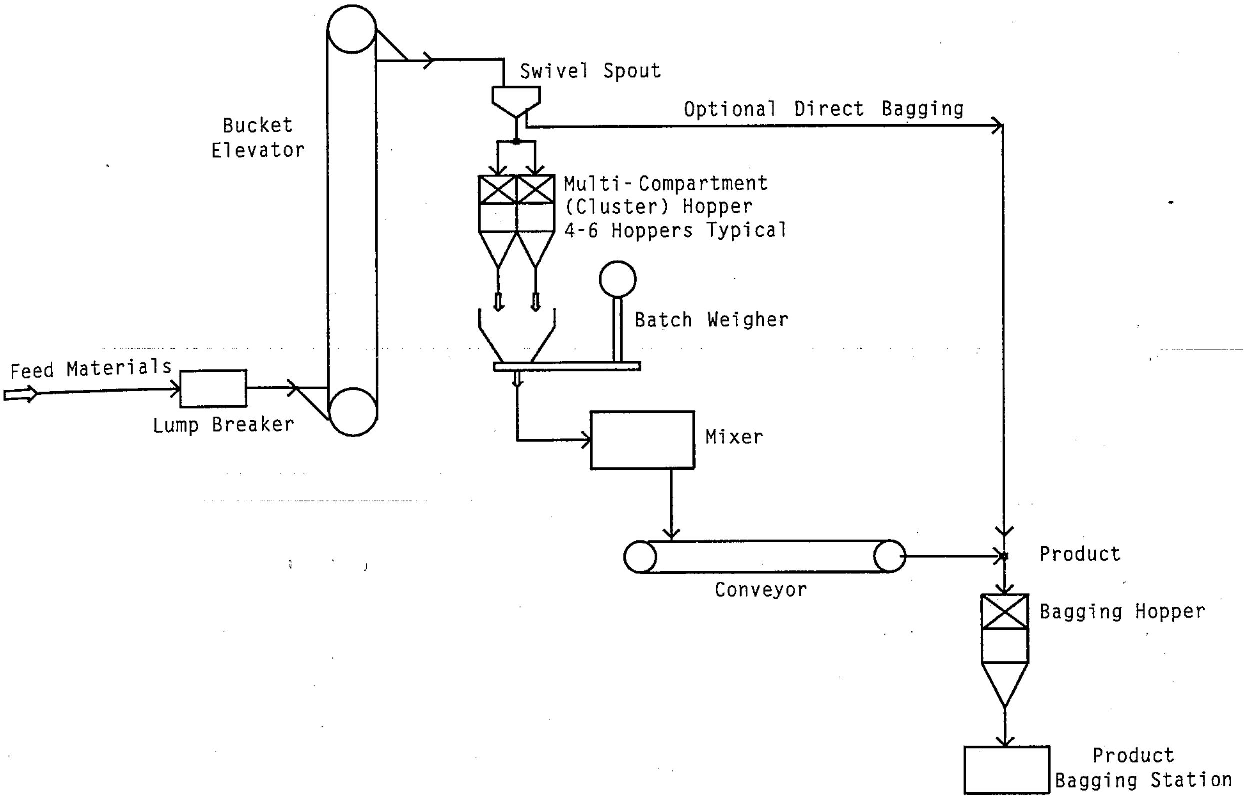


Figure 16.8. Typical Batch-Type NPK Fertilizer Bulk-Blending Plant.

Large, centralized blending plants are also very appropriate in locations where the transport infrastructure is weak. In such instances, it is usually more practical to blend and bag the product near the source of supply (for example, at an ocean or river port, or at a basic fertilizer production complex) and transport the finished product, in bags, to distribution points in lots consistent with the capacity of the transport, storage, and marketing infrastructure.

16.6.5.3 Blending Complements Granulation – The NPK granulation processes (steam/water, chemical, and compaction) all suffer from the lack of being able to economically produce a relatively small quantity of a specific product to meet an individual customer's needs. However, these NPK granulation processes can be used to supply the blender with granular "base formulations" such as ammoniated SSP fortified with such secondary and micronutrients as magnesium, sulfur, boron, and zinc. These granular "base formulations" can be used by the blender to uniformly incorporate small quantities of micronutrients throughout the total blend without fear of segregation, which could result in unbalanced plant nutrition. For example, a blender may use 425 kg of a micronutrient-fortified granular ammoniated SSP mixed with 375 kg of ammonium nitrate and 200 kg of MOP to arrive at a blend containing approximately 12% N, 6% P_2O_5, 12% K_2O, and the desired micronutrients.

The benefits of granulation and blending can often be optimized by operating both processes in concert with each other. In such a system, the granulation unit is used to convert nongranular materials into high-quality granular products, which can be sold directly or incorporated into a wide variety of nutrient ratios by blending with other materials. Such a system offers maximum flexibility in raw material utilization and the ability to produce a large number of nutrient ratios (grades) to meet the often changing needs of the marketplace [9].

16.7 Unique Requirements for Manufacturing Urea-Based Granular Compound Fertilizers

The wide availability of urea at competitive prices makes it an attractive source of nitrogen for the producer of compound fertilizers. If the particle (granule) size of urea is compatible with other fertilizer materials

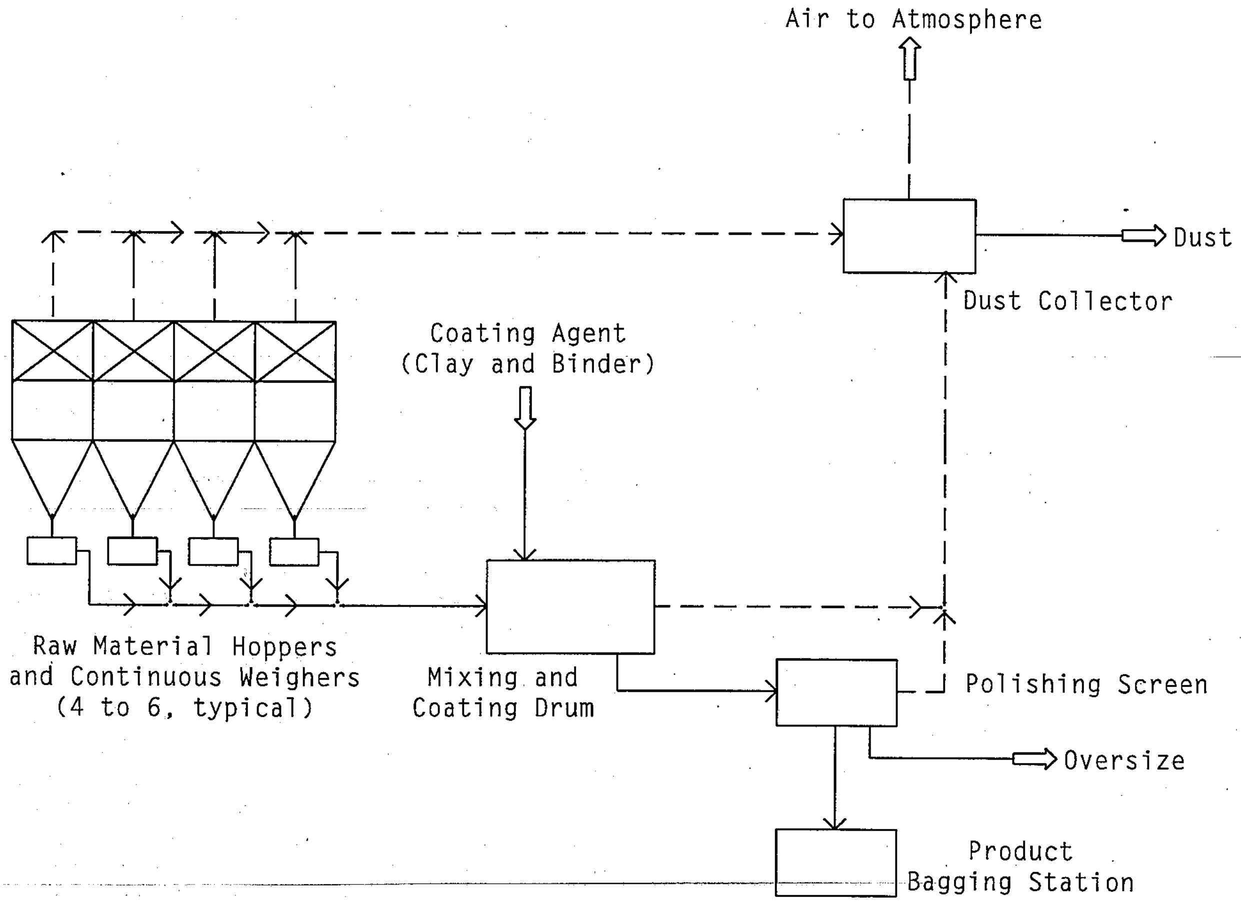


Figure 16.9. Typical Continuous NPK Fertilizer Blending Plant.

and precautions are taken to avoid chemical incompatibility, quality physical mixtures (blends) can be prepared and marketed without incident.

However, when urea is used to produce compound fertilizers using steam/water, chemical, or compaction granulation processes, precautions must be taken to avoid process and product quality problems caused by the presence of urea in the formulation. As little as 2%-5% urea in a compound fertilizer formulation will often be quite noticeable with respect to increased hygroscopicity and plasticity (especially during production) of the product. The adverse impact of urea in a compound fertilizer is significantly increased if MOP and/or kieserite are also present in the formula. The hygroscopicity and plasticity characteristics of urea-containing compound fertilizers may seriously interfere with the operation of the drying, screening, and crushing equipment unless this equipment is specifically designed and operated.

Furthermore, the storage properties of urea-containing compound fertilizers are often inferior to those of compounds that do not contain urea. The tendency to absorb moisture from the atmosphere in the case of bulk product and the caking of bagged product are the two most undesirable characteristics of compound fertilizers containing urea.

Despite these inherent characteristics of urea-based compound fertilizers, high-quality compound products containing more than 30% urea can be successfully produced and marketed provided certain precautions are taken during the production, storage, and bagging steps. The following is a summary of the critical design and operating criteria that should be considered when producing urea-based compound fertilizers. A process flow diagram of an NPK plant specifically designed to accommodate the use of significant amounts of urea in the formulations is shown in Figure 16.6. A discussion of the most important features that should be incorporated into a urea-based NPK granulation process follows [10].

16.7.1 Solid Urea Feedstock

Prilled urea is preferred because its small particle size helps to facilitate its relatively homogeneous incorporation into the NPK granule structure. Very small and broken prills are the most desirable.

16.7.2 Urea Solution or "Melt"

If the urea content of the formula is more than about 20%, it is preferable to dissolve a portion of the urea to produce a hot (105°C) 75%-80% urea solution. The availability of urea solution adds considerable flexibility to the process. The solution is sprayed on top of the bed of material in the granulator. In most instances, a solution of urea is preferred over an almost anhydrous urea "melt" because it is easier to handle and a solution more effectively promotes agglomeration of the other solid materials used in the formulation.

16.7.3 Other Solid Raw Materials

Standard-grade materials are preferred. Nongranular run-of-pile (powdered) monoammonium phosphate (MAP) and superphosphate are recommended. If superphosphate is used in combination with urea, it should be first fully ammoniated to minimize unwanted urea-superphosphate reactions that result in the release of water of crystallization contained in the superphosphate. However, as a general rule, the use of superphosphate in combination with urea should be avoided, even if the superphosphate is ammoniated. Standard-grade muriate of potash is preferred because of its usually good flow characteristics and more optimum particle-size distribution. Good flow characteristics of all solid raw materials are highly desired to facilitate handling and accurate metering.

16.7.4 Preneutralizer

A standard, atmospheric tank-type preneutralizer is preferred. An NH_3:H_3PO_4 mole ratio of about 0.5 to 0.6 is recommended in the preneutralizer to achieve a low free water content while still maintaining a fluid and pumpable slurry. This is especially important if a significant amount of sulfuric acid is also neutralized in the unit. The preneutralized slurry at a mole ratio of about 0.5 to 0.6 should be about 127°C and contain no more than 15% free water. The preneutralizer and its auxiliary equipment (agitator, pumps, and piping) should be constructed of corrosion-resistant materials to facilitate the use of a mixture of phosphoric and sulfuric acid, thus adding considerable flexibility to the process (refer to section 16.5.6.2). In general, if a higher mole ratio (for example 1.5) is used, especially if sulfuric acid is also present, the free water content of the slurry will have to be higher to facilitate pumping because the ammonium sulfate crystals tend to thicken the slurry.

16.7.5 Granulator (Rotary)

The length-to-diameter ratio should be at least 3. The greater length, compared with granulators used in most ammonium phosphate and many North American NPK plants, facilitates granule formation and gives the operator more flexibility in controlling the agglomeration process. The NH_3:H_3PO_4 mole ratio of the material discharged from the granulator may be quite variable depending upon the properties of the raw materials. However, a mole ratio between 1.0 and about 1.8 is expected to be optimum. The lower mole ratio (1.0) will minimize the evolution of ammonia from the granulator and thus simplify operation of the scrubbing system and tend to improve control of the process. The free moisture of the product discharged from the granulator will usually be in the range of about 2% to 3%. The recycle-to-product ratio is expected to vary from about 3 to 6. A ratio of 6 is recommended for design. If the process is based on a solid ammonium phosphate source (for example, powdered MAP) and a preneutralized slurry is not used, then a design recycle-to-product ratio of 3 is usually sufficient.

16.7.6 Cocurrent Dryer

The length-to-diameter ratio of this rotary unit should not exceed about 6. The superficial velocity of the air (at outlet conditions) should not exceed 2.4 m/sec maximum (2.0 m/sec preferred). The maximum temperature of the outlet air should not exceed 80°C, and the RH at this temperature should not exceed 15%. An outlet air temperature of 75°C at 15% RH is recommended as the basis for design. The moisture of the material discharged from the dryer should not exceed 1.0%; a value of 0.8% is recommended for design provided a second-stage dryer (process cooler) is used. The temperature and humidity profile in the dryer is extremely important, and the optimum values will vary from product to product primarily depending on the CRH of the fertilizer material (Figure 16.10). It is important to note that if the material becomes overheated, "melting" begins to occur and material will stick to the interior walls and flights of the dryer near the discharge end, thus a length-to-diameter ratio of no more than 6 is recommended to avoid "overdrying" and possible melting of the material near the discharge end of the dryer.

16.7.7 Countercurrent Process Cooler (Second-Stage Dryer)

This unit is essential because it performs two important functions in a urea-based NPK granulation plant. First, it acts as a low-temperature second-stage dryer to ensure that the product moisture is 0.6% or less; and second, the retention time in the unit allows the relatively soft and plastic material to harden, thus improving the operation of the screening and oversize crushing systems.

The length-to-diameter ratio of the process cooler should not be less than 6; 7 to 8 is preferred. The inlet air should be dehumidified and/or heated to ensure that the RH is 60% or less as it enters the process cooler.

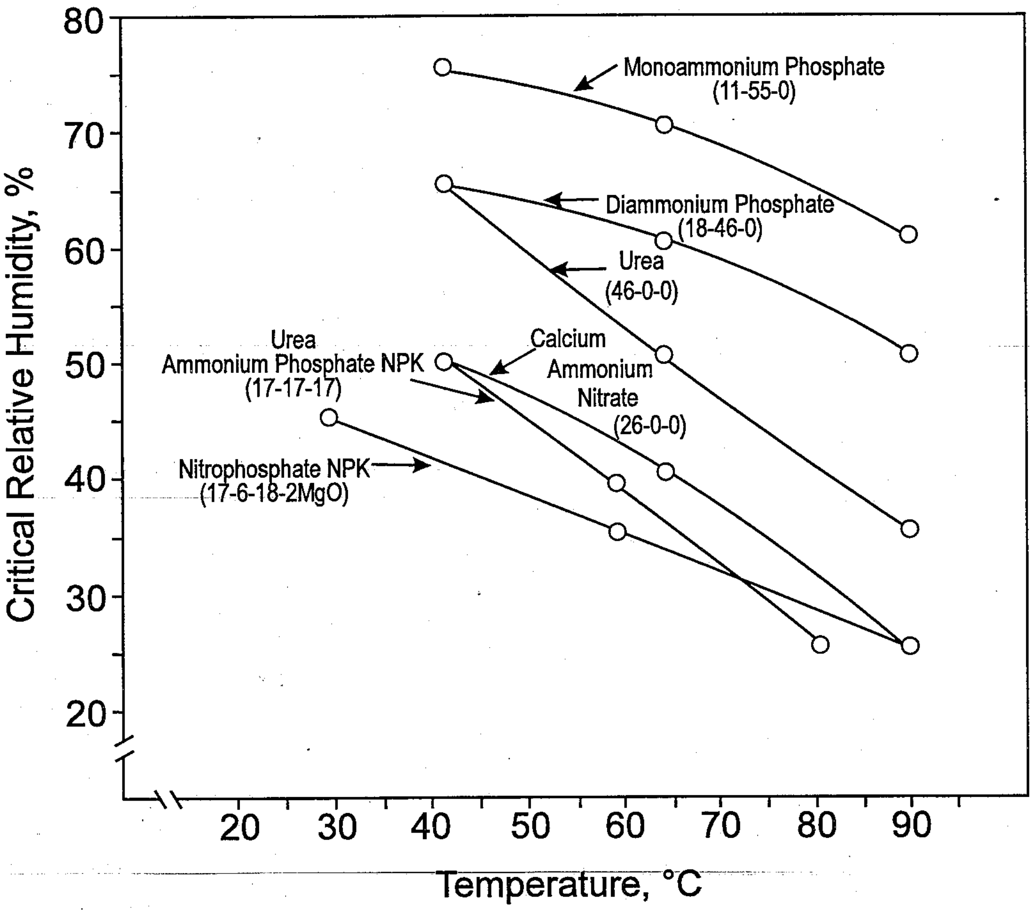


Figure 16.10. Effect of Temperature on Critical Relative Humidity of Selected Fertilizer Products.

The superficial air velocity should not exceed 2.0 m/sec. The low velocity is recommended because of the relatively large amount of minus 1.0-mm particles in the material. It is preferred that these small particles be removed (separated) by the screens rather than by the airflow/dust collection system. The unit should be designed to achieve a material (discharge) temperature of not more than about 54°C at a free moisture content of no more than 0.6%. Further cooling of the product fraction (after screening) is performed in a separate operation.

16.7.8 Screening

Single-deck horizontal gyratory-type screening units are recommended. The screen wire should be stainless steel and of the square-mesh style to obtain "precision screening" and minimize the amount of irregular shaped particles that lead to caking during long-term storage. If inclined, electrically (or motor) vibrated screens are used, they should be for oversize separation only, not for "precision screening" of the product fraction. The hourly loading of the oversize screen should not exceed about 20 t/m^2, and the loading of the horizontal gyratory-type product screen should not exceed 50% of this value (25%-30% preferred).

16.7.9 Oversize Crushers

Double rotor chainmill-type crushers or double row cage mills are preferred. The discharge assembly of the mill should not be restricted and should be constructed of flexible rubber (conveyor belting) panels that can be flexed from the outside by an operator using a hammer. A flared-type discharge assembly for the crushers is recommended to help avoid the accumulation of solids. The crushed oversize should be recycled to the oversize screen on a closed-loop basis to ensure that only the fine-material fraction (undersize) from the screens is returned to the granulator as recycle. With good control of granulation, the production of oversize is minimized. This is important because the production of too much oversize material disturbs the solids surface/liquid-phase ratio in the granulator, which leads to the further production of excessive quantities of oversize material.

16.7.10 Product Cooling

Either a rotary-drum or fluidized-bed unit is recommended. A single-pass, countercurrent, cascade-type cooler is also acceptable. The cooling unit should be located immediately ahead of the product conditioning unit. The RH of the cooling air at inlet conditions should not exceed 50%. The temperature of the product discharged from the cooler should not exceed about 43°C. In all cases the temperature of the cooled product should be about 5°C above the average ambient temperature to avoid absorption of atmospheric moisture on the surface of the material when it is stored in bulk for a short period prior to bagging.

16.7.11 Product Conditioning

A standard rotary drum-type product conditioning unit is recommended. Screw-type mixing units should be avoided because they tend to grind and break the product granules. Kaolin clay applied in the order of about 0.5% (weight bases) is usually sufficient for most urea-based NPKs. An oil- or wax-type liquid binder may also be sprayed into the product prior to the application of the clay conditioner to help adhere the clay to the surface of the granules, thus decreasing the evolution of dust during handling.

16.7.12 Bulk Storage and Process Plant Dehumidification

If ambient conditions normally exceed about 50% RH for extended periods (more than about 8 h), provisions should be made to dehumidify the process plant and bulk storage buildings. Cooling and proper ventilation may also be necessary for worker comfort and safety. Adequate ventilation is especially important because all buildings should be tightly constructed and closed to maintain a dry inside environment (RH of 40%-50%).

16.7.13 Bagging

The urea-based compound fertilizer products should be bagged in moistureproof bags shortly after production. Direct bagging from the production unit is not recommended because off-specification product could inadvertently be bagged and flexibility is lost in handling product during grade-change periods. In addition, bag set (caking) is minimized if the fresh product is allowed to "pile set" for a short period of time (10-12 h).

16.8 Investment and Operating Costs

The economics of the four basic compound fertilizer production processes (bulk blending, compaction granulation, steam/water granulation, and chemical granulation) are compared in terms of (1) required fixed capital investment, (2) conversion cost (not including raw materials), and (3) production cost (conversion cost plus raw material cost). The premises and assumptions used in this evaluation and a discussion of the main economic characteristics of the processes follow.

16.8.1 Premises and Assumptions

All estimates (mid-1995 US $) are based on a grassroots production facility in a developing or transition economy country with an existing industrial infrastructure where the investment cost is assumed to be similar to that of a U.S. Gulf Coast location. Convenient access to an ocean or inland port is assumed and the cost of land is not included. All raw materials are assumed to be purchased from international sources at the indicated free-on-board (f.o.b.) prices which, of course, can vary quite widely. The f.o.b. raw material prices were increased by US $30/tonne for solid materials and US $40/tonne for liquid materials to arrive at an assumed delivered cost at the plant site. Storage facilities (capacity) for dry and liquid raw materials are based on the receipt of raw materials in 3,000- to 5,000-tonne lots and an approximate 2-month inventory at the plant site.

The base case capacity of each NPK production unit is 120,000 tpy while operating at 75% capacity utilization. This translates to 160,000 tpy at 100% capacity utilization assuming 330 days/year.

16.8.2 Fixed Capital Investment Estimates

As indicated in Table 16.8 the estimated total fixed capital investment for the four production schemes varies from a low of US $3.83 million for a batch-type bulk-blending plant to a high of US $19.37 million for the chemical granulation facility. In the case of the bulk-blending plant, the storage facilities represent about 65% of the total fixed capital investment, whereas storage facilities account for only about 20%-24% of the total fixed investment in the more costly compaction, steam/water, and chemical granulation units.

16.8.3 Conversion Cost Estimates

The estimated unit consumptions (not including raw materials) for the four compound fertilizer production processes are summarized in Table 16.9. Using these unit consumptions and typical mid-1995 U.S. costs, the conversion cost, based on a production of 120,000 tpy, including bags and bagging but not raw materials, varies from about US $26/tonne for bulk blending to about US $63/tonne for chemical granulation. In all cases fixed

Table 16.8. Estimated Fixed Capital Investment for Various NPK Production Processes – 120,000 tpy at 75% Capacity Utilization[a]

	NPK Production Process			
	Bulk Blending	Compaction Granulation	Steam Granulation	Chemical Granulation
	(US $ x 1 million)			
Battery-limits process unit	0.47	5.44	6.98	11.12
Bulk storage (dry raw materials and products)[b]	1.89	1.89	1.89	1.30
Bagged product storage[c]	0.59	0.59	0.59	0.59
Liquid storage (ammonia, phosphoric acid, and sulfuric acid)[d]	-	-	-	1.89
Auxiliary and support facilities[e]	0.44	1.19	1.42	2.24
Total Installed Cost	**3.39**	**9.11**	**10.88**	**17.14**
Project management and startup[f]	0.17	0.46	0.54	0.86
Interest during construction[g]	0.27	0.73	0.87	1.37
Total Fixed Capital Investment	**3.83**	**10.30**	**12.29**	**19.37**

a. Mid-1995 costs assuming a U.S. Gulf Coast location.
b. 22,000 tonnes total, except 15,000 tonnes for chemical granulation.
c. 5,000 tonnes total.
d. 3,000 tonnes each for ammonia, phosphoric acid, and sulfuric acid.
e. 15% of cost of process unit and total storage facilities.
f. 5% of total installed cost.
g 8% of total installed cost.

Table 16.9. Estimated Unit Consumptions (Excluding Raw Materials) for Various NPK Production Processes – 120,000 tpy at 75% Capacity Utilization

	NPK Production Process			
	Bulk Blending	Compaction Granulation	Steam Granulation	Chemical Granulation
	(unit consumption/tonne product)			
Labor (includes maintenance), workhours	0.14	0.27	0.28	0.31
Overhead and general expenses	100% of labor	100% of labor	100% of labor	100% of labor
Electricity, kWh	5.0	50.0	30.0	50.0
Steam, t	0.00	0.00	0.06	0.03
Water, t	0.00	0.00	0.25	0.25
Fuel, million kcal	0.00	0.00	0.18	0.10
Bags, each	20.1	20.1	20.1	20.1

capital recovery (based on a 15-year plant life and a 15% annual interest rate) represents the largest fixed conversion cost item and ranges from about 21% of the total conversion cost for bulk blending to about 44% for chemical granulation. It is interesting to note that the cost of bags represents the largest variable conversion cost item.

16.8.4 Estimated Raw Material Cost

Typical production formulas (raw material consumption) for an NPK 15-15-15 produced by the four processes are shown in Table 16.10. It is difficult to precisely evaluate the cost of raw materials for the four compound fertilizer production processes examined because of large variations in prices caused by

Table 16.10. Typical Production Formulas (Raw Material Consumption) for 15-15-15 — Various NPK Production Processes[a]

Raw Material[a]	NPK Production Process Bulk Blending	 Compaction Granulation	 Steam Granulation	Chemical Granulation Feed Basis	 Product Basis
	(kg/tonne)				
Prilled urea – 46-0-0	-	133	133	105	105
Granular urea – 46-0-0	40	-	-	-	-
Nongranular monoammonium phosphate – 10-50-0	-	304	304	-	-
Granular diammonium phosphate – 18-46-0	331	-	-	-	-
Standard ammonium sulfate – 21-0-0	-	288	288	-	-
Granular ammonium sulfate – 21-0-0	354	-	-	-	-
Standard muriate of potash – 0-0-60	-	255	255	255	255
Granular muriate of potash – 0-0-60	255	-	-	-	-
Ammonia – 82-0-0	-	-	-	127	127
Sulfuric acid – 96% H_2SO_4, 4% H_2O	-	-	-	261	251
Phosphoric acid – 52% P_2O_5, 20% H_2O	-	-	-	303	242
Conditioning clay	15	15	15	15	15
Conditioning clay binder	5	5	5	5	5
Total[b]	**1,000**	**1,000**	**1,000**		**1,000**

a. Nutrient content of product (as formulated) is about 1%-2% higher than theoretical to compensate for process losses and/or raw material variations.

b. Free water content of finished product is typically 1.5% to 2.0%.

international market conditions, quantity of purchase, ocean freight rates, and a variety of time- and site-specific conditions. However, for the purpose of illustration, the cost of raw materials, using typical mid-1995 U.S. costs, is the highest for bulk blending (about US $183/tonne of 15-15-15), whereas the raw material cost for compaction, steam/water, and chemical granulation is about US $12-$26 per tonne less than that of blending.

It is important to emphasize that the compaction, steam/water, and chemical granulation processes offer considerable potential for raw material cost savings if the opportunity for buying distressed, off-specification, or byproduct materials exists. Such materials can often be purchased at a significant discount and, then by processing, be upgraded to high-quality compound fertilizer products. Bulk blending does not offer this advantage because the production of high-quality blended products is dependent on the use of high-quality granular raw materials that are priced accordingly. However, as mentioned in section 16.6.5.3, the combination of granulation and bulk blending at the same facility may be very effective in transferring some raw material economies to bulk blending.

16.8.5 Estimated Total Production Cost

Using typical mid-1995 U.S. costs as an example, a summary of the estimated total production cost for the four compound fertilizer production processes, using 15-15-15 as an example, is shown in Table 16.11. These costs include all fixed and variable conversion cost items (including raw materials, bags, and bagging) and vary from a high of about US $234/tonne for chemical granulation to a low of about US $201/tonne for compaction granulation.

16.8.6 Impact of Capacity Utilization

The above example of production cost data is based on an annual production of 120,000 tonnes while operating at 75% capacity utilization (160,000 tpy design capacity). The effect on the total production cost (including bagging) caused by increasing or decreasing the annual plant capacity is shown in Table 16.12. As seen in Table 16.12, in the most capital-intensive plant (chemical granulation), a decrease in capacity utilization to 50% (80,000 tpy) increases the total production cost to US $255/tonne compared with about US $234/tonne at the base case condition. The bulk-blending plant, because of its low fixed capital investment, is least affected by changes in capacity utilization while the

Table 16.11. Estimated Total Production Cost for Producing 15-15-15 Using Various NPK Production Processes at 75% Capacity Utilization[a]

	NPK Production Process			
	Bulk Blending	Compaction	Steam Granulation	Chemical Granulation
	(US $/tonne 15-15-15)			
Fixed conversion cost	9.29	24.64	28.21	42.13
Variable conversion cost (less raw materials)	16.55	18.55	20.49	21.15
Raw material cost	183.48	157.47	157.47	170.78
Total (Bagged Product)	**209.32**	**200.66**	**206.17**	**234.06**

a. Refer to Tables 16.9 and 16.10 for estimated conversion and raw material unit consumption details. Values are indicative of typical mid-1995 U.S. conditions.

Table 16.12. Effect of Capacity Utilization on Production Cost

		NPK Production Process			
Capacity Utilization (%)	Yearly Production (tpy)	Bulk Blending	Compaction Granulation	Steam Granulation	Chemical Granulation
		(US $/tonne 15-15-15)			
25	40,000	227.90	249.94	262.59	318.32
30	48,000	223.26	237.62	248.48	297.25
35	56,000	219.94	228.82	238.41	282.20
40	64,000	217.45	222.22	230.85	270.92
45	72,000	215.52	217.08	224.97	262.14
50	80,000	213.97	212.98	220.27	255.12
55	88,000	212.70	209.62	216.42	249.38
60	96,000	211.65	206.82	213.22	244.59
65	104,000	210.75	204.45	210.51	240.54
70	112,000	209.99	202.42	208.18	237.07
75[a]	**120,000**	**209.32**	**200.66**	**206.17**	**234.06**
80	128,000	208.74	199.12	204.40	231.42
85	136,000	208.23	197.76	202.85	229.10
90	144,000	207.78	196.55	201.46	227.03
95	152,000	207.37	195.47	200.23	225.19
100	160,000	207.00	194.50	199.11	223.52

a. Base case. Illustration based on typical mid-1995 U.S. costs.

compaction and steam/water granulation units are moderately affected compared with the other processes.

16.9 References

1. Food and Agriculture Organization of the United Nations. 1995. FAOSTAT•PC, Computerized Information Series, Rome, Italy.
2. Personal Communications With Various Producers and Industry Associations, March-June 1995.
3. Salladay, D. G., and W. H. Paulson. 1984. "Development of TVA Pressure Reactor for Production of Ammonium Phosphates and Its Retrofit in Conventional Plants," 34th Annual Meeting of the Fertilizer Industry Round Table, October 30 - November 1, 1984.
4. Green, H., D. J. Brunner, R. O. Britt, and A. P. Super. 1978. "Panel Discussion: Recent Pipe Cross Experiences," IN *Proceedings of the 28th Annual Meeting Fertilizer Industry Round Table*, pp. 46-54, Atlanta, GA, U.S.A.

5. Salladay, D. G., M. S. Traweek, and N. H. Louizos. 1985. "Production of Monoammonium Phosphate Sulfate With TVA Pressure Pipe-Cross Reactor," IN *Proceedings of the 35th Annual Meeting Fertilizer Industry Round Table*, pp. 102-113, Atlanta, GA, U.S.A.

6. Cheval, J. L. 1981. "Quality Control in Bulk Blending Blenders Point of View," IN *Proceedings of the 31st Annual Meeting Fertilizer Industry Round Table*, pp. 120-132, Washington, D.C., U.S.A.

7. Canadian Fertilizer Institute. 1986. The CFI Guide of Material Selection for the Production of Quality Granular Blends, Ottawa, Ontario.

8. Leonard, J. E., and T. M. Young. 1989. "Fertilizer Blending in Ireland–Potential Application of Its Unique Features to Developing Country Locations," IN *Supplying Quality Multinutrient Fertilizers in the Latin American and Caribbean Region – Emphasizing Bulk Blending and the Complementary Role of Granulation*, Workshop Proceedings, pp. 142-172, J. J. Schultz and E. D. Frederick (Eds.), SP-14, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

9. Rodriguez, C. M. 1989. "Development of Compaction and Bulk Blending in Guatemala," IN *Supplying Quality Multinutrient Fertilizers in the Latin American and Caribbean Region – Emphasizing Bulk Blending and the Complementary Role of Granulation*, Workshop Proceedings, pp. 72-82, J. J. Schultz and E. D. Frederick (Eds.), SP-14, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

10. Schultz, J. J. 1989. *Production of Granular NPKs in Ammonium Phosphate Plants–Some Important Differences*, Technical Bulletin T-36, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

Chapter 17. Secondary Nutrients and Micronutrients

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Chapter 17. Secondary Nutrients and Micronutrients

Increased knowledge about secondary nutrients and micronutrients, including plant requirements, nutrient sources, and methods of application, has resulted in their increased use. Improvements in soil testing and plant analyses have provided more knowledge about plant needs and the wide variations in plant responses to these nutrients. Higher crop yields and the use of high-analysis NPK fertilizers also have resulted in increased needs for these nutrients.

The secondary nutrients are calcium, magnesium, and sulfur. Concentrations of these nutrients in plant tissues generally are lower than those of the primary nutrients (nitrogen, phosphorus, and potassium) but are higher than those of the micronutrients. The seven micronutrients are boron, chlorine, copper, iron, manganese, molybdenum, and zinc. Because chlorine deficiencies rarely occur in nature, most discussions on supplying micronutrient fertilizers are confined to the other six micronutrients.

17.1 Secondary Nutrients

Calcium, magnesium, and sulfur are designated as secondary nutrients. Plants require these nutrients in fairly substantial quantities for normal growth, but fertilizer sources generally are not applied at rates as high as those of the primary nutrients. Actual requirements and uptake of secondary nutrients vary with plant species and soil conditions. Deficiencies of magnesium and sulfur are becoming more common, while those of calcium are not reported.

17.1.1 Calcium and Magnesium

Calcium is relatively abundant in soils, and calcium rarely limits crop production per se. Low levels of exchangeable calcium in soils result in increased soil acidity, which usually results in reduced growth of most crops. Using lime applications to correct soil acidity to recommended soil pH levels will provide sufficient calcium for crops because liming materials contain calcium (Table 17.1).

Magnesium deficiencies are found mainly on acid, sandy soils and on organic soils containing free calcium carbonate. Magnesium deficiencies also can be accentuated by high levels of available potassium or on soils that have been limed for many years with calcitic limestone, which is very low in magnesium.

Products – Fertilizer sources of calcium include calcium nitrate, a highly soluble nitrogen product, and

Table 17.1. Some Calcium Sources

Source	Chemical Formula	% Ca
Lime Materials		
Blast furnace slag	$CaSiO_3$	29
Calcitic limestone	$CaCO_3$	33
Dolomitic limestone	$CaCO_3 + MgCO_3$	21
Hydrated lime	$Ca(OH)_2$	46
Marl	$CaCO_3$	24
Fertilizers		
Calcium nitrate	$Ca(NO_3)_2$	19
Calcium ammonium nitrate	$NH_4NO_3 + CaCO_3$	
Phosphate rock	$3Ca_3(PO_4)_2 \bullet CaF_2$	33
Superphosphate, normal	$Ca(H_2PO_4)_2 + CaSO_4 \bullet 2H_2O$	20
Superphosphate, triple	$Ca(H_2PO_4)_2 + CaSO_4 \bullet 2H_2O$	13
Soil Amendments		
Gypsum	$CaSO_4 \bullet 2H_2O$	22

Adapted from Follett et al. [1].

Table 17.2. Some Magnesium Sources

Source	Formula	Wt % Mg	Form
Dolomite	$CaCO_3 \bullet MgCO_3$	8-20	Powder
Magnesium chloride	$MgCl_2$	25	Flake
Kieserite	$MgSO_4 \bullet H_2O$	18-26	Powder
Magnesium sulfate (anhydrous)	$MgSO_4$	20	Crystal
Epsom salts	$MgSO_4 \bullet 7H_2O$	10	Crystal
Magnesium hydroxide	$Mg(OH)_2$	35-45	Powder
Magnesium nitrate	$Mg(NO_3)_2 \bullet 2H_2O$	13	Flake
Magnesium oxide	MgO	54-58	Powder
Magnesium oxysulfate	$MgO,MgSO_4$	28 or 36	Granule
Sulfate of potash magnesia	$K_2SO_4 \bullet 2MgSO_4$	11	Powder
Magnesium carbonate (or magnesite)	$MgCO_3$	28	Powder

Adapted from Follett et al. [1].

normal and triple superphosphate. Phosphate rock (PR) also contains calcium; however, because its solubility is quite low, PR must be finely ground and applied to acid soils to be available to plants. Gypsum is an important source of calcium for groundnut. Although its solubility is somewhat limited, gypsum is sufficiently available for plants. Gypsum also is a soil amendment for reclaiming sodic soils for agricultural production.

The most economical way to correct magnesium deficiencies on acid soils is to apply dolomitic limestone. However, if soil pH levels are above 6.0, the sources listed in Table 17.2 can be used. Magnesium sulfate, magnesium oxide, and potassium-magnesium sulfate are the most common magnesium sources [2]. Recommended application rates for magnesium range from 10 to 40 kg/ha, depending on the magnesium requirement of the crop as well as soil test levels [3].

Benefits of Liming – Liming materials provide ample supplies of calcium (and of magnesium if dolomite is used) for crops and also increase the soil pH to recommended levels; thus, liming has additional benefits for plant nutrition [4]. For example, nitrogen fixation by legume crops and nitrification of ammonium-nitrogen to nitrate-nitrogen are microbial processes which are optimal in neutral soils. Similarly, phosphorus availability is highest in soils with a pH of 6 to 7; below this pH range, phosphorus reacts with aluminum and iron oxides to form insoluble compounds in soil, and insoluble calcium phosphates are formed above this range. Likewise, availability of most micronutrients is highest in soil with a pH range of 6 to 7. Except for molybdenum, the availability of the micronutrients decreases with an increase in soil pH. Toxicities of some micronutrients, especially manganese, also occur in very acid soils. Conversely, overliming soils can result in micronutrient deficiencies.

17.1.2 Sulfur

Most of the soil sulfur is in the soil organic matter and is highest in the surface soil. Sulfur in organic matter must be mineralized to the sulfate form to become available to plants. Conversely, sulfate can be immobilized when bacteria decompose crop residues high in carbon. Sulfate-sulfur also can be converted to unavailable sulfides under reducing conditions caused by poor drainage and flooded soil conditions [5].

Recommended application rates for sulfur range from 10 to 50 kg/ha, depending on the level of available sulfur in the soil and the sulfur requirements of the crop. Sometimes a general recommendation for 10 pounds of sulfur per acre is made without conducting soil tests for available sulfur. Knowledge of other inputs, such as sulfur contained in N-P fertilizers, atmospheric deposition of sulfur, and sulfate-sulfur in irrigation water, as well as crop needs and levels of available sulfur in soil should be considered when deciding if sulfur applications to soil are warranted.

Products – There are many sulfur sources for application to soil (Table 17.3). Normal superphosphate contains as much as 12% sulfur as a result of the manufacturing process using sulfuric acid. Most high-analysis phosphate fertilizers contain very little sulfur, although inclusion of sulfuric acid in the granulation process results in 2%-3% sulfur in the final products.

The main sulfur sources are ammonium sulfate, ammonium thiosulfate, potassium sulfate, and potassium-magnesium sulfate, which contain 17%-26% sulfur [6]. Elemental sulfur also is used, but it must be applied to soil in powder form to be quickly oxidized to the sulfate form. This microbial process also results in the formation of acid, which reduces the soil pH. The micronutrient sulfates also provide available sulfur, but their application

Table 17.3. Some Sulfur Sources

Source	Chemical Formula	% S
Ammonium sulfate	$(NH_4)_2SO_4$	24
Ammonium thiosulfate	$(NH_4)_2S_2O_3$	26
Ammonium polysulfide	$(NH_4)_2S_x$	40
Epsom salt	$MgSO_4 \cdot 7H_2O$	13
Gypsum	$CaSO_4 \cdot 2H_2O$	19
Potassium-magnesium sulfate	$K_2SO_4 \cdot 2MgSO_4$	22
Potassium sulfate	K_2SO_4	18
Sulfur, elemental	S	30-100
Sulfuric acid	H_2SO_4	33
Superphosphate, normal	$Ca(H_2PO_4)_2 + CaSO_4 \cdot 2H_2O$	12-14
Superphosphate, triple	$Ca(H_2PO_4)_2 + CaSO_4 \cdot 2H_2O$	1

Adapted from Follett et al. [1].

rate usually is so low that they do not provide adequate sulfur for crop needs on sulfur-deficient soils.

17.1.3 Incorporation in Granular Fertilizers

The International Fertilizer Development Center conducts an annual survey of NPK granulation plants in the United States. By 1995 the number of operating plants decreased to only 25, from about 200 in 1965. No estimate has been made of the number of NPK granulation plants worldwide, but almost all of these plants, plus all nitrophosphate plants, incorporate secondary nutrients, primarily calcium and/or sulfur, in their products as the preferred, least expensive raw materials. Magnesium is different and is usually incorporated as a special additive.

Calcium is most often incorporated in granular NPK grades as single superphosphate (SSP), which contains about 19%-22% calcium depending on the PR source. A grade such as 8-8-8 based on ammoniating solution, sulfuric acid, and SSP contains about 7% calcium. The use of nongranular triple superphosphate (TSP), which contains about 13% Ca, in NPK formulations is declining because production of nongranular TSP is decreasing.

Nitrophosphate products, either granular or prilled, contain calcium in the NP(K) grades and in the ammonium nitrate coproduct (see Chapter 13). NPK grades such as 13-13-13 retain some of the calcium originally in the PR because the calcium nitrate is never completely removed in the Odda process crystallization step. The residual calcium is converted primarily to dicalcium phosphate when ammoniation is carried out to produce the NPK products. The separated crystalline calcium nitrate is dissolved and converted to ammonium nitrate solution and solid calcium carbonate by addition of ammonia and carbon dioxide. The ammonium nitrate solution is concentrated and prilled or granulated with addition of calcium carbonate to produce calcium ammonium nitrate (CAN). CAN typically contains 26% or 27% N and 20% to 24% calcium carbonate. In some processes, a small amount of gypsum is mixed with the calcium carbonate prior to addition to the concentrated ammonium nitrate solution [7].

Most of the magnesium-containing materials shown in Table 17.2 may be used for incorporation in granular fertilizers. Dolomite and kieserite are added to nitrophosphates to obtain grades such as 12-12-17-1.2 Mg and 13-9-16-2.4 Mg [8]. The most common source of magnesium for U.S. granulation plants is probably potassium magnesium sulfate, also called sulfate of potash magnesia. For granulation without a pipe-cross reactor, magnesium chloride should be avoided in formulations using sulfuric acid because of the possibility of producing corrosive hydrogen chloride vapor or ammonium chloride aerosol. Magnesium nitrate should not be used in significant proportion in dry fertilizers because of its fire and explosion risk.

The predominant sources of sulfur in NPK products are sulfuric acid, which forms ammonium sulfate in the ammoniator-granulator, and SSP, which contains about 12% S as gypsum. Byproduct crystalline ammonium sulfate (24% S) is also frequently used. Gypsum is used, including natural gypsum, recovered gypsum from flue gas desulfurization, and, where environmental regulations permit, phosphogypsum. Of course, all the sulfate salts listed as magnesium sources in Table 17.2 may also be used as sulfur sources.

17.1.4 Bulk Blending or Direct Application

In addition to secondary nutrients that are incorporated in granular mixtures, secondary nutrient materials are also used for direct application and bulk blending. Powdered sources are normally used for direct application only; bulk blending requires granules 2-4 mm in size, crystals, or compacted material. These large particle size materials are also excellent secondary nutrient sources for direct application. The following are some of the more important secondary nutrient sources for direct application and bulk blending:

Direct application only
- Crushed dolomite, 20% Ca, 12% Mg
- Basic slag, up to 33% Ca
- SSP, 20% Ca
- Ground phosphate rock, 30%-35% Ca
- Nongranular TSP, 13% Ca
- Calcium nitrate, 19% Ca
- Fine potassium magnesium sulfate, 11% Mg, 22% S
- Gypsum, 23% Ca, 19% S
- Fine ammonium sulfate, 24% S

Bulk blending or direct application
- Granular SSP and TSP
- Pelletized dolomite
- Granular gypsum
- Ammonium sulfate, granular or coarse crystal
- Potassium magnesium sulfate, compacted or coarse crystal
- Calcium ammonium nitrate, granular, 9% Ca

Also, some of the magnesium sources listed in Table 17.2 may be applied directly.

17.1.5 Addition to Fluid Fertilizers

Secondary nutrients are an important component of the fluid fertilizer market, and many source materials are available for use in clear solution and suspension formulations. Most of the materials for clear solutions may also be used in suspensions, but they are seldom used because they are generally more expensive. The polysulfide solutions should not be mixed with acidic materials – dangerous hydrogen sulfide gas may be evolved! The following list gives secondary nutrient sources for solutions and suspensions are [9]:

Calcium in solutions
- Chelate solutions and powders, 5%-10% Ca
- Calcium nitrate, granular or solution
- Calcium nitrate plus ammonium nitrate solutions
- Calcium lignosulfonate solution

Calcium in suspensions
- Fluid lime (limestone-clay suspension)
- Gypsum, 50% flowable emulsion

Magnesium in solutions
- Epsom salts, $MgSO_4 \cdot 7H_2O$
- Chelated solutions and powders, 1%-6% Mg
- Magnesium sucrate solubilized granules
- Magnesium nitrate, flake or solution (7-0-0-6 Mg)
- Magnesium chloride, $MgCl_2 \cdot 6H_2O$, flake or solution

Magnesium in suspensions
- Magnesium oxide
- Potassium magnesium sulfate, fine
- Magnesium carbonate
- Fluid lime (dolomitic)

Sulfur in solutions
- Ammonium thiosulfate, 12-0-0-26S solution
- Ammonium sulfate, crystals or 8-0-0-9S solution
- Epsom salts, 13% S
- Ammonium polysulfide, 20-0-0-40S solution with aqua or anhydrous ammonia
- Potassium polysulfide, 0-0-22-22S solution
- Potassium thiosulfate, 0-0-25-17S

Sulfur in suspensions
- Elemental sulfur, 52%, flowable emulsion
- Elemental sulfur, 90%, wettable powder or degradable granule
- Potassium magnesium sulfate, fine
- Potassium sulfate

17.2 Micronutrients

Deficiencies of micronutrients in crops have been increasing throughout the world. Some reasons include higher crop yields, use of high-analysis NPK fertilizers, and decreased use of animal manures on many agricultural soils. Also, micronutrient deficiencies have been verified in many locations through increased use of soil testing and plant analyses.

17.2.1 Micronutrient Applications for Crops

When micronutrient deficiencies are compared with regard to the worldwide importance of various crops, deficiencies of zinc, manganese, and copper are most important, especially for cereal crops. Boron is of greatest concern for some legume crops, cotton, and root crops such as groundnut and sugarbeets. Iron deficiency is of greatest concern for crops grown on calcareous soils. Molybdenum is especially important for legumes because of its role in nitrogen fixation.

Boron – Recommended boron application rates range from 0.5 to 2.0 kg/ha and should be carefully followed [10]. Crop species vary considerably in their boron requirement as well as in their tolerance to over-applications. Residual effects of applied boron also vary with soil conditions, with the lowest effects found on acidic sandy soils in areas of high rainfall. Some crops with high boron requirements are alfalfa, cotton, peanuts, irrigated corn, root crops, soybean, and some fruits and vegetables.

Copper – Most copper deficiencies are found on organic soils and on sandy soils. Recommended copper application rates range from 1 to 10 kg/ha. Residual effects of copper are very marked, with responses being noted up to 8 years after application, so annual applications usually are not necessary [3]. Soil tests should be used to monitor the copper buildup in soils where copper is applied. Some crops with high copper requirements are cereals, corn, clover, and some fruits and vegetables.

Iron – Although iron is the most abundant element in soils, levels of available iron often are limiting in calcareous soils, and to a much lesser extent in sandy soils in high-rainfall areas. Soil applications of most iron sources are not effective for crops, so foliar sprays are the recommended control method [3]. Plant species vary considerably in their susceptibility to iron chlorosis. Growing iron-tolerant species or varieties within a species is one of the main methods of controlling iron chlorosis on low-iron soils.

Manganese – Deficiencies of manganese are found mainly on well-drained neutral or calcareous soils or organic soils. Recommended manganese application rates range from 2 to 20 kg/ha. There are no residual effects from applied manganese because of oxidation of the available divalent form to the tetravalent form, which is unavailable to plants [3]. Some crops with high manganese requirements are cereals, cotton, peanuts, soybean, sugarcane, and fruits and vegetables.

Molybdenum – Deficiencies of molybdenum are found on acidic soils and may be corrected by liming soils to pH 6.0. Because the amounts needed to correct molybdenum deficiencies are very low, seed treatment (supplying 60-120 g/ha) is the recommended method [3]. Deficiencies are mainly found in legume crops, because molybdenum is essential for nitrogen fixation. However, some vegetable crops also are sensitive to molybdenum deficiencies.

Zinc – Deficiencies of zinc are more widespread than those of the other micronutrients. Deficiencies occur in many soil types with pH levels > 6.0, especially in soils with low organic matter [11]. As with copper, residual effects of applied zinc are substantial, with responses found at least 5 years after application. Recommended zinc application rates range from 1 to 10 kg/ha [3]. Some crops with high zinc requirements are corn, citrus, field beans, rice, and some fruits and vegetables.

17.2.2 Products

Micronutrient sources vary considerably in their physical state, chemical reactivity, cost, and availability to plants [12]. There are four main classes of micronutrient sources – inorganic, synthetic chelates, natural organic complexes, and fritted glass products (frits).

Inorganic sources include oxides, carbonates, borates, molybdates, and metallic salts such as sulfates, nitrates, and chlorides (Table 17.4). The sulfates are the most commonly used inorganic sources and are sold in crystalline or granular form. Oxides of zinc and manganese also are commonly used and are sold as fine powders and in granular form. Because oxides are water-insoluble, their immediate effectiveness for crops is rather low in granular form. Also, the divalent form of manganese will oxidize to unavailable forms in soil, so there is no residual availability of manganese fertilizers.

Synthetic chelates are formed by combining a chelating agent with a metal through coordinate bonding. Stability of the metal-chelate bond affects availability to plants of the chelated micronutrients (copper, iron, manganese, and zinc). An effective chelate is one in which the rate of substitution of the chelated metal for cations in the soil is quite low; thus, the metal is maintained in chelate form. The relative effectiveness for crops per unit of micronutrient as soil-applied chelates may be two to five times higher than that of the inorganic sources, while relative costs may be 5 to 100 times higher.

Natural organic complexes are made by reacting metallic salts with some organic byproducts of the wood-pulp industry or related industries. Several classes of these compounds are the lignosulfonates, phenols, and polyflavonoids. The type of chemical bonding between the metal and the organic compounds is not well understood. Although these complexes are less costly per unit of micronutrient than the chelates, they also are usually less effective than the chelates.

Fritted micronutrients (frits) are glassy products in which solubility is controlled by particle size and matrix composition. Frits generally are used only on sandy soils in regions of high rainfall where leaching occurs. This class of micronutrients is more suited for maintenance programs than for correcting severe micronutrient deficiencies. Therefore, frits have only a very small share of the market.

Industrial byproducts now are being used as micronutrient fertilizers in the United States because they are less costly per unit of micronutrient than products manufactured specifically for the purpose [13]. Oxides of zinc and manganese are the most common byproducts used. Because these oxides are dusty and difficult to handle, they are partially acidulated with sulfuric acid and are called oxysulfates. Acidulation results in formation of water-soluble sulfates, which may be more available to plants. The percentage of water-soluble zinc or manganese in these oxysulfates is directly related to the degree

Table 17.4. Some Micronutrient Sources

Source	Solubility in H_2O	% Element
Boron		
$Na_2B_4O_7 \bullet 5H_2O$ (fertilizer borate)	Soluble	20
$Na_2B_4O_7 \bullet 10H_2O$ (borax)	Soluble	11
$Ca_2B_6O_{11} \bullet 5H_2O$ (colemanite)	Slightly soluble	10
Copper		
$CuSO_4 \bullet 5H_2O$	Soluble	25
CuO	Insoluble	75
Iron		
$FeSO_4 \bullet 7H_2O$	Soluble	20
$Fe_2(SO_4)_3 \bullet 9H_2O$	Soluble	20
FeEDDHA (chelate)	Soluble	6
Manganese		
$MnSO_4 \bullet xH_2O$	Soluble	24-30
$MnCO_3$	Insoluble	31
MnO	Insoluble	41-68
Mn oxysulfate	Variable	30-50
Molybdenum		
$Na_2MoO_4 \bullet 2H_2O$	Soluble	39
$(NH_4)_2MoO_4$	Soluble	49
MoO_3	Insoluble	66
Zinc		
$ZnSO_4 \bullet H_2O$	Soluble	36
$ZnSO_4 \bullet 7H_2O$	Soluble	22
ZnO	Insoluble	60-78
Zn oxysulfate	Variable	18-60
ZnEDTA (chelate)	Soluble	6-14

Adapted from Mortvedt [12].

of acidulation of the oxide by sulfuric acid. Research results have shown that at least 40% of the total zinc or manganese in granular oxysulfates should be in water-soluble form to be effective for crops [11].

17.2.3 Methods of Application

Methods of micronutrient application include application directly to soil, in foliar sprays, and as seed treatment. The most common application method for crops is soil application [12]. Because recommended application rates usually are less than 10 kg/ha (on an elemental basis), it is difficult to achieve uniformity when individual micronutrient sources are applied separately in the field. Therefore, both granular and fluid fertilizers are commonly used as carriers of micronutrients. Including micronutrients with mixed fertilizers is a convenient method of application, and it allows a more uniform distribution with conventional application equipment. Costs also are reduced by eliminating a separate micronutrient application.

Micronutrients can be combined with NPK fertilizers by dry mixing, bulk blending with granular fertilizers, coating onto granular fertilizers, incorporation during the manufacturing process, and mixing with fluid fertilizers [12].

17.3 Preparation of Fertilizers Containing Micronutrients

Micronutrients can be applied in many ways including foliar application, seed treatment, root dipping of transplanted seedlings, and application with pesticides. However, the most popular method is to apply the micronutrients in admixture with the primary nutrient fertilizer that the farmer regularly uses. The first reason for this popularity is convenience; the farmer does not have to devote extra labor to micronutrient application if the micronutrient carrier is a fertilizer that he is already using. A second reason is that uniformity of application is much easier when the micronutrient material is mixed with a much larger volume of fertilizer. The purpose of this section is to describe some of the methods that are used to produce fertilizer mixtures containing micronutrients and to discuss their advantages and disadvantages.

17.3.1 Reactions of Micronutrient Materials With Fertilizers

It should be recognized that when micronutrient materials are mixed with other fertilizers, chemical reactions are likely to occur. Lehr [14] has described many of the numerous chemical reactions. The effect of these chemical reactions may or may not be important. A water-soluble micronutrient source may be partially or wholly converted to a water-insoluble compound. Conversely, water-insoluble sources may be converted to water-soluble forms. The gain or loss of water solubility may or may not be important. Some examples follow.

Soluble salts of copper, manganese, iron, and zinc are likely to become insoluble when incorporated in ammonium phosphates or ammoniated mixed fertilizers. The reaction forms one of several metal ammonium phosphates such as $ZnNH_4PO_4$. In general, the water solubility decreases with increase in pH of the fertilizer product. Loss of water solubility does not necessarily imply loss of effectiveness but may delay it. Sodium borate when incorporated in ammoniated fertilizers containing calcium may become partially or wholly insoluble presumably because of formation of calcium borate. (The boron in calcium borate is insoluble in cold water but soluble in boiling water.) This effect has been noted with nitrophosphate fertilizers and may occur with other formulations.

Many water-insoluble micronutrients (oxides, carbonates, and silicates) become at least partially soluble when incorporated in superphosphates or mixed fertilizers containing unammoniated superphosphate.

Some insoluble oxides become soluble when incorporated in ammonium polyphosphate fertilizers. In practice, the ammonium polyphosphate liquid fertilizers are widely used in some countries, and zinc oxide often is added and dissolved in them. However, solid fertilizers containing ammonium polyphosphate also will convert zinc oxide (or carbonate) to a soluble form.

Zinc oxide and cuprous oxide (Cu_2O) become partially soluble when incorporated in ammonium nitrate or nitrogen solutions such as urea ammonium nitrate solutions. The solubility can be increased by adding enough ammonia to keep the solution pH at 7 to 8. The soluble compounds formed are presumed to be zinc nitrate amine and copper nitrate amine. Because the addition of copper compounds to ammonium nitrate is said to sensitize its decomposition, copper is not used in some countries for solid fertilizers containing a high percentage of both ammonium nitrate and chloride [15]. In TVA tests, the addition of zinc to ammonium nitrate did not cause any increase in explosibility.

Coating of micronutrient materials on granular fertilizers would be expected to result in less reaction than would incorporation, but even so, substantial gain or loss of water solubility of the micronutrient has been found to occur with coated materials.

When chelated micronutrients are incorporated in fertilizers, there is less likelihood of reactions that cause loss of water solubility. Some granulation processes, however, involve high temperature and use of ammonia and acids which can cause decomposition or the organic chelate and consequent loss of availability. Frits are ordinarily insoluble and remain so when incorporated in neutral fertilizers, but an increase in solubility was observed when frits were incorporated in triple superphosphate.

17.3.2 Dry Mixing

Perhaps the simplest method for producing mixtures containing micronutrients is to dry-mix the micronutrient material with the primary nutrient materials. This method works well with nongranular materials. Segregation usually is not serious when all materials are fine, such as less than 1 mm in particle size. Fine materials, however, are likely to cake, and some micronutrient materials may promote caking. Caro et al. [16] noted increased caking of some formulations of dry-mixed fertilizer when zinc sulfate was added.

Nongranular dry-mixed fertilizers are not popular in most areas but are still used in some. One of these areas is in Florida where there are multiple micronutrient deficiencies. Hundreds of formulations are used, often custom mixed, so granulation is impractical.

Dry mixing by farmers may be practical in some countries. Bautista et al. [17] reported that in the Philippines farmers were supplied with fine granular zinc sulfate heptahydrate (22% Zn) in 5-kg bags and were instructed to mix it with the fertilizer used for basal application for rice to provide about 1 kg of Zn per hectare. The paper did not say what the primary nutrient fertilizer was, but prilled urea is the most popular fertilizer in the Philippines.

17.3.3 Bulk Blending

Bulk blending is a form of dry mixing in which all of the nutrients are granular (e.g., 1.0-3.3 or 2-4 mm). Micronutrient materials are available in granular form for use in bulk blends. One problem is segregation; unless all materials are closely matched in particle size, segregation will occur in piles, in bins, in spreader trucks, or during mechanical spreading. If the blends are bagged from a bin, disparity in particle size will lead to wide variation in micronutrient content from one bag to another. This variation can cause poor results because of oversupply in some spots and undersupply in others.

Hoffmeister [18] has outlined some methods for preventing segregation of blends. A blending system that is used in Ireland effectively minimizes segregation. The materials for blending are fed continuously from separate hoppers by weigh belts to a connecting belt where the materials form layers. The collecting belt discharged into a continuous mixer which discharges to a small hopper over the bagging machine. Since the bagging hopper is being continuously filled and emptied, there is little chance of segregation. Segregation can still occur in bags, but it is not likely to be serious unless there is extreme disparity in particle size. Segregation can also occur in the field by the action of some types of mechanical spreaders, but this is not likely to be a problem in developing countries.

Another problem with blends is the sparse distribution of micronutrient carriers. For example, only one granule in thirty may be a micronutrient carrier. The larger the granules the less likely that any one plant will have a micronutrient granule within reach of its root system. Also, the higher the concentration of micronutrient material, the fewer the granules required to provide a given application rate. This problem is not unique to bulk blends but would also be encountered in direct application of granular micronutrient materials. One method for coping with the problem is intentional dilution of the micronutrient with either an inert material or a primary nutrient material. For example, micronutrient chelates are granulated with clay or vermiculite to produce granules containing 1%-5% of a micronutrient element or similar percentages of two or more micronutrients. Several products are available that contain 1%-10% of one or more micronutrients granulated with one or more primary nutrients. These products may be used in blends.

17.3.4 Incorporation of Micronutrients in Granular Fertilizers

In most cases incorporation of micronutrients in granular fertilizers containing one or more primary elements is not technically difficult. However, it is often uneconomical to produce small lots of special grades in large granulation plants, so the practice is economical only when there is a substantial demand for micronutrient-enriched fertilizers. In several countries in Europe, there is a need for boron for root crops such as sugar beets and fodder turnips. Because these crops are important ones, there is sufficient demand to justify an economical scale of operation. The boron often is incorporated in a superphosphate-based PK mixture in amounts to supply 0.2%-0.5% B. One company in Germany produces a granular 0-15-25 grade containing 2.5% borax (about 0.3% B) in which the phosphorus is supplied by Rhenania phosphate. Production of ground and granulated PR containing added "trace elements" has been reported in France. Copper deficiencies often are encountered in Denmark, and NPK fertilizers containing copper are marketed there. One German company has produced an NPK fertilizer in which scrap metal filings or turnings are incorporated (copper, zinc, or brass). One company in Ireland produces a fertilizer based on superphosphate and ammonium sulfate-containing boron added as colemanite.

Several companies in the United States market "premium" fertilizers containing small percentages of two, three, or more micronutrients. For example, mixtures containing manganese, iron, and zinc are intended for soybeans. One company markets premium fertilizer containing polyphosphates with zinc and iron incorporated in the polyphosphate. Boron is recommended for cotton in portions of Alabama, Georgia, and Mississippi, and mixed, granular fertilizers are marketed containing 0.2% or 0.3% B. In general, no important technical problem would be expected in incorporating the small amounts of micronutrients that are commonly used. When larger percentages of micronutrients are incorporated, some problems may occur. TVA has made a series of tests aimed at producing materials with relatively large percentages of micronutrients for use in bulk blending. Concentrated superphosphate was granulated with steam in a conventional drum granulator with addition of anhydrous sodium tetraborate ($Na_2B_4O_7$); a small amount of ammonia was added to decrease the free acid content of the superphosphate. The scale of the operation was 10 tph. The product after drying contained 47% available P_2O_5 and 3.4% B [19]. No unusual problems were encountered when using the anhydrous borate. When the pentahydrate was used, however, large balls formed in the dryer, and the granules were soft and weak. This condition was attributed to release of water of hydration in the dryer. It was concluded that the anhydrous sodium tetraborate should be used for production of this product.

In pilot-plants tests ammonium nitrate was granulated with zinc oxide, borax, or both to produce granules containing 2.3% Zn and 0.5% B, or 1.9% Zn and 0.7 B [20]. The micronutrient materials were added to hot concentrated ammonium nitrate solution (95% NH_4NO_3), and the mixture was granulated in a pan granulator. The granules were dried and screened, and the fines and crushed oversize were recycled to the granulator. The boron content of the products was fully water soluble, and the zinc content was 30%-40% water soluble. The compound $3Zn(OH)_2 \bullet NH_4NO_3$ was identified in the water-insoluble portion of the zinc-containing products. The water-soluble zinc may have been zinc amine nitrate. Tests showed that the physical properties of the products were as good as straight ammonium nitrate and that the sensitivity of ammonium nitrate to detonation was not increased by borax or zinc oxide. In subsequent work, granular ammonium nitrate containing up to 8% Zn was produced by addition of zinc oxide. One company now markets a product containing 30% N and 10% Zn.

Zinc oxide was incorporated in ammonium polyphosphate (15-60-0) during granulation without difficulty at levels of 1%-3% Zn; 80%-100% of the zinc was water soluble [20]. Although the zinc oxide did not react with ammonium polyphosphate in absence of water, when the granules were placed in the soil the ammonium polyphosphate and 80% of the zinc dissolved and diffused in the soil. In similar tests with diammonium phosphate-zinc oxide granules, most of the diammonium phosphate dissolved and diffused into the soil while the zinc remained at the granule site as $ZnNH_4PO_4$.

Substantial percentages of iron, manganese, and copper were soluble when appropriate compounds of these elements were incorporated in granular ammonium polyphosphate.

17.3.5 Coating of Micronutrients on Granular Fertilizers

When small percentages of micronutrient materials are to be added to granular fertilizers, they may be added as a coating on the surface of the granules. This method has several advantages. The coating may be added to homogeneous granular compound fertilizers, to bulk blends, or to straight (single nutrient) fertilizers. The coating may be added just before shipment, thereby avoiding storage of additional grades. Each granule is coated with a micronutrient as opposed to bulk blends containing granular micronutrient materials in which only one granule in thirty may be a micronutrient carrier. The operation is simple, and the equipment is inexpensive. Conceivably the coating could be done at the village level or by individual farmers.

One drawback of the coating method is that the addition of a micronutrient material (whether coated or not) lowers the primary nutrient grade. This is a problem in countries where only prescribed, registered grades can be marketed. Bulk blenders, however, can easily deal with this problem. In areas where they are required to make only registered, whole-numbered grades, the grade is often adjusted by adding a filler such as crushed, screened limestone; thus, dilution by a micronutrient can be compensated for by adding less filler. Another method for grade adjustment is to use two materials of different concentration, such as ammonium sulfate and urea, in varying proportions. Finally, the problem can be solved by legislation or regulation if the appropriate officials recognize the problem.

In some states of the United States, bulk blenders are not required to produce guaranteed grades; the farmer is invoiced for the separate materials, and the merchant is responsible only for the analysis of the materials used in the blend. He will then mix the materials as a service to the farmer. This system has the advantage that prescription mixing is easy. Disadvantages are that infractions such as adulteration or errors in proportions are difficult to detect and the merchant has no incentive to produce uniform mixtures. In addition, bulk blending by local retailers has some disadvantages in developing countries; bulk materials cannot be transported within the country without loss or deterioration of quality. The alternative – to transport materials in bags to a local mixer who will make various mixtures and bag them – is obviously expensive.

Some micronutrient materials will adhere to some granular fertilizers without a binder. One example is a finely powdered zinc oxide (80% Zn) which was applied as a coating to granular ammonium nitrate in a rotary drum such as is commonly used for coating fertilizers with clay or other conditioning agents. Up to 8% Zn was applied as a zinc oxide coating with up to 93% adherence in industrial-scale equipment [19]. However, adherence decreased to 47% after 6 months' bagged storage. The addition of steam in the coating drum increased adherence after 6 months' storage to 72%. More complete adherence was obtained in pilot-plant tests with lower percentages of zinc oxide or by using a small amount of 70% ammonium nitrate solution as a binder. Achorn and Balay [21] have described plant practices for adding micronutrients to bulk blends.

Most micronutrients require a binder for good adherence on the surface of granular fertilizers. The binder may be oil, wax, water, or fertilizer solution. TVA has developed and studied procedures for coating. A batch method was selected because most bulk blenders in the United States use a batch mixer. The batch method consisted of the following steps [22]:

1. Charge the mixer with the granular fertilizer to be blended and the powdered micronutrient.

2. Blend dry for 1 minute by rotating the drum mixer.
3. Add the liquid binder through a spray nozzle while continuing rotation of the mixer (1 minute).
4. Continue mixing for 1 minute.
5. Discharge the coated material.

This procedure gave a more uniform coating than did the addition of the binder before mixing. Silverberg et al. [23] reported the results of tests with this procedure in some detail. In general the best results were obtained when the micronutrient material was finely ground (minus 100-mesh or finer). Oils ranging from No. 2 fuel oil to used motor oil gave good results, but the less viscous oils were absorbed into the more porous granular fertilizer causing some loss of adherence with time. A 1:2 mixture of Nos. 2 and 6 fuel oil and a 1: 2 mixture of microcrystalline wax and No. 2 fuel oil gave the best long-term adherence. The amounts of binder ranged from 0.5% to 5.0% of the mixture. In some cases, the addition of 2% clay improved adherence when water was used as a binder. Ammonium polyphosphate solution (11-37-0) was an excellent binder for zinc, manganese, and iron oxides. The oxides reacted with the solution to give a hard, smooth coating. As much as 13% of a mixture of these oxides was coated on granular TSP using 3% of the APP solution as a binder. Adherence was 100% even after 2 weeks' storage. Achorn and Balay [21] have described some U.S. plant practices for coating micronutrients on blends.

Use of a 64% solution of ammonium nitrate as a binder for coating micronutrients on bulk blends has been described [24]. Over 97% adherence was obtained. The use of liquid fertilizers as a binder was patented [25], and the process – trade named "Micro-Charger" – may still be in commercial use.

Coating with oil and clay is a common practice in European plants for both bulk blends and chemically granulated mixtures. The usual proportions are about 0.5% oil and 1.0% clay. The coating usually is done in a continuous drum mixer. The oil is specially formulated for the purpose. One company in the United States produces specially formulated oils for dust control on granular fertilizer [26]. At least one bulk blender coats micronutrients on blends using clay and water or oil as a binder [27].

In some developing countries an oil coating is objectionable to the farmer because it soils the fertilizer bags which he wishes to reuse for grain storage. A possible solution to this problem is to use a waxy material that is a solid at atmospheric temperatures. For example, adherence of 5% of a powdered micronutrient frit was satisfactory in laboratory tests with 1% of either petrolatum or a petrolatum-rosin-paraffin wax mixture as a binder [28]. The granules were preheated to 49°C, the molten wax mixture was poured over them in a rotating mixer, and then the frit was added. Possible further study is needed to identify acceptable, low-coat binders. Also most Asian farmers use urea, and methods for coating micronutrients on urea seem to have received little attention. Some micronutrient materials (e.g., zinc sulfate) form adducts with urea, which might be advantageous in coating or incorporation.

17.3.6 Fluid Fertilizers

Fluid fertilizers are used in substantial amounts in only a few developing countries. Two types of fluid fertilizers are recognized:

1. Clear liquids are fluids in which all or nearly all of the ingredients are in aqueous solution.
2. Suspensions are fluids that contain solid particles. The solids may be soluble salts suspended in their saturated solution, they may be insoluble materials, or both types of solids may be present.

Fluid fertilizers may be used for foliar application or for application to the soil. Micronutrient sprays are often used for correcting deficiencies particularly for tree crops. A soluble salt or chelate of the micronutrient material may be dissolved in water to form a solution of suitable concentration. Finely powdered insoluble materials also may be used for foliar application. Because some metal salts form acidic solutions, the slightly soluble basic salts may be preferable for foliar application [29]. An example is $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$, a basic copper sulfate.

It is common practice to combine foliar application of micronutrients with pesticide sprays or with foliar application of primary nutrients. When two or more materials are combined for foliar application, care must be taken to ensure that the materials are compatible. Many pesticides are incompatible with solutions of micronutrients. Incompatibility means that some chemical or physical change takes place that renders the mixture unusable or harmful. In general, micronutrient solutions should be applied separately unless compatibility is shown.

Liquid fertilizers containing micronutrients and one or more of the primary nutrients are suitable for application to the soil or for foliar application when diluted sufficiently to avoid leaf burn. Such liquid fertilizers may be produced merely by dissolving fertilizer salts in water. Dry mixtures of water-soluble fertilizer salts are available that may be marketed as such and dissolved in water prior to use. However, for large-scale use, it is more common for the manufacturer to prepare the liquid mixed fertilizer at his plant for shipment to the farmer.

In formulating liquid mixed fertilizers, it is not sufficient to know that all ingredients are water soluble. Many reactions may occur that result in formation of water-insoluble compounds of micronutrients.

In general, most micronutrients are soluble in aqua ammonia or in solutions containing ammonium nitrate and urea provided that proper choice is made of the micronutrient compounds and that free ammonia is present or added to keep the solution pH above 7. Hester [30] describes the formulation and preparation of a solution based on aqua ammonia containing all micronutrients except iron. The solution contained 17.5% N as ammonia and ammonium sulfate, 0.29% Mo, 1.1% Cu, 2.0% Mn, 1.9% Zn, 0.9% B, and 0.12% Co. The metallic elements were added as sulfates, but they were present in the solution as complex metal amine sulfates. Boron and molybdenum were added as boric acid and molybdic acid.

Silverberg et al. [23] have discussed the solubility of micronutrients in nitrogen solutions and in various NP and NPK liquid fertilizers. In general, only boron (borax) and molybdenum (sodium molybdate) were appreciably soluble in nearly neutral ammonium orthophosphate solutions. Copper, iron, and zinc, however, were soluble in ammonium polyphosphate solutions to the extent of 1%-3%, and manganese was soluble to the extent of 0.2%. The production of liquid fertilizers including ammonium polyphosphate solution has been discussed by Hignett [31] and in a group of 12 papers in *Products and Techniques for Plant Nutrient Efficiency* [32]. Several of these papers discuss the potential advantage of liquid fertilizers in tropical countries and the incorporation of micronutrients in liquids.

When micronutrients are incorporated in suspension fertilizers, solubility is not a technical problem although it may be an agronomic problem. Soluble or insoluble compounds of micronutrient elements are added to suspension fertilizers using materials of small enough particle size that they are easily suspended and will not clog spray nozzles. Production of suspension fertilizers containing micronutrients has been described by Silverberg et al. [23].

17.4 Other Useful Elements

Although only 17 elements are considered to be essential for plant nutrition at this time, many other elements are known to occur in plant tissues. Positive effects of some of these elements have been reported by numerous researchers. Whether any of these elements eventually will be discovered to be essential for plant growth remains to be seen. Current criteria for an element to be considered essential are (a) it must be present for the plant to complete its life cycle; (b) its action must be specific and unable to be replaced by that of another element; and (c) its action must be direct [33].

Another term, beneficial elements, has been proposed to describe some elements that appear to have specific functions in plant nutrition but do not meet all of the three criteria required for essentiality as described above. Two such elements (cobalt and silicon) will be discussed here.

17.4.1 Cobalt

Cobalt is essential for animal nutrition, but it has not been established as essential for plant growth. Ruminant animals require cobalt for the synthesis of vitamin B_{12} by their rumen microflora. This was established about 1935, but an essential role of cobalt in plants was not demonstrated until 1960 [33]. Cobalt has been found to be essential for the growth of legumes which rely on symbiotic nitrogen fixation.

Field responses to cobalt applications by subterranean clover were reported on sandy soils of South Australia and Western Australia. Later, it was shown that narrow-leafed lupins were even more sensitive to cobalt deficiency. Concentrations of cobalt are less than 1 ppmw in many plant tissues, which is even lower than those of molybdenum, a micronutrient. Cobalt application rates also are quite low, less than 1 kg/ha. Although it is possible to prevent cobalt deficiency of livestock by applying cobalt-containing fertilizers to pastures, it may be more practical to supply the cobalt directly to animals in the form of a "cobalt bullet" given orally to young animals in cobalt-deficient areas [33].

17.4.2 Silicon

Silicon is the second most abundant element on earth, and there are sufficient supplies of available silicon in most soils. Some plant species absorb large quantities of silicon for example, up to 4% by flooded rice [33]. Grasses grown under upland conditions also absorb significant quantities of silicon. In such crops, silicon is found in leaves and stems and is credited with increasing stalk strength. Sugarcane also is known to have a high silicon requirement.

Highly weathered soils in the tropics and volcanic soils generally contain the least silicon. Growth reductions and "leaf freckle" of sugarcane have been reported on such soils, which are low in extractable silicon. Amending these soils with silicate materials has become a common practice, especially for sugarcane and rice production. Rates of 5 to 30 t/ha have resulted in significant increases in sugar production from sugarcane in Hawaii, for example [34].

Other beneficial effects reported on various plant species include improved resistance to fungus diseases and insect attack. This may be related to deposition of silicon dioxide in cell walls of leaf and stem tissues to give them increased rigidity [33]. Reduction in manganese toxicity symptoms in crops grown on acid, weathered soils also has been reported after silicate applications. Reduced pollen viability due to low silicon uptake has been reported on several crops. Further research is needed to better understand the effects of silicon on plant growth and reproduction.

17.5 Acknowledgment

Section 17.3 of this chapter, Preparation of Fertilizers Containing Micronutrients, and appropriate references, were reprinted from the paper, "Sources and Production of Micronutrient Fertilizers," by T. P. Hignett and G. H. McClellan, 1985, IN *Micronutrients in Tropical Food Crop Production*, P.L.G. Vlek (Ed.), Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht, The Netherlands. All rights reserved. No part of this publication [Section 17.3] may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publishers. Reprinted by permission of Kluwer Academic Publishers.

17.6 References

1. Follett, R. H., L. S. Murphy, and R. L. Donahue. 1980. *Fertilizers and Soil Amendments*, Prentice-Hall Inc., Englewood Cliffs, NJ, U.S.A.
2. Portsch, S. (Ed.). 1991. *The Role of Sulphur, Magnesium and Micronutrients in Balanced Plant Nutrition*, Potash and Phosphate Institute of Canada, Saskatoon, Saskatchewan.
3. Mortvedt, J. J., and F. R. Cox. 1985. "Production, Marketing and Use of Calcium, Magnesium and Micronutrient Fertilizers," IN *Fertilizer Technology and Use*, O. P. Engelstad (Ed.), 3rd. Ed., Soil Science Society of America, Madison, WI, U.S.A.
4. Adams, F. (Ed.). 1984. *Soil Acidity and Liming*, 2nd Ed. Agronomy Monograph 12. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, U.S.A.
5. Tabatabai, A. (Ed.) 1986. *Sulfur in Agriculture*, Agronomy Monograph 27, American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, U.S.A.
6. Beaton, J. D., R. L. Fox, and M. B. Jones. 1985. "Production, Marketing and Use of Sulfur Products," IN *Fertilizer Technology and Use*, O. P. Engelstad (Ed.), 3rd Ed., Soil Science Society of America, Madison, WI, U.S.A.
7. R. Richmann. 1994. "The BASF Nitrophosphate Process," IN *Nitric Acid-Based Fertilizers and the Environment*, Proceedings of an International Workshop, R. G. Lee (Ed.), pp. 203-210, SP-21, IFDC, Muscle Shoals, AL, U.S.A.
8. J. Platz. 1994. "Solid and Liquid Product Formulation Options with the Nitrophosphate Process," IN *Nitric Acid-Based Fertilizers and the Environment*, Proceedings of an International Workshop, R. G. Lee (Ed.), pp. 233-238, SP-21, IFDC, Muscle Shoals, AL, U.S.A.
9. *Farm Chemicals Handbook*. 1995. Vol. 81, Meister Publishing Co., Willoughby, OH, U.S.A.
10. Mortvedt, J. J., and J. R. Woodruff. 1993. "Technology and Application of Boron for Crops," IN *Boron and its Role in Crop Production,* U. C. Gupta (Ed.), CRC Press, Ann Arbor, MI, U.S.A.
11. Mortvedt, J. J., and R. J. Gilkes. 1993. "Zinc Fertilizers," IN *Zinc in Soils and Plants,* A. D. Robson (Ed.), Kluwer Academic Publishers, Dordrecht, The Netherlands.
12. Mortvedt, J. J. 1991. "Micronutrient Fertilizer Technology," IN *Micronutrients in Agriculture,* J. J. Mortvedt et al. (Eds.), 2nd Ed., Soil Science Society of America, Madison, WI, U.S.A.
13. Mortvedt, J. J. 1992. "Use of Industrial By-Products Containing Heavy Metal Contaminants in Agriculture," IN *Residues and Effluents: Processing and Environmental Considerations,* R. G. Reddy, W. P. Imrie, and P. B. Queneau (Eds.), The Minerals, Metals and Materials Society, Lakewood, CO, U.S.A.
14. Lehr, J. R. 1972. "Chemical Reactions of Micronutrients in Fertilizers," IN *Micronutrients in Agriculture,* J. J. Mortvedt et al. (Eds.), Soil Science Society of America, Madison, WI, U.S.A.
15. Knudsen, K. C. 1972. "NPK Production by Ion Exchange," Paper presented at ISMA Technical Conference, Seville, Spain, November 1972.
16. Caro, J. H., H. P. Freeman, and J.H.L. Marshall. 1960. "Zinc Induced Caking in Mixed Fertilizer and its Counteraction," *Agr. Chem.*, January.

17. Bautista, A. C., J. C. Bunoan, Jr., and R. Feuer. 1980. "Development of the Zinc Extension Component for Irrigated Rice in the Philippine Masagana 99 Production Program," Presented at the Symposium on Paddy Soils, Nanjing, China, October 19-24, 1980.

18. Hoffmeister, G. 1973. "Quality Control in a Bulk-Blending Plant," IN *TVA Fertilizer Bulk-Blending Conference*, pp. 59-70, Bull. Y-62, TVA, Muscle Shoals, AL, U.S.A.

19. McCollum, J. A., R. S. Meline, and B. V. Durham. 1966. "Adding Nutrients to Fertilizers," *Chem. Eng. Progress*, 62(9):130-132.

20. Hignett, T. P. 1964. "Problems in Production of Micronutrients Enriched Fertilizers," IN *Proc. 14th Ann. Meeting of the Fertilizer Industry Round Table*, pp. 50-55.

21. Achorn, F. P., and H. L. Balay. 1973. "Plant Experience in Adding Pesticides, Micro- and Secondary Nutrients to Bulk Blends," IN *TVA Bulk Blending Conference*, pp. 70-79, Bull. Y-62, TVA, Muscle Shoals, AL, U.S.A.

22. Young, R. D. 1969. "Providing Micronutrients in Bulk-Blended, Granular Fertilizers," *Commercial Fertilizer,* 118:21-24.

23. Silverberg, J., R. D. Young, and G. Hoffmeister. 1972. "Preparation of Fertilizers Containing Micronutrients," IN *Micronutrients in Agriculture*, J. J. Mortvedt et al. (Eds.), Soil Science Society of America, Madison, WI, U.S.A.

24. Gilbert, R. L., H. H. Nau, and T. R. Cox. 1968. "Coating Micronutrients on Bulk-Blended Fertilizers," IN *Proc. 18th Ann. Meeting of the Fertilizer Industry Round Table*, pp. 66-68.

25. Nau, H. H. 1967. "Method for Preventing Segregation of Mixed Fertilizer," U.S. Patent No. 3,353,949.

26. Frick, J. O. 1977. "Petroleum-Based DCA's to Control Fugitive Dusts," IN *Proc. 27th Ann. Meeting of the Fertilizer Industry Round Table*, pp. 94-97.

27. Poulton, J. W. 1975. "Bulk-Blending Practices in the United Kingdom," IN *Proc. 25th Ann. Meeting of the Fertilizer Industry Round Table*, pp. 136-140.

28. Hignett, T. P. 1965. "Bulk Blending of Fertilizers: Practices and Problems," *Fert. Soc. Proc.* No. 87.

29. Nikitin, A. A. 1960. "Production and Use of Trace Salts in Fertilizers," IN *The Chemistry and Technology of Fertilizers*," V. Sauchelli (Ed.), pp. 435-445, Reinhold Pub. Co., New York, NY, U.S.A.

30. Hester, J. B. 1962. "Ammoniacal Trace Element Solution for Agriculture," *Agricultural Ammonia News*, May-June, pp. 8-9.

31. Hignett, T. P. 1972. "Liquid Fertilizers: Production and Distribution," *Chemtech*, 2:621-637.

32. British Sulphur Corporation, Limited. 1978. *Products and Techniques for Plant Nutrient Efficiency*, British Sulphur Corp. Ltd., London, England.

33. Asher, C. J. 1991. "Beneficial Elements, Functional Nutrients and Possible New Essential Elements," IN *Micronutrients in Agriculture*, J. J. Mortvedt et al. (Eds.), 2nd Ed., Soil Science Society of America, Madison, WI, U.S.A.

34. Fox, R. L., J. A. Silva, O. R. Younge, D. L. Plunknett, and G. D. Sherman. 1967. "Soil and Plant Silicon and Silicate Responses by Sugar Cane," *Soil Sci. Soc. Am. Proc.*, 31:775-779.

Chapter 18. Physical Properties of Fertilizers

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Chapter 18. Physical Properties of Fertilizers

18.1 Introduction

Physical quality is an important criterion used by a consumer in selecting a particular fertilizer. The acceptability of a fertilizer in the marketplace depends not only on its nutrient content but also on its physical quality. Although crop response to the available nutrient content is the ultimate reason for the use of fertilizers, physical quality is often the reason for selecting one fertilizer over another. Good physical condition ensures the consumer of easier, faster, more uniform, and less expensive application to the field. Additionally, in a fertilizer distribution system, it is important that fertilizers remain free-flowing (noncaking), that they be relatively nondusty, and that they withstand a reasonable amount of exposure to normal atmospheric humidity. Many production techniques, including various physical "conditioning" treatments, have been developed especially to provide favorable physical properties [1].

The consumer cannot detect whether a fertilizer actually meets the guaranteed nutrient content; however, federal or state laws normally regulate the nutrient content and thereby give some protection to the consumer. In contrast, physical condition usually is a matter only of agreement between purchaser and supplier. Normally, fertilizer regulatory laws do not regulate fertilizer physical properties. However, the consumer can certainly evaluate the physical condition of a fertilizer. Simply by observation, he can see whether a fertilizer is caked or free-flowing, dusty or dust-free, wet and sticky or dry.

The quality of a fertilizer product is basically judged by two criteria: chemical properties and physical properties. The chemical properties (nutrient content, form, and availability to the crop) and their effectiveness (agronomic response) are the ultimate reasons for the use of a fertilizer. Good chemical properties are reflected in the agronomic response. In contrast, the physical properties of a fertilizer product and its ability to resist deterioration are important with respect to processing, handling, storage, field application, and agronomic response [2].

The most frequently encountered problems resulting from deficiencies in physical properties are caking (agglomeration or lump formation), dustiness, poor flowability, excessive hygroscopicity (moisture absorption characteristics), and segregation (nonuniformity of composition throughout a fertilizer lot).

The physical quality of a fertilizer can be evaluated by many different methods. These methods of measurement can vary from simple observation to sophisticated techniques. Producers have adopted and/or developed methods to evaluate their particular products. International, national, and regional organizations have adopted, developed, and/or published procedures intended for general application to a variety of fertilizer products and raw materials [1,3,4,5,6,7,8,9,10]. The International Organization for Standardization (ISO), Technical Committee 134/Subcommittee 3 (Fertilizers and Soil Conditioners/Physical Properties), has been engaged over the past 15-20 years in developing and adopting international standard methods of analyzing various physical properties of fertilizers. Thus far, only six methods have been designated as international standards [8,10].

This chapter defines the various physical properties; discusses the effects and importance of these physical properties on product quality; briefly reviews the types of methodology used in measuring these properties; and gives some typical values for most of these properties for various fertilizers. Literature references are given, indicating where more detailed information can be obtained.

18.2 Physical Properties of Solid Fertilizers

In the following section, most of the physical properties of solid fertilizers will be discussed.

18.2.1 Particle Size

Particle size distribution of fertilizer products and/or fertilizer raw materials is defined as the particle diameter range of the material. Particle size analysis is typically measured by sieving, a process of separating a mixture of particles according to their size fraction [11]. Particle size affects agronomic response; granulation and process performance; and blending, storage, handling, and application properties. Some of the reasons for size control follow.

18.2.1.1 Effects on Agronomic Response – Fertilizer of very low water solubility generally must be ground to small particle size to ensure sufficiently rapid dissolution in the soil and utilization by plants. For example, the effectiveness of raw phosphate rock generally increases with fine grinding down to a particle diameter of about 150 μm; below that, little further benefit has been established [12]. Other materials of low solubility that require relatively fine grinding include basic slag, limestone, dolomite, dicalcium phosphate, and fused phosphates [13,14]. Micronutrient or secondary nutrient sources of low solubility, such as sulfur, metallic oxides, and glasses ("frits"), likewise require fine grinding [1].

The fine grinding required for these materials often results in undesirable dustiness and other handling difficulties. Therefore, some research and development has been directed toward regranulating the pulverized materials. For example, in the United States, there are currently a few small commercial limestone granulation plants. Methods of dust control other than granulation include spraying the pulverized materials lightly with oil, water, or amine formulations.

Other fertilizers that benefit agronomically from particle size control are some of the sparsely soluble slow-release nitrogen fertilizers such as urea-formaldehyde, isobutylidene diurea, and oxamide. The rate of dissolution, and hence the rate of nitrogen availability from these materials, has been shown to be dependent on particle size; the larger the particles, the slower the release.

18.2.1.2 Effects on Granulation and Process Performance – In the production of granular NPK products, the agglomeration process is one of two principal mechanisms utilized, the other being the slurry-based nitrophosphate-type process. In the agglomeration process, 50%-75% of the raw materials are fed as "dry" solids. Because much of the initial (in-process) and final mechanical strength of the agglomerated granules is obtained by the mechanical interlocking or fitting of the individual particles, the particle size and size distribution of the solid raw materials are very important. If the final product is in the size range of 2-5 mm, then the raw materials should be quite widely distributed within a range of about 0.2-3.0 mm [15].

Compaction is a dry granulation process in which mixed raw materials are agglomerated by pressure. One of the characteristics of the feed raw materials that affects compactibility is particle size. Generally, in order to obtain optimum compaction, the feed raw materials should fall within a wide range of particle sizes, preferably in the range of 0.1-1.0 mm. Material smaller than 0.1 mm will likely contain too much air, and particles larger than 1.0 mm will require energy to crush them to a smaller size [16,17].

18.2.1.3 Effects on Storage, Handling, and Application Properties – Particle-size control of fertilizers is important to ensure satisfactory storage, handling, and application properties. Before about 1950, almost all fertilizers were produced as relatively fine powders or small crystals. As a result, fertilizers usually were dusty during handling and very susceptible to hard caking during storage in piles or bags. Considerable labor usually was required to break up the lumps and make the products suitable for field application. The rapid growth of granulation in the early fifties, however, resulted in great improvement in storage, handling, and application properties. This growth of granulation was paralleled by improvements in application equipment that took advantage of the better flow properties and reduction of caking in granular products [1].

In the United States, the typical size range of granular fertilizer products is around 1.00-3.35 mm. The Association of American Plant Food Control Officials defines "Granular Fertilizer" as one in which 95% or more of the product is retained on a series of sieves within the range of 4.75 mm openings to and including 850 µm openings, and in which the largest particle passes through a sieve having an opening not larger than four times that of the sieve which retains 95% or more of the product [13]. In European countries and Japan, granular fertilizers generally are produced in somewhat larger particle size; sizes reported are generally in the range of 2.0 to 4.0 mm [18,19,20].

Fertilizers preferably should be free from particles so small that they generate air-borne dust during handling and application, not only to ensure farmer acceptance but also to prevent unhealthy working conditions and environmental damage around fertilizer plants and bulk-handling operations.

18.2.1.4 Effects on Blending Properties – Since the advent of bulk blending as an important system of mixing and distributing granular fertilizers, control of particle size has assumed additional importance as a method for reducing the segregation tendency of blends. In some early blending operations, materials were blended without regard to matching of particle sizes, with the result that the blends were very susceptible to segregation (unmixing) during handling. Subsequent studies identified particle-size matching of blend ingredients as by far the most important factor in producing a blend that is resistant to segregation. The effects of mismatches in other physical properties, namely density and particle shape, were insignificant in comparison with the effect of mismatch in particle size [9,21,22,23].

Size range is not sufficiently restrictive to ensure good size matching for bulk blending. It has been found that materials for blending should not only agree in regard to their upper and lower size limits but should also be reasonably similar in particle-size distribution between these limits [24].

Mismatched particle sizes in raw materials used for blending can result in segregation mainly by three mechanisms: (1) vibration, (2) coning, and (3) ballistic action [25,26,27].

Fertilizers are subject to vibration during their transportation by truck, rail, or other means. Various studies have shown, however, that such vibration is not a significant cause of segregation in most fertilizers, including typical bulk blends. Segregation due to vibration becomes significant only when the size differences between blend ingredients are extreme to the extent that particles of one ingredient are small enough to "sift" downward through the void spaces between particles of another, larger ingredient [1].

The type of segregation most often encountered in handling fertilizers is due to flow of material over itself. This often is referred to as segregation due to "coning" because in the buildup of conical storage piles there is a maximum opportunity for this type of segregation to occur when material dropped on the apex of the pile flows downward over the pile surface. Particle-size classification (segregation) occurs as the material flows; the smaller particles in the fertilizer, being retarded to a greater extent by frictional resistance of the pile surface, tend to remain behind and come to rest, whereas the larger particles continue to travel farther down the pile surface before coming to rest. The result is a size-classified (segregated) pile of material [1].

When fertilizer is propelled through the air, such as by the action of fan-type fertilizer spreaders, particles of different physical properties follow different paths because of varying effects of gravity and air drag. The result is segregation due to ballistic action. Particle-size differences are the greatest cause of ballistic segregation of granular fertilizer blends during spreading; the larger granules tend to travel farther from the spreader than do the smaller ones [21,23]. Thus, matching of the particle size of blend ingredients is a sufficient measure to minimize segregation by both coning and ballistic actions, the two most troublesome causes of fertilizer segregation. The fact that fertilizer particle size has a much greater effect on ballistic segregation than does particle density is not surprising when consideration is given to the relative effects on granular weight and thus on inertia of moving granules. Increasing granule diameter from 1.18 mm to 3.35 mm increases granule weight more than twentyfold, whereas the usual range of fertilizer granule densities (1.3 to 2.7 g/cm^3) represents only about a twofold difference [28]. Air drag, although less on a small particle, is, according to Stoke's law, reduced only in direct proportion to particle diameter [29].

18.2.1.5 Particle-Size Analysis – Particle-size distribution is normally measured by conducting a "screen analysis" (sieve analysis) of a representative sample on 20-cm-diameter sieves. The sample size recommended for testing on these sieves varies according to the size range of the material. The sieves selected for use are stacked, with sieve apertures increasing in size from bottom to top in the stack. The sample is placed on the uppermost sieve of the stack, and the stack is placed on a stand which is subjected to controlled shaking. During shaking, each particle in the sample gravitates downward through screen apertures until it reaches a screen with apertures too small to allow its passage. At the end of a specified shaking period, the material on each screen is weighed individually and the particle-size distribution of the sample is thus determined. In cases where sieve analysis of a raw material with micron-size particles is required (such as phosphate rock), it may be necessary to perform a "wet" sieve analysis using a wet sieve shaker [2].

Most countries have standard sieve specifications and sieve analysis procedures. These specifications and procedures are usually generic and can be used for a wide variety of products, including fertilizers. The ISO has a series of international standards for test sieves [10] including (1) Test sieves – Woven metal wire cloth and perforated plate – Nominal sizes of apertures (ISO 565); (2) Test sieves and test sieving – Vocabulary (ISO 2395); (3) Test sieving (ISO 2591); (4) Test sieves – Technical requirements and testing (ISO 3310/1); and (5) Solid fertilizers and soil conditioners – Test sieving (ISO 8397). The ISO sieve series is shown in Table 18.1.

Finally, in the past 10-15 years, methods have been developed to analyze particle size "on-line" to improve process control [30,31,32,33,34].

18.2.2 Density

Density is the mass per unit volume of a material. Three types of density measurements can be determined for fertilizer products and fertilizer raw materials: bulk density, apparent density, and true density.

18.2.2.1 Bulk Density – Bulk density is the mass per unit volume of a fertilizer and includes the voids between particles. It is of interest in bag/package sizing, in calibrating volumetric feeders or applicators, and when considering the capacity of storage bins and transport vehicles. Bulk density is the most commonly used density value for fertilizers.

Bulk density is determined by weighing a container, of a known volume, that is filled level-full with the sample. There are two types of bulk density measurements – "loose pour" and "tapped."

Loose pour bulk density is defined by ISO as the mass per unit volume of a material after it has been tipped freely into a container under clearly specified conditions. Loose pour bulk density represents the minimum density (greatest volume occupancy) expected. To avoid designing equipment and bags that are too small, loose pour bulk density is the most commonly used value.

Tapped bulk density is defined by ISO as the mass per unit volume of a material tipped into a container and

Table 18.1. ISO Sieve Series – Nominal Apertures (ISO 565)

Principal Sizes (R 20/3)[a]	Supplementary Sizes (R 20)[b]	Supplementary Sizes (R 40/3)[c]
(mm)	(mm)	(mm)
125	125	125
	112	
		106
	100	
90.0	90.0	90.0
	80.0	
		75.0
	71.0	
63.0	63.0	63.0
	56.0	
		53.0
	50.0	
45.0	45.0	45.0
	40.0	
		37.5
	35.5	
31.5	31.5	31.5
	28.0	
		26.5
	25.0	
22.4	22.4	22.4
	20.0	
		19.0
	18.0	
16.0	16.0	16.0
	14.0	
		13.2
	12.5	
11.2	11.2	11.2
	10.0	
		9.50
	9.00	
8.00	8.00	8.00
	7.10	
		6.70
	6.30	
5.60	5.60	5.60
	5.00	
		4.75
	4.50	
4.00	4.00	4.00
	3.55	
		3.35
	3.15	
2.80	2.80	2.80
	2.50	
		2.36
	2.24	
2.00	2.00	2.00
	1.80	
		1.70
	1.60	
1.40	1.40	1.40
	1.25	
		1.18
	1.12	
1.00	1.00	1.00

Principal Sizes (R 20/3)[a]	Supplementary Sizes (R 20)[b]	Supplementary Sizes (R 40/3)[c]
(µm)	(µm)	(µm)
	900	
		850
	800	
710	710	710
	630	
		600
	560	
500	500	500
	450	
		425
	400	
355	355	355
	315	
		300
	280	
250	250	250
	224	
		212
	200	
180	180	180
	160	
		150
	140	
125	125	125
	112	
		106
	100	
90	90	90
	80	
		75
	71	
63	63	63
	56	
		53
	50	
45	45	45
	40	
		38
	36	
	32	32
	28	
		26
	25	
	22	22
	20	

a. ISO designation for principal sizes with a ratio difference between sieves of approximately 1.41.
b. ISO designation for principal sizes with a ratio difference between sieves of approximately 1.12.
c. ISO designation for principal sizes with a ratio difference between sieves of approximately 1.19.

then compacted under clearly specified conditions. Tapped bulk density represents the maximum density (smallest volume occupancy) expected. Generally, when measuring the bulk density of granular and prilled fertilizers one can expect tapped bulk density to be 6%-12% higher than loose pour bulk density.

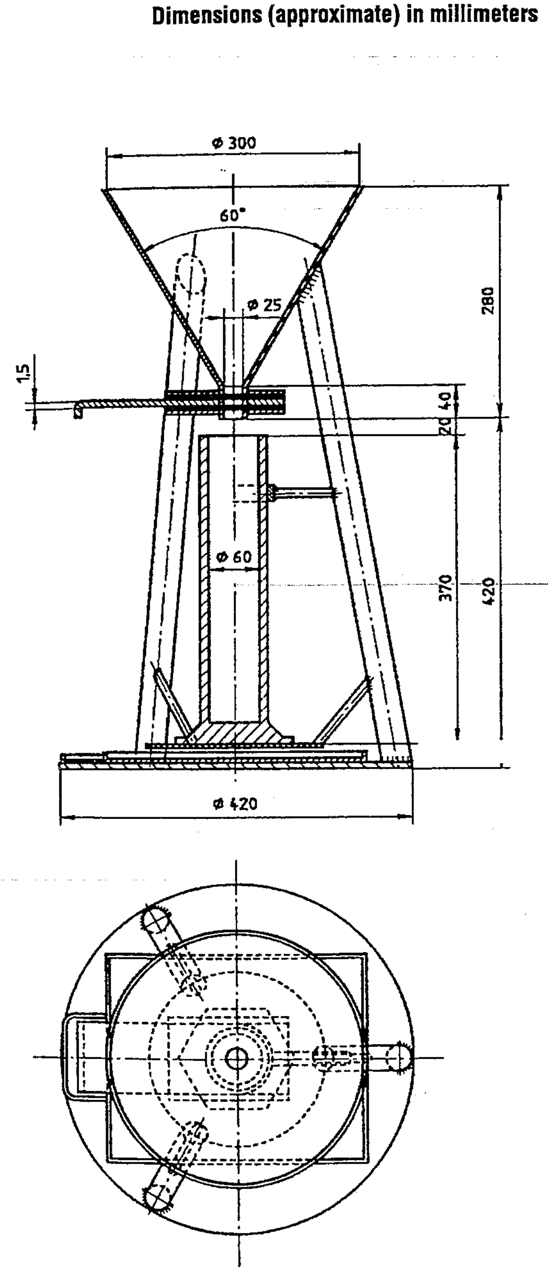


Figure 18.1. Apparatus for the Determination of Bulk Density (Loose) of Fertilizers (ISO-3944).

The ISO has a series of international standards for bulk density [10] including (1) Fertilizers – Determination of bulk density (loose) (ISO 3944); (2) Fertilizers – Determination of bulk density (tapped) (ISO 5311); and (3) Fertilizers – Determination of bulk density (loose) of fine-grained fertilizers (ISO 7837). Figures 18.1, 18.2, and 18.3 illustrate the ISO equipment for measuring bulk density. Figure 18.4 is an illustration of an apparatus developed by the Tennessee Valley Authority (TVA) for measuring bulk density [3].

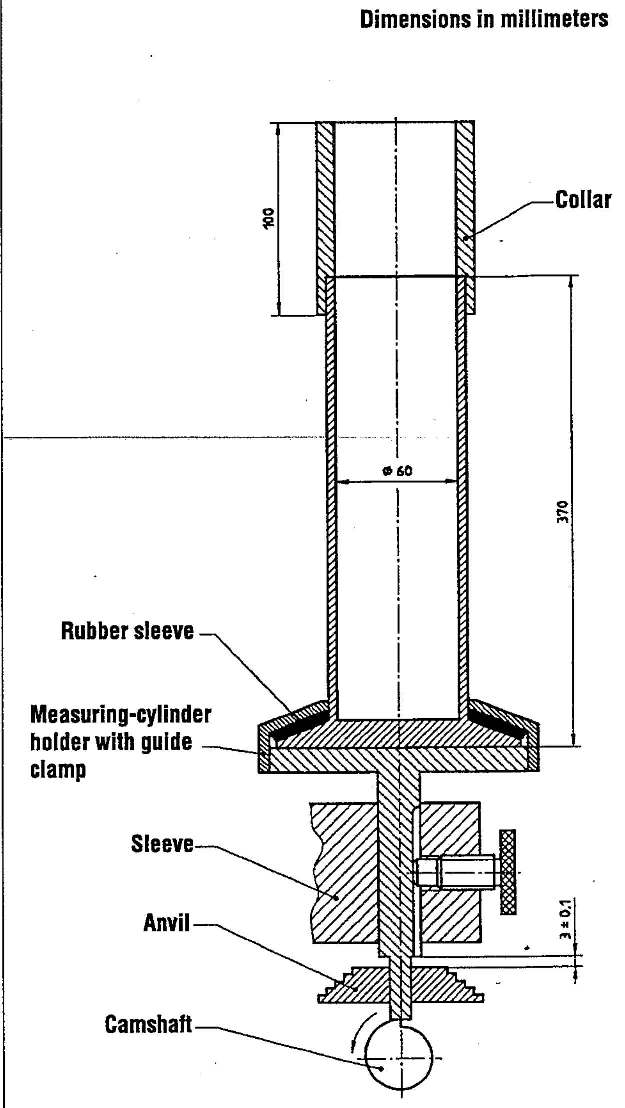
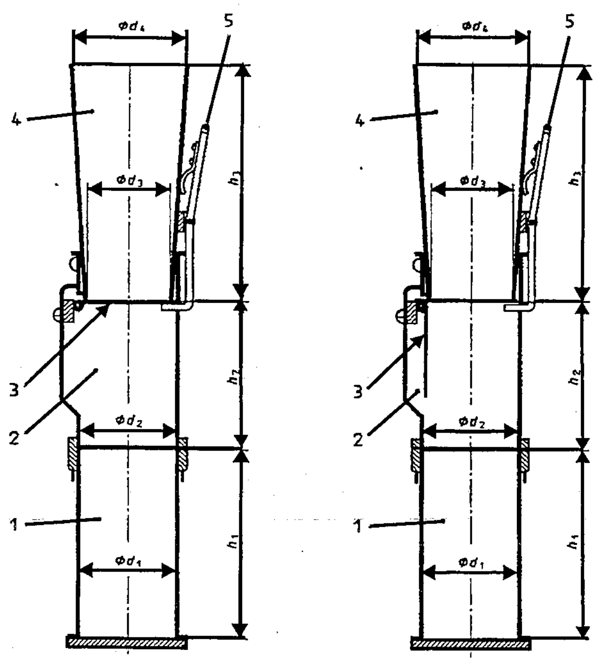


Figure 18.2. Apparatus for the Determination of Bulk Density (Tapped) by Machine Tapping (ISO-5311).



(a) Closed Position (b) Open Position

1 Measuring cylinder	
Internal diameter	d_1 = 87 mm ± 1 mm
Internal height	h_1 corresponding to a capacity of 1,000 cm3 ± 5 cm3
2 Intermediate piece	
Internal diameter	d_2 = 87 mm ± 1 mm
Height	h_2 = 135 mm ± 1 mm
3 Hinged cover	
4 Filling device	
Lower internal diameter	d_3 = 79 mm ± 1 mm
Upper internal diameter	d_4 = 99 mm ± 1 mm
Height	h_3 = 199 mm ± 1 mm
5 Spring-suspended locking lever	

Figure 18.3. Apparatus for the Determination of Bulk Density (Loose) of Fine-Grained Fertilizers (ISO-7837).

Bulk density values for fertilizers normally range from 750 to 1,500 kg/m^3. Typical bulk density values for some common fertilizers are listed in Table 18.2.

18.2.2.2 Apparent Density – Apparent density is the mass per unit volume of a fertilizer, excluding voids between particles. Apparent density is not a property that is measured frequently, but it has been of special interest in connection with studies of particle segregation characteristics and in the development of granulation processes. For a given product, variations in density can result in variations in hardness, moisture-holding capacity, and storage properties.

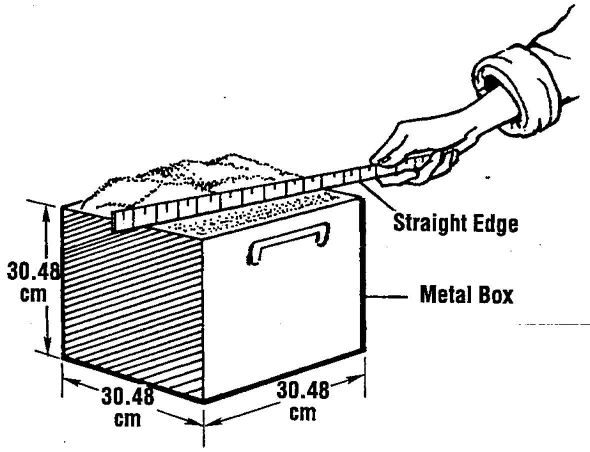


Figure 18.4. Metal Box (0.0283 m^3) for Measuring Bulk Density of Fertilizers.

Determinations of granule apparent density are made in a special apparatus by submerging a known weight of the granules and measuring the volume of mercury that is displaced. Figure 18.5 is an illustration of this apparatus.

Apparent density values for fertilizer granules typically range from 1.22 to 2.65 g/cm^3. Typical apparent density values for some common fertilizer materials are listed in Table 18.3.

18.2.2.3 True Density – True density is the mass per unit volume of a fertilizer material, excluding voids between particles and the pores within the particles. It is of interest in process control and design of process equipment. The true density can be determined with an air-comparison pycnometer. The pycnometer has two sample chambers of equal size. One chamber is flooded with a measured volume of air. The other chamber is filled with a weighed amount of the ground test sample and then flooded with a measured volume of air. The difference in air volumes is equivalent to the sample volume. The sample weight and volume are used to calculate the true density. Figure 18.6 is an illustration of a Beckman air-comparison pycnometer. Typical true density values for some common fertilizer materials are listed in Table 18.4.

Table 18.2. Typical Bulk Density Ranges of Some Common Fertilizer Materials

Fertilizer		Bulk Density	
Type	Grade	Loose-Pour	Tapped
		(kg/m^3)	
Prilled urea	46-0-0	720-820	820-900
Granular urea	46-0-0	720-820	820-900
Prilled ammonium nitrate (high density)	34-0-0	850-975	900-1,025
Crystalline ammonium sulfate	21-0-0	1,000-1,100	1,100-1,200
Granular ammonium sulfate	21-0-0	785-1,040	850-1,100
Granular diammonium phosphate	18-46-0	875-1,100	1,000-1,200
Granular monoammonium phosphate	11-55-0	900-1,100	1,000-1,200
Powdered monoammonium phosphate	10-50-0	850-1,000	-
Granular triple superphosphate	0-46-0	950-1,200	1,050-1,350
Single superphosphate (run-of-pile)	16%-20% P_2O_5	900-1,200	-
Phosphate rock	28%-35% P_2O_5	1,200-1,600	1,400-1,800
Granular potassium chloride	0-0-60	950-1,200	1,000-1,200
Coarse potassium chloride	0-0-60	1,050-1,150	1,100-1,200
Standard potassium chloride	0-0-60	1,075-1,200	1,150-1,300
Granular potassium sulfate	0-0-50	1,150-1,360	1,360-1,500

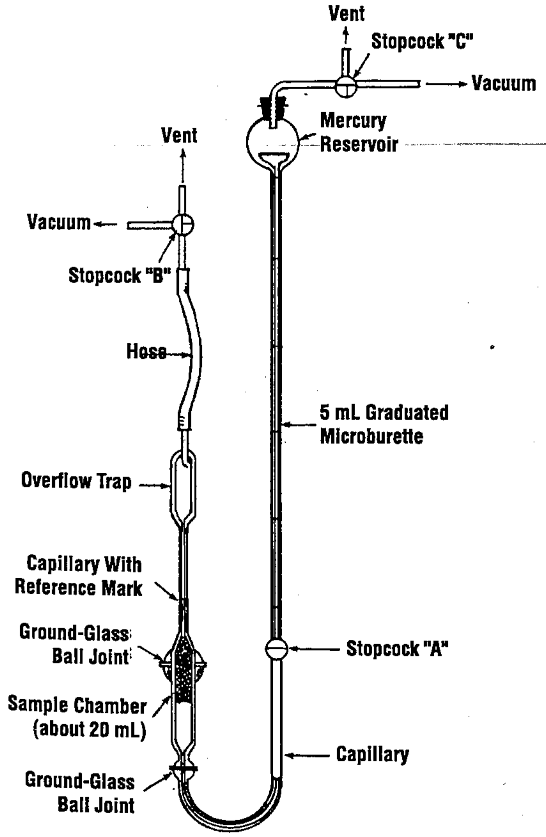


Figure 18.5. Apparatus for Determination of Apparent Density of Fertilizer Granules.

18.2.3 Angle of Repose

Angle of repose (static) is defined by ISO as the angle at the base of a cone of fertilizer obtained by allowing a sample to fall onto a horizontal base-plate under specified conditions. A less rigid definition is the angle with the horizontal at which the fertilizer will stand when poured or dropped into a pile from a fixed overhead point [1]. For the second definition, the pile of fertilizer does not have to form a cone to have an angle of repose and, in fact, this is the most common method of storage for a large quantity of bulk fertilizer.

Angle of repose is of interest when considering storage capacity and the design of hoppers, chutes, conveyors, and sloped roofs of bulk-storage buildings [35,36,37]. The angle of repose of fertilizers is influenced mostly by particle shape, size, and surface texture [38,39].

Angle of repose can be determined by the ISO procedure, "Solid Fertilizers – Measurement of Static Angle of Repose" (ISO 8398). This procedure involves pouring a sample through a fixed funnel onto a level base-plate, measuring the diameter and height of the conical pile, and calculating the base angle of the cone from these measurements. Figure 18.7 is an illustration of the ISO apparatus for measuring the static angle of repose.

Angle of repose values for fertilizers normally range from about 25° to about 40°. Spherical products, such as prilled urea, usually have low angle of repose values (<30°). Irregularly shaped products, such as granular

Table 18.3. Typical Apparent Density Values of Some Common Fertilizers

Fertilizer		Apparent Density
Type	Grade	(g/cm^3)
Prilled urea	46-0-0	1.30-1.32
Granular urea	46-0-0	1.22-1.30
Granular ammonium sulfate	21-0-0	1.58-1.65
Crystalline ammonium sulfate	21-0-0	1.75
Prilled ammonium nitrate (high density)	34-0-0	1.65-1.67
Prilled ammonium nitrate (low density)	34-0-0	1.29
Granular ammonium nitrate	34-0-0	1.50
Granular diammonium phosphate	18-46-0	1.63-1.65
Granular monoammonium phosphate	11-55-0	1.67-1.78
Granular triple superphosphate	0-46-0	1.93-2.12
Granular potassium chloride	0-0-60	1.96-1.99
Coarse potassium chloride	0-0-60	1.96
Granular potassium sulfate	0-0-50	1.76
Potassium-magnesium sulfate	0-0-22	2.65

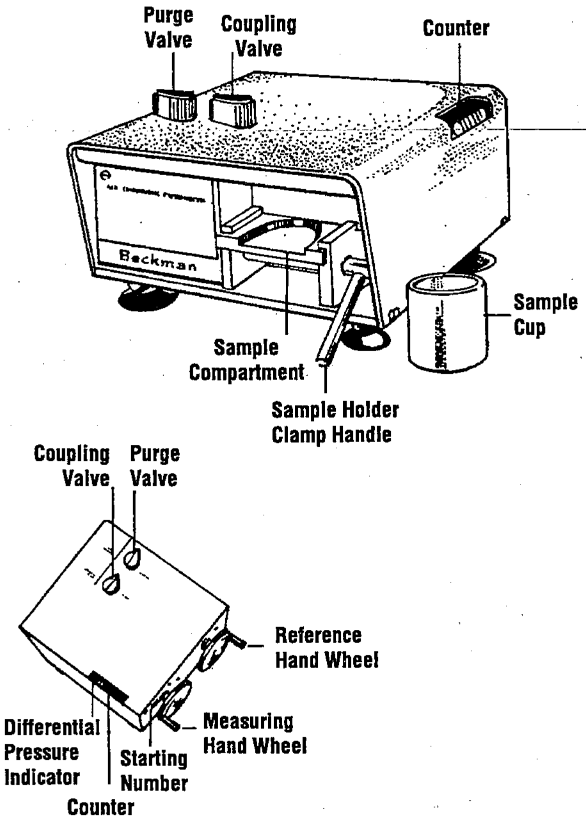


Figure 18.6. Beckman Air-Comparison Pycnometer for Measuring True Density of Solids.

potassium chloride, usually have high angle of repose values (>35°). Typical angle of repose values for some common fertilizers are listed in Table 18.5.

18.2.4 Granule Hardness

Granular fertilizers should have sufficient mechanical strength to withstand normal handling and storage without significant fracturing of granules and creation of excessive dust. The mechanical strength of fertilizer is influenced by its chemical composition, method of production, granule porosity, granule shape, surface crystals, and moisture content. Three distinct types of mechanical strength are recognized as desirable: (1) granule crushing strength, (2) abrasion resistance (sloughing), and (3) impact resistance [40,41,42].

18.2.4.1 Crushing Strength – Crushing strength is defined by ISO as the minimum force required to crush individual particles. It is useful in predicting the expected handling and storage properties of a granular fertilizer.

Crushing strength is measured by applying pressure to individual granules, usually of a specified size range, and noting the pressure required to fracture each granule. The degree of refinement varies from simple application of finger pressure to the use of calibrated crushing test machines [1,8,43,44,45,46]. Use of a simple finger test, which can be quite useful as a quick field measurement, is described as follows [47]:

> A granule which can be crushed between the thumb and forefinger is classified as 'soft.' If it can be crushed

Table 18.4. Typical True Density Values of Some Common Fertilizer Materials

Fertilizer		
Type	Grade	True Density (g/cm^3)
Prilled urea	46-0-0	1.33
Granular urea	46-0-0	1.33
Ammonium sulfate	21-0-0	1.77
Ammonium nitrate	34-0-0	1.71
Diammonium phosphate	18-46-0	1.71
Monoammonium phosphate	11-55-0	1.86
Triple superphosphate	0-46-0	2.22
Potassium chloride	0-0-60	2.00
Phosphate rock, central Florida	31% P_2O_5	2.94
Phosphate rock, Morocco	33% P_2O_5	3.16
Phosphate rock, North Carolina	30% P_2O_5	2.74
Phosphate rock, Senegal	36% P_2O_5	3.11
Phosphogypsum (various rock sources)	-	2.25-2.75

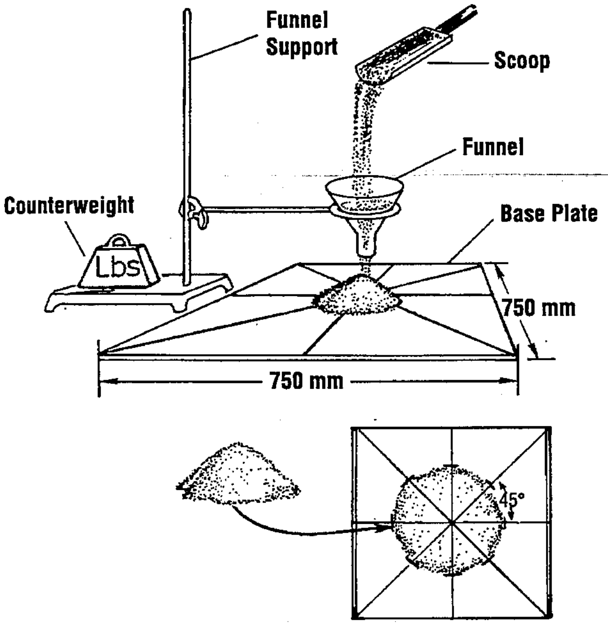


Figure 18.7. Apparatus for the Determination of Angle of Repose of Fertilizer (ISO-8398).

with the forefinger on a hard surface, it is regarded as being of 'medium hardness.' If it remains intact when subjected to pressure by the forefinger against a hard surface, it is classified as 'hard.'

A commercial compression tester or a simple kitchen scale may be used, although the latter is less accurate. Figure 18.8 is an illustration of a typical commercial compression tester.

Experience has shown that particles (2.36-2.80 mm diameter) with a crushing strength less than about 1.5 kg tend to fracture easily and form dust during handling, particles with a crushing strength of about 1.5-2.5 kg are acceptable with special handling precautions, and particles with a crushing strength greater than about 2.5 kg are highly desirable.

Typical crushing strength values for some common fertilizers are listed in Table 18.6. When making comparisons of crushing strength data, it is important to compare only granules of equal size because crushing strength increases significantly with increase in particle size.

18.2.4.2 Abrasion Resistance – Abrasion resistance is the resistance to the formation of dust and fines and to granule fracturing as a result of granule-to-granule and granule-to-equipment contact during handling. Abrasion resistance is determined by measuring the percentage of dust and fines created by subjecting a sample to abrasive-type action. There are numerous methods, mostly developed by producers, for determining abrasion resistance. Generally, these methods can be divided into two types: rotary drum type or screen type. Both types normally use steel balls or steel rods as an abrading medium. Values obtained from such methods are useful in estimating expected product degradation during processing, handling, storage, and application.

In the rotary drum-type methods, a prescreened sample is weighed and placed in a drum with an abrading

Table 18.5. Typical Angle of Repose Values (Ranges) of Some Common Fertilizer Materials

Fertilizer Type	Grade	Angle of Repose (degrees)
Prilled urea	46-0-0	27-28
Granular urea	46-0-0	34-38
Granular ammonium sulfate	21-0-0	36-38
Crystalline ammonium sulfate	21-0-0	29-36
Prilled ammonium nitrate	34-0-0	29-38
Granular diammonium phosphate	18-46-0	27-37
Granular monoammonium phosphate	11-55-0	28-37
Powdered monoammonium phosphate	10-50-0	30-34
Granular triple superphosphate	0-46-0	28-35
Granular potassium chloride	0-0-60	32-41
Coarse potassium chloride	0-0-60	31-35
Standard potassium chloride	0-0-60	28-32
Granular potassium sulfate	0-0-50	28-35
Phosphate rock (various rock sources)	-	30-35

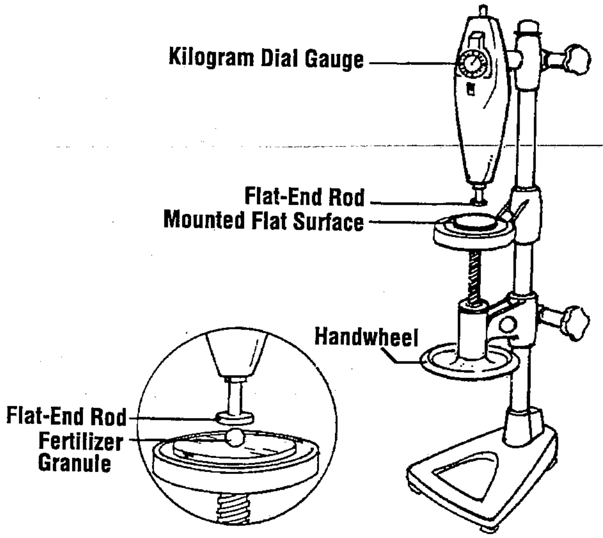


Figure 18.8. Chatillion Compression Tester for Measuring Granule Crushing Strength.

medium. The drum is then rotated at a specified speed for a predetermined period of time. The sample and abrading medium are removed from the drum, and the abrading medium is separated from the sample (usually by hand sieving). The abraded sample is then mechanically sieved to separate the dust, fines, and fractured granules created during the test from the granules that remained intact.

In the screen-type methods, a prescreened sample is weighed and placed on a sieve with an abrading medium. The sieve containing the sample and abrading medium is placed in a mechanical shaker and shaken for a predetermined time at a specified amplitude and frequency. The dust, fines, and fractured granules are collected in a pan nested below the sieve.

The numerous methods used to measure abrasion resistance illustrate very well the need for international standard methods not only for abrasion resistance but for other physical properties as well. In 1981 H. Rieschel and K. Zech of Maschinenfabrik Köppern GmbH & Company KG, Germany, published abrasion resistance data obtained from evaluating four samples with twelve different methods used by various potash producers [48]. One of the potash samples had abrasion resistance values ranging from 3.93% to 70.31% degradation, depending on the method used. Figure 18.9 is an illustration of one type of rotary drum used to determine abrasion resistance.

Typical abrasion resistance values obtained using the rotary drum illustrated are listed in Table 18.7. Urea prills, which have low single-particle crushing strengths (Table 18.6), also showed relatively high degradation in the abrasion resistance test. Likewise, diammonium phosphate granules, which have high single-particle crushing strengths (Table 18.6), also showed relatively

Table 18.6. **Typical Crushing Strength Values (Ranges) of Some Common Fertilizers**

Fertilizer Type	Fertilizer Grade	Crushing Strength (kg/granule)
Prilled urea	46-0-0	0.8-1.2
Granular urea	46-0-0	1.5-3.5
Granular ammonium sulfate	21-0-0	1.5-2.5
Prilled ammonium nitrate	34-0-0	1.2-1.7
Granular diammonium phosphate	18-46-0	3.0-5.0
Granular monoammonium phosphate	11-55-0	2.0-3.0
Granular triple superphosphate (accretion process)	0-46-0	4.5-8.0
Granular triple superphosphate (steam granulation)	0-46-0	1.5-3.0
Prilled potassium nitrate	13-0-44	1.5-2.0
Granular potassium chloride	0-0-60	3.0-5.0
Granular potassium sulfate	0-0-50	3.0-4.0

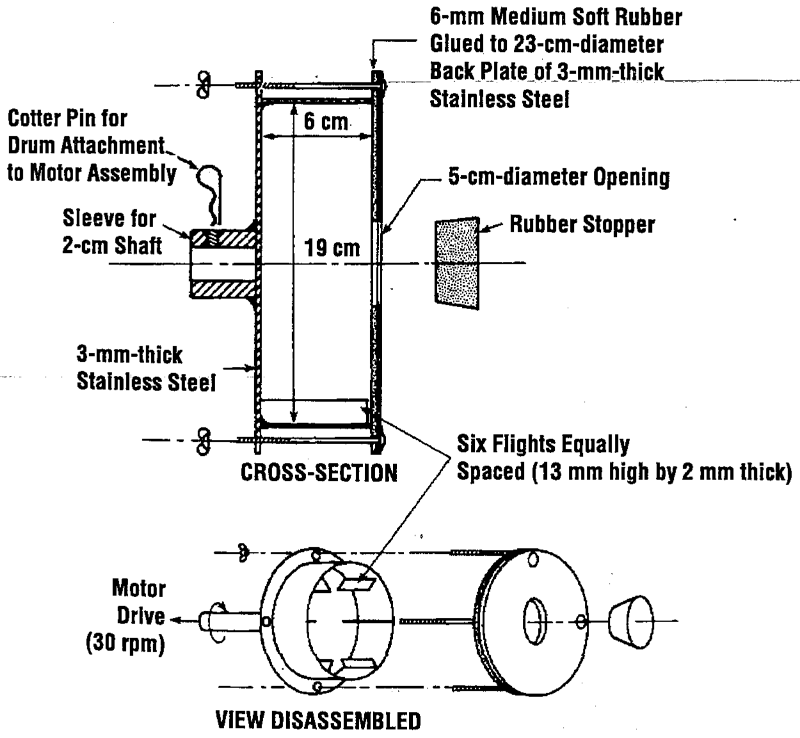


Figure 18.9. **Rotary Drum Used in Abrasion Resistance Test.**

low degradation in the abrasion resistance test. However, potassium chloride granules, which have high single-particle crushing strengths (Table 18.6), showed relatively high degradation in the abrasion resistance test, probably because of the irregular, block-like particle shape.

18.2.4.3 Impact Resistance – Impact resistance is the resistance of granules to breakage upon impact against a hard surface. It is of interest when fan-type fertilizer spreaders are used, when a material is discharged from an overhead point such as loading into a shiphold, and when bags of material are dropped during handling.

Impact strength is determined by measuring granule breakage after a sample is subjected to a standardized impact. The impact can be imparted by dropping a sample from a given height onto a steel plate or by impinging a sample against a steel plate [1,8,46,49]. The impact resistance is normally calculated by determining the

Table 18.7. **Typical Abrasion Resistance (Rotary-Drum Method) Values (Ranges) of Some Common Fertilizers**

Fertilizer Type	Fertilizer Grade	Abrasion Resistance (% degradation)
Prilled urea	46-0-0	10.0-30.0
Granular urea	46-0-0	0.2-3.0
Granular ammonium sulfate	21-0-0	0.2-1.0
Crystalline ammonium sulfate	21-0-0	6.0-10.0
Prilled ammonium nitrate	34-0-0	1.5-27.0
Granular diammonium phosphate	18-46-0	0.5-2.0
Granular monoammonium phosphate	11-55-0	0.5-2.0
Granular triple superphosphate (accretion process)	0-46-0	0.1-1.0
Granular triple superphosphate (steam granulation)	0-46-0	1.0-5.0
Prilled potassium nitrate	13-0-44	10.0-20.0
Granular potassium chloride	0-0-60	2.0-5.0
Granular potassium sulfate	0-0-50	5.0-7.0

percentage difference in round granules (sphericity discussed later in this chapter) before and after the impact test or by prescreening the sample to a specified size before the impact test and then rescreening the sample after the test to determine the amount of breakage.

Figure 18.10 is an illustration of the equipment used in a typical drop-type impact resistance test. Typical impact resistance values (based on the illustrated drop-type equipment using the screening procedure) for some common fertilizers are listed in Table 18.8.

18.2.5 Hygroscopicity

Hygroscopicity is defined as the moisture absorption properties of a fertilizer under specified conditions of humidity and temperature. Most fertilizer products are hygroscopic to some extent because of their normally high water solubility. However, the more hygroscopic a fertilizer is, the more problems one can expect during storage and handling. Factors that normally influence the degree of hygroscopicity in fertilizers are (1) chemical composition, (2) moisture content, (3) ambient temperature, (4) relative humidity, (5) particle structure and porosity, (6) exposure time, and (7) particle surface area [50,51,52].

The hygroscopic properties of a fertilizer can be quantified and qualified by measuring the critical relative humidity and its moisture absorption-penetration characteristics.

18.2.5.1 Critical Relative Humidity (CRH) – The CRH of a material is defined as the relative humidity of the atmosphere at which the material begins to absorb moisture from the atmosphere and below which it will not absorb atmospheric moisture. The major factors that dictate the CRH of a fertilizer are its chemical composition and the ambient air temperature [2].

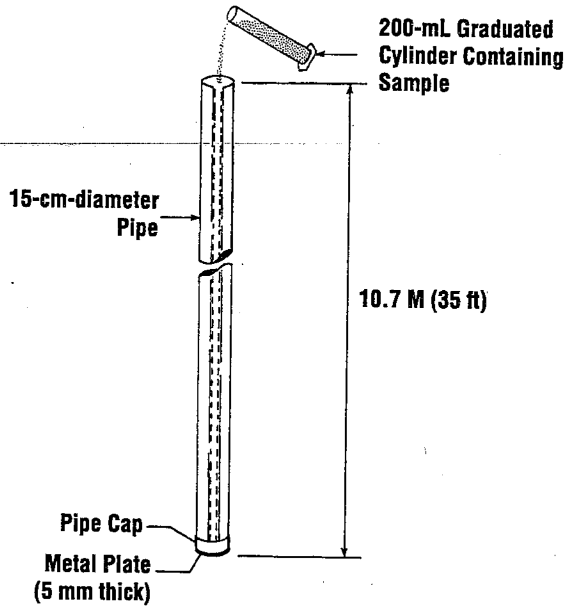


Figure 18.10. **Impact Resistance Test for Measuring Strength of Granules.**

All soluble salts, including fertilizer salts, have characteristic CRHs. Chemically speaking, the CRH of a salt is

Table 18.8. Typical Impact Resistance Values (Ranges) of Some Common Fertilizers

Fertilizer		
Type	Grade	Impact Resistance (% shattered granules)
Prilled urea	46-0-0	5.0-15.0
Granular urea	46-0-0	0.1-1.0
Granular ammonium sulfate	21-0-0	0.1-0.5
Prilled ammonium nitrate	34-0-0	3.0-6.0
Granular diammonium phosphate	18-46-0	0.5-1.5
Granular monoammonium phosphate	11-55-0	0.5-1.5
Granular triple superphosphate	0-46-0	0.0-1.0
Prilled potassium nitrate	13-0-44	5.0-10.0
Granular potassium chloride	0-0-60	2.0-5.0
Granular potassium sulfate	0-0-50	5.0-10.0

that humidity of air at which the partial vapor pressure of water in the air exactly equals the equilibrium water vapor pressure above a saturated solution of the salt at any given temperature [1].

For a fertilizer, a relatively high CRH is an advantage because such a material can be exposed and handled under more humid atmospheric conditions without becoming wet and nonflowable or without absorption of moisture that might later promote caking. The CRH of a fertilizer affects, to a large extent, (1) wetting of bulk-pile surfaces; (2) the mass transfer of moisture within a pile or bag; (3) sticking and buildup on equipment; (4) compatibility in bulk blends; and (5) the choice of handling in bulk or bag and, if bagged, the type of bag required. However, the importance of CRH in other regards should not be overestimated. For example, CRH is sometimes mistakenly considered to be a universal measure of caking tendency in fertilizers. Actually, if a fertilizer is stored in a moisture-resistant bag or in a protected (plastic covered) bulk storage pile, atmospheric humidity is effectively excluded and CRH is of relatively little importance. In those situations, caking when it occurs is related to other factors, such as constituent moisture content of the fertilizer, chemical reactions, ambient air temperature, storage pressure, presence of fines, and efficiency of any conditioning treatment. Even in regard to bulk exposure of fertilizer, CRH is not the only property that governs behavior under humid conditions. CRH is strictly a quantitative measure indicating whether or not moisture will be absorbed by a material at a specified relative humidity and temperature. The CRH says nothing as to how well or how poorly the fertilizer will tolerate the absorbed moisture. A fertilizer has other properties (discussed later in this section) that can be determined to more fully define its hygroscopic properties.

The simplest, most relevant method by which to measure the CRH of a fertilizer is to expose a sample to progressively higher relative humidities at a predetermined temperature. The lowest relative humidity at which a "significant amount of moisture" is absorbed (determined by frequent weight checks) is taken as the CRH. A significant amount of moisture for a fertilizer can vary depending on the type and nature of material being tested. What is significant for one fertilizer may not be significant for another fertilizer. The determination is most conveniently made in a laboratory temperature-humidity chamber equipped with forced air circulation and mechanical refrigeration for humidity control. In the absence of a prefabricated environmental chamber, CRH determinations can be done in a simple, insulated, moisture-tight cabinet equipped with an electric circulating fan, an electric heater, a wire-mesh sample shelf, and a large glass dish to hold a humidity-controlling salt solution. However, use of this equipment can result in data that are not reproducible, and the procedure is slow and time-consuming.

Several other procedures have been reported for determination of CRH of fertilizers and pure fertilizer salts [53,54,55,56,57,58]. In general, these are static, indirect methods that do not simulate practical exposure conditions and cannot distinguish true CRH from secondary absorptions due to impurities.

Data obtained from typical CRH determinations utilizing the method described above are shown in Figure 18.11. The data obtained for prilled urea are typical of relatively pure materials, in that the critical point is quite definite. There was no moisture absorption in 3 hours at 70% relative humidity, but there was continuous absorption at 75%. The data shown for the fertilizer grade diammonium phosphate, on the other hand, illustrate typical behavior of fertilizers that contain small amounts of soluble impurities. It is obvious that the CRH of the main constituent is between 70% and 75%; for practical purposes, however, it would have to be recognized that exposed product would pick up some moisture at relative humidities between 60% and 70%. At 70% relative humidity, a maximum of 2% would be absorbed. For most diammonium phosphate products, this is insufficient to cause intergranule transfer of moisture; thus, only the surface granules would be affected in a bulk pile. One of the chief advantages of this method is this ability to distinguish between true CRH and secondary absorptions due to impurities.

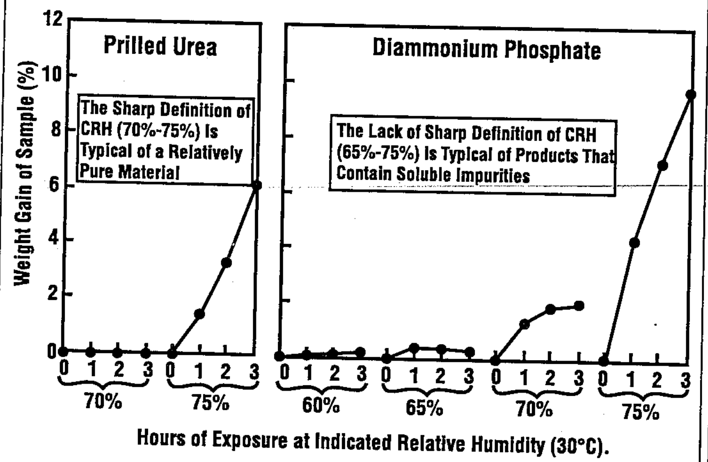


Figure 18.11. Data Obtained From CRH Measurement of Fertilizer Grade Urea and Diammonium Phosphate.

Mixtures of fertilizers usually have lower CRHs than either of the constituents. The chart given in Figure 18.12 shows typical CRH data for commercial fertilizers and mixtures of these fertilizers [59]. The effect of mixing fertilizers is most dramatic in the case of ammonium nitrate (CRH of 55%-60% at 30°C) and urea (CRH of 70%-75% at 30°C) where the CRH of a mixture of these two fertilizers is approximately 18%. Table 18.9 also lists CRH ranges of some commercial fertilizer products [2].

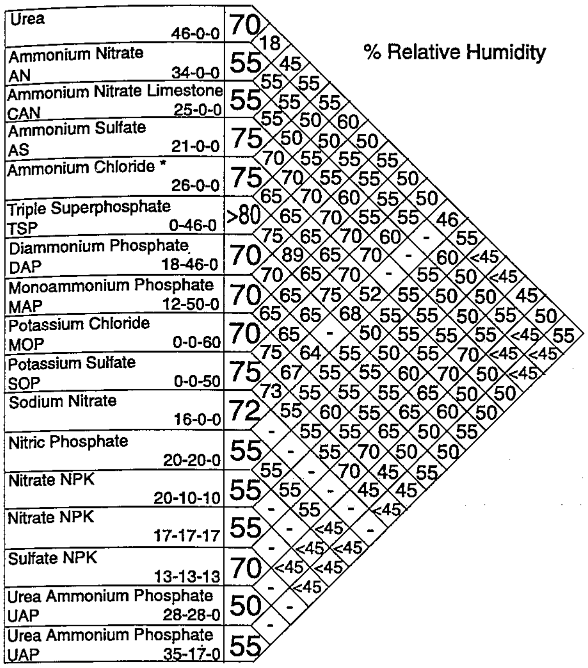
The CRH of most fertilizers decreases with increase in temperature. Figure 18.13 shows the effect of temperature on the CRH of some typical commercial fertilizers [60,61].

18.2.5.2 Moisture Absorption-Penetration Characteristics – Determination of CRH defines the humidity above which a fertilizer will absorb moisture from the atmosphere. However, the CRH gives no information as to how rapidly moisture will be absorbed or what effect the moisture absorption will have on the physical condition of the fertilizer. Fertilizers vary considerably in their ability to tolerate absorbed moisture. When a fertilizer is exposed to relative humidities above its CRH, the factors that most affect the moisture absorption-penetration characteristics of a fertilizer are its chemical composition, particle porosity, particle surface area, and degree of crystallinity. Moisture absorption-penetration characteristics are important when considering conditions at which a fertilizer is to be stored, when predicting its flowability during handling and movement through the distribution system, and during field application [28,62,63,64].

Laboratory Absorption-Penetration Test

The surfaces of bulk storage piles frequently are exposed to humid atmospheres; thus, it is of interest to know how rapidly moisture will be absorbed and how rapidly and to what depth wetting and physical deterioration will progress. The laboratory absorption-penetration test provides a method for evaluating these effects of pile exposure [1,3,8].

The laboratory absorption-penetration test involves exposing a bulk fertilizer surface of known area to moving air at a controlled temperature and humidity for an extended period of time in a constant temperature-humidity chamber. Samples are exposed in glass cylinders as illustrated in Figure 18.14. Samples are normally evaluated periodically during the extended exposure time. The samples are evaluated by measuring (1) the rate of moisture absorption per unit of fertilizer surface; (2) the depth of moisture penetration into the fertilizer; (3) the moisture-holding capacity of the individual fertilizer particles; and (4) the integrity of the wetted granules. Typical data from this test for some common fertilizer materials are given in Table 18.10.



* Reagent Grade Salt

Note: Determinations were made on commercial materials. CRH Values are approximate and may vary several points depending on production method and source of material.

Figure 18.12. Critical Relative Humidities of Commercial Fertilizers and of Mixtures at 30°C.

It is interesting to note that neither rate of moisture absorption nor depth of moisture penetration correlate with CRH. Neither did depth of moisture penetration correlate with rate of moisture absorption; this is a result of differences in "moisture-holding capacity." Moisture-holding capacity represents the maximum amount of moisture that a granule will absorb before it becomes so wet that moisture will be transferred to adjacent granules by capillary action. High moisture-holding capacity is a desirable characteristic that can offset the effects of high rate of moisture absorption. Moisture-holding capacity apparently is related to both the chemical composition and the porosity of the granules. Pure crystalline fertilizer salts such as urea and ammonium nitrate generally are nonporous and have low moisture-holding capacities. Some impurities, for example, iron and aluminum phosphates from wet-process acids, decrease the crystalline phase and increase the amorphous phase in fertilizers and are beneficial in increasing moisture-holding capacity.

Results of the laboratory absorption-penetration tests are indicative of expected bulk fertilizer behavior under steady, high-humidity conditions, but it should be realized that under cycling conditions, such as occur in actual storage, the results may be altered by crusting (self-sealing) of pile surfaces of some materials during dry cycles. Also, it should be realized that under such cycling conditions products with high CRH values will be nonabsorbing a greater portion of the time than will products with low CRH values.

Flowability Test

In addition to pile exposure, fertilizers are also frequently exposed to humid environments during handling and movement through the distribution system and during field application. In those operations, the effect of moisture on flowability is the major concern. Even though two fertilizers may have similar CRH values, they may differ significantly in their ability to remain flowable under humid conditions. The flowability test provides a method for evaluating the ability of a fertilizer to remain free flowing under humid conditions [1,8]. In this test, flowability is determined by measuring the length of time a material will remain flowable in a rotating drum under elevated humidity conditions (in a constant temperature-humidity chamber). Figure 18.15 is an illustration of the rotary drum used in this procedure to measure flowability. Typical flowability data for some common fertilizers are given in Table 18.11. In addition to determination of free-flow time, the sample can be analyzed at the end of the test to determine the moisture content at which the product became nonflowable.

Several other methods have been developed, including small-pile storage tests and drillability tests, to evaluate the degree of moisture tolerance of fertilizers. All of these tests have some merit and can be found in the literature [1,2,3,8,65,66,67,68,69,70].

18.2.6 Caking Tendency

The ISO defines caking as "the formation of a coherent mass from individual particles" [11]. Fertilizers, between the time of production and field application, must be stored, either in bulk or in bags. Storage times can vary from a few days to a year or more. It is essential that, during storage, either the fertilizer remain completely free flowing or the caking be so minimal that a small amount of normal handling will restore the original free-flowing condition. It is not possible to give a universal criterion as to what degree of caking is tolerable because requirements differ widely in different areas and for different uses. Where machine application is employed, complete freedom from lumps is highly desirable, although a few (up to perhaps 15%) light lumps may be acceptable. For hand application, where labor is available and each bag can receive individual treatment, a higher percentage of lumps and the presence of lumps of medium hardness may not be considered intolerable.

Table 18.9. Critical Relative Humidity (CRH) of Some Typical Fertilizer Products

Grade	Composition[a]	CRH (at 30°C)
46-0-0	Urea	70-75
34-0-0	Ammonium nitrate	55-60
21-0-0	Ammonium sulfate	75-85
18-46-0	DAP	65-75
12-50-0	Monoammonium phosphate	70-75
0-46-0	TSP	75-85
0-0-60	KCl	70-80
13-0-44	Potassium nitrate	80-85
0-0-50	Potassium sulfate	75-80
10-10-10	Ammonium sulfate, ammonium phosphate, KCl, sand	65-75
8-32-16	Ammonium sulfate, ammonium phosphate, KCl, sand	65-75
10-5-18-2MgO	Ammonium sulfate, phosphate rock, KCl, kieserite	60-70
20-10-10	Ammonium nitrate based	55-60
28-28-0	Urea, APP	55-65
20-20-0	Urea, DAP, phosphate rock	50-60
16-0-30	Urea, KCl	45-55
18-18-10	Urea, DAP, phosphate rock, KCl, neem cake, filler	45-55
17-17-17	Urea, ammonium sulfate, DAP, KCl	45-55
19-19-19	Urea, APP, KCl	50-60
15-15-15	Urea, DAP, KCl, sand	45-50
12-12-17-2MgO	Urea, phosphate rock, KCl, kieserite	40-50
12-12-17-2MgO	Nitrophosphate	60-65

a. DAP = diammonium phosphate; TSP = triple superphosphate; KCl = potassium chloride; APP = ammonium polyphosphate.

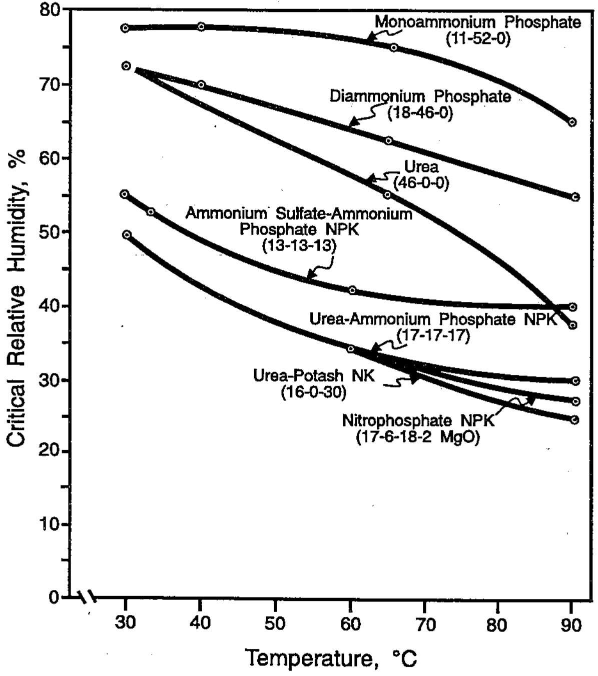


Figure 18.13. Effect of Temperature on Critical Relative Humidity of Selected Fertilizers.

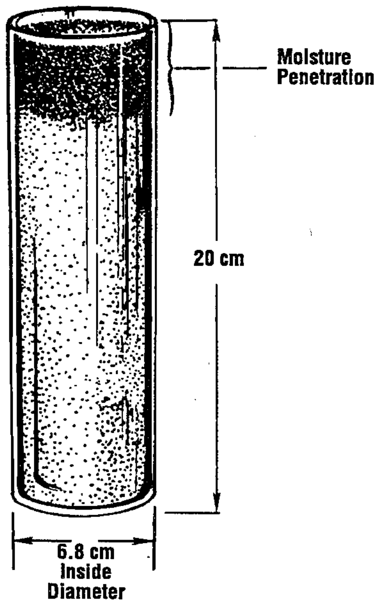


Figure 18.14. Glass Cylinder Used in Measuring Moisture Absorption and Penetration in a Fertilizer.

Table 18.10. Moisture Absorption-Penetration Characteristics of Some Typical Granular Fertilizer Products

Grade	Composition[a]	Moisture Absorption-Penetration Characteristics (30°C, 80% Relative Humidity for 72 h): Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Holding Capacity (%)	Granule Integrity[b]
46-0-0	Urea	350	15	3	Fair-good
21-0-0	Ammonium sulfate	100	0	-	Excellent
18-46-0	DAP	175	2	12	Fair-good
0-46-0	TSP	235	2	12	Excellent
0-0-60	KCl	135	3	5	Good
6-24-24	Ammonium sulfate, ammonium phosphate, KCl, sand	280	2	15	Fair
10-10-10	Ammonium sulfate, ammonium phosphate, KCl, sand	270	4	7	Poor
13-13-13	Ammonium sulfate, ammonium phosphate, KCl, sand	365	4	9	Fair
28-28-0	Urea, APP	370	3	15	Poor
17-17-17	Urea, ammonium sulfate, MAP, KCl	580	6	12	Poor
12-19-9	Urea, phosphate rock, KCl	450	5	8	Poor
15-15-15	Urea, phosphate rock, KCl, sand	490	6	8	Poor
12-12-17-2MgO	Urea, phosphate rock, KCl, kieserite	445	5	7	Poor

a. DAP = diammonium phosphate; TSP = triple superphosphate; KCl = potassium chloride; APP = ammonium polyphosphate; MAP = monoammonium phosphate.

b. Granule integrity is a qualitative observation based on the strength of the top layer (surface) of granules after exposure for 72 h.

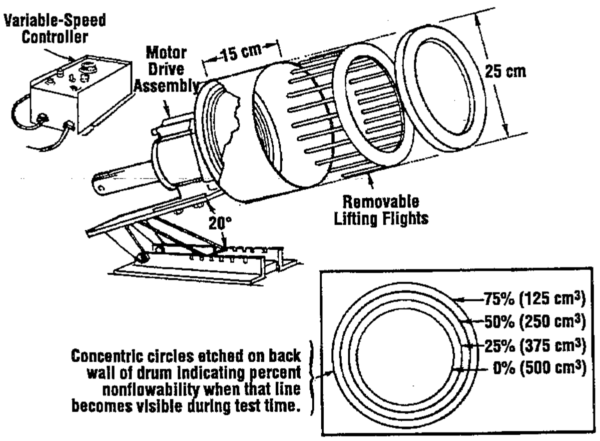


Figure 18.15. Rotary Drum for Measuring Flowability of Fertilizer When Exposed to Humid Conditions.

18.2.6.1 Causes of Caking – Caking of fertilizer is caused by the formation of contact points between the particles (granules, prills, tablets, briquettes, powder, crystals, etc.). These contact points differ in nature and basically have three mechanisms, namely, phase contacts, adhesive contacts, and surface diffusion [71].

Phase contacts (salt bridges) are crystal bridges formed at the contact points between the fertilizer particles [72,73]. The most troublesome caking of fertilizers is believed to be caused by crystal bridging. Crystal bridges develop during storage as a result of continuing internal chemical reactions, dissolution/recrystallization processes, and/or thermal effects [74,75].

Adhesive contacts (capillary adhesion) are formed as a result of molecular attraction between the surfaces in contact [76,77]. The forces of attraction involved in this phenomenon, known as Van der Waals forces, are considered to be relatively weak. This type of contact is influenced mostly by the plasticity of the particles and the pressure exerted on the fertilizer material when it is stacked in bags or piled in bulk, usually referred to as bag or pile set. The material normally reverts to a free-flowing form rather easily with a minimal amount of handling.

Table 18.11. Flowability (During Humid Exposure) of Some Typical Granular Fertilizer Products

Grade	Composition[a]	Flowability (Minutes at 30°C and 90% RH) 25% Nonflowable	50% Nonflowable	75% Nonflowable
46-0-0	Urea	5	10	15
34-0-0	Ammonium nitrate	7	12	16
21-0-0	Ammonium sulfate	175	220	280
18-46-0	DAP	70	130	180
11-52-0	Monoammonium phosphate	80	165	190
0-46-0	TSP	180	240	300
6-24-24	Ammonium sulfate, ammonium phosphate, KCl, sand	155	175	205
10-10-10	Ammonium sulfate, ammonium phosphate, KCl, sand	75	90	105
19-19-19	Urea, APP, KCl	10	20	30
12-6-22-3MgO	Urea, phosphate rock, KCl, kieserite	31	38	40
12-6-22-3MgO	Ammonium nitrate based	37	43	48

a. DAP = diammonium phosphate; TSP = triple superphosphate; KCl = potassium chloride; APP = ammonium polyphosphate.

Surface diffusion is a result of water-salt complexes consisting of pairs of hydrated ions that are transported within an adsorbed phase and then form contacts with adjacent granules. The diffusional mechanism of caking in fertilizers is greatly influenced by the porous structure of the particles [78,79,80].

18.2.6.2 Factors Influencing Caking – A number of factors influence the tendency of a fertilizer to cake. These factors can be divided into internal factors, related to the physical-chemical constitution of the fertilizer, and external factors, related to the environmental conditions to which the fertilizer is exposed during handling and storage. Obviously some of these factors are interrelated. Identification and review of factors that have an influence on caking tendency have been the subject of numerous publications [71,72,73,76,81,82,83,84,85,86].

Internal Factors

1. The chemical composition of fertilizers has an effect on the caking tendency. For example, it has been shown that the caking tendency of ammonium nitrate-based and urea-based NPK fertilizers is greater than that of ammonium sulfate-based and ammonium phosphate-based NPK fertilizers [87,88,89,90]. Even impurities may affect caking. Fertilizer products made from wet-process phosphoric acids characteristically contain significant proportions of iron and aluminum phosphate impurities, which have been shown to serve as effective internal anticaking agents in those products [91,92,93]. The iron and aluminum phosphates are found in the products as amorphous "gels" that harden the products and apparently immobilize solution phases. Formation of the iron and aluminum phosphates under relatively high pH and low temperature conditions promotes the gel-type structure rather than crystalline forms [94].
2. The amount of moisture allowed to remain in a fertilizer at the time of its manufacture has a great effect on its tendency to cake in storage. For most caking mechanisms, the presence of moisture, in the form of solution phase, is essential. The higher the degree of drying at the time of manufacture, the less active the caking mechanisms will be. The extent of drying required to effectively inactivate caking mechanisms varies rather widely with the composition and physical makeup of the fertilizer. Generally, those fertilizers that contain high proportions of nitrogen salts require a greater degree of drying. This is particularly true for fertilizers that contain ammonium nitrate or urea. The following tabulation offers some very general guidelines on maximum product moisture content for granular fertilizers. These values should be used only in a general way because numerous processing variations alter the effects of moisture on storage and handling properties of a given fertilizer composition. The values given represent "free water" content (nonhydrate water).

Product Moisture, 0%-0.5%

Ammonium nitrate
Urea
Ammonium sulfate
Calcium nitrate
Sodium nitrate
Potassium chloride

Product Moisture, 0.5%-1.0%

Mixed fertilizers that contain urea or ammonium nitrate

Product Moisture, 1.0%-1.5%

Mixed fertilizers with $N:P_2O_5$ ratios greater than 1:1 that contain no urea or ammonium nitrate

Product Moisture, 1.5%-2.0%

Mixed fertilizers with $N:P_2O_5$ ratios less than 1:1 that contain no urea or ammonium nitrate

Product Moisture, Above 2.0%

Mixed fertilizers containing little or no nitrogen
Superphosphates

3. The size, shape, and structure of the particles are also important. If the particles are relatively large, well formed, and uniform in shape and size with very little fine material, the specific surface area is reduced [95]. Consequently, forces of attraction and points of contact between adjacent particles are reduced, lowering the tendency to cake.

4. The mechanical strength or hardness of the particles has an effect on the caking tendency. Weak granules may break down under stack or pile pressure (crushing strength) or during handling (abrasion and impact strength) [95]. As a result, a substantial quantity of fines can be created and thereby increase the number of contact points between particles.

5. The hygroscopic properties of the product can have an effect on the degree of caking [96]. All fertilizers have a CRH above which they will absorb moisture. Caking as a result of moisture absorption is usually along the pile surface and with prolonged exposure to elevated humidities can become quite deep.

6. The temperature of the product when placed in storage is another important factor having an effect on caking tendency [97,98,99,100]. Higher temperatures increase the chemical reactivity, such as the re-evaporation of water, which results in recrystallization and formation of solid crystalline bridges. Additionally, a high product temperature can promote the development of plastic-like particles that deform under pressure. This deformation promotes both crystal bridging and capillary adhesion. After conducting extensive research on the caking tendency of urea Van Kijfte stated, "Urea being fed to the stockpile at 50°C to 70°C will definitely form strong cakes. The lower the feed temperature, the lower the tendency to cake. The conclusion of these studies was that if the urea is cooled below 30°C before entering storage, there is less agglomeration and, mainly, the agglomerates are softer" [101]. Diammonium phosphate, on the other hand, usually needs to be cooled only to about 70°C.

External Factors

1. The warehouse or storage temperature is important with respect to caking tendency. Higher ambient temperatures lower the CRH of a fertilizer material and thereby increase its hygroscopicity. For example, the CRH of a 15-15-15 nitrophosphate is approximately 55% at 30°C, whereas it is approximately 45% at 40°C. Conversely, raising the temperature of *existing* warehouse air will reduce the relative humidity (RH). This method can be employed to lower the warehouse RH below the CRH of the fertilizer.

2. The humidity of the surrounding atmosphere has an effect on caking. As mentioned previously, when a fertilizer is exposed to a RH above its CRH, absorption of moisture will take place. Saturated solutions will then be formed at the granule surface, promoting capillary adhesion and crystallization processes due to changes in temperature or subsequent evaporation. Here the severity of caking depends mainly on the rate of absorption. The rate of absorption is dependent on factors such as (1) the difference between the RH of the air and the CRH of the fertilizer, (2) the movement of air with a constant RH over the fertilizer, (3) the moisture-holding capacity of the fertilizer as influenced by the granulometry and porosity, and (4) the rate of penetration into the bulk fertilizer pile [85].

3. The length of storage time influences caking. In most cases, the tendency of a fertilizer to cake is highest during the first few weeks after production. However, if a fertilizer has a tendency to cake, prolonged storage periods will generally result in a significant increase in caking.

4. The pressure exerted at the bottom of a stack or pile of fertilizer has a definite effect on caking [102]. As with storage time, if a fertilizer has a tendency to cake, excessive and prolonged pressure will result in a significant increase in caking. Under pressure,

particle deformation may occur, resulting in increased contact area.

18.2.6.3 Solutions to Alleviate Caking – Various measures by the fertilizer industry have proven beneficial in alleviating caking, including the following:

1. Various drying processes to obtain a product with a low moisture content.
2. Various cooling processes to obtain a product with a low temperature.
3. Various granulation, prilling, and pelletizing processes to produce larger particles thereby decreasing the surface area and number of contact points between particles.
4. The use of screening equipment to obtain a more uniform particle size thereby decreasing the surface area and number of contact points between particles.
5. The control of storage conditions such as RH, temperature, pile height, and storage time.
6. Packaging fertilizer products in moisture-resistant bags.
7. The addition of anticaking agents (conditioners).

As indicated, much can be done to decrease the caking tendency by improving both process and storage conditions. However, there is always a practical and economical limit to the improvements that are possible. Thus, in many cases the use of an anticaking agent in combination with process and storage control is the obvious answer to caking problems. However, it should be emphasized here that an anticaking agent *cannot* be used to compensate for a poorly produced or handled fertilizer.

18.2.6.4 Anticaking Agents – An anticaking agent is a material added to a fertilizer to promote the maintenance of good physical condition (flowability) during storage and handling. Anticaking agents can be classified into two categories according to the method of application: coating agents and internal conditioners.

Coating Agents

Coating agents are conditioning materials that are applied uniformly onto the surface of the fertilizer particles. Most coating agents are either very finely divided inert powders (dusts) that adhere to the particle surfaces or are liquids that are sprayed onto the surface. These anticaking agents function by various mechanisms. Inert powders such as clays (kaolin and china), diatomaceous earth (kieselguhr), and talc (basic magnesium silicate) function as mechanical barriers between particles and also serve to absorb, spread, and inactivate any solution phase that may occur on particle surfaces. Where caking bonds do occur, the presence of dust-type anticaking agents usually weakens the bonds; thus, caking is less severe. Liquid coating agents usually function either as crystal modifiers to inhibit or weaken crystal growth on and between the particles or as hydrophobic barriers to inhibit moisture absorption.

Inert Powders – Clay anticaking agents are extremely fine (typically 90% less than 10 µm and 50% less than 1 µm) and thus adhere well to the fertilizer granules. Kaolin clays are widely available and relatively inexpensive. When used alone, they are usually sufficiently effective for use on NP or NPK fertilizers and on urea. They are not normally considered effective for use on ammonium nitrate or other high-nitrate products. However, kaolin clay combined with certain organic additives can be used with these products; organically treated kaolin is an accepted conditioner for ammonium nitrate [103,104].

Diatomaceous earth (also referred to as kieselguhr) is coarser than most clays (typically 90% minus 20 µm and 50% minus 3 µm) and thus does not usually adhere as well as clay. However, diatomaceous earth has good absorption properties and is an effective anticaking agent for ammonium nitrate. The major disadvantages to using inert powders as anticaking agents are their diluting effect on the product analysis and their dustiness.

Adherence of inert powders often can be improved by spraying the fertilizer with a small amount of oil or wax-free binders (usually 0.1%-0.3%). Results are best with moderately to fairly viscous oils (25 to 200 MPa•s).

Liquid Coating Agents – These agents include organic surface active agents (surfactants) and nonsurface active agents [105].

Surfactants function by altering the interfacial tension between the solid (particles) and liquid (surfactants). Their action as anticaking agents is not clearly understood, and various mechanisms have been proposed – protection from moisture, spreading of liquid film, modification of crystal makeup/behavior, inhibition of dissolution and crystallization, and modification of bond tensile strength.

Because surfactant molecules comprise a nonpolar hydrophobic (water repellent) group and one or more polar hydrophilic (having a strong affinity for water) groups, they can be subdivided into two classes according to their polar structure: (1) ionic, which can be further classified according to the polarity of the charge carried on the active part of the molecule (anionic if the charge is negative or cationic if the charge is positive) and (2) nonionic, where the molecule is electronically neutral.

The anionic surfactants commonly employed are mainly sulfonates, particularly alkyl aryl sulfonates [106,107,108,109,110,111]. It is primarily due to their hydrophobic nature that the anionic surfactants act as anticaking agents; i.e., this increases the contact angle of the fertilizer solution and reduces the tensile strength of the caking bond.

Cationic surfactants are dominated by the fatty amines, especially those with a long carbon chain like octadecyclamine [112,113,114]. Caking is prevented by three different mechanisms: by the formation of a hydrophobic coating on the surface of the particles, thus improving water repellency; by reducing capillary adhesion between particles; and by inhibiting nucleation or otherwise modifying crystal growth.

The largest class of nonionic surfactants is the polyoxyethylene condensates, but these have only a moderate effect and are not widely used. Silicone fluids may be considered as nonionic surfactants; although they are used as anticaking agents for many powders, their use on fertilizers is limited due to their high cost. Other nonionic surfactants include fatty acid esters, substituted ureas, and aldehydes and ketones with low molecular weight [115,116].

Nonsurface active coating agents are organic compounds that do not exhibit surface activity but do form a moisture-resistant layer on the surface of the fertilizer particle [117,118,119,120,121]. Typical nonsurface active coating agents include paraffin wax, synthetic polymers, and oils. They can be used alone or in combination with an inert dust.

Internal or Chemical Conditioners

This type of conditioner (anticaking agent) is added to the fertilizer during processing. These conditioners act internally, usually as hardeners or crystal modifiers to improve storage properties [122,123,124,125,126].

For urea conditioning, a popular practice in some countries is the inclusion of 0.3%-0.5% of formaldehyde in the final product. The formaldehyde is added to the molten urea in the form of a 37% formaldehyde solution or concentrated urea-formaldehyde (UF85 containing 26% urea, 59% formaldehyde, and 15% water). Formaldehyde addition also reduces the formation of dust in the finishing (granulation) process because the granules are harder and more resistant to abrasion and breakage than is untreated material [127,128,129].

In the case of ammonium nitrate fertilizer, internal conditioners are used to inhibit or modify the effects of crystal phase inversions that result from temperature cycling during storage; the inversion that occurs at 32°C, in particular, can cause untreated ammonium nitrate prills to shatter and cake seriously under cycling storage temperatures [126,130,131,132,133,134]. For ammonium nitrate the most popular internal conditioner is magnesium nitrate. A treated product typically contains about 1.8% magnesium nitrate [135].

As discussed previously, fertilizer products made from wet-process phosphoric acid characteristically contain significant quantities of iron and aluminum phosphate impurities, which serve as effective internal conditioners.

18.2.6.5 Evaluation of Caking Tendency – Excessive caking can cause problems in (1) removal of material from storage bins, railcars, trucks, and shipholds; (2) field application; and (3) bagging operations. Methods for evaluating the caking tendency of fertilizers can be divided into three types, namely, large-bag storage tests, small-bag storage tests, and accelerated caking tests.

Large-Bag Storage Test

The caking tendency of a fertilizer can be evaluated by subjecting a standard-size bag to a predetermined pressure for a specified period of time. The time of storage is usually based on what the actual storage period is expected to be (usually 1-12 months). Usually, enough samples are placed in storage so that evaluations can be made at certain intervals (for example, 1, 3, 6, and 12 months) during the test. The storage temperature can be controlled or not controlled, depending on the expected conditions of the fertilizer in actual storage. After storage, the test samples are evaluated for "bag set" and then dropped to simulate normal handling procedures. The caking tendency is then determined by measuring the percentage and hardness of lumps created during storage [1,2,3,8].

Small-Bag Storage Test

The disadvantages of the large-bag method (i.e., need for large quantities of material, a large test area, and a considerable amount of labor) can be avoided by performing a small-bag storage test. In this procedure, an 1,800-cm^3 sample is sealed in a moisture-resistant bag and stored under a predetermined pressure for a specified period of time to simulate actual storage conditions. The remainder of the procedure and evaluation are essentially the same as the large-bag method [1,2,3,8].

Figure 18.16 is an illustration of the equipment used in the small-bag storage tests.

Accelerated Caking Test

The major disadvantage of the large- and small-bag methods is the long period of storage required (usually 1-12 months). There have been numerous attempts at devising a quicker method for evaluating caking tendency in fertilizer [1,3,76,136,137,138,139,140]. Unfortunately, time cannot be accelerated, so most of these

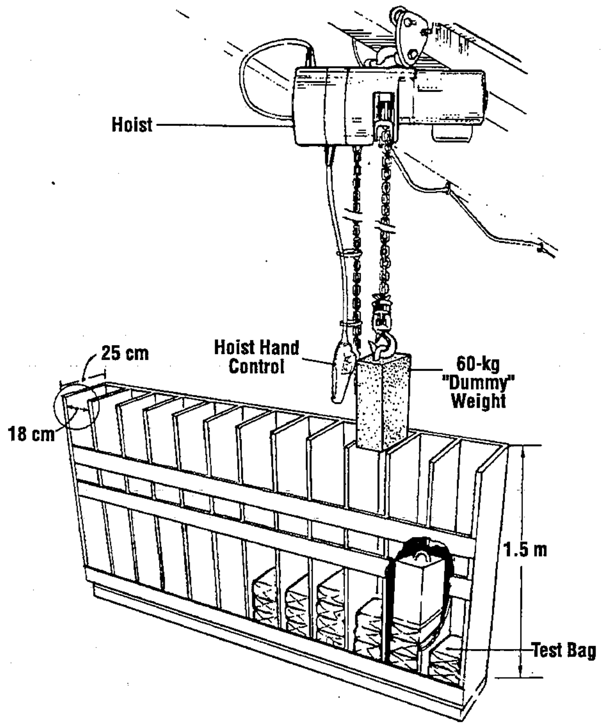


Figure 18.16. Storage Rack to Measure Caking Tendency of Fertilizer Using Small-Bag Method.

methods employ an increase in temperature, pressure, and/or humidity to speed up caking. To date, most of these methods have not produced reliable results. These accelerated methods can be used as "screening methods." That is, if the test sample cakes in an accelerated method, it will probably cake under normal storage conditions; if it does not cake in an accelerated test, it may still cake under normal storage conditions. An accelerated method can also be useful as a "screening method" when evaluating a number of anticaking agents.

18.2.7 Dustiness

Because of the large quantities of fertilizer products and raw materials handled in bulk, their dustiness is of particular concern and can cause significant problems [141,142]. First, significant quantities of material can be lost during processing, handling, and application resulting in lost revenues. Second, environmental pollution and exposure of employees to hazardous levels of dust are not indicative of a responsible organization.

The most common sources of dust in granular fertilizers are (1) inefficient screening operations, (2) weak granules, (3) poor conditioner (anticaking agent) adherence, (4) granule surface crystals which abrade easily when handled, and (5) granule surface dust from the process.

The dustiness of a fertilizer material is normally measured by passing a sample through a countercurrent airflow inside a "dedusting tower" and noting the amount of weight loss [1,3,8]. The countercurrent airflow is typically adjusted so that it will entrain a specified particle size (dust) while allowing the granules to fall to the bottom of the tower. Figure 18.17 is an illustration of a "dedusting tower" used to measure dustiness. This equipment can also be used to evaluate the ability of a powder-type conditioner (anticaking agent), such as kaolin clay, to adhere to a granular fertilizer product.

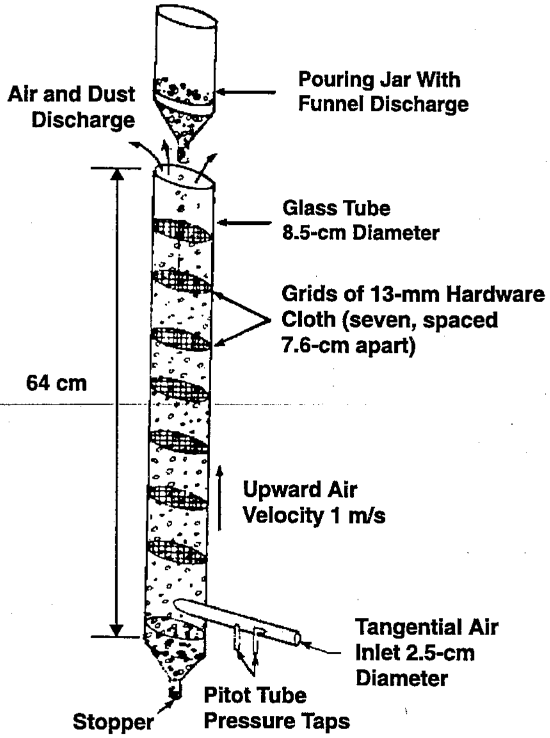


Figure 18.17. Apparatus for Measuring Dustiness.

18.2.7.1 Dust Control Agents – It is preferable to produce nondusty fertilizer without use of dust-control treatment. However, when this cannot be accomplished, it is sometimes necessary to resort to antidust treatments [143,144,145,146,147]. This treatment involves spraying the fertilizer with some liquid that will cause dust particles to adhere to granules or to agglomerate and thus not become airborne during handling. The most common liquids used are petroleum oil-based. The most effective oils are moderately to fairly viscous and consequently have greater binding effectiveness and less tendency to be absorbed into granules during storage with resultant loss of effectiveness.

Oils of high paraffin content are particularly effective. Naphthenic-based oils, if used, require the use of special oil-resistant rubber belting on conveyors. Oils containing added amines are said to have enhanced dust-control properties.

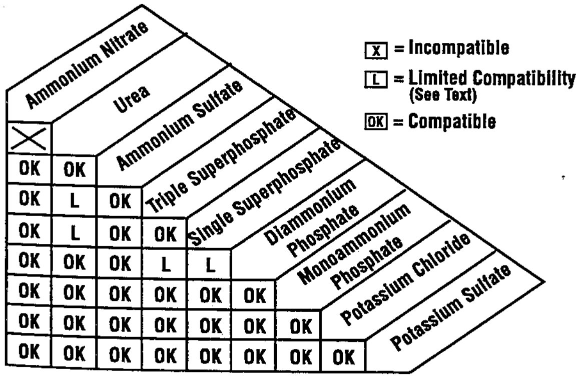
Liquids other than oils that have been used for dust control include lignin sulfonate liquors, liquid fertilizers, and water. These liquids are suitable if the water introduced does not cause caking during subsequent storage. They are sometimes used in bulk-blending plants, where the fertilizer is intended for immediate application.

Some companies market special lines of dust control agents [81].

18.2.8 Other Properties

There are a number of other physical properties of solid fertilizers which are of importance for various reasons. These physical properties are briefly discussed below.

18.2.8.1 Chemical Compatibility in Blends – The first step toward making a bulk-blended fertilizer of good quality is choice of ingredients that are chemically compatible. Fortunately, there are only a few combinations of fertilizer materials that may give trouble in this respect. The chemical compatibility of some common fertilizer materials used in bulk blends is shown in Figure 18.18.



	Ammonium Nitrate	Urea	Ammonium Sulfate	Triple Superphosphate	Single Superphosphate	Diammonium Phosphate	Monoammonium Phosphate	Potassium Chloride
Urea	X							
Ammonium Sulfate	OK	OK						
Triple Superphosphate	OK	L	OK					
Single Superphosphate	OK	L	OK	OK				
Diammonium Phosphate	OK	OK	OK	L	L			
Monoammonium Phosphate	OK	OK	OK	OK	OK	OK		
Potassium Chloride	OK	OK	OK	OK	OK	OK	OK	
Potassium Sulfate	OK	OK	OK	OK	OK	OK	OK	OK

☒ = Incompatible
L = Limited Compatibility (See Text)
OK = Compatible

Figure 18.18. **Chemical Compatibility of Blend Materials.**

The only completely incompatible combination is ammonium nitrate and urea, which results in a mixture with an excessively low CRH of 18%. However, combinations of urea and superphosphate can also be completely incompatible depending on the water content (free water plus hydrate water) of the superphosphate [148]. The cause of the incompatibility is a chemical reaction between urea and monocalcium phosphate monohydrate, the main constituent of superphosphate; this reaction releases water of hydration and causes severe stickiness. Mixtures of diammonium phosphate with superphosphates also are shown in the figure to be of limited compatibility because, in some long-term storage tests in bags, reactions between these materials have caused caking [1,87,88].

Chemical compatibility can be evaluated either in the large- or small-bag storage test described previously or by a simple "bottle test" [8,148]. In the bottle test, a freshly made blend is tightly capped in a glass bottle, stored in a moderately heated cabinet (30°C), and inspected after periods varying from 1 day to several months. Inspection reveals any wetting, caking, disintegration, or noxious gas formation.

18.2.8.2 Physical Compatibility in Blends – The physical compatibility of bulk blends is the ability of two or more materials to remain thoroughly mixed during storage, handling, and application. As discussed previously in the section on particle size, segregation can be a major problem in the handling of bulk-blended fertilizer. Segregation of materials in a bulk blend is normally caused by mismatched particle sizes. The most common method to determine physical compatibility of bulk-blend ingredients is to perform a particle-size analysis of each ingredient and compare the data. There are basically two techniques used to make the data comparison, i.e., the cumulative particle size distribution and the size-guide number [1,7,8,149,150,151,152,153].

The cumulative particle size distribution technique entails comparing each cumulative size fraction of one ingredient with the equivalent cumulative size fraction of the other ingredient(s). For these cumulative size fractions, the differences in percentage retained are noted, and the largest of these differences is used to determine compatibility. The larger this difference, the higher the segregation tendency. The following general guidelines can be used in determining compatibility:

Largest Cumulative Size Fraction Difference	Expected Compatibility
0%-10%	Good compatibility
11%-20%	Moderate compatibility (special handling precautions may reduce segregation tendencies)
>20%	Incompatible

Figure 18.19 illustrates how blend ingredients are evaluated for physical compatibility according to cumulative particle-size distribution.

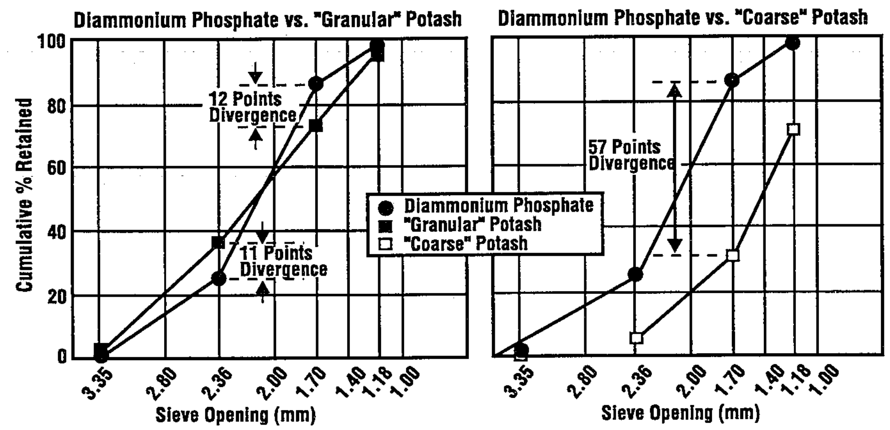


Figure 18.19. Physical Compatibility of Bulk Blend Ingredients According to Cumulative Particle-Size Distribution.

The size-guide number technique, developed by the Canadian Fertilizer Institute, entails determining the median particle size of each blend ingredient by locating the 50% cumulative retained point from the size distribution curve. The particle size (in millimeters) at the 50% cumulative retained point is multiplied by 100 and rounded to the nearest 5. This number is referred to as the SGN (size guide number) of that blend ingredient. The SGN for each bulk-blend ingredient is compared, and the blends are evaluated by the following guidelines.

Size Guide Number Difference	Expected Compatibility
0%-10%	Good compatibility
11%-20%	Moderate compatibility (special handling precautions may reduce segregation tendencies)
>20%	Incompatible

Figure 18.20 illustrates how blends are evaluated for physical compatibility according to the SGN.

18.2.8.3 Sphericity – Sphericity is a measure of particle roundness in granular fertilizers. Sphericity is useful in estimating processing efficiency and coating, handling, and storage properties of a fertilizer. To determine sphericity, a sample of granules is distributed over an inclined moving belt. The round granules roll down the incline and are collected at the bottom of the belt. The irregularly shaped or broken granules are carried upward and discharged at the top of the belt. Figure 18.21 is an illustration of typical sphericity equipment.

18.2.8.4 Surface Area – The specific surface area of a material is its surface area per unit mass; it indicates the fineness and/or porosity of a material. It is particularly useful in determining the fineness and porosity of phosphate rock and phosphogypsum in phosphoric acid production processes. The data can be used to predict reaction efficiencies and filtration rates.

18.2.8.5 Porosity – Porosity is a measure of the pore space in fertilizer granules. Excessive porosity is often the reason for weak granules. Also, in fertilizer compacting and granulating systems, porosity is an indication of the compaction and granulation efficiency. Porosity is determined by measuring a material's apparent density and true density (both discussed previously) and calculating the difference. Typical porosity values are listed in Table 18.12.

18.2.8.6 Melting Point – The melting point of fertilizers is of interest in connection with prilling or other melt-granulation processes in which a fluid melt is necessary. The melting point is also of interest in drying fertilizers that are granulated by other processes because it limits the maximum temperature in the dryer. Typical melting point values are listed in Table 18.13.

18.3 Physical Properties of Fluid Fertilizers

Although fluid fertilizers do not comprise a major part of the market in most countries, some mention should be made of their physical properties. Methods of analyzing physical properties of fluid fertilizers are used to obtain data for (1) controlling product quality; (2) predicting storage, handling, and application characteristics; and (3) providing basic data for pump, tank, and application equipment design [5,6]. A brief description

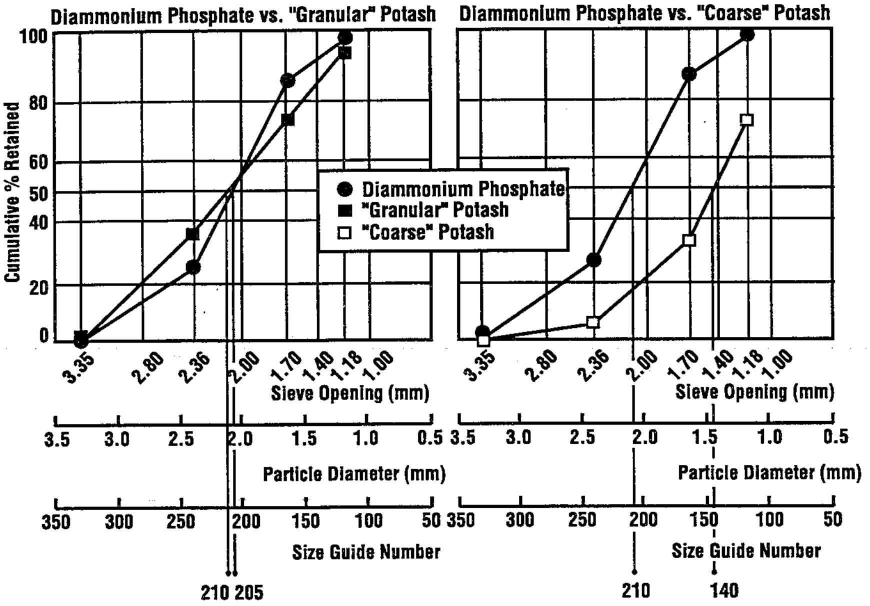


Figure 18.20. Physical Compatibility of Bulk Blend Ingredients According to Size Guide Number.

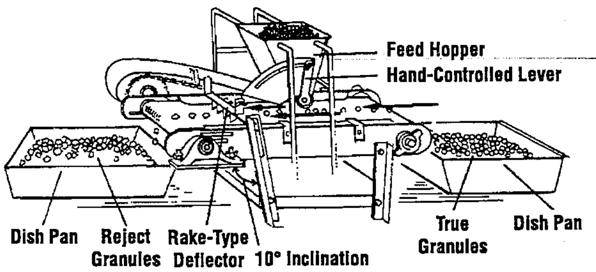


Figure 18.21. Sphericity Apparatus for Measuring Roundness of Granular Fertilizer.

Table 18.12. Typical Porosity Values (Ranges) of Some Common Fertilizers

Fertilizer Type	Grade	Porosity (% of Pores)
Prilled urea	46-0-0	1-3
Granular urea	46-0-0	5-8
Granular ammonium sulfate	21-0-0	8-10
Crystalline ammonium sulfate	21-0-0	0.5-1.0
Prilled ammonium nitrate	34-0-0	2-4
Granular diammonium phosphate	18-46-0	2-6
Granular monoammonium phosphate	11-55-0	5-10
Granular triple superphosphate	0-46-0	10-15
Granular potassium chloride	0-0-60	1-2

of some of the more common physical properties of fluid fertilizers follows.

18.3.1 Density/Specific Gravity

Density is the mass per unit volume of a fluid at a specified temperature. It is of interest in the calibration of volumetric meters, as a quality control method in determining nutrient concentrations of liquid feeds and scrubber liquors, or in evaluating the storage and handling characteristics of a fluid fertilizer. Typical methods for measuring the density of a fluid fertilizer use either a density bottle (pycnometer) or a hydrometer. Figure 18.22 shows a typical pycnometer used for measuring density of fluids.

Typical density values for some common fluid fertilizer grades are listed in Table 18.14 (solution fertilizers) and Table 18.15 (suspension fertilizers).

18.3.2 Viscosity

Viscosity is the internal resistance to flow exhibited by a fluid. Viscosity is a useful measurement in evaluating the storage and handling characteristics of a fluid fertilizer, or as a quality control method in liquid or slurry

Table 18.13. Melting Points of Some Fertilizer Products

	Nominal Grade	Melting Temperature (°C)
Ammonium nitrate	33.5-0.0	167
Urea	46-0-0	136
Sodium nitrate	16-0-0	308
Potassium nitrate	13-44-0	333
Calcium nitrate (tetrahydrate)	12-0-0	43
Sulfur	-	120
Urea-ammonium phosphate	21-42-0	153
Urea-ammonium phosphate	36-18-0	130
Urea-ammonium phosphate	17-27-17	143
Nitrophosphate	26-13-0	148
Nitrophosphate	20-20-0	152

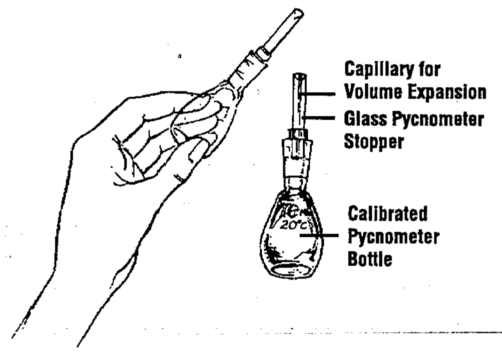


Figure 18.22. Gay-Lussac Type Pycnometer for Measuring True Density of Liquids.

feeds to a granulation process. For solution fertilizers, glass capillary-type viscometers are preferred. For suspension fertilizers, rotating spindle-type viscometers are required.

Typical viscosity values for some common fluid fertilizer grades are listed in Table 18.14 (solution fertilizers) and Table 18.15 (suspension fertilizers). For fluids that are to be applied directly to the soil, the viscosity must not exceed 800 MPa•s at 27°C and 900 MPa•s at 0°C. The viscosity of base grades that are primarily for use in production of fluid blends must not exceed 1,000 MPa•s at 27°C and 1,500 MPa•s at 0°C. Field tests have shown that fluid blends that do not meet the above viscosity criteria usually cannot be uniformly applied to the soil, and base grades that do not meet these viscosity criteria usually cannot be satisfactorily drained from storage tanks

Table 18.14. Typical Physical Properties of Various Solution Fertilizers[a]

Grade	Density (g/ml at 24°C)	Viscosity (MPa.s at 24°C)	Crystallization Temperature (°C)	pH
8-24-0	1.26	30	-8	6.6
10-34-0[b]	1.37	50	<-18	6.0
11-37-0[b]	1.40	80	<-18	6.0
7-21-7[b]	1.33	50	-13	6.5
7-7-7[c]	1.24	40	-5	6.6
5-10-10[c]	1.25	40	-1	6.5
32-0-0[d]	1.33	50	0	7.5[e]
28-0-0[d]	1.27	23	-17	7.5[e]

a. Based on thermal phosphoric acid.
b. Contains polyphosphate.
c. Supplementary nitrogen from urea-ammonium nitrate solution.
d. Urea-ammonium nitrate solution.
e. Ammonia added to control corrosion.

Table 18.15. Typical Properties of Various Suspension Fertilizers[a]

Grade	Density (g/ml at 24°C)	Viscosity (MPa•s at 24°C)	pH
12-40-0[b]	1.44	700	6.0
13-38-0	1.44	800	6.4
9-32-0[b]	1.40	200	6.7
10-30-0	1.37	250	6.3
31-0-0[c]	1.32	150	8.0
18-0-18	1.37	160	7.4
13-13-13	1.40	600	6.3
4-12-24	1.41	400	6.3
0-0-31[d]	1.30	360	6.8

a. Based on wet-process orthophosphoric and polyphosphoric acids. Properties may vary with impurity content of raw materials used and amount of suspending clay added.
b. Contains polyphosphate.
c. Urea-ammonium nitrate solution.
d. Potash suspension.

or transferred from one container to another by pumping [5].

18.3.3 Crystal/Particle Size and Type

Fluid fertilizers are considered to be unsatisfactory if they contain any crystals, either initially or after storage, that exceed 850 µm in size, because the large crystals can stop up distribution pipelines, spray nozzles, orifice meters, and other types of flow metering or flow regulating equipment. Suspension fertilizers require an abundance of small crystals of the precipitating phase to avoid the development of excessively large crystals. The type of crystals in fluid fertilizers is also important because crystals vary in shape from long needle-like to cubical blocks and to thin sheets. The long needle-type crystals are avoided because they cause stoppages in equipment more readily than do crystals of other shapes. The thin rectangular shaped crystals are preferred because they have a higher surface area-to-volume ratio and are therefore less difficult to suspend. The size and shape of crystals can be determined by microscopic analyses [5].

18.3.4 Crystallization Temperature

Crystallization temperature is that temperature at which a component in a solution fertilizer will precipitate or salt-out. This is a useful measurement in determining the optimum storage temperature range of a solution fertilizer. Crystallization temperature is determined by slowly cooling a solution fertilizer until crystallization occurs. Typical crystallization temperatures of some common solution fertilizers are listed in Table 18.14.

18.3.5 Settling (Sedimentation)

The solid phases present in some suspension fertilizers have a tendency to settle. Factors that affect this property are crystal/particle size, nature of the fluid phase, and/or the effectiveness of the suspending agent. It is desirable that all crystals in suspension fertilizers remain suspended at all times. For a suspension to be considered satisfactory, no crystals can settle and pack on the bottom of a container during static storage and a maximum of only 2% by volume of crystals can be settled after vibration, which occurs during transit by rail or truck. A suspension is measured in the laboratory for settled and packed crystals by pressing a stirring rod to the bottom of a test container to determine if any resistance is encountered in reaching the bottom of the container. If settled crystals are very loose and are capable of being redistributed in the suspension by recirculation or air sparging, the suspension is rated satisfactory. If the settled crystals are packed and difficult to redistribute, the product is rated unsatisfactory.

Crystals of any type are undesirable in solution fertilizers. To ensure against nucleation and growth of fertilizer salt crystals in solution fertilizers, crystallization temperatures are determined, and the concentrations of the solutions are adjusted to facilitate production of the highest possible satisfactory solution grades. However, solutions that are prepared from wet-process phosphoric acids contain impurities that precipitate slowly as very fine crystals or sludge. Because precipitation of these impurity materials is almost impossible to avoid, some precipitated solids are permitted [5].

18.3.6 pH

The pH measurement is used in the fluid fertilizer industry as a grade control method and to a lesser extent to evaluate the potential storage and handling properties.

18.3.7 Gel Strength

Suspension fertilizers are composed of a gelling agent dispersed in a solution of fertilizer salts – all of the solution is saturated, and both crystals of fertilizer salts and impurities are present. In production of the suspension fertilizers, a suspending agent, which is usually a gelling-type clay, is incorporated in a slurry to form a gel that is strong enough to suspend the solids in the saturated solution but not too strong to prevent pumping, pouring, and application to the soil. Gel strength is the force required to break the gel [5].

18.3.8 Other Properties

Several other physical properties of fluid fertilizers are of importance for various reasons. Some of these physical properties are briefly discussed.

18.3.8.1 Clarity – Fluid fertilizers that are produced from wet-process phosphoric acids derived from uncalcined phosphate ores are black in color due to the presence of finely divided carbonaceous material. The black color has no effect on the nutrient value of the fertilizers, but it does restrict the sight identification of solid material in solution fertilizers that could clog the equipment used for application. Solution fertilizers are often used for row application, whereas most suspension fertilizers are used for broadcast to the soil. Solution fertilizers often are gravity fed, and the distribution equipment, orifice meters, pipelines, and nozzles used for row application usually are smaller than those used for broadcast application of suspension fertilizers. Because the application equipment is smaller, it is more likely to get stopped up by large crystals or foreign particles; therefore, the need to see these solid particles in the solution fertilizers is much greater than it is in suspension fertilizer.

In production of solution fertilizers, samples of the product are taken and measured for clarity, which is the amount of visible light that passes through the sample without being absorbed. Measurements for clarity are made with a spectrophotometer. The object of the measurement is to determine whether or not the fertilizer is clear enough for fertilizer producers, farmers, or others that handle or apply solution fertilizers to the soil to see large crystals, or foreign matter, that might stop up orifice meters, or other equipment, that is used in handling or applying the solution to the soil.

Clarity is expressed as the percentage of light transmitted at the desired wavelength of the liquid absorption spectrum. A liquid with 25% light transmittance, as compared with 100% transmittance for distilled water, is considered acceptable [5].

18.3.8.2 Syneresis – Suspension fertilizers sometimes are affected by syneresis, which is formation of clear liquid, usually on top of the suspension with the remainder of the suspension being uniform throughout. The presence of the clear liquid layer does not necessarily cause a suspension to be unsatisfactory, but it is undesirable because with decrease or fluctuations in temperature or other conditions that cause changes in the concentration of the liquid phase, growth of excessively large crystals occurs at the clear liquid layer interface. Provided the crystals do not grow to exceed 20 mesh (850 µm) in size, syneresis is not objectionable if recirculation or air sparging will remix the clear liquid and suspension. Generally, syneresis is caused by either insufficient clay concentration or improper gelling of clay [5].

18.3.8.3 Solidification Temperature – If a fluid fertilizer is produced for winter-time storage in the colder regions of a country, its solidification temperature must be lower than the expected low temperature of that region. Solidification temperatures of fluid fertilizers are measured in the laboratory by cooling them to solidification over a period of 1-1/2 to 2 hours with an acetone or ethanol-dry ice bath [5].

18.3.8.4 Pourability – Fluid fertilizers are evaluated in the laboratory for pourability to determine whether or not they can be drained from their container by gravity or pumped or otherwise transferred in the field from one container to another. This determination is made by rotating a stirring rod twice around the inside surface of the storage container, generally an 8- or 16-ounce sample bottle, to apply gentle agitation to the fluid. Rotation of the stirring rod is intended to supply no more agitation than would be supplied by air sparging. The container then is turned downward at a 45° angle for 1 minute and the content (% by volume) that pours out is determined. Field tests have shown that fluid products that are at least 98% pourable by this procedure will flow freely by gravity from their storage container and can be easily transferred from one tank or container to another by pumping [5].

18.3.8.5 Vibrational Settling – Some suspension fertilizers that have been known to store satisfactorily for long periods of time under static conditions have undergone settling when subjected to vibration such as occurs during shipment by rail; the crystals settled excessively and became packed on the bottom of the railroad tank cars. Settling of crystals during vibration is related to the weight, size, and shape of the crystals; the density of the solution phase of the suspension; and the strength of the gel [5].

Other physical properties of fluid fertilizers that may have some specific importance are vapor pressure, specific heat, wettability, surface tension, refractive index, and conductivity.

18.4 References

1. Hoffmeister, G. 1979. *Physical Properties of Fertilizers and Methods for Measuring Them*, TVA Bulletin Y-147, Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, AL, U.S.A.
2. Rutland, David W. 1991. "The Effect of Fertilizer Physical Properties on Product Quality and the Methods Used to Evaluate Them," Presented at the FADINAP Asia Pacific Regional Symposium on Fertilizer Legislation, Ho Chi Minh City, Vietnam.
3. Tennessee Valley Authority. 1970. *TVA Procedures for Determining Physical Properties of Fertilizers*, Special Report No. S-444, Environmental Research Center, Muscle Shoals, AL, U.S.A.
4. The Fertilizer Institute. 1982. *Fertilizer Sampling and Analytical Methods*, Fourth Edition, Product Quality Committee, 1015 18th Street, N.W., Washington, D.C., U.S.A.
5. Potts, J. M. (Ed.). 1984. *Fluid Fertilizers*, TVA Bulletin Y-185, Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, AL, U.S.A.
6. Palgrave, D. A. 1984. "Importance of Measuring Physical Properties in Fluid Fertilizers," Paper No. 203, 98th Meeting of AOAC International, Washington, D.C., U.S.A.
7. Canadian Fertilizer Institute. 1986. *The CFI Guide of Material Selection for the Production of Quality Granular Blends*, Suite 301, 280 Albert Street, Ottawa, Ontario K1P5G8, Canada.
8. Rutland, David W. 1993. *Manual for Determining Physical Properties of Fertilizer*, Reference Manual IFDC-R-10, Second Edition, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.
9. Hofstee, J. S. 1993. *Physical Properties of Fertilizer in Relation to Handling and Spreading*, Wageningen Agricultural University, Wageningen, The Netherlands.
10. International Organization for Standardization. Central Secretariat, 1, rue de Varembe, Case Postale 56, Ch-1211 Geneve 20, Switzerland.
11. International Organization for Standardization. 1984. *Fertilizers and Soil Conditioners – Vocabulary*, ISO 8157, Central Secretariat, 1, rue de Varembe, Case Postale 56, Ch-1211 Geneve 20, Switzerland.
12. Khasawneh, F. E., and E. C. Doll. 1978. "The Use of Phosphate Rock for Direct Application to Soils," *Advances in Agronomy*, 30:159-206.
13. Association of American Plant Food Control Officials. 1994. *Official Publication, No. 47*. Copies may be purchased from North Carolina Department of Agriculture, 4000 Reedy Creek Road, Raleigh, NC, U.S.A.
14. European Union (formerly European Economic Community). 1976. *Official Journal of the European Communities*, Volume 19, No. L24, Council Directive 76/116/EEC, Office of Official Publications of the European Union, L-2985, Luxembourg.
15. Schultz, James J. 1989. *Production of Granular NPKs in Ammonium Phosphate Plants*, T-36, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.
16. Lupin, M. S., and N. D. Le. 1983. *Compaction, Alternative Approach for Granular Fertilizers*, T-25, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.
17. Klein, Maurice O. 1991. "The Manufacture of Fertilizers by Compaction/Granulation," IN *Urea-Based NPK Plant Design and Operating Alternatives*, Workshop Proceedings, pp. 119-132, SP-15, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.
18. Berquin, Y., and J. Burko. 1974. "Hot Spherodizer Processes and Complex Fertilizers: Recent Developments," *Proceedings of the 24th Annual Meeting of the Fertilizer Industry Round Table*, pp. 110-112, Washington, D.C., U.S.A.
19. Kelly, W. J. 1974. *Solids Handling and Metering in an NPK Prilling Plant*, Proceedings of the Fertilizer Society, (London), No. 141.
20. Maartensdijk, Sinte. 1976. "Direct Production of Granulated Superphosphates and PK Compounds from Sulphuric Acid, Phosphoric Acid, Rock Phosphate and Potash," Paper No. TA/76/12, Presented at the International Superphosphate

Manufacturers' Association Technical Conference, The Hague, Netherlands.

21. Hoffmeister, George. 1962. "Compatibility of Raw Materials in Blended Fertilizers Segregation of Raw Materials," *Proceedings of the 12th Annual Meeting of the Fertilizer Industry Round Table*, pp. 83-88, Washington, D.C., U.S.A.

22. Hoffmeister, George. 1973. "Quality Control in a Bulk Blending Plant," *Proceedings of the TVA Fertilizer Bulk Blending Conference*, TVA Bulletin Y-62, pp. 59-70, Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, AL, U.S.A.

23. Hoffmeister, George, S. C. Watkins, and Julius Silverberg. 1964. "Bulk Blending of Fertilizer Material: Effect of Size, Shape, and Density on Segregation," *Journal of Agricultural and Food Chemistry*, 12(1):64-69.

24. Hoffmeister, G. H. 1982. *Particle Size Requirements for Bulk Blend Materials*, TVA Circular Z-146, Paper presented at the 36th annual meeting of the Association of American Plant Food Control Officials, August 3-4, Columbus, OH, U.S.A.

25. Hoffmeister, G. H. 1981. "Evaluating and Correcting Segregation in Bulk Blends," *Custom Applicator*, February.

26. Balay, H. L. 1983. "Fertilizer Properties Related to Bulk Storage and Handling," *Custom Applicator*, February.

27. Cheval, John. 1994. "Top Quality Blends," presented at the 5th Latin America Fertilizer International Conference, April 17-19, Palm Beach, FL, U.S.A.

28. Tikhonovich, Z. A., and N. N. Bogdanova. 1991. "Some Aspects of the Hygroscopicity of Fertilizers," *The Soviet Chemical Industry*, 23(2):89-90.

29. Perry, R. H., C. H. Chilton, and S. D. Kirkpatrick (Eds.). 1984. *Perry's Chemical Engineers Handbook*, Sixth Edition, McGraw-Hill Book Company, New York, NY, U.S.A.

30. Stanley-Wood, N. G., and G. J. Llewellyn. 1982. "In-Stream and On-Line Particle Size Analysis," *Chemical Society, Analytical Proceedings*, 19(11):527-528, November.

31. Bura, K. J. 1984. "Improved Methods of Particle Size Analysis," *Particle Size Analysis of Construction Materials, Analytical Proceedings*, Volume 21, pp. 133-134, April.

32. "Particle Size Analyzers: Out of the Lab, Into the Plant." 1988. *Chemical Engineering*, pp. 95-98, November 7.

33. Frydenberg, Wilhelm. 1989. "The Development and Use of an On-Line Particle Analyses in a Prilling or Granulation Plant," Paper read before The Fertilizer Society of London, October.

34. Jørgensen, T. 1991. "A Particle Analyser for Measuring Particle Size Distribution and Shape, On-Line or in the Laboratory," *Fertilizer Research*, 28:109-114.

35. Carr, R. L. 1965. "Evaluating Flow Properties of Solids," *Chemical Engineering*, pp. 163-168, January 18.

36. Lauzon, Michael. 1983. "How to Avoid Flow Problems in Hoppers and Feeders," *Canadian Chemical Processing*, 67(4):31-32, June.

37. Kühnemund, B. 1984. "Bin Storage of Bulk Materials," *Pit & Quarry*, 76(8):57-59, 62, February.

38. Saxena, R. C., and S. Varma. 1973. "Effect of Moisture on the Flow Characteristics of Granular Fertilizers," *Technology*, 10(1&2):42-45.

39. De, Dipankar. 1989. "Flow Behaviour of Chemical Fertilizers As Affected by Their Properties," *Journal Agricultural Engineering Research*, 42:235-249.

40. Bhatti, Muhammad Essa. 1991. "Quality Control Measures for Developing of 10:20:20 Grade Fertilizer," *Fertilizer Research*, 28:213-216.

41. Ibrahim, Y. A. 1992. "Product Quality Improvement on Urea Prills," Paper presented at the 1991 IFA Technical Conference, The Hague, Netherlands, October 6-8.

42. Rahman, M. Jalilur, P. Bozadjiev, and Y. Pelovski. 1994. "Studies on the Effects of Some Additives on the Physicomechanical Properties of Urea-Ammonium Sulphate (4UAS) Pellets," *Fertilizer Research*, 38:89-93.

43. Smith, P. G. 1980. "Apparatus for Determining the Strength of Granules," *Laboratory Practice*, pp. 743-744, July.

44. Ivanov, M. E., A. Sh. Berkovich, A. B. Ivanov, and T. N. Kozlova. 1985. "Determination of the Static Strength of Ammonium Nitrate Granules," *The Soviet Chemical Industry*, 17(6):348-350.

45. Murthy, D.V.S., and A. P. Rao. 1989. "Effect of Binding Agents in NP Granulation," *Indian Journal of Technology*, Vol. 27:121-124, March.

46. Borisova, L. I., M. P. Talkhaev, and S. Ya Gal'perina. 1989. "Quality Control of Phosphorite Pellets," *Khimicheskaya Promyshlennost*, 21(10):751-754.

47. Fruhstorfer, A. 1961. "Testing Granular Fertilizers for Hardness," Paper No. LE/61/58, The International Superphosphate Manufacturers' Association, Wiesbaden, Germany.

48. Rieschel, H., and K. Zech. 1981. "Comparison of Various Test Methods for the Quality Control of Potash Granulate," *Phosphorus and Potassium* No. 115:33-39, September/October.

49. Willems, M., and R. van Hardevell. 1981. "Production of High Quality Urea Prills," *Proceedings of the 31st Annual Meeting of the Fertilizer Industry Round Table*, pp. 64-72, Washington, D.C., U.S.A.

50. Hegner, P., and L. Jäger. 1976. *Hygroscopicity of Fertilizer Materials*, Research Institute of Inorganic Chemistry, 400 60 Ústi nad Labem, Czechoslovakia.

51. Rutland, D. W. 1984. "Comparison of Hygroscopic Properties of Mixtures of Granular Materials (Bulk Blends) and Granulated Mixtures," *Proceedings of the 34th Annual Meeting of the Fertilizer Industry Round Table*, pp. 89-98, Baltimore, MD, U.S.A.

52. Babin, J. J. 1989. "Contribution of the Understanding of Hygroscopicity of Fertilizers," *Hungarian Journal of Industrial Chemistry*, 17: 61-71.

53. Merz, A. R., W. H. Fry, J. O. Hardesty, and J. R. Adams. 1933. "Hygroscopicity of Fertilizer Salts," *Industrial and Engineering Chemistry*, 25(2):136-138.

54. Yee, J. Y. 1944. "Determining Hygroscopicity of Fertilizers," *Industrial and Engineering Chemistry, Analytical Edition*, 16(6):367-369.

55. Dunmore, F. W. 1939. "An Improved Electric Hygrometer," Research Paper RP1265, *Journal of Research of the National Bureau of Standards*, 23:701-714.

56. Geissler, P. R. 1968. "Hygroscopicity of Complex Fertilizers – Determination of Critical Relative Humidity of Multicomponent Systems," *Journal of Agricultural and Food Chemistry*, 16(3):378-383.

57. Geissler, P. R. 1967. *Method for Determining the Critical Relative Humidity of Fertilizer*, U.S. Patent 3,304,767.

58. Pustil'nik, G. A., V. S. Talanova, and Y. A. Vakhrushev. 1973. "Accelerated Method for Determining Hygroscopic Points of Fertilizers and Salts," *Khim. Prom. (Moscow)*, 49(11):844-845 (Russ.); *Soviet Chemical Industry*, 5(11):708-709.

59. Clayton, W. E. 1984. "Humidity Factors Affecting Storage and Handling of Fertilizers," IFDC-P-5, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.

60. Rutland, D. W. 1991. "Storage and Handling Characteristics of Urea-Based NPK Fertilizers," IN *Urea-Based NPK Plant Design and Operating Alternatives*, Workshop Proceedings, pp. 82-88, SP-15, International Fertilizer Development Center, P.O. Box 2040, Muscle Shoals, AL, U.S.A.

61. Hoffmeister, G., and C. P. Harrison. 1982. "Critical Humidity-Temperature Relationships for Several Fertilizers," TVA circular Z-143, Paper presented at the 184th National Meeting of the American Chemical Society, September 12-17, Kansas City, MO, U.S.A.

62. Idnani, M. A., and O. P. Chawla. 1968. "Moisture Absorption and Caking in Ammonium Sulphate," *Fertiliser News*, pp. 26-28, November.

63. Bach, Bjorn. 1982. "Packaging, Transportation, and Storage of Fertilizers," Seminar on Fertilizer Quality Control and Handling held in New Delhi, India, pp. 313-329.

64. Kuvshinnikov, I. M. 1985. "Quantitative Evaluation of the Hygroscopicity of Fertilizers," *The Soviet Chemical Industry*, 17(3):153-155.

65. Mehring, A. L. 1929. "Factors Affecting the Drillability of Fertilizers," *Industrial and Engineering Chemistry*, 21(12):1219-1223.

66. Mehring, A. L. 1931. "Measurement of Drillability of Fertilizers," *Industrial and Engineering Chemistry, Analytical Edition*, 3(1):34-38.

67. Mehring, A. L., and G. A. Cumings. 1930. *Factors Affecting the Mechanical Application of Fertilizers to the Soil*, U.S. Department of Agriculture, Technical Bulletin No. 182, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., U.S.A.

68. Rapp, H. F., and J. O. Hardesty. 1957. "Granulation of Mixed Fertilizers in Experimental Equipment and Determination of Storage and Drilling Characteristics of the Products," *Journal of Agricultural and Food Chemistry*, 5(6):426-433.

69. Gantt, C. W., W. C. Hulburt, H. F. Rapp, and J. O. Hardesty. 1958. *Determining the Drillability of Fertilizers*, U.S. Department of Agriculture, Production Research Report No. 17, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., U.S.A.

70. Hoffmeister, George, and C. P. Harrison. 1977. "Physical Properties of Granular Urea-Based NP and NPK Fertilizers," *Proceedings of the 27th Annual Meeting of the Fertilizer Industry Round Table*, pp. 162-170, Washington, D.C., U.S.A.

71. Kurshinnikov, I. N., and G. F. Chelikid. 1978. "Methods of Eliminating the Caking of Fertilizers," IN *Proceedings of the Soviet-Swedish Symposium on the Beneficiation of Phosphate Rock*, pp. 180-186, Tallinn, Estonia.

72. Bookey, J. B., and B. Raistrick. 1965. "Caking of Mixed Fertilizers," IN *Chemistry and Technology of Fertilizers*, Vincent Sauchelli (Ed.), pp. 454-479, Reinhold Publishing Corporation, New York, U.S.A.

73. Silverberg, Julius, J. R. Lehr, and George Hoffmeister, Jr. 1958. "Microscopic Study of the Mechanism of Caking and Its Prevention in Some Granular Fertilizers," *Journal of Agricultural and Food Chemistry*, 6(6):442-448.

74. "The Complex Phenomenon of Caking," 1987. *Fertilizer Focus*, pp. 36-37, 39, July.

75. Tikhonovich, Z. A., A. Ya. Syrchenkov, V. F. Kabanov, A. I. Grapas, and I. M. Gurman. 1989. "Study of the Physicomechanical Properties of Nitrophoska," *Khimiya Promyshlennost*, 21(9):671-673.

76. Thompson, D. C. 1972. *Fertilizer Caking and Its Prevention*, Proceedings of the Fertilizer Society (London), No. 125.

77. Mackay, P. A., and K. S. Sharples. 1985. *The Use of Special Oils and Coatings to Prevent Caking of Fertilizers*, Proceedings of the Fertilizer Society, (London), No. 239.

78. Kuvshinnikov, I. M., Z. A. Tikhonovich, S. A. Troitskaya, and V. A. Frolkina. 1984. "Mechanism of the Modifying Action of Surfactants Used to Eliminate the Tendency of Complex Fertilizers to Cake," *The Soviet Chemical Industry*, 16(1):25-27.

79. Kuvshinnikov, I. M., V. A. Timofeev, and M. P. Komarov. 1987. "Theoretical and Technological Foundations of the Elimination of the Cakeability of Mineral Fertilizers," *Mendeleev Chemistry Journal*, 32(4):51-55.

80. Kuvshinnikov, I. M., V. G. Dubinin, L. B. Geladze, V. T. Kukushkin, and M. P. Komarov. 1987. "Structure of Granules of Complex Fertilizers and Their Caking," *Journal of Applied Chemistry of the USSR*, 60(6):1384-1386, June.

81. Rutland, D. W. 1991. "Fertilizer Caking: Mechanisms, Influential Factors, and Methods of Prevention," *Fertilizer Research*, 30:99-114.

82. Adams, J. R., and W. H. Ross. 1941. "Relative Caking Tendency of Fertilizers," *Industrial and Engineering Chemistry*, 33(1):121-127.

83. Whynes, A. L., and T. P. Dee. 1957. "The Caking of Granular Fertilizers: An Investigation on a Laboratory Scale," *Journal of the Science of Food and Agriculture*, 8:577-591.

84. "Using Anticaking Agents." 1983. *Nitrogen*, No. 146:21-23, November-December.

85. Rosenblom, Jan, and Stig Zettervall. 1978. "Anticaking Treatments of Granular Inorganic Salts Such as Phosphate Based Complex Fertilizers and Ammonium Nitrate," IN *Proceedings of the Soviet-Swedish Symposium on the Beneficiation of Phosphate Rock*, pp. 158-179, Tallinn, Estonia.

86. Gamondes, J. P., and J. B. Van't Hoff. 1977. "How to Prevent Fertilizer Caking," *Nitrogen*, No. 105:32-35, January-February.

87. Rutland, D. W., and J. R. Polo. 1990. "Urea in NPK Fertilizers: How Much Can You Use?" *Phosphorus & Potassium*, 166:25-32, March-April.

88. Rutland, D. W., and J. R. Polo. 1989. "Comparative Properties of Urea-Based NPK Fertilizers," *Proceedings of the 39th Annual Meeting of the Fertilizer Industry Round Table*, pp. 159-172, Atlanta, GA, U.S.A.

89. Kuvshinnikov, I. M., A. V. Kononov, V. A. Frolkina, S. A. Troitskaya, M. P. Lobacheva, and L. I. Evdokimova. 1989. "Physical Properties of Diammosphoska," *Khimiya Promyshlennost*, 21(9):674-676.

90. Kuvshinnikov, I. M., A. V. Kononov, L. I. Evdokimova, V. A. Frolkina, M. P. Lobacheva, and S. A. Troitskaya. 1989. "Balanced Compound Fertilizers Made From Ammonium Phosphates and Urea," *Khimicheskaya Promyshlennost*, 21(10):747-748.

91. Tennessee Valley Authority. 1970. "Effect of Aluminum and Iron on the Physical Properties of Ammonium Phosphate Fertilizers," IN *New*

Developments in Fertilizer Technology, 8th Demonstration, p. 14, TVA Bulletin Y-12, TVA, NFDC, Muscle Shoals, AL, U.S.A.

92. Borisov, V. M., Yu. V. Azhikina, and L. S. Gerke. 1978. "Methods for Reducing the Cakeability of Phosphorus-Containing Fertilizers," *The Soviet Chemical Industry*, 10(8):590-591.

93. Borisov, V. M., Yu. V. Azhikina, B. M. Maslennikov, S. B. Kapilevich, L. S. Gerke, and A. A. Brodskii. 1982. "Physicochemical Fundamentals of Technology for Noncaking Complex Fertilizers Based on Monoammonium Phosphate," *The Soviet Chemical Industry*, 14(6):346-348.

94. Ando, Jumpei, Mitsuhiko Omura, and Takashi Akiyama. 1965. "Precipitates from the Ammoniation of Wet-Process Phosphoric Acid and the Viscosity of the Product Slurry," *Kogyo Kagaku Zashi*, 68:2327-2331.

95. "Using Anticaking Agents," 1983. *Nitrogen*, No. 146, November-December.

96. Venkatesan, T. N. 1987. "Fertilizer Conditioning: Need of the Hour," *Fertilizer Industry, Annual Review*, 10:213-216.

97. Koltashov, N. A. 1978. "Caking of Urea as a Function of Loading Temperature and Packaging Method," *Khimiya v sel' skom khozyaistve*, 16(8):25-28.

98. Visvanathan, T. R., S. Balasubramaniam, and J. Bennett. 1978. "Problem of Caking in NPK Granular Fertilizers," *Fertiliser News*, 23(8):37-40.

99. Saxena, R. C. 1982. "Let Your Granules Glide," *Self-Reliance*, 8(3):6-8.

100. "Caking: Complex Problem," 1984. *Fertilizer Focus*.

101. Van Hijfte, Willie H.P. 1981. "The Coating of Straight Nitrogen Fertilizers," IN *Proceedings of the 31st Annual Meeting of the Fertilizer Industry Round Table*, pp. 181-187, Washington, D.C., U.S.A.

102. Ahmed, S. M. 1990. "Caking of CAN Fertilizer – Its Prevention," *Technology and Development (Kuwait)*, 15(1):75-84.

103. Hoff, J. B. van't. 1986. *Practical Approach to Anticaking in Nitrogen Fertilizers*, The British Sulphur Corporation, Ltd.

104. "The Marketing of Coating Agents." 1993. *Fertilizer Focus*, pp. 18, 20-21, 24-25, 27, March.

105. "Conditioning Solid Fertilizers." 1993. *Fertilizer International*, No. 327, pp. 20-23, November.

106. Kuvshinnikov, I. M., S. A. Troitskaya, V. A. Frolkina, G. S. Gol'din, and K. O. Averbakh. 1973. "Effect of Surface-Active Agents in Caking Tendency of Nitrophoska," *The Soviet Chemical Industry*, 5:7, July.

107. Blouin, G. M. 1986. "Production of High-Strength, Storage-Stable Particulate Urea," U.S. Patent 4,587,358, May 6.

108. Krut'ko, N. P., O. V. Shulyakovskaya, F. F. Mozheiko, and V. N. Avilor. 1988. "Effect of Lignosulfonates Modified by Urea on Properties of Granulated Potassium Fertilizers," *Journal of Applied Chemistry of the USSR*, 61:2:2, p. 394-397.

109. Iwasaki, Tetsuji, and Hitoshi Hosokawa. 1989. "Caking - Preventing Agent for Fertilizer," U.S. Patent 4,812,158, March 14.

110. Detriot, William I. 1989. "Lignosulfonate Treated Fertilizer Particles," U.S. Patent 4,846,871, July 11.

111. Sanford, Michael E. 1991. "Modified Lignosulfonate Conditioning Agent for Urea Particles," U.S. Patent 5,032,164, July 16.

112. Kawashima, Kazuo, T. Takeno, and K. Kurita. 1984. "Anticaking Agent Composition for Potassium Salt," Canadian Patent 1,166,436.

113. Aleksandrovich, Kh. M., A. P. Yanovskaya, and G. S. Shakskikh. 1990. "Intensification of the Effect of Amines as Anticaking Agents in Potassium Fertilizers," *Khimicheskaya Promyshlennost*, 22(11):663-665.

114. Spelt, J. K., G. Strathdee, and A. W. Neumann. 1991. "Wetting and Spreading of Conditioning Reagents on Potash Products," Presented at KALI 91, 2nd International Potash Technology Conference, Hamburg, Germany, May 26-29.

115. "Fertilizer Caking: Kao Corp. Tests Decylaldehyde as Urea Anticaking Agent." 1987. *Nitrogen*, No. 166, March-April.

116. Kuvshinnikov, I. M., Z. A. Tikhonovich, N. N. Bogdanova, A. A. Alekseev, and O. V. Bratashova. 1987. "Elimination of Caking of Nitrogen-Phosphorus-Potassium Fertilizer by Encapsulation with Urea-Formaldehyde Resins," *Khimicheskaya Promyshlennost*, 19(2):27-29.

117. Ackermans, Wilhelmus H.J., and Michael H. Willems. 1981. "Process for Reducing the Caking and Dusting Tendencies of Urea Granules as Well as Urea Granules Obtained by this Process," European Patent Application 0047556.

118. Komarov, M. P., and I. M. Kuvshinnikov. 1984. "Conditioning Nitroammophoska with Ammonium Sulfate," *The Soviet Chemical Industry*, 16(4):216-217.

119. Backlund, Peter S. 1986. "Coated Fertilizer Particles," U.S. Patent 4,565,564, January 21.

120. "Product Finishing." 1988. *Fertilizer International*, No. 266, October.

121. Kuvshinnikov, I. M., M. P. Komarov, and V. A. Timofeev. 1991. "Mechanism of Conditioning of Granulated Fertilizer With Inorganic Substances," *Khimicheskaya Promyshlennost*, 22(4):209-212.

122. Tarkhanova, L. S., Z. S. Shpileva, and G. D. Makzushin. 1984. "Improving the Quality of Urea," *The Soviet Chemical Industry*, 16(3):151-153.

123. Van Hijfte, Willie H.P. 1985. "Process for Making Granules Containing Urea as the Main Component," U.S. Patent 4,500,336, February 19.

124. Blouin, G. M., and A. W. Allen. 1985. *A Study of Anticaking Treatments for Urea*, TVA Circular Z-190, Presented at the 190th National Meeting of the American Chemical Society, September 9-12, Chicago, IL, U.S.A.

125. Orlov, N. I., N. G. Zhavoronkova, L. V. Kuznetsov, E. E. Agafonova, M. I. Kucha, and A. F. Il'chenko. 1987. "Study of the Possibility of Using Phosphogypsum as a Conditioning Agent for Ammonium Nitrate," *Khimicheskaya Promyshlennost*, 19(10):21-24.

126. "Ammonium Nitrate: Magnesium Nitrate Used to Improve the Properties of Prills." 1983. *Nitrogen*, No. 141, January-February.

127. Allgever, Kurt, and Ferdinand Weinrotter. 1963. "Free-Flowing, Storage-Stable Granular or Pelletized Urea," U.S. Patent 3,112,343.

128. Tennessee Valley Authority. 1976. "Physical Properties of TVA Granular Urea," IN *New Developments in Fertilizer Technology*, 11th Demonstration, pp. 35-36, TVA Bulletin Y-107, TVA, NFDC, Muscle Shoals, AL, U.S.A.

129. Van Hijfte, Willie H.P., and R. Goethals. 1973. "Improvements in or Relating to Urea Crystals, Pellets, Prills, and the Like," British Patent Specification 1,334,871.

130. Brown, M. L., A. W. Green, and Ladelle Blanton. 1968. "Stabilizing Ammonium Nitrate Against Crystalline Change," *Journal of Agricultural and Food Chemistry*, 16(3):373-377.

131. C&I Girdler Corporation. 1967. "The Stabilization of Ammonium Nitrate Prills," *Nitrogen*, No. 46:33-35.

132. Griffith, E. J. 1963. "Phase Transitions of the Ammonium Nitrate-Magnesium Nitrate System," *Journal of Chemical Engineering Data*, 8(1):22-25.

133. "Conditioning Ammonium Nitrate for Handling and Storage." 1985. *Nitrogen*, No. 156, July-August.

134. Van Hijfte, W. 1988. *Storage and Distribution of Straight Ammonium Nitrate Fertilizers in Bulk*, Proceedings of the Fertilizer Society, (London), No. 265.

135. "Conditioning Ammonium Nitrate for Handling and Storage." 1985. *Nitrogen*, No. 156:28-34, July-August.

136. Gilbert, Richard L., Jr., and Paul W. Knapp. 1970. "Development of an Accelerated Caking Test for Urea," *Journal of Agriculture and Food Chemistry*, 18(3):397-400.

137. Ha cour, Ph., and J. van't Hoff. 1983. "The Prevention of Fertilizer Caking: An Original Method to Determine Its Effectiveness," *Nitrogen*, No. 145, September-October.

138. Masse, Gary M.J., and Cheng H. Chuang. 1984. *A New Accelerated Caking Test for Granular Urea*, CIL Inc., Chemical Research Laboratory, 2101 Hadwen Road, Mississauga, Ontario, Canada LSK 2L3.

139. Lafei, Ali, K. Güriz, and H. Yücel. 1988. "Investigation of Factors Affecting Caking Tendency of Calcium Ammonium Nitrate Fertilizer and Coating Experiments," *Fertilizer Research*, 18(1):63-70.

140. "The Latest in Fertilizer Cake Prevention." 1990. *Nitrogen*, No. 187, September-October.

141. Bhatti, Muhammad Essa. 1992. "Physical Properties Comparative Study of Urea of Different Companies in Pakistan," *Fertilizer Research*, 32:13-17.

142. Strathdee, Graeme G. 1994. "Managing Potash Product Quality in Global Markets," *Phosphorus & Potassium*, No. 193, September-October.

143. "Anti-Dust Conditioning of Difficult-to-Granulate Fertilizer Materials." 1981. *Phosphorus and Potassium*, No. 114:33-34, July-August.

144. Robinson, Susan K. 1989. "Edible Oils Prove Value as Dust Suppressants," *Agribusiness Worldwide*, pp. 12-13, 15-17, April.

145. Krut'ko, N. P., O. N. Opanasenko, F. F. Mozbeiko, V. N. Avilov, T. A. Zus'kova, I. I. Basalyga, and E. V. Moshkova. 1989. "The Effect of Petroleum Hydrocarbons on the Properties of Potassium Fertilizers," *Khimicheskaya Promyshlennost*, 21(6):430-434.

146. Van de Walle, Richard H. 1990. "The Benefits of Using Binders/Conditioners in Fertilizer Granulation," *Fertilizer Focus*, pp. 86, 88-89, 91, September.

147. Skvirski, L. I., A. A. Chistyakov, and Z. L. Kozel. 1991. "Production of Non-Dusting and Non-Caking Potash Fertilizers," Presented at Kali 91, 2nd International Potash Technology Conference, Hamburg, Germany, May 26-29.

148. Hoffmeister, George, and G. H. Megar. 1975. "Use of Urea in Bulk Blends," *Proceedings of the 25th Annual Meeting of the Fertilizer Industry Round Table*, pp. 212-226, Washington, D.C., U.S.A.

149. Cheval, J. L. 1986. "Material Selection for the Production of High Quality Blends," Paper presented at the 36th Annual Meeting of the Fertilizer Industry Round Table, Baltimore, MD, U.S.A.

150. Hester, Lance, Michael F. Broder, and Carl A. Cole. 1990. *Particle Size Characteristics of Alabama Fertilizer Materials - 1989*, TVA Circular Z-285, Paper presented at the 40th Annual Meeting of the Fertilizer Industry Round Table, November 12-14, Baltimore, MD, U.S.A.

151. Cheval, J. L. 1991. *Update on the Canadian Fertilizer Quality Assurance Program and SGN Industry View*, Association of American Plant Food Control Officials, Official Publication No. 44.

152. Terry, D. C. 1993. "Size Guide Number and Bulk Blend Quality," Paper presented at the 43rd Annual Meeting of the Fertilizer Industry Round Table, October 25-27, New Orleans, LA, U.S.A.

153. Cheval, J. L. 1994. "A Blender's Tool for Quick SGN Determination," Paper presented at the 44th Annual Meeting of the Fertilizer Industry Round Table, Orlando, FL, U.S.A.

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Chapter 19. Environmental Protection and Pollution Prevention

19.1 Introduction

The concept of ecologically sustainable industrial development motivates producers and consumers to use products and operate industry using the best technologies and techniques to minimize adverse environmental impact [1].

Production and use of fertilizers require activities including mining, mechanical and/or chemical processing, material transport and handling, and, ultimately, soil application. Therefore, fertilizer producers and users are faced with a number of potential points where adverse impacts on the environment may occur. For example, fertilizer production processes may release emissions containing potential pollutants that may have local environmental impact (e.g., acid rain, water acidification and eutrophication, groundwater contamination, etc.) and theoretically may contribute to global environmental problems (e.g., greenhouse effect).

It is extremely difficult to generalize about the adverse environmental impact of fertilizer production, distribution, and use activities. This difficulty arises from several factors. Primarily among these is the fact that the industry has evolved over the course of more than a century and over time has responded to changing public interest and concerns. Conversely, current environmental awareness has evolved and intensified only in the past 2-3 decades. The fertilizer industry operates facilities with different levels of environmental safety and, consequently, varies considerably from one production complex to another. Similarly, fertilizer use practices have evolved over time and under changing crop production systems and public concerns (e.g., low-cost food and fiber, reducing adverse environmental impacts, budget consideration, etc.). Thus, fertilizer use practices vary considerably as to real or potential adverse environmental impact(s). Therefore, if fertilizer production processes and use practices are to minimize adverse environmental impact, both locally and globally, it is important that a full range of pollution prevention processes are used and operated with the highest standards of operation and maintenance. The same criteria apply to fertilizer use practices.

Although new, more environmentally friendly technologies have been developed for all basic fertilizer production processes, these have not been fully adopted and implemented in all potential applications. This relatively slower rate of adoption (as compared to other industries) can be attributed, in large part, to the economic conditions faced by the industry in the past few years. Due to a general slackening of demand and the resulting excess capacity, few completely new fertilizer factories have been constructed. In addition, until recently, governmental regulations and international standards emphasized limits on industrial emissions and "end-of-pipe solutions." There are similar parallels to the adoption of more environmentally sensitive fertilizer use practices.

However, as environmental awareness and sensitivity intensifies, priority is being placed on minimizing total adverse environmental impact. This shift in frame of reference necessitates that environmental protection is a priority in all stages of industrial development (process development, design, construction, and operation) and in fertilizer use. In this setting, pollution control is only an instrument to ensure that the industry complies with local regulations.

Increasingly, local standards and regulations are complying with internationally adopted standards and guidelines. At the same time, fertilizer traders and financial institutions are considering the environmental impact of alternative suppliers in making purchase and financial decisions to avoid unfair competition and reduce the chance of being an unwilling contributor to environmental exploitation.

The net effect of these factors is that all producers and users are under increasing pressure to develop and implement environmentally sensitive fertilizer production and use, technologies, and more efficient pollution abatement processes and installations. As retrofitting and expansions of existing facilities and new developments are contemplated, there will be significant scope for improving the contribution of the fertilizer industry to sustainable development.

This chapter is technology oriented. In subchapters the emissions from each production process are described, and available limits are given for selected countries. These limits (targets) have only indicative character; however, it remains that locally developed and approved standards on limits and guidelines on targets should consider the following issues:

- Trends of the limitations in the regulations of developed countries and professional organizations (IFA, EMFA, etc.).
- Trends and limitations recommended by the international organizations.

- Concentration limits of harmful substances in air, water, and soil indicated by the World Health Organization and United Nations Environment Programme (UNEP).
- Protection of water and soil from nonremovable impurities.
- Protection of the aesthetic values of the environment.

In some cases costs of the environmental protection installations are given. However, it is difficult to generalize on the costs of environmental protection measures in the fertilizer industry because the costs depend on several factors:

a. The emission target or limit to be achieved.
b. Raw materials used.
c. Type of process and plant capacity.
d. Any other industrial emissions in the production area.
e. Whether the plant is new and environmental protection has been included in plant design, or if it is an existing plant, the additional pollution abatement investments required.

Hence, costs given are indicative; an environmental impact assessment should be prepared as a part of the feasibility study to reveal the most economical approaches to resolving environmental protection issues.

19.2 Environmental Issues Related to the Use of Fertilizers

There are concerns, both genuine and imaginary, that soil fertility management practices of modern, high-yielding cropping systems are harmful to the soil environment and, as a consequence, only conventional agricultural production is sustainable. Results from long-term fertilizer experiments, designed to assess the influence of fertilization on various soil properties in relation to sustainable yields, tend to dispel such concerns. For example, Japanese research reveals that NPK fertilization did not negatively affect physical, chemical, and biological soil properties, and yields were increased and maintained at levels double those of unfertilized soils [2]. NPK fertilizers, organic materials, and soil amendments have resulted in additional yield increases. While the relative merits of fertilizer use and the sustainability of agriculture are subject to debate, it is evident that the potential adverse impact of fertilizer use practices for both organic and chemical fertilizers can be minimized and the sustainability of agriculture enhanced by increased environmental sensitivity.

19.2.1 Soil Protection by Nutrient Balance

Nitrogen forms a part of chlorophyll, the focal element in plant photosynthesis. Nitrogen is needed in DNA and RNA for storing and processing genetic information, in the amino acids that constitute all proteins, and in enzymes that control all the transformations in the living world.

Phosphorus is involved in a wide range of plant processes – from permitting cell division to the development of a good root system to ensuring timely and uniform ripening of the crop. It is needed primarily by young, fast-growing tissues and performs a number of functions related to growth, development, photosynthesis, and use of carbohydrates. It is a constituent of ADP and ATP, two of the most important substances in the life processes.

Gains and losses of nutrients in natural ecosystems are roughly in balance so that continued biological growth or net fixation of carbon depends upon the cycling of nutrients between the biomass and the organic and inorganic stores. Removing or harvesting portions of the biomass from the ecosystem without replacing the nutrients contained in the harvested biomass fraction ultimately depletes one or more of the nutrients. Consequently, the biological yields are reduced.

It is obvious that nutrients are lost in the ecosystem through crop removal, leaching, denitrification, volatilization, and erosion.

Nutrient removal by the crop is the largest factor accounting for nutrient depletion from well-managed crops. Fertilization practices are generally targeted to replenishing these nutrients consistent with economic considerations.

Leaching is a serious factor in all light-textured and well-drained soils. Leaching primarily affects potassium, magnesium, and calcium but can also be a factor for other nutrients, in particular, boron and nitrogen.

Denitrification occurs as a result of the conversion of nitrate N into nitrous oxide and nitrogen. Under poorly aerated conditions where an initially well-aerated soil becomes wet and poorly aerated, losses of N can be large.

Volatilization only affects ammonia. Losses can be very high where ammonia or ammonia-producing fertilizers are improperly applied.

Erosion is the largest single factor responsible for soil degradation, including nutrient loss. Phosphorus is the nutrient most affected by erosion.

Nutrient depletion and soil fertility can result in degradation of the environment. Depletion of soil nutrients is a worldwide concern. In Africa there is an annual nutrient deficit, in Brazil nutrients applied by fertilizers meet 35% of the computed nutrient needs, and in India only 24%. In China large-scale depletion of phosphorus and potassium is observed. Even in the United States the nutrient budget shows a deficit.

The application of fertilizers to protect the soil from depletion and to enhance the environment requires that several conditions be fulfilled:

- Nutrient ratio, e.g., proper fertilizer quantity.
- Ratio of biomass:mineral fertilizers.
- Time of fertilizer application.

Consequences of plant nutrient mismanagement for the environment at the farm level result from plant nutrient transfer out of the soil/crop system, and induce harmful modification of the conditions prevailing in the system affected by those transfers:

Nitrogen in the surface water:	quality of the drinking water eutrophication
Nitrogen in ground water:	quality of drinkable water
Phosphorus in surface water:	eutrophication
Greenhouse gases to atmosphere:	theoretical climate change

Nutrient Ratio

The soil provides at least 13 essential nutrients to the plants, partly from its own resources and partly by channelling nutrients added through fertilizers, manures, and other sources. All of these nutrients are needed in the specific proportions to satisfy demand of different plants.

Nitrogen is the nutrient most widely deficient, and its initial application often results in very large yield increases. However, nitrogen application does not contribute to a buildup of soil fertility. On the contrary, the unbalanced use of nitrogen relative to other nutrients is currently causing soil nutrient depletion. It has been shown that application of 174 kg/ha of N increased the rice yield by a factor of 2.9 but increased removal of P, K, and S by factors of 2.6, 3.7, and 4.6, respectively [3]. The results are given in Table 19.1.

On the other hand, a deficit of P in soil can reduce nitrogen efficiency. In addition, inadequate supplies of P may lead to higher amounts of nitrate carryover in the soil and increase the probability of nitrate leaching into groundwater. In a large number of trials there were no responses to K in the absence of P application. Negative interaction between P and Zn is observed where high levels of P application reduce the concentration of available Zn; therefore, a balance of all nutrients must be ensured by good soil management.

Table 19.1. Depletion of Nutrients at Single Nitrogen Application

	Nutrient Removed by the Crop kg/ha Without Fertilizer			Nutrient Removed by the Crop kg/ha With 174 kg/ha N		
Nutrient	Straw	Grain	Total	Straw	Grain	Total
N	18	34	52	75	145	218
P_2O_5	2	10	12	5	26	31
K_2O	59	10	69	232	26	258
S	0.8	1.0	1.8	3.3	4.9	8.2
Grain yield	3.4 t/ha			9.8 t/ha		
Straw yield	2.8 t/ha			8.2 t/ha		

Ratio of Biomass to Mineral Fertilizers

The sources of natural nutrients are soil, water, atmosphere and biomass and farmyard manures (FYM).

The sources of nitrogen for worldwide crop production are given in Table 19.2 [4]. Soils are the source of multiple nutrients; however, resources of nutrients in the soil are always limited and must be supplemented. The atmosphere supplies some nitrogen, sulfur dioxide, and chlorides near ocean shores. Water supplies some quantities of calcium, magnesium, and potassium. All of these sources should be considered in the selection of soil management practices.

Organic fertilizers (biomass and FYM) are important elements of the nutrient contribution. The organic matter that is applied has a very complex effect on soils and plant growth. In general, the effects are as follows:

- Improvement of the soil physical properties (better soil structure, water-holding capacity, soil aeration, buffering soil surface temperature, erosion reduction, etc.).
- Improvement of chemical properties (supply of nutrients in balanced ratios, slow release of nutrients, etc.).

Table 19.2. Sources of Nitrogen for Crop Production

Source of N	%	Amount (million of tonnes)
Biological N-fixation	16.3	30
Mineral fertilizers	45.7	84
Aerial fixation	8.1	15
FYM/biomass	13.6	25
Mineralization of soil organic matter	16.3	30
Total	**100**	**184**

- Improvement of the soil's biological activity (stimulation of soil flora and fauna).

However, the amount of biomass and FYM is limited, and with increasing urbanization more and more organic matter is not recycled to the farm site.

The substitution of the present supply of mineral fertilizers by FYM would require a fourfold increase of the livestock worldwide. This is not possible due to the limitation of the feed available, and it is not advisable because of environmental pollution. For example, some European countries have developed very large livestock herds based on imported feed, and manures from concentrated production have resulted in incidences of water and air pollution. This has led the European Community to limit the number of livestock per hectare of land.

Application of organic matter as a fertilizer has some negative aspects:

- Under continuously reducing conditions (poorly drained rice fields) organic acids and other organic products may retard plant growth.
- City compost and sewage slurries may be contaminated by the toxic organic compounds and heavy metals.
- FYM is a source of cadmium.
- Heavy use of FYM may cause bacterial pollution of groundwater and eutrophication of surface waters.
- The application of biomass requires transportation and disposal of large volumes; thus, it is a labor- and energy-intensive operation.

19.2.2 Adequate Time of Application of Fertilizers

Over their life cycle plants require different nutrients with varying intensity; when the supply does not cover the demand, yields are lower and in case of oversupply the unused part of nutrients may pollute the environment, e.g., there is generally no agronomic reason to exceed 150 kg/ha of N in grain production. From an environmental perspective it is risky to apply more than 200 kg/ha of N under European climatic conditions [5].

Plant nutrient supply from various sources should cover immediate plant nutrient demand. If the risks from leaching, volatilization, denitrification, or fixation are high, such as in rainy, tropical climates, it is important to operate in a supply/demand mode rather than in terms of total nutrient doses. The uptake of nutrients by cereals during their developmental phases is given in Figure 19.1 [5].

Daily uptake of N shows an important increase between tillering and jointing in the amount of 6.4 kg/ha/day of N. The second crucial period is between panicle initiation and flowering (demand equals 1.6-1.8 kg/N/ha/day of N).

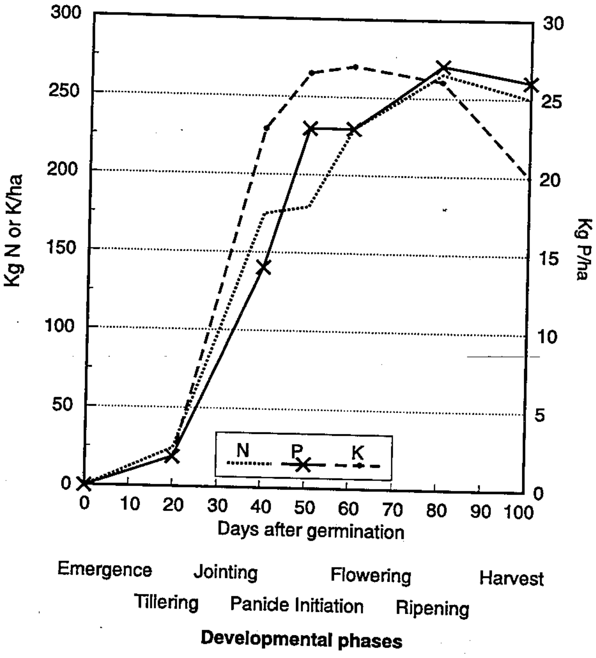


Figure 19.1. Dynamics of the Uptake of Nutrients by Cereals.

Phosphorus demand grows after sucker settlement; however, to produce rich roots phosphorus is necessary from the very beginning. Between half-time tillering and jointing and the preparatory phase of panicle initiation, the demand is about 1 kg/ha/day of the P_2O_5. After flowering, initiation and grain growth, the demand is 0.2-0.3 kg/ha/day of the P_2O_5.

The consumption of K_2O takes place during the first 2 weeks, and supply must reach 15 kg/ha/day of K_2O.

19.2.3 Nitrogenous Fertilizer Use and the Environment

Nitrogen in mineral and organic fertilizers is converted by soil microorganisms to ammonium and nitrate since these are almost the only forms of N that can be used by crops. They are highly soluble in water and are readily available for plant uptake. The ammonium form is attracted to and held by soil particles. If the ammonium form is not used by the plant, it is converted to nitrate. The unused nitrates move with the soil water and can lead to accumulation in the groundwater. Heavy rains may remove nitrogen in any form and deposit it into surface waters. Organic nitrogen, especially that originating from mineralization of the organic matter, is the main source of N loss into the water. Leaching of the nitrogen leads to eutrophication of the surface water and the contamination of drinking water.

Increasing biological production in the surface waters consumes dissolved oxygen and causes eutrophication. Algae present in the waters with excess nutrients (mainly leached nitrogen and phosphorus from soil erosion) grow rapidly and consume most of the oxygen preventing development of other forms of life, e.g., fishes. In some cases eutrophication can lead to the total extinction of life in the waters and can make surface waters unusable.

Nitrate leached from the soil may be present in the drinking water supplies since the standard treatment processes do not remove nitrates from water. Nitrates in the human alimentary system are reduced to nitrites, which transform blood hemoglobin into an inactive form that is unable to participate in the oxygen-exchange process. This is particularly dangerous for bottle-fed babies. Therefore, the amount of nitrates in drinking water is limited by the European Union to the amount of 50 mg of NO_3/l. The WHO advisable limit is 45 mg of NO_3/l. However, water is not the only source of nitrates in the human diet, and the daily dose of nitrate may amount to 200 mg of NO_3 per day. Fruits and vegetables transform nitrates into harmless compounds [6]. The leaching of nitrogen by coincidence is minimal at the economic optimum of the fertilizer application as shown in Figure 19.2.

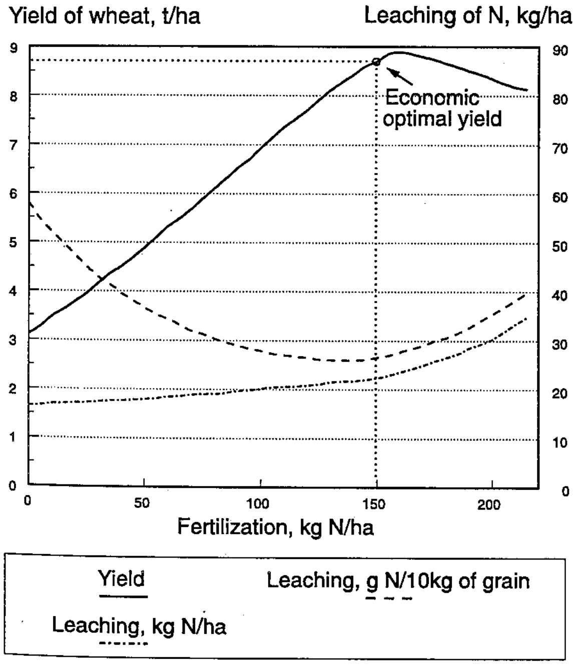


Figure 19.2. Leaching of Nitrogen From Soil at Agronomically Optimal Conditions.

Use of fertilizers also causes emission of gases to the atmosphere. Nitrous oxide and other oxides of nitrogen in the atmosphere are transformed into NO_2, which reacts with ozone in the upper zones. However, the impact of nitrogen oxides on the ozone layer is insignificant in comparison with that of other gases [4].

Use of urea may cause emission of ammonia into the atmosphere. In some cases emission of 50% of the dose applied has been reported. Ammonia emissions (estimated total of 4.5 million tonne/year) do not contribute significantly to the greenhouse effect. Ammonia is quickly removed from the atmosphere by wet and dry surfaces and by dissolution in precipitation. It is estimated that only 10%-20% of ammonia emissions reach the atmosphere and are oxidized to the various nitrogen gases.

19.2.4 Phosphorus Fertilizer Use and the Environment

Phosphorus fertilizers may contain impurities; among those are some heavy metals that are of concern. In particular, cadmium (Cd) has received attention during the past few years. The level of cadmium content in fertilizers has been more or less arbitrarily limited to the concentration of 50 mg Cd/kg of P_2O_5 [7]. WHO has limited the daily intake of Cd to 1 microgram/kg of body weight per day [7]. The current average intake in Europe is lower than this limit [8].

Detailed studies of the origin of cadmium and its content in crops have been carried out in Great Britain [9].

Research has not yet solved the problems of origin and transformation of cadmium in the soil and crops. It has been observed that deposition of the Cd from air is higher than that from mineral fertilizers. Where FYM has been used the total deposition of Cd has been higher than the combined atmospheric deposition and the contribution of mineral fertilizers. However, the behavior of Cd of different origins in the soil has not been investigated. Soil organic matter increases the retention of Cd in the soil. The content of cadmium in grain (wheat and barley) has been of the same magnitude (about 40 micrograms/kg) when mineral fertilizers or FYM has been used. In the case of herbage, NPK contributed a cadmium concentration of 81 micrograms/kg of dry matter, and for FYM reported data are 227 micrograms/kg.

Phosphorus also contributes to the eutrophication process of the surface waters. The eutrophic "threshold value" is considered to be in the range of 0.020-0.050 ppmw of P; most surface waters exceed this value [10]. The P content in sewage waters containing detergents, animal wastes, and plant residues contributes to the high phosphorus content of surface waters. Phosphorus from fertilizers could reach the surface waters only by erosion since P does not leach through the soils in a significant amount [11]. To prevent phosphorus losses in agriculture, soil erosion control measures should be employed.

19.2.5 Fertilizer Benefits to the Human Environment

The potential negative environmental aspects of fertilizers as presented in previous paragraphs are minor when fertilizers are used in the proper quality, at the proper time of the cropping season, and in the adequate quantity. The misuse and overuse of fertilizers could not be an argument against their application. The proper use of fertilizers requires the active participation of governments in broad-based education and advertising programs.

Fertilizers make significant positive contributions to the human environment [12]. Some of these contributions are described in the following sections.

- **Improvement of Farming Efficiency**
  Farmers' incomes can be increased by the use of adequate land management procedures. Application of fertilizers is one of the leading parameters of successful land management. Use of the economic optimum levels of fertilizer is consistent with a minimum of nitrate leaching.

- **Improvement of Soil Quality**
  Long-term experiments in Great Britain, Denmark, and Japan have shown that adequate fertilization improves soil quality. The soils that are tested are more productive after many years of fertilizer application than at any time before. The aggregating action from enhanced root proliferation and the greater amount of decaying residues have been reported to help make soils more friable, tillable, and water retentive.

- **Improvement of Crop Quality**
  The mineral, protein, and vitamin contents of crops may be improved by judicious fertilization.

- **Retardation of Soil Erosion**
  Densely growing crops on slopes are less erosion prone and have a more prolific root system, which protects the soil against water and wind loss. The residual effects of greater organic production improves soil aggregation.

- **Conservation of Water**
  Efficient cropping systems using fertilizers require minimum amounts of water per volume of product. Only well-nourished plants use water efficiently through the expanded root system and decreased evaporation.

- **Air Purification**
  Plants absorb carbon dioxide and produce oxygen. A maize field yielding 6 tonnes/ha of grain may produce about 15 tonnes of oxygen when adequate amounts of carbon dioxide are used. This is approximately the amount of oxygen used annually by 30 people.

Issues of agricultural sustainability and minimal environmental hazards should be addressed simultaneously. Efficient fertilizer use can be the key to sustainable productivity. A well-fertilized soil supports a dense canopy, which protects the soil from erosion, absorbs more carbon dioxide from the atmosphere, and releases more oxygen. Minimizing leaching, erosion, and volatilization losses of mineral and organic fertilizers and preventing overfertilization should be future agricultural strategies.

19.3 Environmental Impact of the Fertilizer Industry

The fertilizer production processes considered in this chapter are shown in Figure 19.3.

Obviously a qualitative description of the emissions would be given for the standard process. The quantitative measure of emissions derives from the process basic

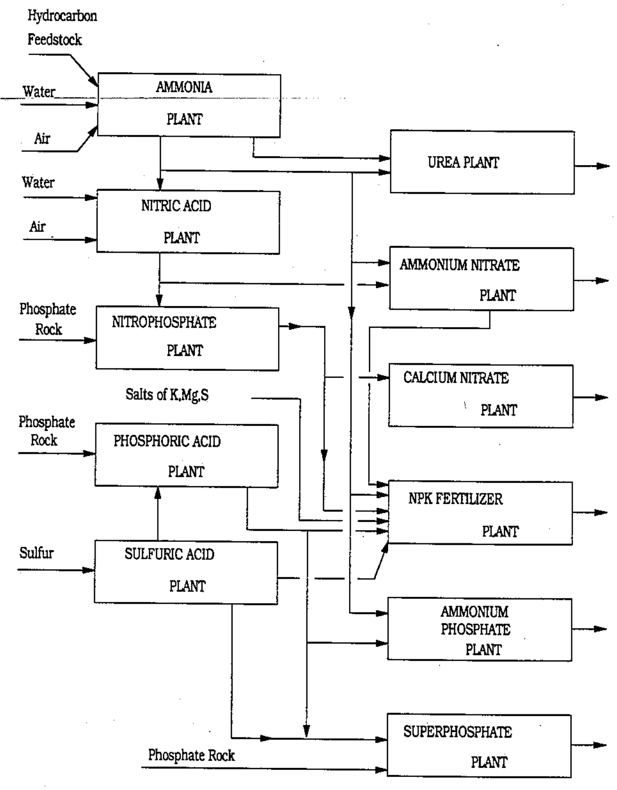


Figure 19.3. General Scheme of Fertilizer Production.

design where relevance to the process alternatives and capacity emissions could be calculated. These should be compared with the limits and targets defined in local regulations (standards or guidelines) and respective additional pollution-abating equipment selected and added to the process design.

19.3.1 Ammonia

Raw Materials

Ammonia is produced from three basic raw materials:

1. Natural gas by the reforming or partial oxidation processes.
2. High viscosity, sulfur-rich crude oil residue by the partial oxidation process.
3. Coal by the gasification process.

Utilities

An ammonia plant needs water of two qualities: process water for boilers and cooling water. Water-treatment installations do not produce harmful wastes.

Waste Characteristics and Impacts

Atmospheric Emissions [13] – The main emission to the atmosphere is carbon dioxide and small quantities of nitrogen and sulfur oxides. A modern steam-reforming process unit generates 2.2 tonnes of carbon dioxide per tonne of ammonia, whereas, the emission of NO_x (as NO_2) is less than 1 kg/tonne of ammonia. The sulfur oxide emission is low (0.2 kg as SO_2/tonne of ammonia) and depends on the efficiency of the desulfurization process. The partial oxidation of fuel and coal gasification produce more carbon dioxide (2.7-2.8 t/tonne of ammonia), 1.8 kg of NO_2 and 3 kg of SO_2/ tonne of ammonia. The increased amount of emissions originates from additional boilers and the Claus SO_2 reduction process.

In principle no ammonia should occur in the atmospheric emissions of a modern ammonia plant because any flow containing ammonia is scrubbed and degasified and the ammonia is recycled. However, because of leakages from the faulty operation of equipment and maintenance activities, some ammonia may be released to the plant atmosphere.

The odor concentration of ammonia is between 18 and 35 mg/Nm^3, and the limit on the workplace concentration is below 10 mg/Nm^3. Ammonia becomes explosive at concentrations of 16%-25% volume in air, which can occur as a result of indiscriminate liquid ammonia loading and unloading operations and catastrophic leakages from ammonia storage vessels [14].

Wastewater – Modern steam-reforming plants recycle process condensate and hence produce no wastes except those from boiler blowdown, boiler water, and cooling water treatments with negligible environmental impact. Partial oxidation and gasification processes produce water with suspended and dissolved impurities and therefore must be treated in a full three-stage water treatment plant (mechanical, chemical, and biological) to meet the standards of the effluent to be disposed into open waters.

Solid Waste – The steam-reforming process contains up to 8-9 catalytic steps; catalysts are replaced after 2-6 years of service. Partial oxidation and coal gasification use 3-4 catalysts. The catalysts contain hexavalent chromium, nickel, zinc, iron, and mineral supports; therefore these materials could not be disposed into landfills. Companies that specialize in producing catalysts or metal-processing companies customarily recycle catalysts.

Spent resins from boiler feedwater treatment plants may be returned to the resin producer or burned in high-temperature kilns.

Hazardous Wastes – The metals contained in the spent catalyst may be hazardous waste if disposed indiscriminately.

The potassium carbonate solution used in carbon dioxide removal contains inorganic and organic additives that could be hazardous when released in larger quantities. The process itself does not provide this opportunity.

Fugitive Emissions – Minor amounts of light hydrocarbons, ammonia, hydrogen, and carbon oxides may be released due to leaks from flanges and stuffing boxes, especially during maintenance operations. The handling of catalysts and chemicals may also cause minor releases.

Contaminants of Concern – No contaminants of concern are present in the product.

Environmental Impact – Carbon dioxide is a greenhouse gas, and sulfur dioxide and nitrogen oxides may contribute to acid rain. In an aquatic environment ammonia concentrations over 1.25 mg/l are harmful to fish.

Pollution Prevention and Control

a. **Source Reduction** – New ammonia plants consume as little as 28 GJ/t of ammonia; therefore, further reduction of carbon dioxide emissions will be difficult. The same relates to the NO_x and SO_x from a reforming unit.

b. **Recycling and Byproduct Recovery** – Atmospheric emissions of carbon dioxide are decreased by nearly one-half by its use in urea or nitrophosphate plants. Spent catalysts should be recycled for metal reclamation.

c. **Hazardous Materials Handling, Management, and Disposal** – The only hazardous material occurring in large quantities is ammonia, which must be stored, transported, and handled in special tanks under specific instructions and guidelines. The handling and recycling of spent catalysts also require specific guidelines.

d. **Treatment Technologies** – A new ammonia plant can achieve a satisfactory level of emissions from reforming sections without abatement of fuel gases. Partial oxidation and gasification plants require treatment of both gaseous and liquid discharges.

Occupational Health and Safety Issues

Natural gas, ammonia, and hydrogen present during the process are explosive in mixtures with the air. Leaks of gas mixtures may self-ignite and may cause explosions; therefore, respective stations of the automatic firefighting equipment must be located in critical areas. Ammonia is stored at low temperatures in large-volume tanks or under pressure in smaller storage tanks. In consideration of the toxic properties of ammonia in concentrations over 10 mg/l, the necessary safety equipment (gas masks, eye wash bottles, showers, etc.) must be located at the workplaces. Operators of ammonia plants should be highly trained workers and have experience in industrial operations. Detailed operating manuals and guidelines should be prepared and workers must be retrained regularly.

Guidelines of Discharge Requirements

There are no specific emission limits and guidelines for ammonia plants in Europe; however, because of their high thermal input, they have limits corresponding to those of electric power plants. Examples of such standards for Germany are given in Table 19.3 [13].

Target/Projected Guidelines

At present the target technology is an ammonia synthesis plant that uses desulfurized natural gas and a reforming (with pre-reforming and partial oxidation) process that requires low amounts of energy (28 GJ/t) and has special burner facilities to decrease NO_x to nil concentrations.

Table 19.3. Emission Limit Values Applied for Combustion Plants in Germany

Pollutant	Type of Plant Gaseous Fuel Installations		Limit Value
SO_3	>100 MW		35 mg/Nm^3
NO_x	New:	>100 MW	200 mg/Nm^3
		>300 MW	100 mg/Nm^3
	Existing:	>100 MW	350 mg/Nm^3
		>300 MW	100 mg/Nm^3

Monitoring Requirements

The reformer units, auxiliary boilers, and sulfur recovery units should be monitored for NO_x and SO_x concentrations. The monitoring frequency depends on local regulations.

19.3.2 Nitric Acid

Raw Materials

Nitric acid is produced from the three basic raw materials – anhydrous ammonia, air, and process water.

Utilities

A nitric acid plant needs water that has three qualities: process water for steam turbine condensation, process makeup water, and cooling water. The water treatment installations do not produce harmful wastes. Recycled process condensate or demineralized water is used by the absorption tower. The cooling water must also be of high quality especially regarding the concentration of chlorides. Sometimes cooling water operates in a closed circuit and is cooled by poor-quality water. The production of nitric acid produces a surplus of energy in the form of high-pressure steam.

Characteristics and Impacts of Wastes

Atmospheric Emissions [13] – The main emissions to the atmosphere are oxides of nitrogen (NO_x) and nitrous oxide (N_2O). The concentration of NO_x in emissions varies between 75 and 2,000 ppmv. The concentration of NO_x depends on final acid concentration, absorption tower pressure and design, temperatures of the cooling tower water, quantity and quality of process water, and degree of tail-gas treatment, if any.

Wastewater – Wastewater from the process can originate from blowdown of cooling tower water to control dissolved solids and from boiler blowdown and water treatment plants. In all cases the water will contain dissolved salts that have a low environmental effect.

Solid Waste – The platinum/rhodium catalyst requires treatment after a certain campaign length depending on the combustion pressure and, due to its high cost, is returned to the manufacturer for credit. Deposits of catalysts can be recovered from various parts of the plant; these are also returned to the catalysts' manufacturer for recovery of platinum and rhodium. Spent water treatment resins may be returned to the resin producer or burned in high-temperature kilns.

Hazardous Wastes – The process does not produce hazardous solid wastes.

Fugitive Emissions – Small amounts of ammonia are released from vaporizer blowdown and from maintenance operations. Similarly, there can be small amounts of nitric acid released during maintenance.

Contaminants of Concern – There are no contaminants of concern present in the product.

Environmental Impact [14] – The main impact on the environment is from NO_x emissions to the atmosphere. NO_x may contribute to acid rain and ground-level ozone. Nitrous oxide could theoretically contribute to greenhouse effects or affect the stratospheric ozone layer; however, N_2O emissions from nitric acid plants are small compared with other sources.

Of the total N converted in the nitric acid plants, 0.6%-0.9% is lost as NO_x and 0.4%-1.5% is lost as N_2O to the atmosphere.

Pollution Prevention and Control

a. **Source Reduction** – Most emissions to the atmosphere can be reduced by plant design and optimal operation. Makeup and cooling water temperature will affect the absorption stage and hence emissions of NO_x.

b. **Recycling and Byproduct Recovery** – Catalyst wastes are recycled.

c. **Hazardous Materials Handling, Management, and Disposal** – Nitric acid should be stored in closed-top stainless steel tanks. The plant areas should have impermeable flooring with all surfaces draining to a neutralization pit to deal with small acid discharges from maintenance operations. It is also important to prevent ammonia vapor emissions from unloading, storage, and handling facilities. Small amounts of nitrate salts produced from the neutralization pit would normally be discharged with cooling water blowdown to waste.

d. **Treatment Technologies** – New high-pressure nitric acid plants can achieve satisfactory emission levels of NO_x without treatment of the tail gas.

For various other plants abatement methods are available to reduce NO_x emissions:

- **Alkaline Absorption and Extended Absorption** – Alkaline absorption involves treating the tail gas with sodium hydroxide in a scrubber. After washing, concentrations of NO_x as low as 200 ppmv in tail gas can be achieved. The byproduct of the washing process is a low concentration solution of sodium nitrite/nitrate that requires safe disposal or further use. The capital cost of the absorption process is 4.3% of the total investment cost of a dual-pressure nitric acid plant. The net operating cost, considering higher maintenance costs yet higher acid recovery, is not expected to increase. Depending on the absorption pressure, the processes of BASF, ICI, and others may use alkaline absorption. Ammonia scrubbing is used in the United States. Goodpasture (U.S.A.) developed a process in which the tail gas is scrubbed with an ammonium nitrate solution with the addition of ammonia in the scrubbing unit. Part of the NO_x may be recovered as ammonium nitrate, and part may be reduced to nitrogen. Norsk Hydro developed a scrubbing process in which the scrubbing medium is an aqueous solution of urea and nitric acid; the loss of fixed nitrogen in the process is a disadvantage [15].

  In the industrialized countries there is a growing preference for extended absorption as a method to control NO_x in tail gas. The method consists simply of increasing the efficiency of the absorption system by adding a second absorption tower, by adding more sections to the absorption tower, or in some cases by reducing the temperature in the last absorption stages by cooling coils using chilled water or other coolant. One company uses refrigerated potassium carbonate solution as the coolant. Hydrogen peroxide can also be used in the end stage of absorption to increase the efficiency of the process. These methods can be used with either new or existing plants; with new plants there is greater flexibility in selecting the economic optimum combination of parameters, including increased pressure. It has been reported by Chemical Works Tarnow (Poland) that substantial reduction of NO_x has been achieved by saturation of scrubbing liquids with oxygen [16]. Several organizations, including Friedrich Uhde (Germany), Société Chimique de Grande Paroisse (France), C&I Girdler (United States), D. M. Weatherly and Co. (United States), and Institute of Mineral Fertilizers (INS - Poland), offer nitric acid plant designs with extended absorption, which will give tail-gas NO_x concentrations below 200 ppmv. This concentration is low enough to satisfy the present requirements of the United States or any West European country. The extended absorption method has the obvious advantage that recovery of nitrogen as nitric acid is increased by 1.0%-1.5% as compared with the former practice.

- **Non-Selective Catalytic Reduction (NSCR) [17]** – Hydrogen or hydrocarbons are burned in tail gas over platinum/rhodium catalysts to remove NO_x using excess oxygen. Reduction to nitrogen requires 1.1-1.25 excess fuel component in relation to the NO_x amount. Application of hydrogen is environmentally safe; however, it is a rather costly process. Utilization of the hydrocarbons produces tail gas containing carbon monoxide and hydrocarbons. Natural gas is usually used as a fuel for the NSCR method. The following reactions are illustrative for this method:

1. $2\,O_4 + CH_4 \rightarrow CO_2 + 2\,H_2O + 802$ kJ [1]
2. $2\,NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2\,H_2O + 331$ kJ [2]
3. $4\,NO + CH_4 \rightarrow 2\,N_2 + CO_2 + 2\,H_2O + 443$ kJ [3]

Tail gas contains about 2%-4% oxygen, which also reacts with the added fuel (reaction 1). For complete reduction of NO_x (reactions 2 and 3), enough fuel gas must be added to consume all of the oxygen in the tail gas. Being highly exothermic this method is often designed with two or more catalyst beds in a series with intercooling to prevent excessive temperatures.

The NSCR process supplied by the State Institute of Nitrogen Industry (GIAP) incorporates a catalyst reactor with two catalyst beds without intercooling to create a high reaction temperature for more efficient energy recovery. This is possible because of the composition of the catalyst; Al_2O_3 with 2% Pd is used for the first bed and Al_2O_3 for the second. The temperature of the gas leaving the reactor is in the range of 680°-800°C, depending on the modification of the process. This method generates much heat at a high-temperature level. The energy is recovered by a high-temperature tail-gas expansion turbine and wasteheat boiler. The tail gas vented to the atmosphere may contain up to 0.15% CO and 0.02% CH_4. More than 100 nitric acid plants in Russia and other Central and East European countries are equipped with GIAP NSCR units.

- **Selective Catalytic Reduction (SCR) [17]** – Ammonia is used as a reducing agent over a catalyst to convert the NO_x gases to nitrogen. These processes can reduce the concentration of NO_x in tail gas to 100 ppmv and lower. Existing plants with medium-pressure absorption can be economically revamped using this process. The capital cost of the selective catalytic reduction (SCR) process to remove NO_x from a concentration of 500-200 ppmv would increase the capital costs of a dual-pressure nitric acid plant by 2% and operational costs by US $0.30/tonne of nitric acid. The SCR method needs ammonia for reduction of NO_x. The following reactions occur in the process of selective reduction of NO_x:

1. $4\,NH_3 + 6\,NO \rightarrow 5\,N_2 + 6\,H_2O + 1810.6$ kJ [4]
2. $8\,NH_3 + 6\,NO_2 \rightarrow 7\,N_2 + 12\,H_2O + 2743$ kJ [5]

If the correct catalyst is chosen, ammonia does not react with the oxygen present in the tail-gas; as a result less heat is generated. The temperature of reaction is usually in the range of 200°-450°C.

For the processes developed in Russia (GIAP), two different catalysts are used: alumo-vanadium (AVK) and alumo-copper-zinc (AMC) catalysts.

SCR has also been used successfully in several commercial plants in Japan, the United States, and Western Europe. Commercial processes are offered by Gulf Oil Chemicals, Inc. (United States); Mitsubishi (Japan); BASF (Germany); Grand Paroisse and Rhone-Poulenc (both France); Espindesa (Spain); and others. A small residual quantity of NH_3 may be present in the tail gas vented to the atmosphere after the SCR unit.

Because of more strict pollution control regulations in Russia [17], preference was given to NSCR and SCR NO_x abatement methods. Since the early 1970s catalytic reduction units, either NSCR or SCR, were incorporated in all Russian-designed nitric acid plants. At the same time, all older plants (except those operating at atmospheric pressure and already equipped with alkali scrubbing) were supplied with SCR units. Both methods, NSCR and SCR, are effective in reducing the tail-gas NO_x concentration well below 100 ppmv.

- **Adsorption Processes** – Adsorption by silica gel or molecular sieves is possible. The process requires regeneration of the adsorbent and permits return of the NO_x to the process. An interesting version of "wet" adsorption scrubbing principle is the Compagnie Française de l'Azote (COFAZ) process [18].

Two examples of the NO_x treatment process units that combine the high efficiency absorption columns and SCR reactor implemented by Uhde and Rhone-Poulenc are described in the next section.

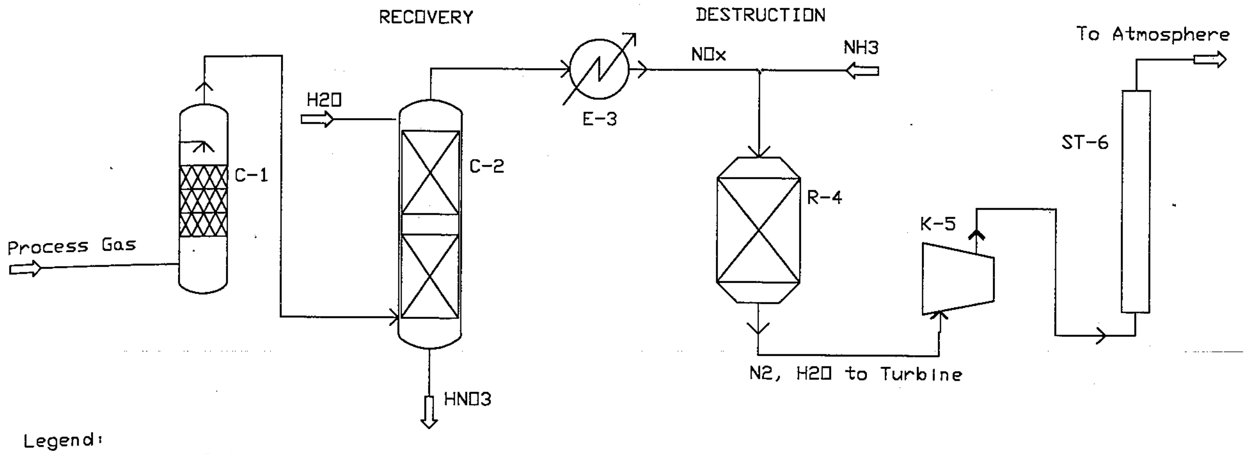
Rhone-Poulenc Processes (RP France) [19]

NO_x abatement of tail gases from nitric acid plants and other NO_x sources (e.g., adipic acid, nicotinic acid, nitrates calcination, etc.) has been implemented during the past 10 years in about 40 projects in 18 countries by applying two processes:

1. High-efficiency absorption (HEA column).
2. Catalytic destruction of NO_x (DCN process).

These two processes which are applied to gases from the absorption tower, are given in Figure 19.4 and could be applied separately or jointly depending on the local NO_x emission limits.

The principle of the high-efficiency absorption (HEA) column is liquid-phase oxidation and absorption. The product is a dilute nitric acid, which is recycled to the main absorption system. The nonabsorbed gases are heated and directed to the catalytic reactor (Rhone-



Legend:
C-1 Absorption Column
C-2 High Efficiency Absorption (HEA)
E-3 Heat Exchanger
R-4 DCN Reactor
K-5 Turbine
ST-6 Stack

HEA Column - Reduction of the NOx content in the tail gas with NOx recovery as nitric acid

DCN Reactor - Destruction of remaining NOx according to level required by the most stringent international standards

Figure 19.4. Rhone-Poulenc NO_x Abatement Process.

Poulenc code: DN110 and DN115). The reaction between the NO_x and NH_3 ensures full reduction of the oxides. The reduced tail gas passes through the turbine and out the stack.

The cost of NO_x pollution abatement depends on the efficiency of the original absorption system; estimated costs for a 365-tpd nitric acid unit are given in Table 19.4 [19].

Institute of Mineral Fertilizers (INS Poland) Process [20]

The process is a double-pressure 0.5/1.5 MPa process. A high-efficiency absorption tower ensures 99.9% efficiency. After treatment the gas contains 40 ppmv of NO_x. The double catalyst system (I step: Pt-RH, II step: Pd) ensures the minimum losses of platinum (20-40 mg/t HNO_3).

Table 19.4. NO_x Abatement Cost Estimate

Process	Investment Cost (US $ million)	Consumption Per Tonne of 100% Nitric Acid	
		Energy, kWh/tonne	NH_3 kg/tonne
HEA	0.4	5	–
DCN	1.0	–	4.5

Total cost of tail-gas cleaning: HEA 0.6 US \$/tonne
DCN 1.3 US \$/tonne

Occupational Health and Safety Issues

NO_x fumes are highly toxic. The exposure threshold limit value (TLV) during an 8-hour period is 3 ppmv and 10 minutes limit of 5 ppmv. Breathing NO_x fumes should be avoided, and a breathing apparatus should be worn whenever necessary. Nitric acid is extremely corrosive to all materials. When handling the acid a fully protective suit, goggles, face shields, PVC gloves, and boots must be worn.

Eye wash bottles and showers should be provided at strategic places throughout the plant. Gaseous emissions from safety devices such as ammonia gas relief valves must be vented to a safe place.

Operators of the nitric acid plant should be highly trained workers with experience in industrial operations. Detailed operating manuals and guidelines should be prepared and workers regularly retrained.

Guidelines of Discharge Requirements

The specific air emission limits and guidelines for existing nitric acid plants in Europe are given in Table 19.5 and for new plants in Table 19.6 [13].

Target and Projected Guidelines

At present the target technology is a nitric acid plant without a special abatement process unit with an NO_x concentration of 200 ppmv in the tail gas. Medium-pressure plants can vent 500-800 ppmv of NO_x in tail

Table 19.5. Air Emission Limits for Existing Nitric Acid Plants

Country	Limit Value	Averaging Time	Implementation Date	Remarks
Germany	450 mg/m^3 dry NO_x as NO_2 (219 ppmv)	24 h	3/1986	
France	4.5 kg HNO_3/tonne of 100% HNO_3			Case by case
Netherlands	600 ppmv	1 h	1992	
United Kingdom	1,000 ppmv		1992	Limit not to be exceeded at any time of operation
Ireland	200 ppmv (NO_x)		1976	
Denmark	Limit values set for each plant			
Spain	20 kg NO_x/tonne HNO_3			
India	3 kg NO_x/tonne of weak acid			
Turkey	800 mg/m^3			
Thailand	2,000 mg/m^3			
U.S.A.	1.5 kg NO_x/tonne HNO_3			
Greece	8 kg NO_x/tonne 100% HNO_3		1981	

Table 19.6. Air Emission Guidelines for New Nitric Acid Plants in Europe

Country	Limit Value	Averaging Time	Implementation Date	Remarks
Germany	450 mg/m^3 dry NO_x as NO_2 (219 ppmv)	24 h	3/1986	Double 2% time
France	4.5 kg HNO_3/tonne of 100% HNO_3		7/1974	400 h/year 48 h 6 kg/tonne
Netherlands >500 tpd	220 ppmv	1 h	1987	No limits at shutdown and startup
United Kingdom	200 ppmv		1987	Limit not to be exceeded at any time of operation
Denmark	200-225 ppmv		Expected	
Spain	3 kg/NO_x/tonne of 100% HNO_3	2 h	1975	
Portugal	400 mg/m^3 NO_2			
Greece	5 kg NO_x/tonne of 100% HNO_3			

gas. A smaller low-pressure plant may emit up to 2,000 ppmv when unabated. The standard of 200 ppmv for new plants is recommended as a realistic target.

Monitoring Requirements

Continuous monitoring of NO_x levels in the stack gas should be provided. The system that measures the sum of all NO_x and NO_2 separately is recommended to allow for a higher degree of plant operational control.

19.3.3 Sulfuric Acid

Raw Materials

Sulfuric acid is produced from three basic raw materials:

a. Elementary sulfur.

b. Pyrites.

c. Tail gases from the metallurgical industry.

Utilities

The production of 1 tonne of 100% sulfuric acid requires 0.33 tonne of sulfur and creates up to 1.8 tonnes of high-pressure steam.

Sulfuric acid plants need water that has three qualities: demineralized water for boiler feed, process makeup water to absorb SO_3, and cooling water. The water treatment installations do not produce harmful wastes. Recycled process condensate or demineralized water is used for the absorption tower. The cooling water amount and quality depend on the type of heat exchangers used and water available.

Waste Characteristics and Impacts

Atmospheric Emissions – The process has two emissions to the atmosphere: sulfur dioxide and acid mist, both of which are released with the waste gas from the final absorber tower.

Wastewater – Apart from boiler blowdowns and water treatment plant regeneration, this process does not produce liquid effluent if the basic raw material is elemental sulfur. If other raw materials are used, there are waters containing chemicals that must be treated.

Aqueous effluent from the sulfuric acid plant can originate from spills, leaking pumps, or flanges; the degree of contamination depends on the operating and maintenance standards.

Solid Waste – The oxidation process uses vanadium catalyst that must be periodically removed and screened for dusts. A 1,500-tpd plant produces 20 m^3 of the spent catalyst annually.

Used catalyst and dusts are returned to the catalyst manufacturer for recovery of vanadium or safe disposal. Vanadium compounds, especially oxides and the sulfide, are toxic if inhaled.

In case of other raw materials (metal sulfides), solid wastes are quite extensive; however, they are also used in metallurgical operations.

Hazardous Waste – The process does not produce hazardous solid waste if the spent catalyst is handled carefully.

Fugitive Emissions – Small amounts of sulfur dust are produced when the sulfur is stored in the open air. Similarly, small amounts of sulfuric acid can be released during maintenance.

Contaminants of Concern – There are no contaminants of concern present in the product.

Environmental Impact – Sulfur dioxide and acid mist released to the atmosphere contribute to local and regional acidification of the atmosphere and may contribute to acid rain. However, SO_x emissions from sulfuric acid plants are small compared with large-scale power stations burning coal and high-sulfur fuel oil.

There is little impact on local groundwaters if leaks are collected such as by a sump and returned to the process.

Pollution Prevention and Control

a. **Source Reduction** – Most emissions to the atmosphere can be reduced by selection of the raw materials. Low ash sulfur requires less screening of catalyst and less solid waste. In other cases liquid sulfur filtration and SO_2 gas filtration are necessary before conversion. Yellow sulfur is preferred before other colors that have organic impurities. The latter produces a mist, which exits the absorption towers and is difficult to remove.

b. **Recycling and Byproduct Recovery** – Catalyst waste is recycled or vanadium is removed from dumped catalyst.

c. **Hazardous Materials Handling, Management, and Disposal** – Sulfuric acid of 96% strength and higher may be stored in mild steel tanks. The plant areas should have impermeable flooring with all surfaces draining to a neutralization pit to deal with small acid discharges from maintenance operations.

d. **Treatment Technologies** – The new sulfuric acid plants can achieve satisfactory emission levels of SO_2 and mist using a double conversion/double absorption system with high efficiency mist eliminators after the final absorption. Fiber mist eliminators having low gas velocities are used to remove all particles above 9 microns and 99% of all smaller size.

Electrostatic precipitators are very efficient; however, they have a high capital cost. In specific locations final tail-gas scrubbing with ammonia or caustic soda solutions is necessary.

For the upgrading of existing facilities based on single absorption, three options exist:

1. Conversion to double absorption.
2. Switching to a cesium-type catalyst.
3. Addition of alkaline tail-gas scrubbing.

All of these changes may account for about 20%-25% of the investment costs of a new installation. Tail-gas scrubbing is the lowest cost option (15% of the total revamping cost); however, this generates a liquid effluent that needs to be processed.

The full revamping program increases the efficiency of operation but not to the extent of being justifiable on economic grounds alone.

Occupational Health and Safety Issues

Concentrations of sulfur dioxide in excess of 27 mg/Nm^3 are known to be strong irritants, and the maximum safe concentration for industrial safety is considered to be one-half of this value.

For sulfuric acid mist, maximum safe concentrations for a 24-hour period are considered to be 0.14 ppmv.

When the acid is handled, a fully protective suit, goggles, face shields, PVC gloves, and boots should be worn. Eye wash bottles and showers must be provided at strategic places throughout the plant.

Operators of the sulfuric acid plant should be highly trained workers with experience in industrial operations. Detailed operation manuals and guidelines should be prepared, and workers should be regularly retrained.

Guidelines of Discharge Requirements

The specific air emission limits and guidelines for existing sulfuric acid plants in several countries are given in Table 19.7 [13].

Target and Projected Guidelines

At present the target technology is a sulfuric acid plant with double conversion and double absorption with mist elimination. The 99.5% sulfur recovery may be achieved by this process structure. This gives a release of 3.3 kg SO_2/tonne of 100% sulfuric acid.

Monitoring Requirements

Continuous monitoring, displaying, and recording of the SO_2 level in the stack gas should be ensured to control the efficiency of the plant.

Acid mist and SO_3 slip from the final absorber demister should be measured at least weekly.

19.3.4 Phosphoric Acid

Raw Materials

Phosphoric acid is produced from two basic raw materials: sulfuric acid and phosphate rock concentrate.

The sulfuric acid does not introduce harmful impurities. The phosphate rock depending on origin can contain either radioactive elements [U, Th, Rd] or heavy metals such as cadmium nickel, copper, etc. Also, the crystalline structure of the phosphate rock influences the process, its efficiency, and the composition of the byproducts. The source of the raw material should be considered carefully when a phosphoric acid plant is established, and the technology should be adapted to this particular source.

Utilities

The production of 1 tonne of P_2O_5 in phosphoric acid requires 7.1 tonnes of makeup water; this includes the acidulation process and washing requirements. The additional water may be necessary to pump the phosphogypsum slurry to the dumping site or sea. A phosphoric acid plant needs water that has two qualities: process water and cooling water. The water treatment installations do not produce harmful waste.

Waste Characteristics and Impacts

Atmospheric Emissions – Phosphate rock usually contains 3%-4.5% of fluorine by weight. Hydrogen fluoride released during the acidulation of the phosphate rock combines immediately with the available silica contained in the reaction slurry. Use of low-silicate phosphate rock produces free hydrogen fluoride also.

Both are harmful fluoride emissions. The reactor fluorides are usually absorbed in water or in diluted solutions of fluosilicic acid. The modern absorbing equipment allows production of concentrated solutions, which could be processed to synthetic cryolite, aluminum fluoride, and various fluorosilicates. If not sold as a byproduct, the fluosilicic acid can be neutralized by liming. The neutralized slurry may require further treatment, such as settling, before it is discharged.

Wastewater – In most cases the water used to transport phosphogypsum to storage is recirculated back to the process. The phosphogypsum stacks require treatment of the run-off water for several years after the phosphoric acid plant has ceased production.

Maintaining the water in the phosphoric acid plant is an important part of the know-how of plant operation.

Table 19.7. Sulfuric Acid Emission Guidelines

Country	SO_2	SO_3	Acid Mist
Denmark	5 kg/t H_2SO_4 (1)	0.5 kg/t H_2SO_4 (1)	
Germany	97.5-99.5 sulfur conversion reate (4)	60-120 mg/m^3	
Greece	6 kg/t H_2SO_4 (1)		
	10 kg/t H_2SO_4 (2)	0.5 kg/t H_2SO_4 (1)	
		0.8 kg/t H_2SO_4 (2)	615 mg/Nm^3
Spain	1,425 mg/m^3 (2)	500 mg/m^3 (2)	
	2,858 mg/m^3 (1)	300 mg/m^3 (1)	
	1,425 mg/m^3 (3)	150 mg/m^3 (3)	
France	6 kg/t H_2SO_4 (7)	0.5 kg/t H_2SO_4 (7)	
United Kingdom	Sulfur as SO_2+SO_3 <0.5% sulfur burned		
India	4 kg/t H_2SO_4		50 mg/m^3
Thailand	500 ppmv	35 mg/m^3	35 mg/m^3
Tunisia	13 kg/t H_2SO_4 (8)	1.5 kg/t H_2SO_4 (8)	
	2 kg/t H_2SO_4 (9)	72 g/t H_2SO_4	
Turkey		0.5 kg/t H_2SO_4	
Jordan	2 kg/t H_2SO_4	75 g/t H_2SO_4	75 g/t H_2SO_4
Mexico	3 kg/t H_2SO_4		
U.S.A.	2 kg/t H_2SO_4		75 g/t H_2SO_4

(1) New plants.
(2) Existing plants.
(3) Plants built after 1980.
(4) Depending on SO_2.
(5) No limitation.
(6) H_2SO_4.
(7) These figures are used as guidelines by licensing authorities.
(8) Single absorption.
(9) Double absorption.

Aqueous effluent from the phosphoric acid plant can originate from spills, leaking pumps, or flanges; contamination depends on the operation and maintenance standards.

Solid Waste – Approximately 5 tonnes of phosphogypsum dry mass is made per tonne of phosphoric acid (calculated per 1 t of P_2O_5). When it is deposited, this waste contains about 40% water, some phosphoric acid, and trace elements from the rock: radioactive elements and heavy metals like cadmium. Other solid waste is produced during plant cleaning from scale deposits and deposits of phosphogypsum in storage tanks. The problem of phosphogypsum waste treatment is given in section 19.4.

Hazardous Waste – Radioactive elements and heavy metals may leach if phosphogypsum stacks are not isolated from groundwater.

Fugitive Emissions – Small amounts of fluorine derivatives are released into the atmosphere. Similarly there can be small amounts of phosphoric acid and sludge released during maintenance.

Contaminants of Concern – All phosphate ore contains traces of radioactive elements, and some contain a number of metals. These impurities are studied in relation to their impact on health and the environment. During the processing of the phosphate rock they are partitioned between ore beneficiation process waste, acid process waste, and final product.

The cadmium level in fertilizers made from phosphoric acid is increasingly causing concern, and this may influence the choice of raw materials. Igneous phosphate rock typically contains very little cadmium (<1 mg Cd/kg P), whereas sedimentary sources contain much higher but widely varying amounts (from 43 mg Cd/kg P to

380 mg Cd/kg P). However, the amount of Cd entering into the ecosystem in Europe (European Union countries) with fertilizers accounts for only 6% of the total balance of cadmium. It has been shown that the deposition of cadmium from the air in Great Britain during the last 40 years has been equal to that introduced with the fertilizers [9].

The regulations or voluntary limits on cadmium for selected countries are given in Table 19.8 [13].

Because cadmium sulfate is water-soluble and cadmium phosphate is acid soluble, most of the cadmium in phosphate rock concentrate stays in phosphoric acid and in the products made from the acid.

Environmental Impact – The phosphoric acid process produces large amounts of phosphogypsum. The latter requires either a large land surface for disposal or a transportation system for disposal into deep sea. Disposal into the sea is controversial, and some governments established limits for this operation.

Table 19.8. Limits on Cadmium in European Countries in mg Cd/kg P_2O_5 in Fertilizers

Country	Value
Austria	120
Denmark	48
Finland	22
Germany	75
Norway	44
Switzerland	22 (NP-NPK) 44 (TSP)
Sweden	22 (NP-NPK) 44 (PK)

The phosphogypsum stacks should be deposited on specially lined surfaces to prevent leakage of contaminated wastewater to the groundwater. Any excess water from the stack, especially from the rain deposits, must be drained and neutralized by liming before being released.

Typical impurities in phosphoric acid used in the fertilizer industry are given in Table 19.9.

Table 19.9. Range of Impurities in Phosphoric Acid

Components	Content, %
H_3PO_4	69-77
P_2O_5	50-56
Heavy metals	0.5-1.5
CaO	0.014-0.35
Fe_2O_3	0.86-2.30
Al_2O_3	0.30-2.45
Mg	0.00-0.80
H_2SO_4	1.0-5.6
SiO_2	0.04-0.1
F	0.25-1.10

Pollution Prevention and Control

a. **Source Reduction** – Most of the emissions of fluorides to the atmosphere can be reduced by selection of efficient absorption equipment.

The hemihydrate (HH) process produces lower quantities of phosphogypsum and a higher concentration of phosphoric acid; however, differences in pollution problems are not substantial.

The wastewater released from the transportation of the phosphogypsum slurry must be carefully circulated.

b. **Recycling and Byproduct Recovery** – The proper recycling of wastewaters from the process and maintaining the water balance should be two of the technology targets.

Fluorides should be transformed into useful industrial products whenever possible. In critical cases when there is no market for such a product, wash waters must be returned to the process and discharged with phosphogypsum.

Phosphogypsum can be processed and used as a construction material or converted to cement and sulfuric acid. The assessment of this process is given in Chapter 11.

c. **Hazardous Materials Handling, Management, and Disposal** – Phosphoric acid is highly corrosive to mild steel. Much of the plant is fabricated using stainless steel, rubber-lined mild steel, plastic piping and valving, and vessels. All storage tanks should be inside containment areas.

The plant areas should have impermeable flooring; all surfaces should drain to a neutralization pit to deal with small acid discharges from maintenance operations.

d. **Treatment Technologies** – Processes are in commercial use for recovery of uranium from phosphoric acid.

There are presently no commercial processes for removal of cadmium from phosphoric acid; however, extensive research is carried out in view of expected stricter regulations on cadmium content.

Gaseous contaminants (fluorides) are removed by scrubbing the gases and transforming fluorides into useful products. The remaining fluorides from sewage waters and from phosphogypsum stacks are removed by two-stage lime treatment.

The existing dihydrate plants could be converted to the hemihydrate-dihydrate (HDH) process at a cost of about 50% of a new HDH facility. The cost of liming the recirculated water to pH 3.5 is one of the primary cost elements and equals US $70/tonne of P_2O_5. The cost of building a new gypsum stack, which has a single-bottom liner, a 20-year life, for a production of 3 million tonnes of gypsum/year, is about US $20 million. The cost of closing a gypsum stack is site dependent, but a recent closure in the United States cost US $5.5 million with an annual maintenance budget of US $250,000 [21].

Occupational Health and Safety Issues

Phosphate rock dust, fluorides, acid, and radioactive elements are the main health hazards in a phosphoric acid plant. The threshold limit value (TLV) of industrial exposure to hydrogen fluoride for daily intake has been established at 5-6 mg/Nm^3; however, considering other inputs from drinking water and food, the reasonable limit of daily intake has been established at levels of 2 mg/day of fluorides ingestion.

The testing of workers must be conducted at regular intervals. The first signs of chronic fluorosis in man is mottling of the teeth and later ossification of the ligaments.

Animals such as cattle are known to be affected by concentrations of fluorides in excess of 30 mg/Nm^3; however, there are other sources of intake, artificial or natural, and in case of overdoses the animals contract osteosclerosis.

Vegetation is more sensitive to exposure than animals or human beings. Fluoride concentrations as low as 0.015-0.04 mg/Nm^3 will damage some pine and fruit trees.

If instrument control of emissions is not possible near the phosphoric acid plant, the industrial sites should use garden plots to assess pollution by fluorides near the plant.

The radionuclides concentration in phosphate rock varies considerably, depending on the geographical area from which it was mined. The median content of the radionuclides surveyed in 1968 in the United States had the following values:

U 59 mg/kg
Th 8 mg/kg
Ra 18 mg/kg

It has been established that about 60% of the radionuclides remain in beneficiation tails. Two-thirds of those remaining in the beneficiated phosphate rock is transferred to the phosphoric acid, and the remaining third is disposed of with the phosphogypsum [22].

There are processes allowing, through the concentration of the phosphoric acid, sedimentation of the uranium in the form of "yellow cake"; however, the process is not economically viable. The analytical review of NPK produced in Finland has shown that the annual contribution of U-238 contained in NPK fertilizers was about 0.25% of the total U naturally occurring in the surface 10 cm of soil layer. Similar results have been reported in Belgium where it was found that Ra-226 contamination in phosphate fertilizers added to the soil represents only 0.25% for 14 kg/ha of P and 0.96% for 54 kg/ha of P of the total Ra-226 in the upper 20-cm layer of the soil [22].

The long-term effects of phosphate fertilization on radioactivity have been studied in the United States. TSP produced from Florida phosphate rock and applied at the rate of 30 kg/ha of P during more than 50 years did not change the concentrations of U, Th, and Ra in corn leaves and grain, wheat grain and straw, or soybean leaves and bean in comparison with nonfertilized plots. The soil conditions facilitating radionuclides uptake by the crops have not been studied in detail; however, it is obvious that radionuclides present in the soil solutions are absorbed by the plants.

In case of use of phosphate rock containing higher radionuclides in production of fertilizers, the radioactivity of phosphoric acid and phosphogypsum must be measured because the radioactive components of the rock are concentrated to a degree in various parts of the plant during processing, particularly during vacuum filtration. To avoid ingestion of radioactive elements, a high level of hygiene should be observed when maintenance is carried out in these parts of the plant and when scale is removed.

The limits of radiation that should be observed are as follows: when handling the acid a fully protective suit, goggles, face shields, PVC gloves, and boots must be worn. Eye wash bottles and showers should be provided at strategic places throughout the plant.

Operators of the phosphoric acid plant should be highly trained workers with experience in industrial operations. Detailed operating manuals and guidelines should be prepared and workers regularly retrained.

Guidelines of Discharge Requirements

Some fluorine discharge limits for phosphoric acid plants are given in Table 19.10.

Table 19.10. Guidelines on Fluorine Emissions From Phosphoric Acid Plants

Effluents	F	HF in mg/m^3
Liquid	50 ppmw	–
Gaseous	25 ppmv	5–10
Total (U.S.A.)	10 g/t P_2O_5	–

Target and Projected Guidelines

At present the target technology of phosphoric acid will depend on the rock sources, the site, and the discharge point of the effluent. The water balance of the plant and further use of phosphoric acid would play a primary role in determining the possible (potential) targets for effluent. Disposal of phosphogypsum to the sea is only agreed upon in Europe. The North Sea Declaration calls for 70% reduction of cadmium to the North Sea by 1995 and further reduction has been targeted to 90% by the year 2000. The established target for plants near the North Sea is 0.5 g cadmium/tonne of gypsum disposed to the sea, and this can serve as a guide elsewhere.

Regarding fluoride emissions to the air from the phosphoric acid plant, the recommended target should be 10 g/tonne P_2O_5.

Monitoring Requirements

Daily monitoring, displaying, and recording of the fluoride level is obligatory. Typical monitoring of the discharge waters from the phosphogypsum storage is given in section 19.4.

19.3.5 Fertilizers

Solid fertilizers are produced in two stages:

1. Synthesis is performed by the following:
    - Reaction of ammonia and CO_2 (ammonium carbonate and urea).
    - Reaction between sulfuric and/or phosphoric acid with phosphate rock (SSP and TSP).
    - Reaction between acids (sulfuric, phosphoric, and nitric) and ammonia.
2. Providing the physical form of the product by crystallization, granulation, or prilling.

It is not economically feasible to eliminate all effluents and emissions during production of fertilizers.

Raw Materials

The principal raw materials for finished solid fertilizers are ammonia; nitric, sulfuric, and phosphoric acids; phosphate rock; and potassium chloride.

Utilities

The production of fertilizers requires steam, fuel for drying, and water for scrubbing of gases, mist, and dust from granulation or prilling units.

Waste Characteristics and Impacts

Atmospheric Emissions

1. ***Simple Superphosphate/Triple Superphosphate*** – Phosphate rock usually contains between 3% and 4.5% of fluorine by weight. Released during the acidulation of phosphate rock, hydrogen fluoride is usually converted into fluosilicic acid by silica in the rock, most of which is retained in the TSP process, but about 25% is released in SSP production. Wet scrubbers are required for production of SSP. In addition, fluoride emission continues during the curing process. Feedstock-handling bins for phosphate rock must be equipped with individual bag filters from which recovered dust is recycled.

    Efficient scrubber designs allow recovery of the H_2SiF_6 as a concentrated solution, which could be processed to synthetic cryolite, aluminium fluoride, and various fluorosilicates. If no market is available for the acid or fluoride derivatives, the fluosilicic acid can be neutralized by liming. The neutralized slurry may require further treatment before discharge.
2. ***Ammonium Phosphates (DAP/MAP)*** – The ammonia-acid reaction produces steam containing ammonia and fluorine; these are scrubbed by water and/or acids. In granulation and prilling equipment the gases from dryers contain dust; they must be filtered by cyclone and bag filter systems when dry. To prevent condensation of water from drying gases, dust recovery equipment is insulated and heated externally. Most of the recovered material is recycled to the process.
3. ***Nitrophosphates*** – The production of nitrophosphate in all stages of production emits the following gases:

a. Acidulation of the phosphate rock with nitric acid produces NO_x and fluorine compounds. An example of NO_x treatment for a nitrophosphate plant is shown in Figure 19.5.

Off gases from the nitric acid attack section and from calcium nitrate filtration are scrubbed; the remaining nitrites are decomposed in the reactor. Ammonium nitrate solution is recycled to the process.

b. Evaporation (condensation) produces emission of fluorine compounds and ammonia.

c. Prilling and granulation processes produce dust and ammonia emissions.

4. ***Ammonium Nitrate, Calcium Ammonium Nitrate, Ammonium Sulfate (AN/CAN/AS)*** – The main emissions to the atmosphere include the following:

- From the reaction and evaporation systems: steam containing ammonia and ammonium nitrate; these are in small quantities and treated in the scrubbing system. Scrubbing waters are recycled to the reaction/evaporation system.
- Ammonium nitrate mist is released from the prilling tower. The dust in the cooling air disperses into the atmosphere and reaches soil many kilometers in radius from the prilling tower. Ammonium nitrate dust can be extremely harmful to pine trees.

The amount emitted from specially equipped prilling towers (dust collection and Brinks filter system) may be between 0.25 and 0.5 kg of AN/tonne of fertilizer.

5. ***Urea*** – The main air pollution in urea plants originates from the prilling tower. The vented hot air amounts to 10,000-15,000 Nm^3/tonne of urea containing an average of 500-1,000 mg of urea/Nm^3 of air before treatment. Dust removal systems such as the impinger-type baffle-plate system may decrease concentrations of dust to 200-300 mg of urea/Nm^3 of air. The remaining dust is very fine (less than 10 micrometers); therefore, dry cyclones are not effective in further reducing emissions.

Improved dust removal systems developed recently may reduce the emissions down to 30 mg of urea/Nm^3 of air and bring the losses to 0.3 kg/tonne of urea.

Wastewater – Direct-process liquid effluents originating from fertilizer processes are rare. In most cases in urea and ammonium nitrate production, wet scrubbers are operated at low concentrations to allow economic recovery. Solutions from scrubbers are concentrated by adding screened fines and dust to

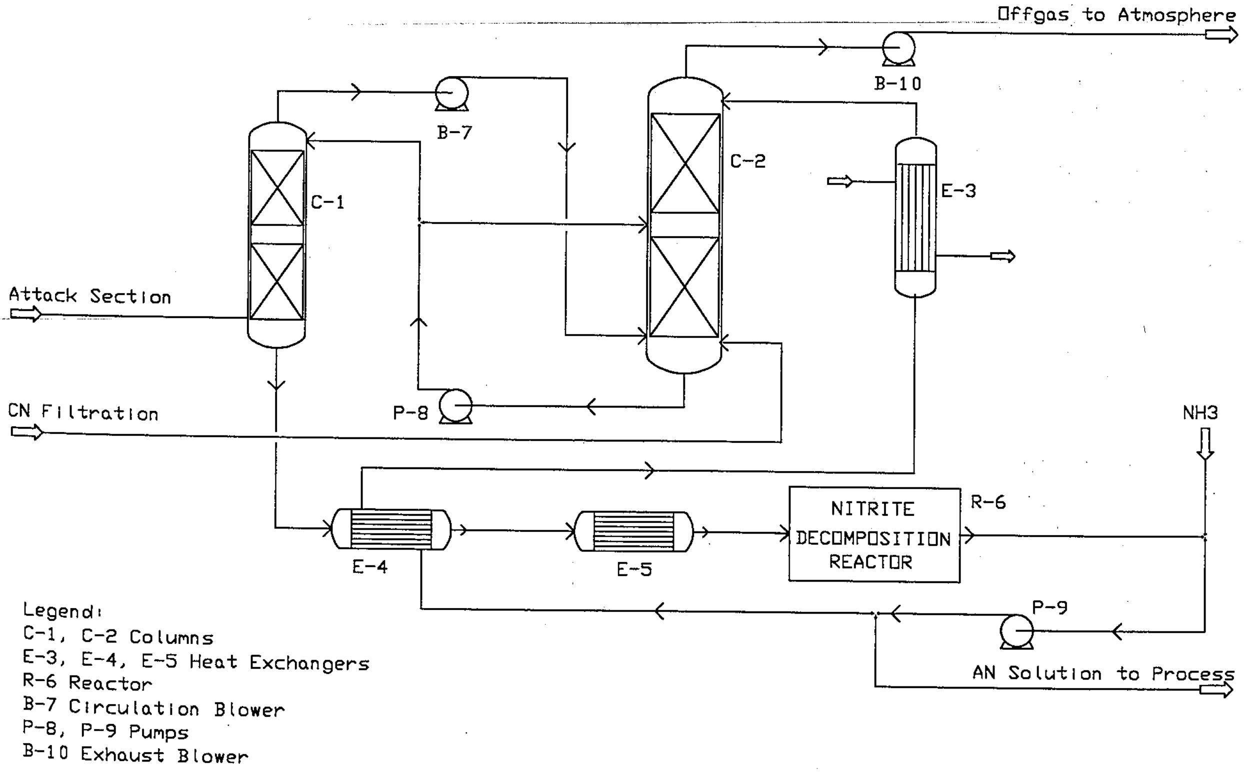


Figure 19.5. The NO_x Treatment Section From the Uhde Nitrophosphate Plant.

increase the concentration for recycling. Adequately sized holding tanks are required to prevent recyclable effluent from overflowing to the sewer during shutdown or abnormal conditions. Aqueous effluent from the fertilizer plant can originate from spills, leaking pumps, or flanges. The severity of leakage depends on operating and maintenance standards.

Solid Waste – Solid wastes are not generally produced in finished fertilizer production processes because offsize material is recycled to the process.

Hazardous Waste – There are no hazardous wastes in fertilizer production other than the cadmium contained in certain fertilizers.

Fugitive Emissions – Small amounts of fluorine derivatives are released into the atmosphere. Similarly there can be small amounts of fertilizers released during maintenance.

Contaminants of Concern– There are no contaminants of major concern in fertilizer production. The cadmium level in fertilizers produced using phosphoric acid is increasingly causing concern, and this may influence the choice of raw materials.

Environmental Impact – Fertilizer production processes that are suitably abating emissions do not release material in harmful quantities to the atmosphere. The following emissions that have negative impact on the environment could be expected:

- Ammonia and acidic fumes may create mists in the plant's vicinity and can cause damage to vegetation.
- Fluoride emissions cause damage to vegetation and harm to livestock that consume vegetation.
- If the dust released into the atmosphere is excessive, it may cause damage to vegetation, especially to the pine forests.
- If plant nutrients are released to the aquatic environment from the scrubber system or runoff water, it is possible that eutrophication of water resources may take place, especially in lakes and closed reservoirs.

Pollution Prevention and Control

The legal limits on emissions in selected countries are given in Table 19.11 [13].

a. **Source Reduction** – Most emissions of fluorides into the atmosphere can be reduced by selecting efficient absorption equipment.

NO_2 emissions from the nitrophosphate process can be controlled by adding urea to the digestion

Table 19.11. Fertilizer Processes – Discharge Guidelines in Selected Countries

Components	Belgium	India	Germany	Taiwan Province	Turkey	Tunisia
Dust		150 mg/Nm^3	55-75 mg/Nm^3	50 mg/Nm^3	200 mg/Nm^3	200-700 mg/m^3
NH_3			50-300 mg/Nm^3 (1)	50 mg/Nm^3		200-700 mg/m^3
Nm^3						
HF			5 mg/Nm^3			
F	300-600 mg/l	10 mg/l	1 kg/t P_2O_5 (2)	15 mg/l	15 mg/l	3-4 kg/t P_2O_5 (3)
NH_4^+ as N	150 mg/l	50 mg/l	2 kg/t N		50 mg/l	
NO_3^- as N	225 mg/l	10-20 mg/l (4)	2 kg/t N	30 mg/l	800 mg/m^3	
Cd	0.3 mg/l (5)					
	2 mg/l		100 mg/t P_2O_5		0.5 mg/l	11 mg/l
P	300 mg/l (5)					
	50 mg/l	5 mg/l	0.5 kg/t P_2O_5		35 mg/l	20 mg/l
COD (6)	450 mg/l (5)					
	300 mg/l		100 mg/l	200 mg/l		
Suspended solids	200-600 mg/l	100 mg/l		30 mg/l	100 mg/l	
pH	5-9.5	6.5-8		6-9	6-9	6-7

(1) Limit at discretion of local authorities.
(2) Limit at the best available technology.
(3) Phosphoric acid production.
(4) Higher value is applicable to phosphate fertilizers unit.
(5) Lower value pertains to brackish water applications.
(6) Chemical oxygen demand.

stage. Gases from the digestion stage are treated in wet scrubbers.

Waste can be minimized by a high level of operation and maintenance to avoid spillages. Any spillage, whether solid or liquid, should be returned to the process.

b. **Recycling and Byproduct Recovery** – All materials resulting from fertilizer production can be recycled. Efficient equipment for scrubbing and dust recovery must be utilized.

c. **Hazardous Materials Handling, Management, and Disposal** – If they are manufactured according to international standards, fertilizer products are generally of low hazard. Ammonium nitrate and high ammonium nitrate fertilizers are considered to be oxidizing agents and require special transport and storage measures. They should not in any case be mixed with hydrocarbons or carbohydrates. It is necessary to avoid any contact of ammonium nitrate with open flame.

   As much as possible, the fluorides should be transformed into useful industrial products. In critical cases when there is no market for such a product, wash waters must be returned to the process and discharged with phosphogypsum.

d. **Treatment Technologies** – The precise combination of abatement installations and the required treatment will be dependent on the types of processes available and limits and targets of the pollution allowed.

To remove ammonium nitrate fumes, low-velocity filters (Brinks mist eliminators) may be necessary. The cost of such an installation for a 1,200-tpd plant amounts to US $750,000 with a filter replacement cost of US $90,000 every 3 years.

For urea dust a venturi plate scrubbing unit may be used with an expected cost of US $1.2 million and an additional annual operating and maintenance cost of US $155,000 and US $12,000, respectively, for a plant of 1,000-tpd capacity.

Dust generated in the process can be passed through cyclones to return the larger particles to the process. For finer particles a bag filter or wet scrubber may be required.

Other gases, mist, and fumes may be treated by water scrubbing or, in case of ammonia, water containing phosphoric acid. In this case installation requires an anticorrosive lining. The scrubber liquors may be concentrated and recycled to the process. When recycling is not possible, wastewaters must be treated before they are returned to the aquatic environment. Removal of the radionuclides from phosphoric acid is operational industrially by the concentration of the phosphoric acid or extraction. There are at present no commercial processes for the removal of cadmium from phosphoric fertilizers; however, extensive research is being conducted in view of expected stricter regulations on cadmium emissions.

Gaseous contaminants (fluorides) are removed by scrubbing the gases and transforming fluorides into useful products. The remaining fluorides from sewage waters are removed by a two-stage lime treatment.

The cost of pollution abatement equipment added to the existing plants can be 10%-20% of the total cost of the fertilizer plants. The operating and maintenance costs relating to environmental protection can be 10%-20% of the total production cost.

In new plants the process design would include the environmental protection measures in all process units with the need for high efficiency and productivity; however, environmental protection costs can hardly be expected to be lower than 10% of total investment and operation costs.

In the next section the commercial processes will be discussed. UNIDO has either received information on these processes directly from licensors or collected it from papers presented at international conferences. Unfortunately not all licensing companies surveyed by UNIDO provided information; therefore, the technology presentation given in the next section does not represent the complete package of technologies presently available on the market. However, concerning the principles applied in pollution abatement, the presented sample seems to be fairly representative from an engineering point of view.

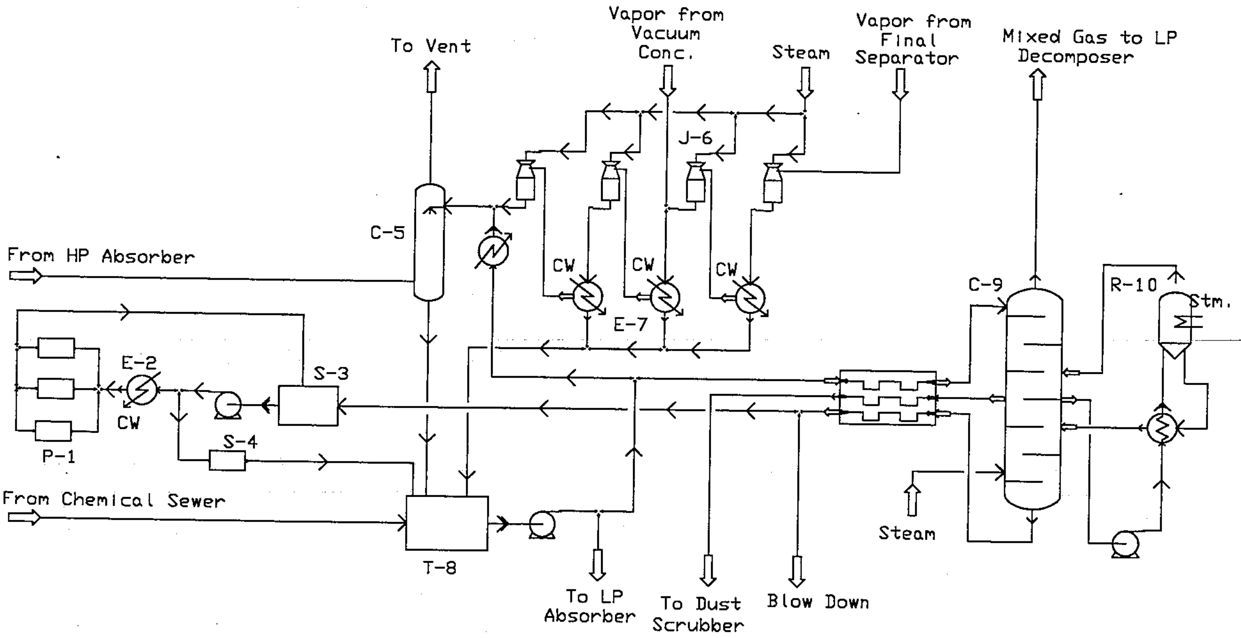
A. **Urea**

Toyo Engineering ACES Process (TEC Japan) [23]

Major pollutants from the urea plant are NH_3 and urea in the liquid and gaseous effluents. The sources of pollution are as follows:

1. Gland cooling water from the reciprocating and centrifugal pumps.
2. Process condensate from the concentration section.
3. Effluent air from the prilling tower or granulator.

To improve treatment of these streams, Toyo Engineering Company and Mitsui Toatsu Company developed an integrated pollution control system of a urea plant, which is given in Figure 19.6.



Legend:
P-1 Reciprocating Pump Stuffing Box
E-2 Cooler
S-3 Oil Separator - 1
S-4 Oil Separator - 2
C-5 Final Absorber
J-6 Ejectors
E-7 Surface Condensers
T-8 PC Tank
C-9 PC Stripper
R-10 Urea Hydrolyzer

Figure 19.6. TEC Integrated Pollution Control System in a Urea Plant.

1. ***Gland Cooling Water From the Pumps*** – Gland cooling water from the stuffing boxes of the reciprocating NH_3 and carbamate pumps is contaminated with ammonia, urea, and lubrication oil, but this is not the case when centrifugal pumps are used. The leakage of the process fluids to cooling water through the seals of pumps may cause a high concentration of urea in cooling water depending on the types of seals and maintenance adequacy. To abate this contamination a closed circuit of the gland cooling water system has been adopted. The lubrication oil in gland cooling water is removed through an oil separator installed on the cooling water circulation line. A blowdown stream containing urea and ammonia is discharged to the process condensate treatment section.

2. ***Process Condensate*** – The largest source of liquid pollution in the urea plant is process condensate in the concentration section.

   Water formed by urea synthesis and that fed to the recovery system as an absorbent is evaporated under a vacuum in the concentrator or evaporator. Evaporated water with an entrained mist of urea is condensed in a multistage surface condenser.

   The uncondensed gas from the surface condenser is vented to the atmosphere through the final absorber where CO_2 and NH_3 accompanied by the inerts are absorbed into process condensate from the first stage of the surface condenser under atmospheric pressure. The emission of NH_3 from the scrubber is less than 0.15 kg NH_3/tonne of urea. The process condensate formed in the second stage of the surface condenser is treated in the process condensate stripper at 3 MPa to remove NH_3 and CO_2. Gas is fed into the urea hydrolyzer at 16 MPa. The overhead gaseous mixture from the process condensate stripper is sent to the low-pressure decomposer for recovery of NH_3, CO_2, and heat of water vapors.

3. **Urea Dust** – A primary source of the emissions is the urea dust in the effluent air from the prilling tower or the urea granulator. Without any treatment the amount of urea dust contained in the emitted air varies within the range of 50-100 mg/Nm^3 of air. The engineering design to reduce this dust must consider the following parameters:
   - The amount of air handled is substantial (e.g., 600,000 Nm^3/h for a 1,500-tpd urea plant).
   - Urea dust contains fine particles of less than 1 micron in diameter.

- Lower pressure drop through the urea dust scrubber minimizes the operational cost.

Considering these parameters TEC constructed a dust scrubber to meet more strict environmental requirements; the scrubber is shown in Chapter 9

The air from the prilling tower or granulator is scrubbed on a packed bed with aqueous urea solution (approximately 20% urea concentration). Any mist in the exit air is caught by a demister. Process condensate is used as makeup water for the scrubber.

The combination of the above control methods allows achievement of the following levels of effluents and emissions.

- Liquid effluents.
  - urea (3-5 ppmw).
  - free ammonia (3-5 ppmw).
- Gas effluents.
  - urea (30-50 mg/Nm^3 of air).

The cost of implementing these measures is determined by the following variables:

- Depreciation of the pollution control installation (investment cost, US $4.5 million for a 1,500- tpd urea plant).
- Utilities cost.
  - electrical energy (6 kWh/tonne of urea).
  - steam (0.02 tonne/tonne of urea).
- The total operations cost increase of urea production is estimated at about US $1.60/tonne.

Foster Wheeler (FW USA) Process [24]

The Foster Wheeler process combines condensate purification with air dedusting and is shown in Figure 19.7.

The key process unit is an FW Evaporative Scrubbing System (ESS). The raw process condensate from the urea unit is first steam stripped to reduce ammonia content. The stripped process condensate is mixed with a circulating stream of urea solution and enters the distribution system of the ESS, which also acts as a cooling tower. The air from the finishing process (prilling or granulation) is introduced into the bottom of the ESS. Particles entrained in the air are dissolved in the urea

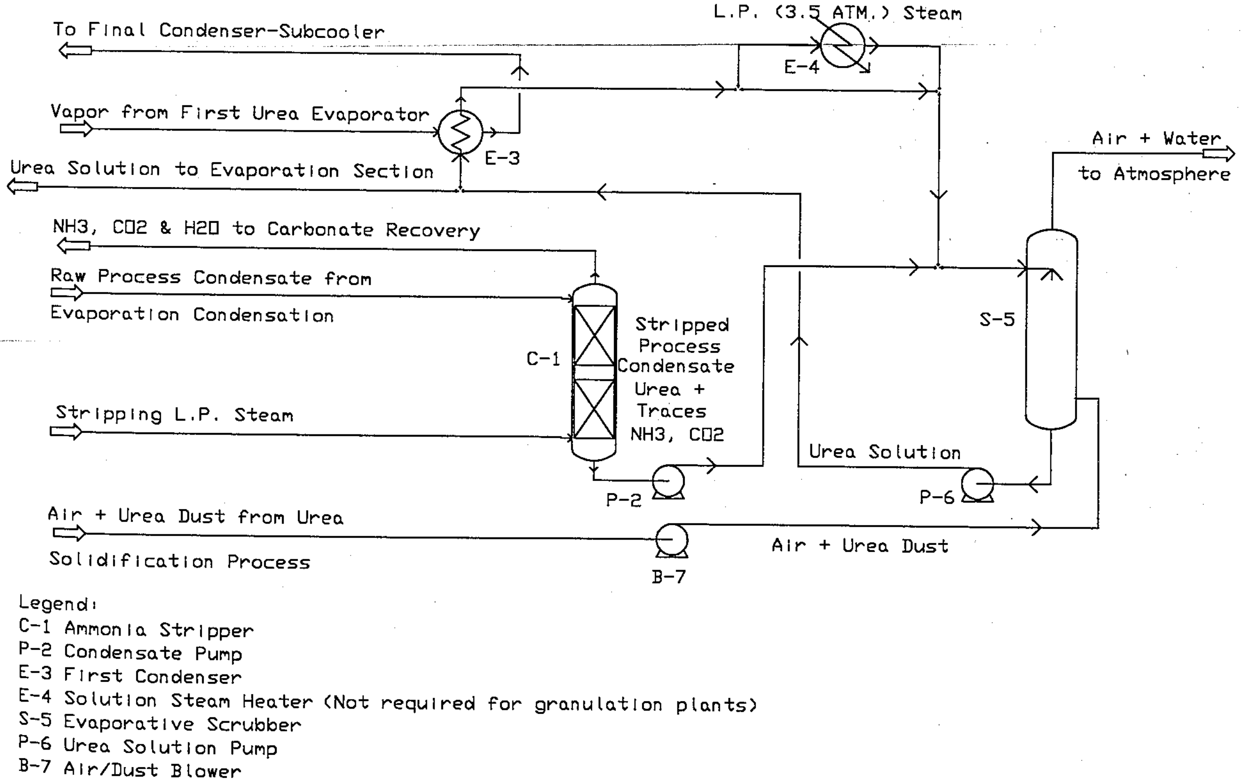


Figure 19.7. Foster Wheeler Combined Dedusting Process.

solution. The solution is also cooled in the scrubber as a result of water evaporation. A portion of rich urea solution from the bottom of the scrubber is sent to the urea plant. The main stream from the scrubber is circulated through a condenser in which most of the vapor from the first urea evaporator is condensed and the circulating scrubber solution is heated.

The amount of heat required for the operation of the ESS is determined by the desired concentration of the rich urea solution. In a practical design the heat from the vapor condenser is sufficient to vaporize the process condensate in the scrubber; therefore, in most cases external heat is not necessary.

In a granulation system some additional heat is necessary and is supplied by a small steam heater (the balance is under 10% of total heat requirements). The integrated system has advantages over the design with separate condensate and dust treatment systems:

- Smaller synthesis equipment.
- Reduced cooling water consumption.
- Elimination of medium-pressure steam for urea hydrolysis.

The above described system has been also applied in dedusting of air from ammonium nitrate prilling or a granulation plant.

The estimated cost for retrofitting the ESS system to an existing plant is:

- Investment cost (BL) US $3.2 million for a 1,350-tpd urea unit
- Depreciation US $0.74/tonne
  - saving on utilities (US $0.40/tonne)
  - credit on urea (US $0.20/tonne)

The total cost of the introduction of a new scheme: increase US $0.14/tonne.

The cost of integrating the system in a new urea plant is composed of the following elements:

- saving on utilities (US $0.40/tonne)
- urea credit (US $0.20/tonne)

The total saving in new urea plant operating costs: US $0.60/tonne.

Stamicarbon bv Process Water Treatment Unit [25]

The process water containing ammonia (about 6%), carbon dioxide (about 4%), and urea (about 1%) is processed in a separate unit, which can be attached to any existing installation. The process is composed of desorption and hydrolyzing units and is shown on Figure 19.8.

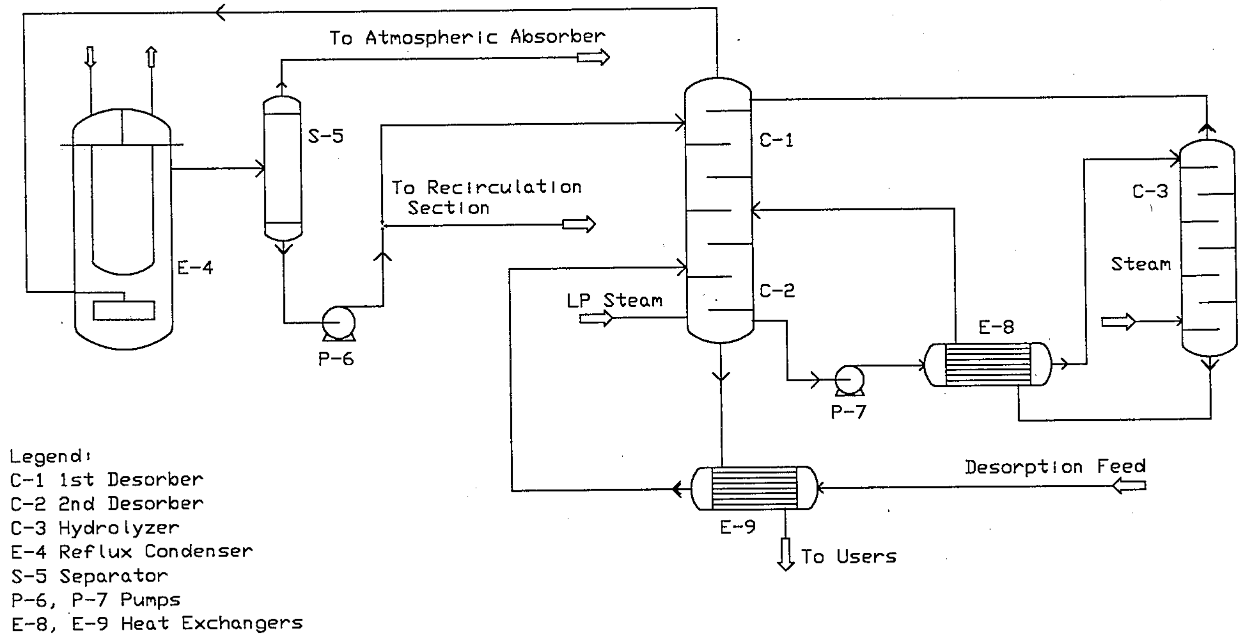


Figure 19.8. Stamicarbon bv's Urea Process Water Treatment.

Process water (desorption feed) enters through the heater to the first desorber where ammonia and carbon dioxide are removed. The urea-containing effluent is sent to the hydrolyzer where urea is decomposed at 200°C. The liquid portion is sent to the second desorber and the gaseous portion is sent to the upper part of the first desorber and the vapor serves as a stripping agent in the first desorber. All vapors are condensed in the condenser where basically carbamate is produced. Part of the carbamate is sent as reflux to the first absorber to maintain its concentration at the required level. The gases are vented after treatment in the atmospheric absorber. The water effluent from the bottom of the second absorber after cooling may be used as process water. The amount of 0.4 MPa steam is about 200 kg/t of process water and 1.8 MPa steam for the hydrolyzer is equivalent to about 40 kg/t of process water. The operating conditions are mild; therefore, regular stainless steel would be used. The design value of the urea and ammonia content in the effluent is 5 ppmw each. The experience of operating installations has shown that it is possible to maintain these levels below 1 ppmw.

B. AN/CAN

GIAP pollution abatement system [26]

A typical pollution abatement system for high-density AN prilling used in many countries of the Commonwealth of Independent States (CIS) is shown in Chapter 8 in Figure 8.14.

Vapor and hot air from the neutralizer and evaporator contaminated with ammonia and AN are treated in the same system with air from the prilling tower. The scrubber solution is recirculated to increase its concentration and eventually recycled to the AN solution preparation step. The recovery of AN and ammonia is reportedly up to 85%. The system meets the pollution control requirements enforced in these countries. Unfortunately, construction of a very large scrubber on top of the prill tower notably increases the capital cost of the plant. A very effective method of solving this problem has been developed by the Co-Operative Farm Chemical Association (CFCA) and is in use at its plants. The fume abatement system consists of installing a bell-shaped shroud around the spray head in the upper part of the prill tower to collect fume-laden air from that part of the tower where fume is formed when air contacts hot AN solution or prills in the solidification process. The airflow through this shroud is only about 25% of the total airflow through the tower; the remaining 75% is practically free of dust and fume and is discharged directly to the atmosphere. The air from the shroud is drawn through a scrubber and Brinks high-efficiency mist eliminators. Fume and vapor from the neutralizer and evaporators are collected to the same scrubbing system.

The system recovers 3-7 kg of AN/tonne of product from all sources; this recovery more than offsets the operating cost (excluding capital cost). From a pollution abatement viewpoint the system has met applicable standards; an atmospheric emission of less than 0.5 kg/tonne of product and opacity of less than 10% have been attained.

C. Complex Fertilizers (NP/NPK)

There are several process variations of NP/NPK plants. They have been constructed in different periods of environmental legislation; and no one possible solution exists to allow a plant to meet the present required level of emissions.

Uhde Methodology

Therefore, Uhde [27] has developed a four-step approach to evaluate and reduce plant emissions. They consider the potential emissions related to specific equipment and technological parameters that are listed in Table 19.12.

Table 19.12. Sources of Emissions on NP/NPK Plant

Process	Pollutant	Parameters
Reactor	NO_x, fluor compounds	Temperature, type of acid, organic matter
Neutralizer	NH_3, fluor compounds	Temperature, molar ratio
Granulator	NH_3, NO_x, dust	Temperature, molar ratio, granulation parameters
Drying	NH_3, dust	Temperature, molar ratio, granulation parameters
Solids handling	Dust	Granulation parameters
Scrubbers	Fluor compounds	Temperature, molar ratio

The steps to evaluate optional methods of improvement are as follows:

Step 1. Reduce or avoid the formation of pollutants at the source.

Step 2. Select process conditions and/or equipment to minimize emissions at the source.

Step 3. Contain pollutants in a minimum of carriers.

Step 4. Recover airborne pollutants.

The methodology used has proven efficient in several plants when Uhde has been involved in the emissions reduction program.

Beladune Fertilizers Limited Process (BFL Canada)

The process is exclusively licensed to HiTech Solutions, Inc., Lakeland, Florida, U.S.A. [28].

During the production of DAP about 110 kg of condensate/tonne of DAP containing 2.5%-3.0% of ammonia is released. This condensate must be internally consumed in the plant with minimal heat losses. The double mol scrubbing (DMS) system and BFL vaporizer scrubber resolve the problem of the reactor/granulator (RG) off-products. The system utilizes waste heat to vaporize ammonia, scrub the fluorine, and provide hot water for cake washing in the phosphoric acid plant (see Figure 19.9).

The off-gases from the DAP reactor and granulator are scrubbed separately in pipe (duct) sprays using as a scrubbing liquor the recycle from the low mol scrubber.

Both flows enter the cyclonic separator (Hi Mol Scrubber-HMS) where the liquor is separated from the gas stream. The liquor drains back to the recirculation tank. The gases then enter a Venturi scrubber followed by a cyclonic separator (Low Mol Scrubber-LMS). The low strength phosphoric acid is pumped and recirculated to the venturi cyclone.

The excess of the low strength phosphoric acid is recycled to the reactor. The gases from LMS enter the BFL Vaporizer/Scrubber.

All the condensate water is drained to the seal tank and recirculated to a single large spray nozzle at the heat exchange inlet. The off-gases flow through the heat exchanger, and the gas stream/condensed water enters

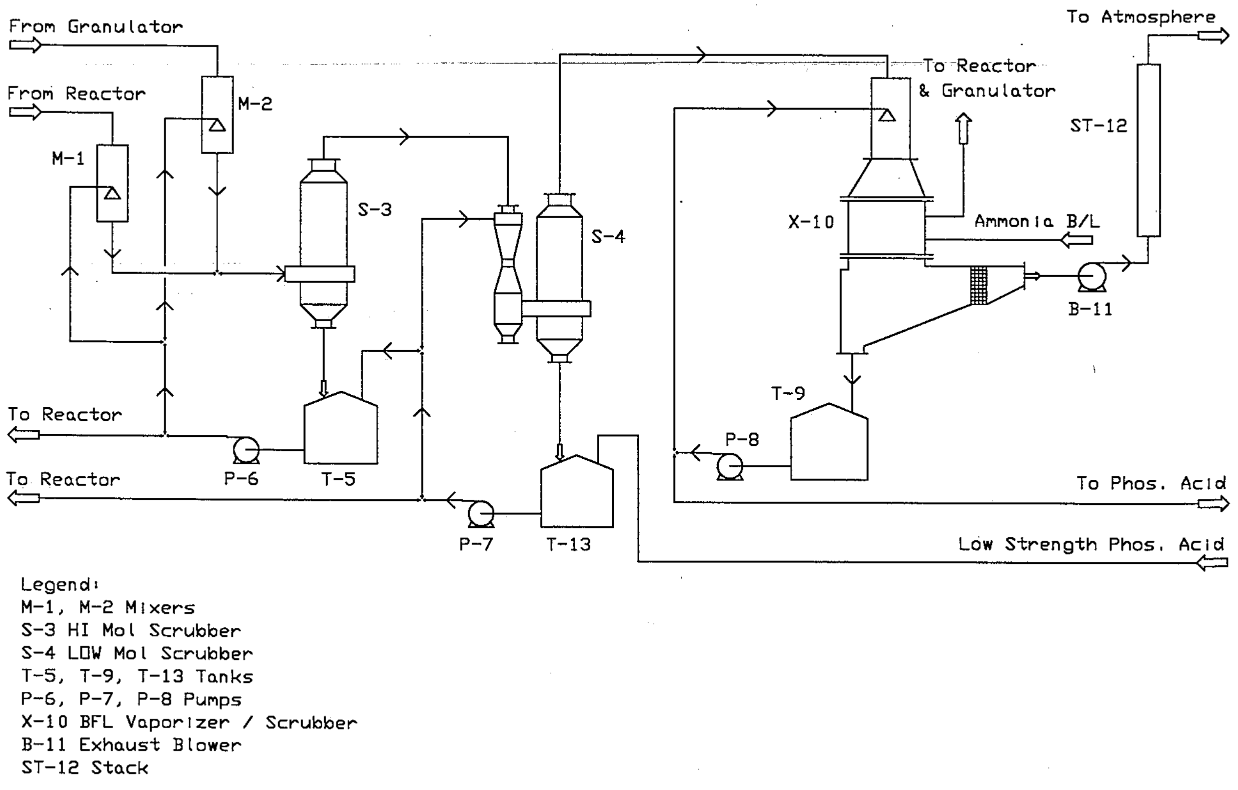


Figure 19.9. BFL DMS Process.

a separator chamber equipped with a demister. The acidic water is returned to the plant, and purified gas is ventilated to the stack.

The following process parameters are published:

LMS
Mole ratio (NH_3:P_2O_5), 0.4-0.8
Scrubbing liquor temperature, 70°C
Recirculation ratio, 215 liters/100 m^3
Scrubber gas exit temperature, 82°-90°C
HMS
Mol ratio (NH_3:P_2O_5), 1.6-2.0
Scrubbing liquor temperature, 85°C
Recirculation ratio, 160 liters/100 m^3
Scrubber gas exit temperature, 82°- 90°C
BFL vaporizer/scrubber
Entering gas temperature, 82°- 90°C
Exit gas temperature, 77°- 82°C
Recirculation rate, 1.4 m^3/min
Condensate composition: 0.02-0.2% F
<2,000 ppmw NH_3
<1,000 ppmw P_2O_5
Yield of condensate, 2 liters/tonne DAP
Emissions meet all regulated amounts.

The costs of the full scheme are as follows:

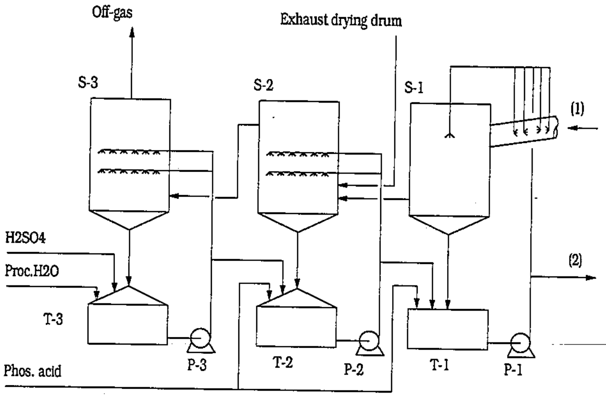
- Investment cost for 1,000-tpd DAP plant: US $8 million
- Electrical energy consumption, 14 kWh/tonne
- Heat recovery, 0.5 GJ/tonne
- Water saving, 36 l/tonne

The total cost of implementing the BFL scheme compared with that of the standard scheme, which does not meet the emission regulations: US $1.40/tonne.

Uhde Closed Scrubber System [29]

The concept of a closed system has been applied in the BGF AS plant in Turkey. The principal scheme is given on Figure 19.10.

The exhaust gases from the pipe reactor (or preneutralizer) and granulator enter the granulation scrubber for cleaning by a recirculated solution. Gases from the granulation scrubber enter the main scrubber along with exhaust from the drying drum, and they are washed by a circulating solution to which phosphoric acid is added. The off-gases are washed in the final scrubber with water and sulfuric acid. The surplus circulating solution is returned to the pipe reactor or preneutralizer.



(1) - Exhaust pipe reactor or preneutralizer + granulator
(2) - To pipe reactor or preneutralizer

Legend:
S-1 Granul. scrubber
S-2 Main scrubber
S-3 Final scrubber
T-1, T-2, T-3 Tanks
P-1, P-2, P-3 Pumps

Figure 19.10. Uhde's Closed Scrubber System for NPK/DAP Plants.

D. Nitrophosphate Fertilizers

Norsk Hydro nitrophosphate process emissions treatment:

1. Liquid Effluents [30]

All washwaters from the wet section are collected, and calcium hydroxide and calcium carbonate are added to precipitate phosphates and fluorides in a settling cone. A flocculant is added to increase the rate of precipitation. The slurry is recycled to the process, and water is reused as washwater. Thus, two objectives are achieved:

- All liquid effluents are eliminated from the digestion section.
- The efficiency of raw materials use is increased (99.9% for P_2O_5).

The water vapors removed from neutralization and evaporation stages are scrubbed with a recirculated ammonium nitrate solution (60%); the vapors are then condensed and ammonia is stripped and returned to the neutralization section. The clean condensate is discharged.

The typical composition of liquid effluents from a NH nitrophosphate plant is given in Table 19.13.

Table 19.13. Effluent Limits From NH Nitrophosphate Plant

Effluent	Level of Impurities
NH_3	<100 ppmw of N
NO_3	<200 ppmw of N
F	<50 ppmw

2. Gaseous Emissions

The gaseous emissions are treated separately:

- The emissions from digestion, crystallization, separation, and filtration are scrubbed in several stages by wash water, which is recycled as described above. To cope with the excessive amounts of NO_x, some amount of urea is added to the scrubbing water.
- The emissions from the conversion section are first scrubbed with recycled acidic ammonium nitrate solution and in the second stage by recycled acidic water.
- The emissions from granulation are cleaned with conventional cyclones.

The emissions to the atmosphere from the NH nitrophosphate plant are given in Table 19.14.

Total effluents from the NH nitrophosphate plant are given in Table 19.15.

The BASF Method of Nitrophosphate Process Emissions Treatment [31]

Treatment of gaseous emissions is divided into two systems:

- NO_x removal
- NH_3 and dust removal

Table 19.14. Emission to Atmosphere From NH Nitrophosphate Plant

Effluent	Level of Impurities
Dust	<100 ppmv
NH_3	<150 ppmv of N
NO_3	<150 ppmv of N
F	<25 ppmv

Table 19.15. Total Effluents From NH Nitrophosphate Plant

Element	Process Condensate	Vents to Atmosphere
	(kg/t P_2O_5)	
Nitrogen as N	4.4	1.4
Phosphorus as P	0.6	–

NO_x-containing waste air is treated in a two-stage scrubbing system. Air from the digestion and inert separation sections containing concentrated NO_x enters the first scrubber for washing by solution from the second absorber. The concentration of NO_x emerging from the first scrubber can be as high as 2,000 mg/Nm^3 calculated as NO_2 but existing in the NO form. The air from the cooling section and belt filters contains a high proportion of NO_2.

Gas from the first scrubber is mixed with that from the cooling section and calcium nitrate filters; the resulting mixture has an oxidation level of 40%-60%, which is easy to absorb. The second scrubber is fed with ammonium nitrate solution and makeup water. The ammonium nitrite that forms may be decomposed by adding urea.

The nearly saturated waste air from the neutralization and evaporation sections and the waste air from the granulation and drying sections are fed to a special construction scrubber by means of separate gas distributors. The scrubber is shown in Figure 19.11.

The recirculating AN solution liquor is kept acidic by addition of 60% HNO_3. The AN solution produced is recycled. The results of the treatment process are given in Table 19.16.

Occupational Health and Safety Issues

As described previously, phosphate rock dust, fluorides, acids, ammonia, and radioactive elements are the main health hazards in fertilizer production. Fertilizer products are of low hazard; however, ammonium nitrate storage areas must be kept free of organic materials. Coating materials such as crystalline silica are hazardous if inhaled.

When handling acid a fully protective suit, goggles, face shields, PVC gloves, and boots must be worn. Eye wash bottles and showers should be provided at strategic places throughout the plant.

19.4.2 Disposal of Phosphogypsum

The storage area for phosphogypsum disposal depends on local conditions and regulations. The most modern deposits can store 0.5 million tonnes of phosphogypsum/ha of land. Even though it is acceptable under the present regulations in the United States and European Union, establishment of a phosphogypsum pond and stack requires high investment expenditures. Table 19.18 gives examples of current establishment of three phosphogypsum deposits [33,34].

Sufficient comparable data do not exist to assess the unit investment and operation costs of modern phosphogypsum stacks. However, it would be safe to consider that any technology of phosphogypsum processing requiring US \$75/tonne P_2O_5 (±50%) investment and US \$15/tonne (±50%) of operation cost would be competitive with phosphogypsum storage.

The water system of the phosphoric acid plant is one of the important issues to be tackled and resolved. Water is required (1) for cooling the phosphoric acid processing units and (2) for absorbing gaseous and particulate emissions. The resulting wastewater is used for pumping the phosphogypsum as a slurry to the storage site.

Table 19.18. Gypsum Pond Economics

Cost Component	Cases U.S.A. (1)	France (2)	Sweden (3)
Investment US \$ million (1994)			
Permits and approvals	7.1	–	–
Engineering/control	6.9	–	–
Land and improvements	25.4	12.0	54.0
Pump station	9.51	7.9	1.7
Plastics liner	16.9	42.9	51.8
Drainage/miscellaneous	9.2	1.6	3.6
Contingency	2.8	–	–
Total	**77.8**	**74.5**	**111.0**
Operation Cost US \$/t of P_2O_5 (1994)			
Utilities	0.6(4)	1.1	0.2
Labor/maintenance	0.6(4)	6.3	2.8
Land royalties	4.3		0.9
Miscellaneous	0.7(4)	0.7	0.8
Depreciation and financial charges	8.2	8.9	13.7
Total	**10.1**	**21.3**	**18.4**

(1) IMC Fertilizers Inc., Tampa, Florida. Capacity 1.5 million tpy of P_2O_5.
(2) Medium-size plant. Pond 14 km from plant.
(3) Pond close to small plant.
(4) UNIDO assessment.

A closed circuit water system is desirable; rainfall, however, usually exceeds evaporation, resulting in a surplus of pond water. This surplus is contaminated and must be treated before discharge. The recycled phosphogypsum water composition is given in Table 19.19 [34].

The excess pond water must be neutralized and filtered. This problem is not yet properly developed, and costs of neutralization were assessed at the value of about US \$70/tonne of P_2O_5.

Disposal of phosphogypsum in the sea raises consideration of the impacts of gypsum, trace elements, and the pH of the discharged water. It has been shown that in good tidal conditions or at open sea gypsum is quickly dissolved in the water without changing the calcium concentration. In addition, all heavy metals present in phosphogypsum are already in the seawater, and phosphogypsum disposal would increase the concentration of these metals in 1 km^3 of water by 0.1%-3%. Changes of pH in the same volume have also been found to be insignificant.

Table 19.19. Pond Water Composition

Component	Ranges Low	High	Average
	(mg/l)		
P_2O_5	8,000	20,000	12,000
F	900	12,000	10,000
SO_3	2,400	9,000	4,000
CaO/MgO	560	5,280	2,400
Na_2O/K_2O	292	3,140	2,250
Fe_2O_3/Al_2O_3	230	1,500	450
pH	1.2	2.5	1.5

19.4.3 Other Applications

The other following applications have been described in Chapter 11.

- Agricultural applications
- Cement retardant and other construction materials additives
- Plasterboard products

19.4.4 Transformation Technologies

Phosphogypsum may be converted to lime and elemental sulfur by heating it in a neutral atmosphere with a reducing agent such as coal. The basic technological process has been described in the Chapter 11. Below is given an example of phosphogypsum processing in an NPK plant.

Gujarat State Fertilizer Complex Process [35,36]
Another example of complex solid waste processing originating from a phosphoric acid plant is the Gujarat State Fertilizer Company, Ltd., Baroda, India. The complex is composed of a Chemico DH phosphoric acid plant, with an installed capacity of 165 tpd, two trains of DAP with a capacity of 460 tpd, and an AS (ammonium sulfate plant) with a capacity of 470 tpd.

The phosphogypsum originating from the phosphoric acid plant is purified by repulping and filtering to remove traces of P_2O_5 and make it suitable for use in the ammonium sulfate (AS) process. Senegal phosphate rock is used; thus, minimum impurities and adequate crystal form are ensured. The AS production process from phosphogypsum has been licensed by ICI (UK) and designed by Hitachi Zosen, Ltd. (Japan). The ammonium carbonate is produced from ammonia, water, and carbon dioxide.

The ammonium carbonate solution is then mixed with washed fine phosphogypsum crystals to form a slurry of calcium carbonate in AS liquor. The slurry is filtered, and the filtrate is clarified in a settler. The filter cake is repulped with process effluent water and disposed of in chalk pond. Excess ammonia in the filtrate is removed, and the liquor is sent to a triple-effect evaporative crystallization system to produce ammonium sulfate crystals, which are centrifuged, dried, and bagged.

Extensive work has been done to use waste calcium carbonate, and the following applications have been found to be technically feasible:

- chemical lime 50% CaO
- building lime
- activated lime pozzolanic mixture
- cementation binder
- bitumen mastic (55% calcium carbonate)
- flooring tiles

Again the availability of natural chalk, credit for the disposal costs, and transportation costs determine the economic feasibility of any of these applications.

19.5 Environmental Impact Assessment [37]

An environmental impact assessment (EIA) and an officially presented document entitled "Environmental Impact Statement (EIS)" are the instruments of risk management at the enterprise or regional levels.

19.5.1 Objectives of EIA (EIS)

All chemical installations should be subject to a periodical environmental impact review. The frequency of the evaluation is established either by law or by internal company regulations. The EIA becomes an EIS when it is formally released by the company to the controlling government organizations.

The objectives to be achieved by conducting an EIA are as follows:

1. Determine the achieved level of protection of man and the environment.
2. Identify discrepancies and their sources relative to established legislation and internal rules.
3. Analyze emergency cases and check implementation of the recommendations.
4. Check the implementation of related policies and decisions.
5. Determine necessary adjustments and provide information on justification and the efficiency of their implementation.
6. Provide a basis for recognizing good and inadequate performance.
7. Demonstrate management's commitment to environmental protection and provide motivation for improvement.
8. Provide information on achievements in environmental protection to public authorities and community shareholders.
9. Provide input into the company's education and training activities.

19.5.2 Methodology

Methodology of the EIA preparation differs from company to company depending on its size and organizational system. The point is who should prepare the EIA. The three basic methodological approaches to determine the preparer of the EIA are as follows:

1. In large companies a special safety or environmental department assumes the responsibility for preparing a regular EIS.
2. In medium-size companies a task force is convened; this group is composed of the operational staff, safety staff, and maintenance staff under the responsibility of a technical manager.
3. In small companies a specialized auditing company may be contracted; however, in this case participation of the local staff is crucial for the success of the study and implementation of the recommendations.

In all cases the group should be given access to all technical documentation, environmental reports, and regular water and air analysis results, reports of technical deviations, accident reports, and all legislative background related to factory operations.

Operational hazard studies or similar reviews should be provided. Group members during the period of EIA preparation should be freed from their everyday functions and responsibilities.

The EIA group should act in the following sequence:

- Review the documents.
- Conduct a detailed physical audit of the installation.
- Prepare the questionnaire and discuss it with workers and staff.
- Prepare the statistical review of the crucial parameters.
- Prepare the identification chapter for:
  - Normal operation
  - Incidents/accidents
- Discuss the identification chapter with plant management.
- Review new legislation and identify new industrial obligations.
- Prepare the recommendations chapter:
  - Technology adjustment.
  - Training and education.
  - Equipment revamping.
  - Adjustment of management procedures.
- Prepare the economic/financial analysis report:
  - Specification of costs.
  - Specification of penalties.
  - Specification of yields.
  - Economic efficiency of the adjustments.
  - Financial resources and modalities of implementation.
- Discussion of the draft report with management.
- Editing and printing of the report.
- Dissemination and advertising.

19.5.3 Content of EIA (EIS)

A unified, obligatory format of the EIA does not exist. Countries that introduced the regular auditing obligation only recommended general issues that should be reported in EIA.

Through a series of workshops, international organizations (UNEP, UNIDO) are disseminating a general methodology; however, the formal format of the EIA table of contents has not been established. The number of industries and their specific technological features prevent such regulation.

Therefore, the format below should be tentatively considered. In specific cases it should be adjusted to local conditions, technical culture, and management rules to comply with the objectives of EIA.

Executive Summary

Chapter I. Review of the legislation and internal company rules

- Risk assessment data
- Provisions for penalties
- Legislation in the preparation process

Chapter II. Review of statistical data

- Statistical data on production
- Statistical data on controlled inside and outside factory emissions
- Statistical data on penalties
- Statistical data on accidents/incidents and their gravity
- Labor health statistics
- Training and education reports

Chapter III. Review of the technological process

Review of the technological process is carried out in a specific way:

- Analytical assessment of the raw materials and contents of hazardous materials
- Technological tracing of the hazardous materials and their end form
- Technological scheme of the emissions (the flowsheet is analyzed from the point of view of emissions)
- Material and energy balance
- Balance of emissions and comparative analysis of both
- Elimination of discrepancies
- Product quality and content of the hazardous materials
- Byproduct quality and content of the hazardous materials

- Options to further processing of the byproducts
- Emissions and content of the hazardous materials
- Review of the emissions processing (washing and treatment)
- Review of the new processes/equipment for the emissions treatment
- Comparison of the technical process data with the statistical analytical data
- Review of failures and accident reports
- Listing of the hazardous operations and review of the preventive measures
- Review of the records and the standards of the maintenance works, especially in the emission areas
- Review of processes/equipment eliminating or diminishing emissions
- Proposal for revised technological scheme
- Revamping proposal (modalities of implementation)

Chapter IV. Emissions, effluents and disposal – This chapter describes the present situation outside the factory area at the local control points

- The air analysis
- Wastewater treatment efficiency
- Solid waste deposits

Chapter V. Economic and financial analysis

- Cost of environmental protection
  - Pretreatment and treatment installations
  - Regulated disposal costs
  - Specific raw materials purchases
- Revamping proposals
  - Operation costs
  - Results
- Investment costs
- Economic efficiency of the adjustments
- Financial resources and modalities of implementation

19.5.4 Instrumental Application of EIA/EIS

The cost of preparing an EIA/EIS is high. Considering that an installation of average complexity includes 60-100 pieces of equipment, thousands of valves and fittings, and processes three to ten substances, the process review may require 3-6 months and cost approximately US $60,000-US $100,000. Therefore, legislation must consider this cost, and frequency requirements must be reasonable. In addition, utilization of EIA must be much wider than the scope of its preparation. Instrumental applications of the EIA above the primary scope allowing the recovery of part of all of the costs, are given in the following section.

19.5.5 Investment in Revamping and Improvements

Any installation requires regular updating. In principle this is performed annually or during major maintenance to improve product quality, decrease consumption of raw materials and energy, and decrease labor requirements. However, revamping of the installation requires complex technical and financial documentation (e.g., a feasibility study).

Preparation of an EIA gives basic technical information for the intended revamping. Therefore, management of the enterprise should instruct an auditing team to consider and evaluate a wider scope of revamping. This requires better cooperation with licensers, updating their processes, and formal contacts (inquiries and offers) with equipment suppliers.

Widening the scope of the EIA would involve very little extra time and cost of preparation. In the meantime the costs of the EIA preparation may be considered part of the investment cost of a newly revamped installation; consequently, every company may easily find the necessary financial resources (own or credit facilities). This is also valid for Eastern and Central European countries with economy in transition when they are looking for strategic investors to change their production strategy. Therefore, the preparation of the EIA study should be combined with the restructuring program of an industrial enterprise.

19.5.6 Prevention/Preparedness

As mentioned above an EIA may be prepared in the case of accidents. This requires preparation of an operational hazards (HAZOP) study, which indicates the emissions during the accident. Obviously the concentrations of the chemical substances in this case would greatly exceed allowable levels inside the factory site and outside the fences. The duration of this exposure would have an impact on the environment and health of the local population. This case requires preparation of special plans, e.g., contingency plans. Because modern societies use advanced technologies, the danger of a disaster is much higher than the pre-industrial era. Therefore, governments are preparing national contingency plans which will mainly be implemented by local civil defense organizations, fire departments, national guards, etc. For preparation of a good contingency plan, the following information is necessary:

- Identification and analysis of hazards and risk assessment
- Definition of the emergency response resources
- Instructions on the emergency actions

Obviously plan preparation is financed from the budget, but the crucial information required to develop such a plan is included in the preparation of the HAZOP and EIA studies. This may be a case whereby enterprises may use state financial resources to improve the environmental situation in everyday and emergency cases.

19.6 The Role of International Organizations

The United Nations and its agencies and organizations (UNEP, UNIDO, WHO) have undertaken practical actions to improve environmental protection in concert with industrialization progress. The challenge of reconciling the demands of population growth, the desire for continued industrial development, and the need to preserve our environment can be met only by an approach that fosters development and sustains the environment.

UNIDO has taken the general United Nations call for sustainable development, contained in, for example, General Assembly resolution 42/187, and translated it into practical terms that relate to industrial development. UNIDO calls this ecologically sustainable industrial development, or ESID. ESID is a new approach to industrial development that allows industry to contribute economic and social benefits to the present generation without compromising the ability of future generations to meet their own needs and without impairing basic ecological processes. To secure views of member states on the issue of sustainable industrial development, UNIDO convened the Conference on Ecologically Sustainable Development at Copenhagen during 14-18 October 1991.

At the Conference, the member States agreed that reduction of pollution intensity across all media (air, water and land) within industry through cleaner production was the key to achieving ESID. To secure the views of the business community on sustainable industrial development and to contribute to the United Nations Conference on Environment and Development (UNCED), UNIDO in cooperation with UNEP organized the Second World Industry Conference on Environmental Management (EICEM II) at Rotterdam during 10-12 April 1991. The delegates to EICEM II agreed to support the Business Charter for Sustainable Development and thereby committed themselves to improving their environmental performance and to working towards achieving sustainable development. The Industry Forum on Environment and Development was organized and conducted in Rio de Janeiro a few days before UNCED. The 350-page book *From Ideas to Action* contains over 150 examples of how industry has implemented the Business Charter. The UNCED conference was held in Rio de Janeiro during 3-14 June 1992. At UNCED, international governments agreed on several nonbinding documents, including the Rio Declaration on the Environment and Development and Agenda 21. Agenda 21 is a global action program designed to implement the Rio declaration. In December 1992, the General Assembly noted with satisfaction the report of UNCED and endorsed the recommendations of the Rio Declaration.

This manual fulfills one of the recommendations on the information and awareness dissemination in the field of safe fertilizer production and agricultural application.

19.7 Best Available Technology (BAT)

The European Fertilizers Manufacturers' Association (EFMA) has carried out extensive studies and published guidelines on BAT that are agreed to by member companies. The BAT comprises the achievable environmental emissions levels and energy consumption figures for the principal fertilizer manufacturing processes in Europe. The BAT, being a combination of different proprietary and public domain processes, should be available for purchase by all operators at a price not entailing excessive costs. These activities are supporting the European Union in the framework of an Integrated Pollution and Control Directive (PPC), where emissions limit values will be set based on the BAT. For the fertilizer industry, EFMA has prepared eight BAT booklets. They cover the production processes of the following products:

- Booklet 1: Ammonia
- Booklet 2: Nitric acid
- Booklet 3: Sulfuric acid
- Booklet 4: Phosphoric acid
- Booklet 5: Urea and UAN
- Booklet 6: AN and CAN
- Booklet 7: NPKs by the nitrophosphate technology
- Booklet 8: NPKs by the mixed acid route

The booklets are available from EFMA [38]. The BAT references would be approved by the EU Commission by 1998. The achievable emission levels for the European fertilizer industry using BAT are given in Table 19.20.

Table 19.20. Achievable Emission Levels for the European Fertilizer Industry Using BAT

Ammonia

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
NO_x to air	75 (150)	150 (300)		0.45 (0.9)
SO_2 to air	as for combustion plants			
NH_3 to water				
Spent catalysts			100 (100)	0.2 (0.2)

Energy consumption: 32.5 GJ/t NH_3 (new plants)

Nitric Acid

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
NO_x to air	150 (400)	300 (800)		1.6 (4.2) as 100%

Sulfuric Acid

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
SO_2 to air				2-4 (10)
SO_3 to air				0.15 (0.6)

Phosphoric Acid

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
Fluoride to air		5 (30)		0.04 of P_2O_5
Dust to air		50 (150)		

Note: Gypsum re-use or disposal on land may be allowed to continue.

Urea

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
Granulator				0.25 (04)
Urea dust		50 (80)		
NH_3 to air	75 (250)	50 (165)		0.25 (0.83)
Prill tower				0.5 (1.5)
Urea dust		50 (150)		
NH_3 to air	75 (150)	50 (100)		0.5 (1.0)
Vents NH_3 to air				0.06 (0.75)
Urea to water			1 (150)	0.0005 (0.1)
NH_3 to water			5 (150)	0.0025 (0.1)

(Continued)

Table 19.20. Achievable Emission Levels for the European Fertilizer Industry Using BAT (Continued)

Ammonium Nitrate

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
Granulator/Prill Tower				**Total to Air**
Dust		15 (15)		Dust 0.5 (0.5)
NH_3 to air		10 (10)		NH_3 0.2 (0.2)
Neutralizer Cooler/ Dryer				
Dust		30 (30)		
NH_3 to air		50 (50)		
Solids and CAN				
Dust		50 (50)		
NH_3 to air		50 (50)		
N to water			100 (100)	0.2 (0.2)

Nitrophosphate (NPK

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
NH_3 to air		50 (250)		0.3 (1)
NO_x to air		500 (500)		0.2 (0.2)
Fluoride to air		5 (5)		0.02 (0.02)
Dust to air		50 (50)		0.3 (0.3)
P_2O_5 to water			28 (30)	0.06 (0.11)
NH_3 to N to water			60 (120)	0.12 (0.5)
NO_3 as N to water			15 (150)	0.03 (0.3)
Fluoride to water			13 (26)	0.05 (0.05)

NPK (Mixed Acids)

Type of Emission	ppmv	mg/Nm^3	mg/l	kg/t of Product
NH_3 to air		50 (50)		0.2 (0.2)
NO_x to air		70 (70)		0.3 (0.3)
Fluoride to air		5 (5)		0.02 (0.02)
Dust to air		50 (50)		0.2 (0.2)
N to water			0 (100)	0.0 (0.2)

Note: The first value is for new plants; values in parenthesis are for existing plants.

19.8 ISO 14000

In 1993, the International Organization for Standardization (ISO) set up a Technical Committee on Environmental Management, TC 207, to develop standards on a broad range of topics related to environmental management. These standards were to become a group of standards referred to as the "ISO 14000 series of Environmental Management Standards." In 1996, five standards in the ISO 14000 series were published with the remaining 16 draft standards scheduled to be published sometime between 1997 and 1999. All of the standards except ISO 14001 will be guidance documents. Companies only become registered to ISO 14001. The ISO 14000 series is intended to help companies improve environmental performance and to keep environmental issues from becoming trade barriers.

The motivation to prepare this group of standards is to introduce uniform requirements for the operation of industrial plants and establish a framework for managing environmental impact. The standards or draft standards feature a wide variety of environmental discipines including these six major components [39]:

1. Environmental Management System (EMS)
2. Environmental Auditing
3. Environmental Performance Evaluation
4. Environmental Labeling
5. Life-Cycle Assessment
6. Environmental Aspects in Product Standards

As with all ISO standards, ISO 14000 standards will be voluntary; however, it is expected that the European Union as well as agencies of the U.S. Government will decide upon registration. Therefore, companies who fail to implement an effective environmental management system may not be able to compete in many markets.

Companies intending to be certified under ISO 14001 should meet the specific requirements of the standard. The basic activities under the EMS should be implemented, documented in a special manual, and respective training of all the personnel carried out. The company should apply for registration with an acredited certifying body; certain steps would be involved in obtaining the registration:

- Document review
- Assessment/Registration Audit
- Registration
- Surveillance

It is assumed that a company may prepare the necessary documents by internal auditing or using special consultants. The audit for registration, however, would be prepared by an authorized certifying body. The standard term of the registration would be 3 years, after which time a review/audit would be done to verify continuous implementation of the environmental management plan.

Many analysts of ISO 14000 and ISO 9000 (the ISO quality system series of standards) believe that the two series of standards will be streamlined in some manner. A joint task force has already been formed by the ISO to study this possibility. Some believe that ISO 14000 will conform to ISO 9000 in theory and structure. It is also possible that the provisions of ISO 14000 might eventually become a portion of the overall ISO 9000 series. Incorporating ISO 14001 into the ISO 9000 series could provide some benefits for companies. In the future, it might be possible to become registered to both standards at once.

19.9 References

1. Conference on Ecologically Sustainable Industrial Development. 1991. UNIDO ID/WG.516, Copenhagen, Denmark.
2. Fukushima Prefecture Agricultural Research Station. 1989. "Effect of Long Term Fertilization Management on Physical, Chemical and Biological Properties of Soil," Research Report, Japan.
3. De Datta, S. K. 1985. "Nutrient Requirement for Sustained High Yields of Rice and Other Cereals," Proceedings of Colloquium Potassium in Agricultural Systems of the Humid Tropics, pp. 97-120, International Potash Institute, Switzerland.
4. Kimmo, I. J. 1993. "Nitrogenous Fertilizers and the Environment," Proceedings of the Regional FADINAP Seminar on Fertilization and Environment, ST/ESCAP/1256, conducted September 7-12, 1992, United Nations, New York, U.S.A.
5. Ange, A. L. 1993. "Environmental Risks of Fertilizer Use, Overuse or Misuse," Proceedings of the Regional FADINAP Seminar on Fertilization and Environment, ST/ESCAP/1256, conducted September 7-12, 1992, United Nations, New York, U.S.A.
6. WHO. 1985. "Health Hazards From Nitrates in Drinking Water," WHO meeting report, conducted March 1984, Copenhagen, Denmark.
7. WHO. 1972. Technical Report Series N 505, Geneva, Switzerland.
8. Hutton, M. 1982. "Cadmium in the European Community," Monitoring and Assessment Research Centre Technical Report N 26, University of London, England.
9. Johnson, A. E., and K. C. Jones. 1992. "The Cadmium Issue – Long Term Changes in the Cadmium Content of Soils and the Crops Grown on Them," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 255-269, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.
10. Karim, Z. 1993. "Phosphatic Fertilizers and the Environment," Proceedings of the Regional FADINAP Seminar on Fertilization and Environment, ST/ESCAP/1256, held September 7-12, 1992, United Nations, New York, U.S.A.
11. Miller, F. P. 1982. "Fertilizers and our Environment," pp. 21-44, The Fertilizer Handbook, The Fertilizer Institute, Washington, D.C., U.S.A.
12. UNEP. 1993. "Fertilization," Terrestrial Ecosystem Branch of UNEP, Proceedings of the Regional FADINAP Seminar on Fertilization and Environment, ST/ESCAP/1256, September 7-12, 1992, United Nations, New York.
13. Norsk Hydro AG. 1993. "Pollution Prevention and Abatement Guidelines for the Fertilizer Industry," UNIDO report UC/GLO/91/202, Vienna, Austria.
14. UNIDO. 1980. *Fertilizer Manual*, Development and Transfer of Technology Series N13, N.Y.1980 67.II.B.1.
15. "Urea as a Pollution Control Agent." 1975. *Nitrogen*, 93:32-36.
16. Polish Chemical Industry Restructuring Conference. 1995. Zakopane, Private communication.
17. Aleinov, D. P. 1993. "Environmental Issues of the Nitric Acid-Based Fertilizer Industry in Russia," IN *Nitric Acid-Based Fertilizers and the Environment*, Workshop Proceedings, pp. 285-292, R. G. Lee (Ed.), SP-21, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

18. Roudier, L., M. Durand, and B. Mouille. 1982. "Nitric Acid Recovery From Waste Nitrous Gases by COFAZ Process," Proceedings of the Nitrogen Fertilizers 4th British Sulphur International Conference, pp. 561-565, British Sulphur 2.

19. Boisne, M. 1994. Rhone Poulenc SA, Private Communication.

20. Instytu Nawozow Sztucznych. 1995. Private Communication, Pulawy, Poland.

21. Kleinschmidt, D. 1992. "Phosphogypsum Stack Closure," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 185-192, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

22. Mortvedt, J. J. 1992. "The Radioactivity Issue – Effects on Crops Grown on Mined Phosphate Lands, P-Fertilized Soils, and Phosphogypsum-Treated Soils," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 271-278, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

23. Uchino, Hidetoshi, and Haruyuki Morikawa. 1994. "Advanced Technologies for Urea Production: 'The ACES process,' " Unpublished technical information.

24. Pomfret, J. G. 1992. "Zero Water Discharge From Urea and Ammonium Nitrate Plants," Unpublished, European fertilizer plant retrofitting conference, Budapest, Hungary.

25. Lemmen, W. 1994. "The Environmental Impact of a Stamicarbon 2000 MTPD Urea Plant," Unpublished, Stamicarbon B.V., AIChE Ammonia Safety Symposium, Vancouver BC, Canada.

26. Plevsky, V. M., and M. K. Rustankov. 1991. "New Technology Development in the Field of Production of Nitric Fertilizers," Proceedings from IFA-AGrichim Conference, held October 8-10, 1991, Moscow, Russia.

27. Benes, J. A., and H. Franzrahe. 1994. "Modifying Existing DAP/NPK Fertilizer Plants to Comply With New Environmental Regulations," UHDE GmbH, IFA Workshop, held September 1994, Amman, Jordan.

28. Houghtaling, S. V., and V. S. Margitt, Jr. 1994. "Advanced Ammonium Phosphate Scrubbing With Minimum Water Discharge," HiTEch Solutions U.S.A., Workshop, held September 1994, Amman, Jordan.

29. Hopfer, Klaus. 1994. "Environmental Aspects: Closed Scrubber System for NPK/DAP Plants," Private Communication, UHDE GmbH, Germany.

30. Storen, H. 1992. "The Nitrophosphate Process – An Alternative Route to Phosphate Fertilizers," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 223-229, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

31. Diehl, L., R. E. Nitzschmann, and J.G.A. Reuvers. 1992. "The BASF Nitrophosphate Concept: Experience and Environmental Aspects Related to Three Recently Commissioned NPK Plants," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 241-250, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

32. McFarlin, R. F. 1992. "Current and Anticipated Research Priorities for the Utilization and Management of Phosphate Process Byproducts and Wastes," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 179-184, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

33. Baretincic, J. M. 1992. "Engineering and Cost Data for Lined Phosphogypsum Storage Site Being Installed by IMC Fertilizer, Inc.," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 193-195, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

34. Isherwood, K. F. 1992. "Phosphate Industry and the Environment," IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 115-124, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

35. Vyas, V. M. 1992. "Environmental Management of Phosphatic Group of Plants – Gujarat State Fertilizers Company Limited (GSFC), India, IN *Phosphate Fertilizers and the Environment*, Workshop Proceedings, pp. 197-207, J. J. Schultz (Ed.), SP-18, International Fertilizer Development Center, Muscle Shoals, AL, U.S.A.

36. Economic Commission For Europe. 1988. *Use and Disposal of Wastes From Phosphoric Acid and Titanium Dioxide Production*, ISBN 92-1-116433-1, ECE/CHEM/65, New York, NY, U.S.A.

37. Kopytowski, J. A. 1994. "Environment Impact Assessment: Methodology and Practice," Unpublished, Regional Workshop on Chemical Safety, held July 1994, Warsaw, Poland.

38. EMFA, Avenue E. Van Nieuwenhuyse 4, B-1160 Brussels, Belgium, Fax (0322) 6753961.

39. ISO 14000. 1995. "The Groundwork for Environmental Management" Perry Johnson Inc. WP/9/95.

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Chapter 20. Planning for the Development of a Fertilizer Industry

20.1 Introduction

The fertilizer industry is a special kind of technical operation; it belongs to the so-called agroindustrial complex, which is composed of agricultural and industrial sectors. Therefore, it is difficult to find the necessary data and their assessment in many national statistical reports. The management of the sector and available data are dispersed among different ministries, government agencies, international agencies, research institutions, industrialists, wholesalers, and farmers. However, the development and implementation of an intensified agricultural production program requires an integrated approach. The development of the agroindustrial sector should be based on macroeconomic, agricultural, and industrial assumptions and indicators.

20.1.1 Macroeconomic Assumptions and Indicators

Macroeconomic assumptions and indicators have a strategic character and correspond to the political trends and decisions in the country. They are related to the trends in the growth of the assumed gross domestic product (GDP) per capita and distribution of the GDP between the agricultural and nonagricultural GDP and the investment ratios to be provided for agricultural development and processing of agricultural products. The energy input of the food consumed by the population and its distribution between the cereals and animal proteins influence the structure of the country's agricultural production.

20.1.2 Agricultural Assumptions and Indicators

The agricultural assumptions and indicators depend on the actual and projected resources, including arable land, harvested land, irrigated land, cropping intensity, available labor, level of mechanization of agricultural labor, crop diversification related to the kind and number of livestock, permanent crops, etc.

These indicators would allow the calculation of the agricultural production profile and the necessary investment and inputs. Some of the inputs such as certified seeds and animal breeds have an agricultural origin; others have an industrial origin. Also environmental protection measures originating from agricultural development must be considered.

20.1.3 Industrial Assumptions and Indicators

The industrial subsectors contributing to the increase of agricultural inputs should be identified and examined collectively to evaluate the potential and organization of the increase in agricultural production.

The industries and semi-industrial activities contributing to increased food production include the following:

- Manufacture of agricultural machinery.
- Semi-industrial activities such as irrigation and soil improvement.
- Fertilizer industry.
- Pesticide industry.
- Animal feed additives industry.
- Food processing industry.
- Packaging industry.

Therefore, to observe closely the development of the fertilizer industry requires the identification of the conditions under which the agroindustrial complex will be operated. The collective contribution of all elements is so important that a nonintegrated approach to the solution of the problem will not suffice.

If the high-yielding varieties of seeds continue to be introduced, i.e., genetically more efficient, then the availability of all industrial inputs must be increased accordingly. High-yielding varieties quickly consume soil nutrients, and without inputs of fertilizers (including micronutrients) soil fertility will rapidly decrease. The intensive species are more susceptible to animal and plant pests. Therefore, intensive agriculture is impossible without very selective, planned pesticide applications.

Commercial agriculture often requires mechanized harvesting of agricultural products. Also waste materials resulting from large-scale food production can be used as animal feed. If this is to be carried out in the most efficient way, special fertilizers, pharmaceuticals, and other chemicals are required.

Therefore, only an integrated approach can provide the means to efficient food production. The production of fertilizers and their beneficial use is only one of the problems to be solved. However, to identify the analytical data for complex studies, the impact of fertilizer industry development must be assessed to provide the following inputs:

- Projected amount and profile of crop production. This information allows the assessment of the needs for transportation, storage, and agricultural machinery.
- Program of crop processing into food and feed products. This information would help establish the food processing industry and develop the industry of food and feed additives.
- Program of crop processing into industrial raw materials and intermediates.
- Yields assessment (an extensive test program is necessary), establishment of the optimum fertilization, benefit:cost evaluation, and planning of policy measures.
- An optimal fertilizer production program, which would be adequate for consumption requirements and considers import-export elements. This information would allow the assessment of investment costs and promotional policies for fertilizer application.
- Marketing and distribution network planning and development, including the dealers' network and the application of the necessary policy measures regarding the storage of fertilizers.

Obviously, local production of fertilizers is an alternative to importation. The decision to construct a local fertilizer plant would depend not only on consumption requirements but also on the international market situation and the nearest point of potential importation.

A detailed review of international fertilizer market trends has been given in Chapter 3.

20.2 Strategies and Policies of Fertilizer Industry Development

20.2.1 General Methodology

The establishment of the development program, and in particular the development program of the fertilizer industry, requires not only the collection of data to be processed using a specific methodology but also requires self-control in the feedback system. There are numerous examples of development programs established on the basis of future or expected demand, which are not correlated with the macroeconomic options and features of the country's economy.

These programs were either never implemented or their implementation increased debts or generated other economic crises. On the other hand, there are examples of failures when separate projects were implemented based on the commercial feasibility of a specific project. These examples have also proven to be inefficient because of their deficiencies in technology, economy, market assessment, or selection of priorities. This case-by-case approach was transferred from developed countries where a basic industrial structure already existed and competing innovations change the industrial structure and the overall consumption/production patterns of the economy.

However, a perfect method of development programming does not exist. The decisionmaker involved in the industrialization process should not seek ideal or optimum solutions but establishment of a reliable system for monitoring program implementation. Political, economic, logistic, and technological constraints impose such pressure on any of the development programs that only a proven, realistic and easy-to-test development thesis can be implemented. This closed circuit of the programming process should therefore follow the procedure that can be institutionalized as the monitoring methodology. However, when establishing such a methodology, one should remember what are the objective parameters/variables of the system and which are subjective and dependent on the position and opinion of the politicians or decisionmakers. Therefore, before the procedure is analyzed, the features of the potentially implementable methodology should be investigated. A well-proven methodology of the programming process establishes certain choices that must be made before determining the industrialization process. The strategies, industrial structure, and appropriate policies must be selected.

20.2.2 Strategic Issues of Fertilizer Industry Development

Strategies are partially subjective and partially objective elements of the programming methodology. Their objective character is related to the country's macroeconomic patterns, and their subjective character is related to the choices of goals to be achieved. The strategic issues of fertilizer industry development include the following topics:

- Import substitution.
- Export promotion.
- Resource utilization.
- Technological options – labor intensive, capital intensive, or advanced (high) versus standard (proven) technology.
- Energy source and use efficiency.
- Market share selection (basic industries versus consumer industries).

- Property (private or public sector support).
- Development financing.

Obviously, in each country the establishment of the ranges of quantitative variables must be adjusted to a particular economic feature. Establishment of the fertilizer complex usually requires a mixture of several strategies, namely import substitution combined with export promotion, capital-intensive industrial development addressed to the consumer, and oriented to involve both private and public capital with selective participation of foreign companies.

Implementation of the strategies requires selection and application of a set of industrial policies, but simple repetition of the existing policies established in industrialized countries will not be feasible for many reasons, e.g., lack of capital market, lack of savings, and nonconvertibility of the national currency. Therefore, policies should be specific for the promotion of the optimum, specific industrial structure and would not suffice for the development of any other type of structure.

20.2.3 Search for Industrial Structure

The second step in the programming methodology is therefore the establishment of the optional (multi-alternative) industrial structure (a technological network for processing raw materials into fertilizers). This programming step is an objective element of the methodology, which is based on an existing set of technological processes with well-defined production and investment costs. Their analytical assessment will give insight into the options and will also influence the strategy selected. An example of a simple fertilizer network is given in Figure 20.1.

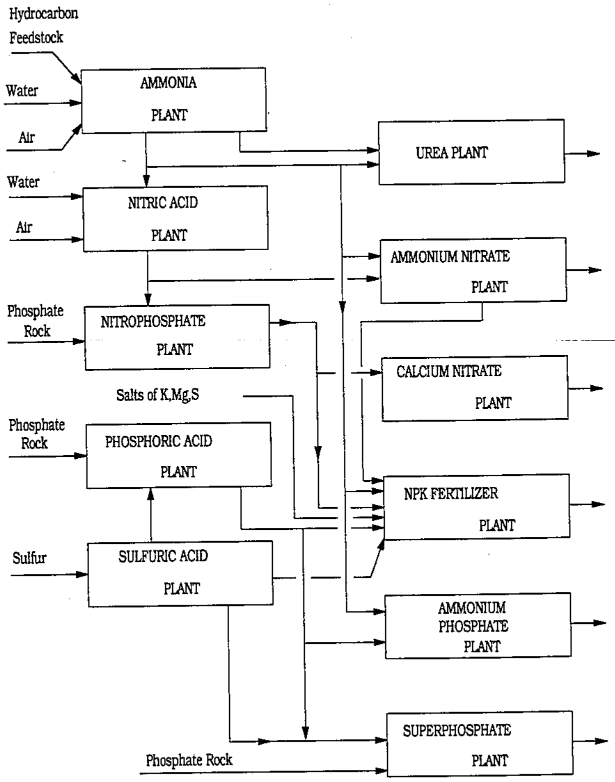

Figure 20.1. Fertilizer Production Network.

If any of the options analyzed for the future industrial structure do not meet objective efficiency parameters, such as manufacturing value added (MVA) profits and their ratios to investment, salaries, or capital formation, the selected strategy should be revised or another one selected to meet the needs of the given country. However, the comprehensive strategy with the selected option for the industrial structure depends on implementation of appropriate policies.

20.2.4 Policies to Ensure a Positive Benefit:Cost Ratio

This third methodological element requires another consideration. Industrial policies are the indisputable part of the instrument with which government controls the trends of industrial development because many economic processes are exponential in nature and they also lack continuity. One important example of this feature is a change of financial efficiency of the installation at decreasing utilization of capacity (operation at a break-even point is not feasible). General industrial policies serve to adjust economic process more or less to the linearity.

Two types of policies support industrial development. The two categories of the industrial policy instruments are general macroeconomic and microeconomic policies. General macroeconomic policies relate to taxation, rate of interest, customs duties, depreciation and dividends, exchange rate, and individual versus social income. The selective, microeconomic policies include special policies pertaining to subsidies on raw material prices and rate of interest.

Each of the policies have several options and a selection of policy implies the need for the establishment of the necessary parameter expressed in a specific value. If the policies are an objective element of the programming process, the establishment of their parameters is a subjective exercise if econometric models, allowing even simple simulation, are not available. In our case, the policies and their parameters can be checked in the technological structures, preselected from the previous step.

Therefore, when considering the policies before establishment of the fertilizer complex, computer simulation should be made of the possible impacts of selected policies on the program itself and also on the country's budget and trade balance. Table 20.1 gives the basic limits of the industrial policies to be applied before the establishment of a fertilizer complex. Using the econometric models, the necessary agreement between the strategies, industrial structure, and policies could be established. Certain examples show that a few repetitions of the methodological steps may give full agreement between the development objectives, strategies, policies, and industrial structure.

Table 20.1. Policy Measures (Trends and Limits)

Policy Parameters	Recommended Values for Low Added Value Products	Recommended Values for High Value Added Products
Custom duties	Min. 0%	Max. 35%
Capital tax	Min. 0%	Max. 15%
Income tax	Uniform	Uniform
MVA tax	Min. 0%	Max. 24%
Export credit facilities	Min. 1 month	Max. 6 months
Interest rate subsidies (as part of prevailing rate of interest)	Max. 50%	Min. 0%
Depreciation time	15-20 years	3-4 years
Subsidies on raw material prices	Max. 20%	Min. 0%

20.2.5 Procedural Steps

The macroeconomic planning features presented in the UNIDO methodology, published in the *Guidelines for Industrial Planning in Developing Countries* [1], show that the identification of an industrial structure optional model is a central element of the comprehensive program, which can be presented as a package to national and foreign investors. Such models were developed by several scientific institutes and consulting/engineering companies. One particular specialized package, Multicriterial Industrial Development Aid (MIDA), was used in UNIDO projects to identify the business opportunities in several developing countries [2].

However, every methodology used to establish the production structure of the future industry needs to identify some patterns of the actual and projected consumption, which is well correlated with the country's or region's situation. Thus, an estimate of the potential market for the final consumer goods is necessary. Methods of compiling these data are crucial for any programming exercise in the chemical industry.

Establishment of the goals based on strategies and respective supporting policies requires application of a monitoring system, the "feedback" methodology. Therefore, the whole investment promotion system (independent of the economic pattern of the country) should be based on trial-and-error, stepwise procedures. The reason for such an approach is that it is impossible to establish simultaneously the strategies (which are independent variables of the development equation) and to check the policies without having the evaluation of the set of priority projects and their impact on the strategy implementation results. Therefore, the following basic steps are necessary to ensure identification of appropriate business opportunities and promote foreign investment:

1. Identification of the strategic goals and their definition in the measurable parameters (macroeconomic parameterization).
2. A sectoral/subsectoral consumption projection based on macroeconomic individual patterns of consumption or on the Leontieff matrix to identify markets.
3. Establishment of the technological network ensuring consumption needs of the final consumer commodities and goods, analytical evaluation of the network, optimization of the industrial structure giving certain scenarios of the constraints, and selection of the priority investment projects.
4. Simulation of the resulting structure efficiency under different packages of policies and risk analysis testing the impact of external variables such as prices and demand changes.

The results, which may be presented in the form of the master business plan, should be checked again through the intersectoral flows and reviewed in terms of the macroproportions elaborated by the strategies. Of course, because of changeable external parameters (prices and other countries' decisions influencing the market situation), it is impossible to achieve full integrity and stability of such a program. It is sufficient to concentrate the planner's attention on two or three basic industrial subsectors to elaborate the package of policies supporting the main development strategy. A well-integrated package of policies will also serve as a motivation in other subsectors in following the given development pattern.

20.3 Estimates of Demand and Requirements

20.3.1 Demand Estimates

Multiple studies have proven that the growth of agricultural crops primarily depends on the timely application of properly selected fertilizers in the best potentially available climatic conditions. Proper seeds and seedlings must be selected, the necessary quantity of water ensured during the growth period, proper plant protection products used, and collection of the crops without unnecessary losses ensured. Only then would the positive impact of fertilizers be observed, without a negative impact on the environment.

No unified methodology exists for assessing fertilizer demand. In fact, when demand is assessed in a given country, a very basic study must be prepared considering all aspects of the operation of the agroindustrial complex. However, the methodological approaches are limited, and examples related to the target and time of the projection include the following:

1. The World Bank/FAO/UNIDO/Industry Fertilizer Working Group.
2. Regional assessment by the East-West Centre, Honolulu, Hawaii, of the demand in Southeast Asia.
3. FAO's country projection of the development of the agroindustrial complex.
4. FERTIS, the UNIDO system of the fertilizer industrial development as a part of an agroindustrial complex.

There are well-established demand projection methodologies developed by industrial organizations and companies, however, they were not disseminated for public use.

20.3.1.1 FAO, UNIDO, and World Bank "World and Regional Supply and Demand Balances for Nitrogen, Phosphate, and Potash" [3] – The FAO/UNIDO World Bank Industry Fertilizer Working Group includes a number of specialists who are experienced in the analysis of trends in the production and consumption of the primary fertilizer nutrients and fertilizer raw materials. Other members of the Group represent major industrial associations of the nitrogen, phosphate, potash, and sulfur industries. Technical, production, marketing, and agricultural interests are also represented within the Group.

Demand projections result as a consensus of the Group and consider a variety of methodologies, including trend analyses, market surveys, agricultural programs, and economic modeling. The Group's demand projections are based on the scenario that considers these elements:

- Global economic growth projections.
- Specific policy measures (e.g., environmental protection measures).
- The balance of agricultural stocks and their reduction.
- Foreign exchange availability in developing countries.
- The transition to a free market economy in Central and Eastern Europe and other policy measures in the developing countries.
- Loss of capacities due to different reasons.
- Raw material prices (natural gas and crude oil) and their impact on the benefit:cost ratio of fertilizer application.

The Group provides statistical data for the following geographical areas:

- World.
- Africa.
- America (with the subdivisions of North, South, and Central America).
- Asia (with the subdivisions of West, South, and East Asia).
- Europe (with the subdivisions of East, West Europe, and the former Soviet Union [FSU]).
- Oceania.

Separate tables refer to countries in the regions.

Statistics on the following fertilizer components are reported:

- Ammonia (including nonfertilizer use).
- Phosphoric acid (including nonfertilizer use).
- Other phosphate fertilizers.
- Potash (including nonfertilizer use).

Table 20.2 compares the demand of nutrients as projected by the Group with the statistically reported achieved demand. Substantial differences in projections occurred due to the disruption of the fertilizer use system after the introduction of world prices and the removal of subsidies in Central and Eastern Europe and the FSU. This transformation was not possible to foresee in 1989 when projections were prepared. For the case of stable consumption in Central and Eastern Europe and FSU countries, the absolute error for the world consumption projected in 1989 by the year 1992/93 would be for N +2.3%, P_2O_5 -2%, and K_2O 6.9%.

20.3.1.2 East-West Centre (EWC): The "Need-Based" Approach for Projecting Long-Term Fertilizer Demand Based on Agronomic Considerations [4] – When considering the options of committing scarce financial resources for fertilizer production or other nation-building investments, decisionmakers need to assess the long-term fertilizer demand/supply outlook. However, fertilizer demand projection models based on trend analysis, while effective for short-term

Table 20.2. World Bank/UNIDO/FAO Fertilizer Consumption Projections [3]

Nutrients	1987/88 Production (N, P_2O_5, K_2O) (million tonnes of nutrient)	Consumption, 1992/93 Projection	Consumption, 1992/93 Recorded	Absolute Error (%)
		- -(million tonnes of nutrient) -		
World Total				
Nitrogen	73.84	83.54	73.63	- 11.8
P_2O_5	35.84	40.80	31.50	- 22.8
K_2O	26.54	29.38	20.66	- 29.7
North America				
Nitrogen	10.85	11.12	11.58	+ 4.2
P_2O_5	4.35	4.60	4.64	+ 0.8
K_2O	5.00	5.30	4.95	- 6.6
Central and South America				
Nitrogen	3.95	4.68	3.58	-23.5
P_2O_5	2.80	3.21	2.34	-27.1
K_2O	1.90	2.33	1.95	-16.3
Western Europe				
Nitrogen	10.60	10.10	9.22	-8.7
P_2O_5	4.75	4.75	3.75	-21.0
K_2O	5.17	5.17	4.11	-24.0
Eastern Europe and CIS				
Nitrogen	16.34	19.50	7.20	-62.1
P_2O_5	11.42	13.12	4.37	-66.0
K_2O	9.93	10.81	3.85	-63.5

Note: To obtain the annual report of the Fertilizer Working Group, write to the IBRD/The World Bank, 1818 H Street NW, Washington, DC 20433, U.S.A.

projections, may be of limited value for such long-term tasks. Thus, alternative approaches are needed. While making any projection is "crystal ball gazing," investment decisions could be reinforced if a "second opinion" confirms the first. A summary of the EWC method for projecting long-term fertilizer demand based on agronomic considerations follows [4]. The model has been tested for Asian countries.

The model uses the following relationship:

$$NPK(D) = \frac{APD - APRF}{CR}$$

Where:

NPK(D) = Total fertilizer demand projected, expressed in million tonnes.

APD = Total agricultural production of crops desired, expressed in million tonnes.

APRF = Agricultural production on residual soil fertility, expressed in million tonnes.

CR = National average crop response to fertilizer use.

An evaluation of all three elements of the equation is made using the following procedures:

1. Total agricultural production desired – The concept of the agricultural crop production per capita (APC) is used to project total production in a similar fashion as the FAO methodology uses calories per capita to project food-grain needed. This is a typical national parameter showing the crop consumption per capita. Because of differences in crops grown, however, APC should not be compared across the countries. By multiplying the APC by the projected year's population, it is possible to approximate total agricultural target desired for each country and by the projected year. In testing the model, projections and

actual consumption for 1990 are compared. The value of APC during long periods remained stable in Asia. The stability of the APC parameter may be explained either because quick growth of population does not create the possibility of increasing foodgrain consumption and/or the consumption pattern does not change even when more food is available.

2. Agricultural production on residual soil fertility (APRF) – The theoretical agricultural production on residual soil fertility has been introduced to the model. The average crop yield per hectare in any country years ago when no chemical fertilizer was used would approximate the yields. However, changes in seed selection or new techniques changed the APRF. Therefore, to approximate the current APRF, the average crop yield per hectare is regressed with the average fertilizer use per hectare over a certain period of time (in testing the model the 1965-90 period has been used). The theoretical crop yield at the NPK intensity of zero approximates the past APRC (by extrapolation).

   It is possible to consider better crop management practices by assuming slight improvement of the APRC in future years. By subtracting APRC from the total agricultural production of specific crops, the approximate gap in agricultural production that has to be filled with fertilizer use is determined.

3. Crop response to fertilizer use (CR) – The regression analysis of the relationship between the outputs and fertilization mentioned above gives the possibility of establishing the function of CR against fertilization intensity. The slope of the regression curve is the CR for certain fertilization intensity, following the normal pattern of the decreasing crop response with fertilization intensity. However, this parameter is dependent on the climatic and soil conditions of each specific country. The value of this parameter also may indicate the achievements in crop management practices.

4. The projected long-term fertilizer demand: NPK(D) – The NPK(D) is derived by dividing the gap in the agricultural production to be met with fertilizer use by the national crop response to fertilizers (CR).

Validation of EWC model – The regression analysis yielded high R^2 values (0.8 or better) in six countries (Bangladesh, India, Pakistan, Indonesia, Malaysia, and China) and somewhat lower values (0.77 to 0.67) in another two countries (Sri Lanka and Thailand), thereby indicating that a real relationship exists between agricultural productivity and fertilizer use in these countries. In some countries lack of relationship or difference in CR can be explained by imprecise statistical data available, due to the nonregistered trade in fertilizers between some of the countries.

Consultation on practical implementation of the methodology can be obtained from the East-West Centre, 1777 East-West Road, Honolulu, Hawaii 96848, U.S.A.

Comparison of the Calculated 1990 Fertilizer Projection With Actual Data – The calculated and reported data are given in Table 20.3. Differences between the 1990 actual and projected values are 7% or less in nine countries. Only in Sri Lanka is the difference (23%) higher because of the very low level of initial fertilization considered by the model.

20.3.1.3 The Food and Agriculture Organization Projection Methodology [5] – After the FAO conference in 1987 the document, *Agriculture: Towards 2000*, was prepared and published. The country documents prepared in 1988 by the Global Perspective Studies Unit (ESDG) describe the historical data and provide projections on the production of different crops and livestock and describe the economic parameters of local agriculture at present and by the year 1990 and 2000. One of the projection elements is fertilizer consumption.

The detailed methodology for preparing country tables is described in the FAO publication [5]. A short summary of the methodology is given here.

The country tables, prepared using statistical data from the FAO AGROSTAT data base, have been standardized. The projections have been made for the period May 1986 to April 1987 and were based on data for the 3-year average (1982-84); some data from 1986 have been used.

The general methodology is based on the scenario method; three scenarios are developed for each country (central case, pessimistic, and optimistic).

The production projections are made by estimating net and gross cumulative investment for the projected period to allow assessment of the macroeconomic proportions. The gross value of crops is calculated and inputs are analyzed. The crop production growth is estimated by assessment of the sources of growth such as yield per hectare, arable land growth, and cropping intensity. This produces projected crops and, in particular, cereal yield per hectare.

The projections of inputs growth rate are made by the scenario method; the most probable dynamics of the growth are selected. By comparing the ratio of the fertilizer input contribution to the crops (in particular cereals), the yield growth of the fertilizer input or its efficiency at a given intensity could be analyzed.

The projections for the year 2000 for each country are confidential and could not be published. To assess the validity of the methodology, the results of projected

Table 20.3. Validation of the East-West Centre Model

Parameters	Bangladesh	India	Nepal	Pakistan	Sri Lanka
Population (in millions)	115.6	853.0	19.1	122.6	17.2
APC/capita (tonnes/capita)	0.36	0.66	0.49	0.58	0.48
Total APD (million tonnes)	41.1	562.3	9.3	71.1	8.2
Total HA (million ha)	13.7	163.9	3.5	71.1	8.2
APRF (t/ha)	2.3	1.8	1.8	2.5	2.8
APRF (million tonnes)	31.3	295.0	6.3	44.2	3.9
APC-APRF (million tonnes)	10.0	267.3	3.0	26.9	4.3
CR (tonne/tonne)	11.5	20.9	40.0	13.5	21.0
NPK(D) (million tonnes)	0.87	12.78	0.075	1.99	0.21
1990 TFC[a] (million tonnes)	0.93	12.56	0.073	1.89	0.17
Error, %	- 6.4	+ 1.8	+ 2.7	+ 5.3	+23.5

Parameters	Indonesia	Philippines	Malaysia	Thailand	China
Population (in millions)	184.2	62.4	17.9	55.7	1,139.1
APC/capita (tonnes/capita)	0.7	1.0	0.76	1.58	0.71
Total APD (million tonnes)	128.9	62.4	13.6	88.0	808.8
Total HA (million ha)	23.2	11.4	4.9	16.9	137.7
APRF (tonne/ha)	3.5	4.4	1.0	2.8	2.9
APRF (million tonnes)	81.2	50.2	4.9	47.3	399.3
APC-APRF (million tonnes)	47.7	12.2	8.7	40.7	409.5
CR (tonne/tonne)	18.6	21.0	9.0	38.0	15.5
NPK(D) (million tonnes)	2.56	0.58	0.97	1.07	26.42
1990 TFC[a] (million tonnes)	2.51	0.59	0.95	1.04	27.08
Error, %	+ 2.0	- 1.7	+ 2.1	+2.9	- 2.8

a. Total fertilizer consumption.

data for selected countries by the year 1990 are given in Table 20.4 [6].

Country data and consultation on the methodological issues can be obtained from the Global Perspective Studies Unit, FAO, Via delle Terme di Caracalla, Rome 00100, Italy.

20.3.1.4 FERTIS: UNIDO System of the Fertilizer Industry Development as Part of an Agroindustrial Complex [7] – The FERTIS program was undertaken by UNIDO during 1990-92 in the framework of the Industrial Development Decade for Africa (IDDA), United Nations Program for Action for African Recovery and Development (UNPAAERD) and the

Table 20.4. FAO Projection of Fertilizer (NPK) Consumption (1984) [6,21,22]

Country	FAO Projection for 1990	FAO Projection for 1990	Recorded in 1990	Error
	(kg/ha)	(tpy)	(tpy)	%
Benin	5.6	7,600	11,000	+30
Burkina Faso	4.6	13,400	21,000	+36
Mali	8.9	18,245	15,000	-21
Niger	0.6	2,100	2,000	-5
Togo	7.7	15,400	12,000	+28

African Priority Program of Economic Recovery (APPER). The program has been primarily oriented toward African countries; however, it has developed tools that could be used universally.

The basic equations were applied as reported by M. S. Mudahar [8].

The FERTIS program combined the analytical evaluation of the resource side, infrastructural elements, technological elements, demand/production side, and the Government strategies for the countries and assessment of the policies necessary to increase the use and efficiency of fertilizers in agriculture. The methodology allowed the development of certain patterns of fertilizer consumption/production.

The projections apply the economic parameters for evaluation of the potential demand and define the local policies necessary to transform the potential demand into real consumption. The demand assessment could be prepared in an integrated manner for all types of crops (e.g., for all cereals) or could be oriented toward the specific dominating crops in the country.

From the farmer's point of view the efficiency of fertilizer application is determined by two factors:

1. Crop response to increased fertilization.
2. Price ratio between crops and inputs.

The evaluation of both elements establishes a benefit:cost ratio that may motivate the farmer to use fertilizer. The FAO uses three parameters to define this benefit:cost ratio [9]:

1. Marginal rate of return (MRR).
2. Value:cost ratio (VCR).
3. Fertilizer-crop price ratios.

The FERTIS program uses *corrected* VCR parameters or

$$\text{VCR''} = \frac{[\text{Value of the yield increase x r}] - (\text{cost of fertilizer})}{\text{Cost of fertilizer applied}}$$

Where:

r = scaling coefficient of the yield increase from fertilization; its purpose is to adjust for differences in yield observed between the test fields and large area fertilizer applications.

At the long-term planning of the consumption/production development, the unified methodology for the crop response should be used, and the prices should be assessed.

An integrated analytical review of the crop responses has been elaborated by FAO in the late seventies and the early eighties during the implementation of the FAO Fertilizer Program [10,11]. A sigma-type function is well acknowledged as the crop response relationship. This function shows saturation when the marginal growth of yields is equal to zero at a certain fertilization intensity. This point is considered the agronomic optimum; however, a direct relationship between the yields expressed in kilograms per hectare (or monetary units per hectare) and fertilization intensity expressed as kilograms per hectare of NPK shows certain divergences for many countries, e.g., approximation is not satisfactory. This is obvious because the crop response greatly depends on climatic conditions, soil conditions, crop variety (response of high-yielding varieties is different from that of standard varieties), and cereals represent different species reacting in a different way. The soil/crop management level differs from country to country.

These divergences are partially smoothed by the application of proper proportions of NPK in applied fertilizer. In many countries extension services have developed recommended proportions and doses of nutrients for different crops, soil conditions, and regions of the countries [12].

Therefore, during the FERTIS system implementation, better correlation can be obtained if yields from harvested land are considered and if a relational function is derived from the published or test data. Obviously this function also has a sigmoidal character; however, the results obtained are always related to specific agronomic and climatic situations.

That function considers that at "no fertilization" on specific soil and climatic conditions and at a specific level of agronomic management, a specific level of soil productivity can be retained. This concept is similar to that used by EWC methodology production on residual soil fertility. The "no fertilization" means that mineral fertilizers are not used. The crops always receive some amount of nutrients from air and rain and by decomposition of soil minerals. On the maximum side the agronomic optimum is used. The argument and function are both expressed in percentages: the use of fertilizers in the percent of fertilization ratio between zero and agronomic optimum and the yield increase related to the "no fertilization" and agronomic optimum. The exemplification of the function is shown in Figure 20.2.

The function shown below has been prepared using the data from the FAO Fertilizer Programme [9]. However, in each country local extension services can elaborate its own function related to specific crops and use it for the purpose of demand assessment.

The economic level of fertilization would depend on the VCR" value. However, calculation of projected VCR"

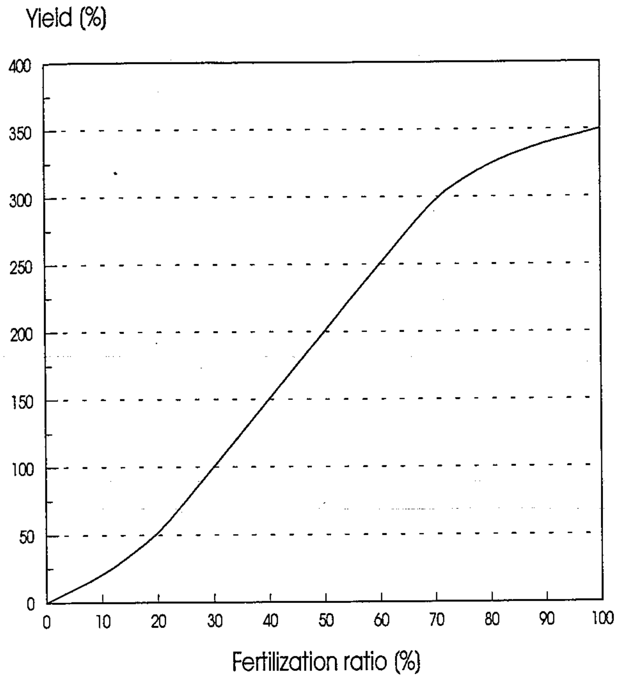

Figure 20.2. Fertilization-Yield FERTIS Function.

does not give the assurance of the use of fertilizers. Therefore, it has been proposed to use the pattern VCR" value (or alternative values) to establish Government policy measures necessary to motivate farmers to use fertilizers.

The pattern VCR" value depends on Government strategy. The optional exemplification of the strategies and VCR" value is given in Table 20.5 [13].

It may be expected that at VCR" equal 4, all marginal land would be harvested if other constraints are not present (manpower availability, water availability, storage, and transportation system). In other marginal cases at very low VCR" values, the farmers would limit or even abandon the use of fertilizers, bringing the soil to residual fertility.

Which of the VCR" to select in the ranges of the given strategy cannot be predicted by econometric analysis and each Government must experiment. However, the economic impact of these experiments may only lead to the shift of the incomes from other sectors of the national economy to agriculture.

Table 20.5. VCR Values at Different Strategies

Country Strategy	VCR" Values
Maximum food independence	3.0 - 4.0
Economically efficient food production	2.0 - 2.5
Liquidation of food surpluses	1.2 - 1.5

Obviously, the VCR" value can be regulated either by establishing local prices for crops (by establishing custom duties on imported products if cheaper than in-country or establishing a complicated system of food subsidies) or by fertilizer subsidies. These options will be discussed later in the chapter.

The procedure for establishing the projections of fertilizer demand in FERTIS methodology is as follows:

1. Following demographic projections and food availability (kcal/capita), establish the target in time of the production output of the concerned crop.
2. Following the harvested land availability, establish the required crop yield.
3. Using the increased crop yield function, establish the required growth in fertilization.
4. Check the agronomic optimum with the extension services, and calculate the amount of fertilizer required.
5. Assume the VCR" value (optional).
6. Using international prices for NPK (specific for crop proportion), establish the farm-gate price of the given crop or VCR".
7. Compare the farm-gate price with the international crop price or VCR" value with the strategic issues.
8. Establish possible custom duties on the crop and determine if it is the internationally (WTO) accepted value.
9. Determine if fertilizer importation is an alternative.
10. Prepare feasibility studies of fertilizer industry development.

The validation of the FERTIS projections is given in the Table 20.6.

Consultation and further information on the FERTIS methodology of fertilizer demand assessment can be obtained from UNIDO, Chemical Industries Branch, P.O. Box 300, A-1400 Vienna, Austria.

All above-mentioned methodologies give approximate results, which should be used for strategic planning only. The particular, short-term and locally adjusted recommendations on fertilizer application could be issued by the local extension services only.

Table 20.6. Validation of the FERTIS Model (1988 Projection) [13,22]

	NPK		
Country	Projection for 1993/94 (tpy)	Recorded for 1993/94 (tpy)	Error[a] %
Indonesia	2,930,000	2,627,000	-11
Korea Republic	1,150,000	975,000	-18
Malaysia	930,000	1,035,000	+11
Thailand	850,000	1,126,000	+25
Vietnam	660,000	900,000	+27

a. Error is calculated as ratio of difference between recorded and projections consumption to the recorded consumption.

20.3.2 Other Factors Affecting the Use of Fertilizers

20.3.2.1 Quality Assurance – Most Governments have established laws and regulations to specify and enforce quality standards of fertilizers to ensure that products of satisfactory quality are available for farmers and that farmers know what they are buying and get what they pay for.

Most regulations are concerned with such subjects as adherence to guaranteed analysis within specified limits of tolerance; guaranteed weights; identification of product source; and specification of grades, nutrients, and methods of sampling and analysis.

Most laws specify penalties such as fines or revocation of trading license for failure to conform to specified standards. The special duties of regulatory officials should be provided by legislation to control the quality of fertilizers at any time and place. This is so important because misrepresentation of fertilizer quality not only destroys farmers financially but also the credibility of food production programs. Special control must be ensured when individual nutrients are imported and blended locally.

The role of the extension service on farm-level use cannot be overestimated because it educates farmers on fertilizer quality and also promotes proper fertilizer use. In some countries the extension service carries out fertilizer tests to show the farmer the benefits and the costs of using fertilizer. The farmer pays for fertilizers only in cases when positive results and promised yields have been achieved. Therefore, it is important that the extension services employ highly qualified specialists, who are paid adequately. The cost of fraud in agriculture and respective losses of the budget are so high that it is worthwhile to ensure properly operating government extension services. Only in countries where farmers are rich can they afford private advisory services.

20.3.2.2 Types of Fertilizers Required – At present the number of variations of the composition of fertilizers is very high. Even standard NPK products are numerous, but any granulation plant could produce special compositions of fertilizers upon request. The selection of the NPK composition depends on the following parameters:

- Type of crop and season of growth.
- Soil properties.
- Climatic conditions.
- Agronomic management.
- Marketing system organization and efficiency.

A diversified country situation requires large efforts by the extension service to advise farmers on the proper selection of fertilizer and requires the distribution system to deliver on time. The balance of nutrients and micronutrients plays a decisive role in the economic efficiency of fertilizers. Efficiency of nutrient uptake by crops has enormous economic value. Specific crops are using ammoniacal nitrogen at certain periods of growth in a specific quantity and nitrate nitrogen during the entire growth period. Therefore, for many crops ammoniacal nitrogen in fertilizer must be transformed into nitrate, which induces certain losses.

It has been proven that in some tropical conditions nitrogen uptake from urea for rice is as low as 20%-40%. Large fertilizer granules that have been coated with sulfur and other nonsoluble agents are the first answer in this field. A similar phenomenon is observed when phosphate fertilizers are used on calcareous soils and, especially in the presence of aluminum and iron, the soluble phosphate will revert to insoluble compounds, which are less available to the plant.

Therefore, proper agronomic management may save farmers and the country millions of dollars in valuable imports or production.

20.3.2.3 Marketing and Distribution Network and Costs – Expanded fertilizer use requires unconstrained availability of product at the farm level. Fertilizer supply at the right time and price depends on an efficient marketing and delivery system. In most developing countries these systems are underdeveloped and very costly.

The costs and logistic elements included in a marketing and delivery system are given in Table 20.7.

Marketing costs vary from country to country. In many countries delivery systems are still organized by the public sector. This is the case in many Asian and African countries. Other countries have developed a system owned by farmer cooperatives. In other countries the dealer system is in private hands. A discussion of the advantages and conditions for application of any system is beyond the scope of this publication. However, if any system is expected to be efficient for the farmer, it must be highly competitive because any kind of monopoly would lead to extravagant charges, aiming at high profits not at turnovers. The importance of these costs may indicate that fertilizer price in many developing countries is twice as high as ex-factory (or f.o.b., foreign port of supplier) price, and threefold prices in specific cases of landlocked countries have also been observed [14].

Table 20.8 gives a summary of the evaluation of delivery costs in selected Asian and African countries.

Table 20.7. Fertilizer Marketing and Distribution Costs

Fixed Costs	Additional Fixed Costs for Imports
Factory storage	Port storages
Transportation system:	
• roads	
• vehicles	
Intermediate storage	
Unloading equipment	
Final storage	

Operating Costs	Additional Operating Costs for Imports
Ex-factory price	C.I.F. price
Loading/unloading costs	Port costs
Working capital storage costs	Custom duties
Dealers' fees (margins)	
Transportation costs	
Interest rate on farm credit	
Distribution losses	
Advertising	
Promotional activities and training	
Extension service to the marketing system	

Table 20.8. Logistic Costs of Fertilizer Supply (1995)

	Landlocked Countries	Other Countries
	---- (US $ per tonne) ---	
Africa		
Handling and storage	15-20	10-15
Transportation	60-120	40-60
Interest charges	18-30	18-30
Physical losses	15-20	6-9
Other costs	30-60	15-30
Asia (landlocked and other countries)		
Handling and storage	4-10	
Transportation	6-20	
Interest charges	16-22	
Physical losses	2-3	
Other	15-30	

The prevailing freight costs of transporting fertilizers from producer to the destination port are given in Table 20.9 [15].

The involvement of banks is crucial for the success of marketing fertilizer. Positive Asian examples show that banks organized at the village level can provide profitable credits for small-scale local industries and farmers. This can be more efficient if a government credit subsidy exists.

Table 20.9. Prevailing Freight Costs Between the Most Common Ports (1994) [15]

Product	From	To	Cost (US $/tonne)
Ammonia	Yushny (CIS)	Greece	23-25
Ammonia	Umm Said	Tuticorin	23-25
Urea	Yuzhny	China	21-22
Urea	Persian Gulf	India (WC)	14
Phosphate rock	Casablanca	Mexico (EC)	10
DAP	Tampa	China	22
DAP	Tampa	Viet Nam	42
Sulfur	Jubail	Alexandria	16.5
Sulfur	Jubail	Coromandel	12.5
Potash	Hamburg	Bombay	29.5
Potash	Hamburg	Nhava Sheva	36

The expected investment costs to establish a reliable delivery system must be evaluated depending on local conditions and the number of distribution stages.

Scenario parameters are given in Table 20.10 of the case study of the establishment of a marketing and delivery system that includes an area, which is 30 km radius and covers 60% of the land for farming, located 200 km from the fertilizer factory. The two-step delivery system (intermediate regional storage and local storages) operates at the medium fertilization rate of 120 kg NPK/ha.

Marketing and delivery costs in this case study amount to between 30% to 50% of the cost of ex-factory fertilizer. This assessment is similar to the reported costs of Asian marketing systems. These costs are moderate only in the case of adequate Government policy of support and strict control of the monopolistic activities.

Integration of the delivery system for fertilizer with that of other agri-inputs (pesticides and animal feed) and outputs from farmers' cereals (rice, maize, wheat) may substantially decrease the operational costs of the delivery system. If crop surpluses obtained through fertilizer application can be handled by the same system, a 50% reduction in the costs can be expected.

Obviously the investment costs of roads and railways and their maintenance have been excluded from marketing costs.

Establishment or development of the marketing and delivery system requires accurate estimates of fertilizer consumption in a given area (region). However, this is a typical "egg and hen" case. Precise assessment of local demand without an operational delivery system is very difficult, and investment in this system is always considered risky. Local piloting schemes must be supported by the Government to show private entrepreneurs the scheme's profitability; at the same time privatization of the system must be allowed. In case competitive private systems do not exist, profit margins must be controlled by fiscal authorities to avoid overcharging the farmer.

A transportation network is a condition for a good delivery system. In many developing countries the density of the roads is scarce (Africa 5 km/100 km^2, Asia 45 km/100 km^2, United States 95 km/km^2, Europe 350 km/km^2; therefore, the problem of plant location is of strategic importance.

20.4 Establishment and Development of the Fertilizer Industry

20.4.1 Options to Establish a Fertilizer Plant

Worldwide production of fertilizers has achieved a highly sophisticated level, and improvements in the technological processes are still observed. The production patterns are well established; therefore, selection of certain alternatives for particular countries does not pose special risks. However, every country presents its own

Table 20.10. Scenario Parameters of the Case Study to Establish Distribution System

Infrastructure Elements	Units	Volumes
Storages:	m^2	
– Regional		3,000
– Local		5 x 600
Laboratory		200
Offices		200
Trucks, 40 tonnes	units	4
Working capital	US $	2 months storage volume financing
Depreciation	% of fixed capital cost	5% building 10 trucks
Transportation costs		
– Fuel	liters	40
– Spare parts/maintenance	% of trucks cost	5
Labor (service, drivers and laboratory)	men	27
Staff	men	3
Insurance	% of fixed capital cost	1
Return on sales	% of sales cost	5
Other	% of total	10

Table 20.11. Investment and Operational Costs of Fertilizer Distribution as in Case Study

Investment Cost Element	US $
Buildings	
– Storages	2,000,000
– Laboratory	120,000
– Offices	100,000
Trucks	800,000
Operation cost element	US $/t
Labor and staff	18.0
Transportation	8.5
Depreciation	5.0
Financial costs	5.5
Insurance	1.4
Market promotion	5.0
ROS	15.0
Total	**58.4**

unique set of options and constraints. Therefore, any consideration by the government to promote the concept of fertilizer industry development must be studied very carefully. As many years of experience shows, the time lag between the first decision to establish any kind of fertilizer industry and factory startup may cover 8-10 years. From the beginning the programming studies must be carried out in a professional manner to avoid later discrepancies and investment inaccuracies. The amount of information to be collected by the country planning/promotional body is very extensive and related to the different scientific and technical matters including geological, mining, agronomic, marketing, engineering, and economic know-how.

Therefore, the government planning/promotional body must assemble a multiprofessional group to develop a program and define a necessary plan of action in manageable components. Technical assistance from experienced expatriates is advisable; however, the entire exercise must be formulated and prepared by national experts. If found feasible in a given environment, the following options to develop a fertilizer industry are open for implementation.

20.4.1.1 Granulation/Compounding Network – Small granulation compounding plants are established in regions serving farmers in a radius of about 30 km. At a ratio of harvested land to total area equal to 0.4-0.6, the capacity of the granulation/compounding plant may reach 6,000 to 8,000 tpy at the medium- to high-fertilization rate (150 kg NPK/ha). Development of this alternative requires the following:

- Establishment of the "mother" ammonia and phosphoric acid plants supplying raw materials to the granulation plants. Supplies of single-nutrient fertilizers are also possible. In the beginning inputs to the granulation plants could be imported. Regional plants are also playing the role of extension services by advising farmers on fertilizer use and adapting production profiles (NPK ratios) to local crop requirements and periods of necessary fertilization. Simple granulation fertilizers are adding to the c.i.f. cost between US $18-$25/tonne of bulk material.
- Establishment of the logistical structure (necessary means of transportation, roads to regions, specialized staff settlements, laboratories, storage, and granulation facilities).

20.4.1.2 Small-Scale Ammonia Plants and Granulation/Compounding Network – This alternative may be considered in landlocked countries or regions where raw materials are dispersed in the primary fertilizer-consuming areas, e.g., small quantities of natural gas resources or small but high-quality deposits of phosphate rock. Demand in such an area should be high enough to use the production from 500-tpd ammonia and 100-tpd phosphoric acid installations without excessive transportation costs. Development of this alternative requires that the following infrastructure be established.

- Small-scale ammonia plants at the source of raw materials.
- Supplies of imported phosphoric acid or locally produced phosphoric acid.
- Affiliated complex fertilizer granulation/compounding plants.

In this case logistic problems are of limited importance. The local centers are also playing the role of extension services for farmers and are flexible enough to adapt to local crop production patterns.

Basic parameters that will influence the technical and economic solutions follow.

- Local natural gas and phosphate rock cost/price.
- Logistics of fertilizer distribution to the farmer from the small-scale plant (own distribution network, utilization/extension of existing network).
- Equity structure of the project (shareholders: public/private, distributors, and importers).

- Ability and conditions of fertilizer credit sales to individual farmers by the fertilizer company (directly or through a local bank).
- Detailed specification of the price difference between the c.i.f. price of fertilizers (different grades needed by the local agricultural production profile) and the farm-gate price.

20.4.1.3 Technological Concept for a Minifertilizer Plant With Integration of the Local Materials and Markets – In fact, all fertilizer plants established before 1960 may be considered minifertilizer plants because only after this date were high-pressure turbocompressors introduced, which solved the problem of a high-capacity ammonia unit.

Although there is no theoretical definition of the "minicapacity" of a fertilizer plant, in practice each installation producing from 100 to 600 tpy of ammonia is considered a small unit. All downstream ammonia processing operations of this size are also considered to be minifertilizer plants. The main technical differences between small- and large-scale ammonia units are summarized in Table 20.12 [16]. These differences (others of minor importance were omitted) influence the production cost, which is qualitatively assessed in Table 20.13.

Breakthroughs in small-scale capacity processes are the Kellogg (KRES system) and ICI Leading Concept Ammonia (LCA) process. The capacity of the referenced installation is 457 tpd, and the total energy consumption is estimated at 7.22 Gcal/tonne of ammonia. Installation also produces carbon dioxide that has more than 99% purity. The processes are described in Chapter 6.

In the developing countries small-scale fertilizer production has been practiced for many years. The number of ammonia plants of 100- to 500-tpd capacity by region was as follows (1977):

Latin America	9
Indian Subcontinent	18
Southeast Asia	8
Middle East	8
Africa	5

In 1991 there were more than 1,000 small-scale ammonia plants in China with a total capacity of 12 million tpy. The unit capacity of such a plant is 30-60 tpd. The basic products of the plant are ammonium carbonate or other ammonium salts. Although the current integrated data are not available, published cases show that many of these old plants are closed. A complete economic evaluation of the operation of such plants has not been published.

The following countries have had valuable experience in the construction and operation of small-scale fertilizer plants: China, India, Pakistan, Indonesia, Turkey, Peru, Mexico, Egypt, Syria, and Zimbabwe (electrolytical hydrogen).

Basic technological and technical data collected during the UNIDO workshop on "Minifertilizer Plant Establishment," held in Lahore in 1983, show an alternative means of developing the fertilizer industry and allow the preliminary technical assessment of such a concept. However, it is not possible to recommend an economical size fertilizer plant if only unit production costs are known. The cost of the marketing and delivery system is a second component of the fertilizer price at the farm gate,. and this price should be considered when determining the size of the fertilizer industry operation.

Advantages of smaller plant establishments, which are not always considered by financial analysis, are as follows:

1. Shorter construction time (2-3 years). This saves the cost of pre-operating interest and recovers the invested

Table 20.12. Technical Patterns of Large/Small Scale Fertilizer Installation [16]

Process Unit	Large Scale	Small Scale
a. Reforming and gas processing	Synthesis gas and high-pressure steam closed loop Pre-reforming optional	Synthesis gas production and steam as a byproduct, LCA system obligatory
b. Gas compression	Turbocompressors	Electrically-driven compressors
c. Purge gas recovery	Included in installation	Only in higher capacity installations
d. Synthesis	Multilayer ammonia reactor optional	Multilayer reactor obligatory. New catalyst to be considered

Table 20.13. Cost Advantages of Large-/Small-Scale Fertilizer Installations

Battery Limits:

Cost Component	Advantage of the Large Scale
Depreciation	Lower due to lower unit investment cost
Labor cost	Lower due to higher labor efficiency
Energy cost	Lower due to closed loop

Cost Component	Advantage of Small-Scale Unit
Shorter construction period	Lower financial cost
Capacity utilization	Higher
Unit depreciation	Higher
Maintenance cost	Lower (spare parts locally produced)

Offsites:

Cost Item	Large Scale	Small Scale
Distribution cost	Higher	Lower
Produced grades	Limited	Wider split
Commercial chain	Long	Short

capital more quickly, thus influencing positively the discounted NPV.

2. Higher capacity utilization of the small-scale plant. Three factors influence this feature. They include (a) an available market, (b) available infrastructure for small-scale distribution, and (c) shorter plant shutdowns because of operational difficulties.

   This is especially true during the startup and the first 3-4 years of operation when the on-stream factor (40%-50% denoted for large-scale plants) has a consequent disastrous effect upon revenue, earnings, and profitability.

3. Lower costs of spare parts (partially produced in the country).

4. Lower cost of expatriate personnel and training costs of local personnel.

In addition, the skid-mounted "serial" installations concept (sometimes called modular) was practically applied. The installation is constructed at the industrialized area in the form of modules and later transported on barges to the operation area. This is especially important in cases where the small-scale plant is constructed in a remote place without the necessary industrial infrastructure. Standardized plants using skid-mounting will have a positive impact on short-time leads, lower engineering costs, ease of training, quicker startups, and more precise prediction of the construction costs. However, transportation difficulties and potential damages to the equipment and piping/instrumentation excluded this concept from wider implementation.

20.4.1.4 Production of Multicomponent Fertilizers in a Moderately Centralized Manner – A moderately centralized production alternative assumes the establishment of large- (medium) scale complex producing multicomponent fertilizers. All raw materials must be transported to the large industrial complex, and also large amounts of complex, multinutrient fertilizers have to be transported to the farmer. The number of alternative grades is obviously limited; therefore, only a general application system has to be applied. Fertilizer production takes place at long distances from the consumer market. Extension services of ministries of agriculture (MOA) would serve as intermediaries between the producer and farmer. Industrial structures that must be developed include: a system for transporting raw materials to the large-scale fertilizer factories, large-scale complex fertilizer factories, a transportation system between factories and intermediate regional storage warehouses, a transportation system between local distributors and their storage facilities, and MOA extension services or dealers.

Multinutrient fertilizers offer a number of agronomic and logistic advantages; therefore, they have largely replaced straight fertilizers for the purpose of basic fertilization. Among these advantages are a simplified and reduced workload for farmers, a more uniform nutrient distribution in the field, and easier logistics at the distribution/purchase level. However, different methods of producing multinutrient fertilizers have a theoretical and practical impact on fertilizer efficiency. The technology of producing complex fertilizers is described in relevant chapters.

The early fascination with complex fertilizers has been presently moderated. The seasonal requirements of the crops are different, and the optimum ratio of NPK also differs substantially. Therefore, more and more often options of establishing local granulation plants to meet the requirements of the local agriculture are discussed.

20.4.2 Raw Material Resources

Raw material resources and the location of their deposits have been discussed in detail in Chapter 5. In this chapter only problems related to planning the development of the fertilizer industry in a given country will be discussed. In fact, the availability of national raw materials is not a condition of the establishment of the local fertilizer industry. Many countries import natural gas, phosphate rock, and potash and are competitively producing fertilizers. Actually, import of intermediates (ammonia, concentrated phosphoric acid) is also possible at a large scale and at competitive prices. Therefore, fertilizer production should be established in cases where imported fertilizers (bulk or bagged) would be more expensive to the farmer than locally produced materials. The possibility of producing more cheaply depends on the implementation of modern technology that is competitive to the world average, lower cost of energy due to local energy production (e.g., hydropower), lower labor costs, and lower logistic costs.

Obviously if a country possesses natural gas resources, which have already been exploited, the advantage of producing ammonia would increase and perhaps fertilizers could also be exported. The cyclic fluctuation of ammonia prices originates from voluntary investment decisions that create oversupply and low prices. Less efficient plants are closed, and a supply deficit occurs, which causes prices to rise. Higher prices stimulate new capacity, but up to 3 years is required to plan, build, and start up the new plants.

Establishment of the phosphate mining and beneficiation operations only for one medium-size plant may not prove competitive with imported phosphate raw materials. Therefore, countries with large phosphate rock deposits have developed national industries that export phosphate rock, phosphoric acid, and fertilizers. These industries would supply the world market with stable volumes of raw materials at comparatively stable prices. A similar situation exists with beneficiation of potash and potash muriate.

20.4.3 Location of the Fertilizer Plant

Kendrick and Stoutjestijk [17] in 1978 developed uniform, computerized methodology for selecting a plant location and provided examples of optimal locations for Egyptian fertilizer industries. The linear model considers all production and logistic costs of raw material supply and product distribution. Similar models have been widely used [18]. It has been proven that fertilizer plant location depends on the product and the location of raw material resources. Low nutrient-containing fertilizers should be produced near the users' area (e.g., SSP, ammonium carbonate, ammonium sulfate). High-nutrient fertilizers, in particular phosphate fertilizers, should be produced as near as possible to the raw material source to minimize transportation costs. In many cases it would be feasible to produce ammonia and concentrated phosphoric acid in a "mother" plant and process intermediates into fertilizers in small granulation plants, providing fertilizers to meet the requirements of local crops. In the case of imported sulfur and phosphate rock, the plant may be located near port facilities. The origin of natural gas is not as critical because pipe transportation of natural gas is much cheaper than transportation of bulk fertilizers.

The availability of utilities, such as water, steam, electricity at the selected location, presents an advantage. Fertilizer plants use much energy and water and dispose substantial amounts of wastewater. The consumption of external energy also depends on the production structure of the plant. Sulfuric acid production may provide steam and energy to a phosphoric acid plant, and a nitric acid plant may provide energy and steam to an ammonium nitrate plant. In any case the establishment of the fertilizer complex near existing electric power stations provides a better opportunity for process selection and optimization of overall energy use. Establishing utility installations for the fertilizer plant alone would increase a plant's investment cost by 30%-50%, as compared with locating it near developed infrastructure. Environmental protection units are cheaper when joint (industrial and communal) water treatment stations are constructed or utilized. In many cases, industrial wastewaters from fertilizer plants provide the feed for active bacteria in the treatment of communal sewage waters.

Some elements of plant location are related to site parameters. A complex fertilizer factory may require 25-60 ha of land surface; therefore, the land cost would be an important investment element. The problem of property is also crucial and very much depends on local regulations regarding converting from agricultural to industrial use of land. The local community may have problems accepting the location of a plant near dwellings; sometimes protests are raised only after a plant has been constructed. Therefore, the investor must consider this sociopsychological element and advertise the construction of a plant in advance to achieve a general consensus.

The soil's character and the underground water level are important factors. High water levels and heavy soils could increase plant construction costs by 7%-12% in comparison with light sands with low water levels.

Existing transportation infrastructure, such as road networks, navigable rivers, and railways, presents a great advantage for locating a fertilizer plant. Today even medium-scale plants should expect to transport more than 1 million tonnes of material per year. Therefore, access to a transportation network is very important for investment costs and future farm-gate fertilizer prices. Construction of a 1-km (6-m width) road may cost from US $1-3 million, and no investor would be able to recover these costs from the profits of fertilizer production. Construction of railway or port facilities should always be considered infrastructure development, which is not the duty of a private investor.

Labor availability and education level are two of the most important elements of selecting a plant location. Construction of a plant in an uninhabited area requires construction of the towns with dwellings and all the necessary infrastructure. Today, the selection of a location in an uninhabited area is rather unlikely, except in the case of an industry/energy linked closely with natural resources; however, it was very common in the 1950s and 1960s in many countries. On the other hand, a plant should be located outside the safety zone of the inhabited areas, also taking into consideration future community development. The community in which a plant is to be located should at least have a high school and a developed system of professional training. It has been proven by multiple examples that the higher the general civilization level of the community in which a plant is located the sooner the plant will achieve full capacity, and it would be less likely to sustain industrial accidents. Investors should consider the means to recruit professional staff. The problem with professional staff recruitment is always less acute when a plant is located near a city with general infrastructure, and staff may decide to settle there for a longer period of time. In principle an investor must provide professional staff with expensive specialized training abroad; therefore, stability of the professional staff also represents a substantial cost saving. General industrial infrastructure in a selected location is important from the perspective of plant operation. In cases of poor industrial infrastructure, an investor must consider establishing a maintenance workshop, which requires additional employment, machinery, and buildings. When the industrial infrastructure is sufficient, all maintenance work and the production of selected spare parts could be subcontracted on a competitive basis. An assessment of these elements of selecting a location has often produced the so-called "Newton's law of location," which states: "The force of attraction of location for industrial development is proportional to the size and diversity of its infrastructure."

20.4.4 Optional Government Policies

There are many types of government policies, but basically they are indirect and direct involvement. Indirect involvement relates to the establishment of a political atmosphere supporting increased food production using different means such as fertilizers. This indirect involvement includes the establishment and operation of research and development programs related to soil fertility and increased crop production. This is realized by the establishment of an agricultural research institute and agro-extension services within the MOA. An extension service that has local laboratories should be authorized to control and certify fertilizer quality (imported or from a local dealer network). Indirect involvement also includes promotion and support of farmer education and local organizations, publication of the agricultural research results, promotion of the use of agricultural inputs, the organization of countrywide competitions and prized expositions, and support of local financial institutions (cooperative banks and cooperative trade organizations). Indirect involvement likewise includes the establishment of the stock exchange(s) for agricultural inputs and for agricultural products with the possibility of concluding future transactions. In addition, support of the organization of a dealer network by training and credit to establish the trade infrastructure would avoid the establishment of a local parastatal or private distribution monopoly.

The direct involvement of the Government is controversial. A liberal policy promotes the position of total Government neutrality concerning agricultural production and applied inputs; however, this theoretical position is not practical in industrialized countries that provide direct financial support to agricultural prices. The system of subsidies used by the European Union countries and the United States is very complicated and perhaps should not be reproduced in developing countries. It is not the purpose of this manual to discuss these systems. However, all countries should consider the possibility of introducing selected policy instruments of direct involvement to stabilize agricultural production in the country, which would also influence the worldwide food situation.

Direct involvement is related to the following policies [8]:

1. Establishment of an agricultural fund as a public (or mixed) trading organization. The task of the fund is to buy agricultural products when prices are declining, endangering farmers' income and their intentions to produce in the following season. The fund would sell the products at the change of seasons when prices of food products on the market are increasing. Therefore, the fund plays a double role – ensuring the stability of farmers' income parity and ensuring the stability of food prices at the local market in the interest of the population. The regulatory role of the prices of imported agricultural products is reduced because food production in developing countries is less costly than in international markets, even considering the export price subsidies.

2. Establishment of an agricultural credit system to facilitate the access of credit to farmers. Considering the seasonal nature of agricultural production and the risk factors, credit facilities should offer preferential interest rates to farmers. The difference between the market interest and agricultural credit cost should be financed from the profits of the agricultural fund or

directly from the budget. Repayment of the debt should be allowed in the form of products supplied to the agricultural fund.

3. Establishment of a comprehensive, flexible system of custom duties. The role of custom duties is to motivate local production at a competitive level inside the country; the export subsidies of other countries should be considered; however, the market should be open to process imported raw materials and exported products.

4. Direct support to establish the fertilizer industry. The fertilizer industry, as a raw material processing branch, is highly capital-consuming with a smaller return on investment than many other industries. Therefore, if the establishment of the fertilizer industry in a country has shown strategic values, the Government should consider two options of support: (a) establishment of a parastatal shareholding company and construction of a plant from budgetary sources or using international financing. At the latter stage the company could be privatized either by selling it to a strategic investor or by the sale of stock exchange shares; (b) establishment of a joint venture between public and private capital (also foreign) and issuing Industrial Development Bank guarantees to financial institutions. In this case, preferential interest rates could be considered for the local financing. Imported equipment and materials could be free from custom duties and other local taxes; and (c) establishment of a preferential industrial situation allowing a private investor to undertake the establishment of the fertilizer plant. This requires the establishment of long-term tax relief, opening local credit facilities with preferential conditions, government-financed technical support for the investor, and special customs arrangements for imported equipment and materials for export of the product at the first stage of plant operation when demand would not be equal to plant capacity.

   The option should be selected on the basis of a detailed economic and financial study covering macroeconomic factors (e.g., food self-sufficiency, foreign trade balance, export promotion, employment, and use of local resources).

5. Direct support to the marketing and distribution system. Establishment of regional trading companies (public or mixed). Initial investments should be organized on preferential conditions similar to those of fertilizer plant establishment.

20.5 Paving the Way to Plant Operation

There are numerous publications dealing with industrial plant construction processes; therefore, the decisionmaker is reminded of the crucial elements of this process.

20.5.1 Decisionmaking Stage

Search for the optimum solution should be performed to show the investor, Government departments, all financial authorities, and other economic institutions the alternatives and consequences at each decision stage. Therefore, three stages of study leading to positive conclusions and allowing a consensus to be reached regarding the construction of a fertilizer plant among different groups can be delineated as follows:

1. Programming study composed of at least the following elements:
   - Review and evaluation of the present and forecasted demand by type of fertilizer, related to the types of soils and crops.
   - Review and delineation of present sources of fertilizer supply and an assessment of the adequacy for future consumption.
   - Review and evaluation of the logistic and financial costs of the present and future modes of fertilizer supply to the farmer and society.
   - Establishment of a credible forecast of regional fertilizer consumption.
   - Evaluation of the cost:benefit application of increasing amounts of fertilizer and delineation of the policy measures necessary to increase demand.
   - Assessment of the availability of raw materials by quantity, quality, and regional distribution.
   - Evaluation of the cost:price situation in different raw material deposits.
   - Technological profiles of the fertilizer production processes, allowing evaluation of technological, technical, and economic features.
   - Review and evaluation of the location of a potential fertilizer installation, accounting for market and raw material availability and other physical and economic factors of plant location.
   - Specification of potential investment projects in hierarchical order:
     - Basic products (ammonia and phosphoric acid).
     - Other products (urea, DAP, CAN/AN, etc.).
     - Final NPK compounds and compositions (granulation compounding installations).
2. Study of the optimization and selection of priority projects (composed of the following elements):

- Establish criteria and policy measures necessary for project selection.
- Prepare econometric model of fertilizer production/distribution.
- Prepare the development scenarios.
- Assess and evaluate the scenario's features by simulation experiments.
- Assess the project's priority taking into account production, distribution, and consumption features in the forecasted period.
- Select priority projects.
- Propose a strategy for fertilizer market development and establishment of an effective distribution network, promoting regional fertilizer consumption.
- Establish the methodological capability to continue studies for future projects.

3. Feasibility study of the selected priority project. The feasibility study should be prepared according to the UNIDO manual on project preparation, evaluation, and financing [19].

20.5.2 Contractual Arrangements

Establishment of a fertilizer plant in most cases is based on technical assistance and design and delivery of the equipment from industrialized countries. Therefore, the conditions outlined in the contracts are important for the project's success. UNIDO also has developed a standard format for contractual arrangements between licenser, contractor, and investor to facilitate the negotiations and organize the transaction in a fair manner [20]. Very few developing countries can organize and manage construction of a fertilizer plant using national staff (e.g., provide technical design, produce/purchase equipment, and supervise the construction and startup). Therefore, in practice a local investor selects the general contractor from engineering/contracting companies in industrialized countries having a good reputation in the industrial specialization required to implement the project. Although it is not the task of this manual to discuss advantages or disadvantages of different forms of contracted execution of the fertilizer plant, the principal forms of contracts will be identified. There are three typical patterns of contracting construction of the fertilizer plant.

1. ***Cost Plus Fee Contract*** – After the investor selects the technology and purchases the licenses and basic engineering, the contract is executed with the general contractor for a complete set of services necessary for the construction of the plant. The contractor is paid either a firm fee for all services budgeted or a percentage over the realized services. Selection of this type of contract ensures the competition of the construction on time and budget only when an investor has enough qualified staff to control the subcontracting process, has a good review of the equipment and services market, and is able to coordinate the civil works. During the implementation of the project, permanent bidding for all equipment and services is carried out, which at certain times may lead to the establishment of the "zoological garden" of types and trademarks of equipment in the plant leading to negative consequences for maintenance services. An investor is obliged to train the labor and staff in plant operation and maintenance.
2. ***Equipment and Services Contract*** – This contract is concluded with an engineering/contracting company from an industrialized country after selecting the technology. All supplies and services are listed in the contract, and a firm price is decided at the signing of the contract (in some cases a price escalation formula is also agreed upon). The civil works are executed by local companies based on competitive bidding, using the technical documentation prepared by the general contractor. However, because the design of civil works could be available at the end of the overall engineering process but should be first at the construction site, a realistic timetable for the documentation supply and overall construction period should be decided. In many cases at the beginning of the construction, the civil work companies are employed on the basis of cost reimbursable contracts, using piecemeal documentation for foundations, underground piping, and building structures. Five to seven revisions of different documentation elements with necessary changes in executed works should be obtained from the general contractors. The investor should have a national professional team capable of supervising and coordinating the construction, basically on the civil works and assembling sites. The investor is obliged to train labor and staff in plant operation and maintenance.
3. ***Turn-Key Contract*** – The contract is concluded after the technology has been selected. This is a firm price contract (with a possible price escalation formula) for all deliveries and services including civil works, startup, and guaranteed test runs of the complete fertilizer plant. The contract preparation requires a large volume of work and time to define the scope and specifics of deliveries and services. The investor has little involvement in the construction process; primarily the investor concentrates on training the labor and staff for plant operation and maintenance.

20.5.3 Project Implementation

The process of contracting and designing the fertilizer plant is complex, and timely implementation of the project requires an experienced staff and good management of the project. Before the feasibility study is completed, offers from licensers and engineering companies (which also normally undertake the function of the general contractor to supply a complete set of equipment) should be collected. However, this process should be divided into two stages:

1. Collection of the preliminary offers from a wide range of suppliers. The offers are not addressed to a specific location but present only the basic technological issues. The investment cost for "battery limits" is provided with low accuracy; these offers serve for preliminary selection of a few (two-three) suppliers of each process.
2. Collection of the final offers will serve as the basis for contractual negotiations. The preparation of the final offer may cost US $150,000-$200,000; therefore, the inquiries must be detailed and well prepared, and the amount of investment should already be decided by the investor. Otherwise, the engineering company may ask for reimbursement of the cost of proposal preparation if the plant is not constructed. Preparation of a full-fledged inquiry requires the preparation of a detailed locational study, definition of the standards for equipment execution, indication of local safety regulations, an estimate of labor efficiency, and definition of the climatic conditions.

For the purpose of preselection and final selection of the supplier, a uniform methodology of assessment should be developed and approved by the decisionmaker. Then the final offers may be requested. The activities related to the preparation of inquiries and offers may require 9-18 months. The data received from the offers should be included in the feasibility study. The feasibility study will serve as an instrument for negotiating loans from banks and other financial institutions. The contract is prepared and negotiated. It is not advisable to have the supplier prepare the contract. The UNIDO format for contracts should be adjusted to local conditions and the type of contract, and the contract should be negotiated. The local team of negotiators should be established with precise terms of references. Although the contract is an entity, in principle, negotiations are carried out in two stages: a technical part and a commercial part. During the negotiations all annexes are completed using information from offers and additional information supplied by the contractor. In principle negotiations should be carried out with at least two competing contractors. The final contractor selection is made on the basis of a comparative evaluation of the prepared contracts. The evaluation should be prepared by an external group to the negotiation team. The methodology of the comparative evaluation should be approved by a decisionmaker before the startup of negotiations. After the contract with the equipment supplier has been signed, the following implementation procedure is performed:

1. Preparation of the basic engineering (licenser and general contractor).
2. Preparation of the civil works engineering data (general contractor).
3. Preparation of the inquiries for the civil works execution (investor).
4. Preparation of the technical design (general contractor).
5. Subcontracting the equipment deliveries (general contractor).
6. Conclusions of the civil works contracts (investor).
7. Site preparations (investor).
8. Construction (investor).
9. Deliveries and services (general contractor).
10. Startup of operation and guarantee test run (general contractor).

The 3-5 years' duration of the fertilizer plant construction after the contract is signed should be considered realistic, depending on the contract scheme and the local infrastructure. An adequate financial scheme should be developed to minimize credit costs.

All of the activities on the investor side would require a special department to be organized within the company. The typical composition of this department is as follows:

- Planning and coordination section including supervision of contract implementation (computerized control systems).
- Documentation section.
- Technical supervision section, including quality and safety control.
- Materials handling and storage (computerized control system).
- Finance and accounting section (computerized control system).
- Technological section.
- Recruitment and training section.

Experience shows that a minimum of 24-35 staff should be employed in the fertilizer plant construction department at the beginning; this number would be increased later to the full operational plant assignments.

Different types of multiple tasks – technical and managerial – require special training of the investor's personnel. However, practical experience in plant construction cannot be substituted by any kind of training; therefore, recruitment of expatriate personnel in "seed" positions is recommended when the local professional market cannot provide enough specialists.

Technical assistance provided by experienced experts from international organizations is highly recommended. Professional staff working under the auspices of UNIDO could be recruited from among the best multinational specialists in each activity area. Therefore, their advice would be neutral and would always consider the investor's benefit. On the other hand, UNIDO could also provide training of the investor's staff in a similar plant construction abroad.

The managerial capability of the investor organization is a deciding factor in the success of the fertilizer plant construction.

20.6 References

1. UNIDO. 1988. *Guidelines for Industrial Planning in Developing Countries*, Vienna, Austria.
2. Kopytowski, J. A., and M. Zébrowski. 1989. "MIDA: Experience in Theory, Software and Applications of Decision Support Systems in the Chemical Industry," IN *Lecture Notes in Economic and Mathematic System*, A. Lewandowski and A. P. Wierzbicki (Eds.), pp. 271-287, Springer Verlag, New York, NY, U.S.A.
3. The World Bank/FAO/UNIDO/Industry Fertilizer Working Group. 1991. "World and Regional Supply and Demand Balance for Nitrogen, Phosphorus and Potash," World Bank Technical Paper N144, Washington, D.C., U.S.A.
4. Ahmed, S. 1994. "The Needs-Based Approach for Projecting Long-Term Fertilizer Demand," Private Communication, Paper presented at APO-RSI Seminar on Fertilizer Policy, Manila, Philippines.
5. FAO. 1988. *World Agriculture Towards 2000*, Alexandrotos, N. (Ed.), Behaven Press, London, England.
6. FAO. 1988. *World Agriculture Towards 2000*, Country Tables, (unpublished), FAO Global Perspectives Study Unit, Rome, Italy.
7. UNIDO. 1990. "Industrial Development Strategies for Fertilizer Industrial Systems in Africa," (unpublished), Programme Development Support Unit, Vienna, Austria.
8. Mudahar, M. S. 1984. "Fertilizer Prices and Subsidies Policy," (unpublished), IFDC Fertilizer Marketing Management Programme, IFDC, Muscle Shoals, AL, U.S.A.
9. Survo, I. 1993. "Economics of Balanced Fertilizer Use," IN *Proceedings of the Regional FADINAP Seminar on Fertilizers and Environment*, Bangkok, Thailand.
10. FAO. 1981. "FAO Fertilizer Programme: 20 Years of Increasing Crop Yields, 1961-1981," Rome, Italy.
11. *Agri-Chemicals, News in Brief*, ESCAP/FAO/UNIDO. 1990. ESCAP UN Building Bangkok, Thailand.
12. Ministry of Agriculture, Government of Thailand. 1984. "Agricultural Statistics of Thailand Crops, 1982/1983," Ministry of Agriculture and Cooperatives Agricultural Statistics, No. 202, Bangkok, Thailand.
13. Kopytowski, J. A. 1990. "Methodological Note on Projections of Fertilizer Demand and Cost:Benefit Ratios," Paper presented at APO-RSI Seminar on Fertilizer Policy, Manila, Philippines.
14. IFDC-Africa and Agricultural Economics Research Institute, LEI, 1988-90. Reports of annual meetings of AFTMIN, Lomé, Togo.
15. *Fertilizer International*. 1994. 335:8, British Sulphur, London, England.
16. Davister, A. 1991. "Technological Options for Construction of Fertilizer Plants – Miniplants," UNIDO-NFC Pakistan Workshop on Appropriate Strategies for Fertilizer Technology and Development, Lahore, Pakistan.
17. Kendrick, D. A., and A. J. Stoutjestijk. 1978. "The Planning of Industrial Investment Programmes," Volume I, Johns Hopkins University Press, Baltimore, MD, U.S.A.
18. Skocz, M., M. Zébrowski, and W. Ziembla. 1989. "Spatial Allocations and Investment Scheduling in Development Programmes," IN *Lecture Notes in Economic and Mathematic Systems*, A. Lewandowski and A. P. Wierzbicki (Eds.), Springer Verlag, New York, NY, U.S.A.
19. UNIDO. 1979. *Manual on Feasibility Studies Preparation*, United Nations, New York, NY, U.S.A.
20. UNIDO. 1984. *UNIDO Model Form for the Contracts of a Fertilizer Plant*, Vienna, Austria.
21. *FAO Yearbook*. 1994. Vol. 48, Rome, Italy.
22. *FAO Yearbook*. 1994. Vol. 44, Rome, Italy.

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Chapter 21. Economics of Fertilizer Manufacture

21.1 Introduction

The capital-intensive nature of fertilizer production, combined with seasonality and uncertainty of demand and international prices, requires careful evaluation of the financial and economic viability of industry investments that form an essential part of both an individual firm's operations and national economic development programs. For the individual firm, the investment opportunity objectives should always be the best alternative use of funds for both the immediate and long-term benefit of stakeholders – private and public equity holders, farmer customers, employees, and society at large. The long-term nature of fertilizer sector investments and the continuing need for increased fertilizer supply mean that each firm must generate sufficient capital formation through retained earnings, new equity, and attractiveness to lenders for sustaining business growth, improving efficiency, and replacing assets.

From the viewpoint of national economic development, complete appraisal of a project should encompass at least six areas of analysis: sectoral framework; market analysis; process technology; project scope; management and personnel; and finance and economics [1]. Sectoral framework analysis assesses the impact of sectoral and macroeconomic policies on the project and the impact of the project on sectoral development. This chapter is not intended to provide a complete guideline to project appraisal and evaluation, as there are many comprehensive published references available [2,3,4]. Rather the purpose is to provide a guide to the structure of fertilizer production economics and investment cost.

Commercial profitability analysis is the first step in the economic appraisal of a project from a national viewpoint. It is concerned with assessing the feasibility of an investment based on its likely financial results for the individual firm. This analysis comprises two parts: (a) investment profitability analysis and (b) financial analysis. These are complementary and non-substitutable. Investment profitability analysis is a measure of the return on a capital investment irrespective of the sources of finance. Financial analysis takes into consideration the sources of finance and disposal of the net cash flows that accrue to service the finance in a manner that allows smooth implementation and operation of a project. Figure 21.1 summarizes this dichotomy.

The range of national development objectives, both economic and social, also varies widely between countries and over time. This requires a standard analytical format in order to make comparisons between alternative investment projects. Although many national objectives often cannot be measured in monetary terms and for this reason are not directly comparable, economic evaluation attempts to identify as much as possible the

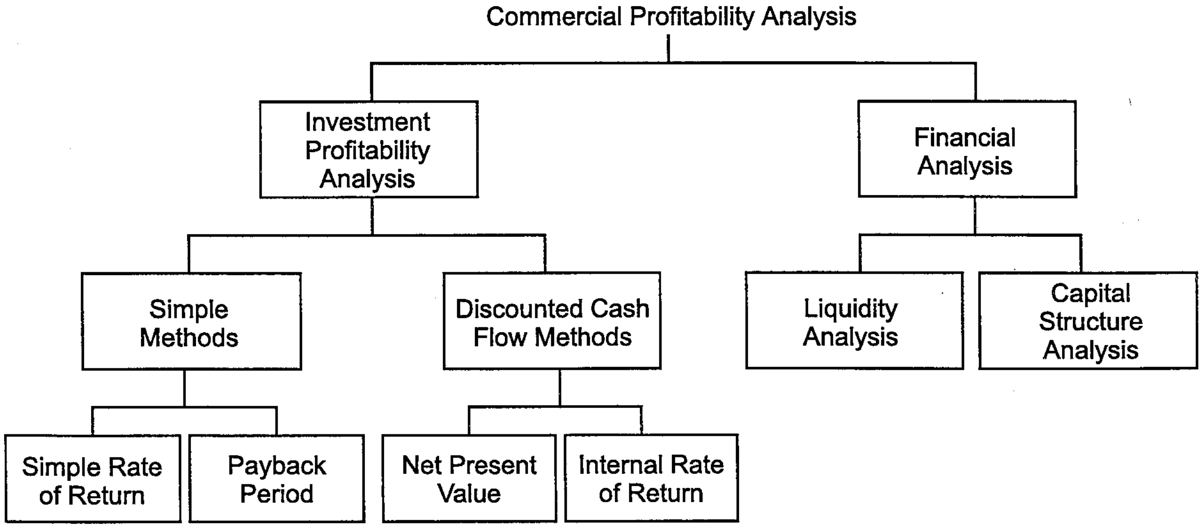


Figure 21.1 Commercial Profitability Analysis.

relationship between national development objectives and the measurable characteristics of individual investment projects.

21.2 The Structure of Investment Cost

A business strategy is essential for both the preparation and evaluation of an investment project and the development of a marketing strategy. A business strategy has a determining impact on the choice of location, technical plant parameters, and resource requirements [2]. Alternative project strategies should encompass business objectives, cost and price competitiveness, product quality differentiation and positioning in target markets, and marketing structures. Market research examines a preliminary project strategy from the marketing point of view to identify alternative strategies and is an essential early requirement in the prefeasibility research for an investment project. This market research should encompass the following:

- Assessment of the target market structure.
- Customer analysis and market segmentation.
- Analysis of distribution channels.
- Analysis of competition.
- Analysis of the socioeconomic environment including government policies.
- Projections of marketing data, including gross product demand, sales forecasts, and prices net of discounts.
- Risk analysis.

When alternative strategies have been identified and the scope of projects established, preliminary cost estimates for the investment project alternatives can follow for opportunity or prefeasibility studies, together with a preliminary **Environmental Impact Assessment**. Reliability of capital and production cost estimates increase as projects progress from one stage to the next. Acceptable ranges of reliability are:

Opportunity study	+/- 30%
Prefeasibility study	+/- 20%
Feasibility study	+/- 10%

In the development of investment cost estimates the following terms are used.

Erected Battery-Limits Plant is the main production unit and includes all process equipment, delivered and installed, with all instrumentation and controls, piping, and electrical tie-ins. Battery-limits takes its name from the concept that the main production unit lies within boundaries or limits that raw materials, catalysts, chemicals, utilities, product and byproducts must cross.

Utility Facilities are the facilities required to support the battery-limits plant. This may include water treatment, steam generation, electricity, and cooling for process water and waste water treatment. Utility facilities support production. Utility facilities can range from 35% of the battery-limits plant cost for grass-roots installations to 10% for an addition to an existing production site.

Raw Material and Product Storage are on-site storage facilities for raw materials and for product. Commonly, when on-site storage is required, storage capacity is provided for 30 days, or more, of raw materials or product. Typical storage investment costs are $90/t of material for bulk storage and $140/t for bagged material. If dehumidified storage is necessary, these costs are about 10% higher.

General Service Facilities are nonproduction facilities, and include administration buildings, security fencing and lighting, fire-fighting equipment, laboratories, maintenance shops, and change houses for personnel. General service facilities can typically range from 15% of the total battery-limits plant, storage, and utility facilities for a grass-roots installation to 5% for an addition to an existing site.

The **Total Installed Cost** is the sum of the costs for the battery-limits plant, storage, utilities facilities, and general service facilities.

Other Cost Components include (a) owners' **Project Management** cost, which includes technical and economic feasibility studies, environmental impact studies, plant site selection, land procurement, financing negotiations, preparation of technical specifications, selection or recommendation of contractors, and contract negotiations; (b) **Preoperation and Startup Expense**, which provides for the costs incurred between the end of construction and the production of a quality product at design capacity; and (c) **Spare Parts.**

Preoperation expenses include training of personnel, testing equipment and instruments, and adjusting or modifying the process. The time and expense depend on the complexity of the plant and the maturity of the technology. Typically these expenses can be between 6% and 10% of the combined capital investment for battery-limits plant and utility facilities.

A supply of spare parts is necessary for maintenance and repairs. The amount of spare parts in inventory depends on availability. In industrialized countries, spare parts investment can generally be small, but in developing countries a larger inventory is often required. Typically, spare parts can range from less than 2% of the total cost for a battery-limits plant and utility facilities in an industrialized area to 4% in developing countries. The investment in spare parts is sometimes included in working capital. After construction is complete, the **Initial Charge of Catalysts and Chemicals** is placed in the plant. These form part of the operating expenses and not initial capital investment; however, when there is a likelihood of rapid consumption, a complete spare replacement may need to be in inventory. Such inventory forms part of the working capital, not the investment capital.

When a paid-up or lump sum **royalty** is paid to the owner of a process technology, this forms part of the capital investment. Running royalties based on production form part of operating costs. From project initiation through construction and startup of a plant, capital costs are incurred. Usually the funds to pay for these costs are borrowed, and interest charges are incurred. These **Interest Charges During Construction** are considered part of the capital investment. Interest during construction is dependent on the interest rate, the length of the construction period, and when funds are borrowed. For simplicity, it is usual to calculate interest during construction as though funds were borrowed from the mid-point of construction.

The **Total Fixed Investment** is the total capital cost of the plant. It includes land, the battery-limits costs, storage, utilities and general service facilities, spare parts, preoperational and startup cost, project management and interest during construction. The **Total Depreciable Fixed Investment** excludes the cost of land, which is not a depreciable cost item.

Working Capital is the capital required to fund operations over and above the fixed investment capital in land, buildings, plant and equipment. It is the capital needed for cash in hand and to finance inventories of raw materials, work in progress, finished products and spare parts, and accounts receivable less accounts payable. Working capital is part of the investment, and a return must be earned on it. It is not deductible as an expense, and it is not depreciable. It is not part of the startup expenses, which are non-recurring. It is considered a liquid asset that can be converted into a positive cash flow when a project ends. During the life of a project, working capital requirements will vary with production rates, sales levels, accounts receivable management, and other factors.

Total Capital Investment is the total of total fixed investment and working capital.

21.2.1 Estimating Total Fixed Investment

All cost estimates should be made with separation of national currency and foreign exchange components to allow for later economic analysis. Order of magnitude capital cost estimates for a battery-limits plant can be made provided plant capacities are set at fairly standardized levels and prices are available for plant and equipment at such capacities. A schedule for a battery-limits plant investment is prepared for a particular place, time, and capacity as shown in Table 21.1 for an ammonia plant in a US Gulf Coast location in 1994. Cost estimates can be adjusted to account for changes in any of these parameters.

The cost of a fertilizer plant is influenced by location. Cost data are generally available for the United States and for Western Europe but not for developing countries. Costs in developing countries are generally higher because of imported materials and equipment, expatriate labor, and higher engineering and project manage-

Table 21.1. Ammonia Plant Investment Cost

Product Capacity, tonnes/day	Ammonia 1,500
Investment Cost	Thousands US $
1. **Battery-Limits Cost**	**170,000**
2. Raw material and product storage (30 days at $90/t)	4,000
3. Utilities facilities (10% of 1)	17,000
4. General service facilities (5% of 1, 2, and 3)	9,600
5. **Total Installed Cost**	**200,600**
6. Spare parts (4% of 1 and 3)	7,500
7. Preoperation and startup expense (6% of 1 and 3)	11,200
8. Project management (5% of 5)	10,000
9. Interest during construction (18% of 5)	36,100
10. **Total Fixed Investment**	**265,400**

ment cost. Depending on the level of development, the relative location factor with respect to the U.S. Gulf Coast can be typically assumed as follows:

	Location Factor
U.S. Gulf Coast	1.0
Western Europe	1.0
Developing Countries	
Type I	1.10
Type II	1.25
Type III	1.50

where Type I comprises countries already having industrial experience for which outside help consists of supervision and supplying personnel (e.g., Brazil, Venezuela, Mexico).

Type II comprises countries with local labor having good experience in civil engineering and public works and with modern equipment in those fields (e.g., Indonesia, Philippines, Thailand)

Type III comprises those countries where the labor is poorly qualified and where the equipment for civil engineering and erection is nonexistent (e.g., some African countries).

The above factors apply to capital cost of fertilizer projects within 160 km of a major industrial or import center, or both, in the designated country type. Within a country, there may be considerable variations in costs that can be attributed to remoteness. Adjustments for remoteness can be made by increasing the location factor by increments of 10% for each 1,600 km that the new site is situated away from a major industrial or import center.

Factors that influence a capital investment cost estimate over time are inflation, workforce productivity, and changing construction standards. The combined effects of these factors are reflected in widely published indices. The main indices in use are:

Chemical Engineering (CE) Plant Cost, U.S.A.
Chemical Engineering Equipment, Machinery, Supports
Chemical Engineering Buildings
Chemical Engineering, Engineering and Supervision
Chemische Industrie, West Germany
Engineering News-Record (ENR) Building Cost, U.S.A.
Marshall & Swift (M&S) Equipment Cost, U.S.A.
Nelson Materials, U.S.A.
Nelson Refinery Cost, U.S.A.
Process Engineering, United Kingdom
WEBCI, The Netherlands

The U.S. indices are prepared using various price indicators published by the U.S. Department of Labor. The most commonly used indices are the CE Plant Cost Index for plant cost estimates. If the plant cost at some time in the past is known, the equivalent present cost can be determined by multiplying the original costs by the ratio of the present index value to the index value applicable when the original cost was obtained, as follows:

$$\text{Present Cost} = \text{Original Cost} \times \frac{\text{(Present Index Value)}}{\text{(Original Index Value)}}$$

If the cost is known at one capacity, the cost for another capacity can be determined by applying a power factor, for example 0.6, to the ratio of the two capacities and multiplying the original cost as follows:

$$\text{Cost at New Capacity} = \text{Cost at Old Capacity} \times \left\{\frac{\text{New Capacity}}{\text{Old Capacity}}\right\}^{0.6}$$

The power factor method can be applied to individual pieces of equipment, to process units, and to battery-limits plant costs. The use of a power factor requires some judgement. Generally 0.6 can be used as an average for many applications, but the power factor can be as high as 0.8 or 1.0 for such items as multiple units or where costs depend strongly on capacity. The power factor can be as low as 0.0 to 0.3 for very small plants or where costs do not depend strongly on capacity. Some power factors for types of equipment are as shown in Table 21.2. Use of these indices should be checked regularly against prices obtained from tendering.

Table 21.2 Power Factors for Individual Items

Item	Power Factor
Air fin coolers	0.80
Agitators	0.50
Blowers	0.65
Bucket elevators	0.85
Compressors	0.75
Conveyors(belt)	0.85
Conveyors (screw)	0.82
Cooling towers	0.80
Distillation towers	0.70
Drums	0.65
Dryers	0.50
Electric motors	0.80
Ejectors (5 stage)	0.50
Evaporators	0.50
Heaters	0.80
Heat exchangers	0.60-0.95
Instruments and controls	0.00
Piping	0.70-0.90
Pumps	0.60
Refrigeration units	0.75
Screens	0.70
Tanks(carbon steel)	0.44
Tanks (stainless steel)	0.68

Source: J. R. Polo. 1986."Cost Estimates: Definitions, Types, Accuracies," IFDC Fertilizer Process Economics Training Program, June 1986.

Table 21.3. Peters and Timmerhaus Method for Plant Cost Estimates

	Solid	Solid-Fluid	Fluid
Direct Costs			
1. Purchased equipment delivered, including fabricated equipment and process machinery	100	100	100
2. Purchased equipment installation	45	39	47
3. Instrumentation and controls (installed)	9	13	18
4. Piping (installed)	16	31	66
5. Electrical (installed)	10	10	11
6. Building (including services)	25	29	18
7. Yard improvements	13	10	10
8. Service facilities (installed)	40	55	70
9. Land (if purchase is required)	6	6	6
10. **Total Direct Plant Costs**	**264**	**293**	**346**
	(224)[a]	**(238)**	**(276)**
Indirect Costs			
11. Engineering and supervision	33	32	33
12. Construction expenses	39	34	41
13. **Total Direct and Indirect Costs**	**336**	**359**	**420**
	(296)	**(304)**	**(350)**
14. Contractor's fee (about 5% of direct/indirect costs)	17	18	21
	(15)	(15)	(18)
15. Contingency (about 10% of direct/indirect costs)	34	36	42
	(30)	(31)	(35)
16. **Total Fixed Capital (Installed Cost)**	**387**	**413**	**483**
	(341)	**(350)**	**(403)**

a. Number in parentheses represents the corresponding cost without service facilities (i.e., battery limits process unit only).

Source: M. S. Peters and K. K. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 3rd ed., p. 180, McGraw-Hill Book Company, Inc., New York, 1980.

Various factoral methods for estimating costs have been advocated. These include the Lang Method, which varies factors with the type of processing plant: solid, solid-fluid, or fluid plant; the Hand Method, which uses varying factors for equipment grouped by type, such as heat exchangers, reactors, and pumps, and then uses an installation factor for each group of equipment; the Chauvel and Rueil Method, which recommends that an additional size correction factor be applied for equipment cost in mild steel and that the additional cost due to use of other materials of construction be added later to the total installed cost; the Chiltern Method, which begins with the equipment installed cost; and the Peters and Timmerhaus Method, which is a combination of the Lang and Chiltern methods. It is based on delivered equipment cost, but it retains Lang's classification of solid, solid-fluid, and fluid plants. Table 21.3 shows the factors to be used in estimating major process plant additions to an existing site. The factors should be varied within the ranges described previously for different locational and other factors for prefeasibility and opportunity studies. The most accurate estimate of fixed capital investment cost is based on a detailed and complete design of each project component. Competitive quotations are usually not appropriate for a feasibility study but occur during the implementation phase.

The schedule in Table 21.1 uses the battery-limits plant cost as a starting point for determining total plant investment, including all auxiliary and support facilities. These include utilities, storage and handling facilities, and general service facilities. Factoral estimating is used in this example to estimate other investment costs as a percentage of the battery-limits plant cost. Typical factors for auxillary/support facilities added to battery-limits plants for existing and greenfield sites are provided in Table 21.4. These do not include infrastructure and support facilities outside the plant site boundary. These, in developing countries, may include access road and railroads; waterways and harbors; facilities for raw material delivery; employee housing; educational, recreational, and school facilities; temporary housing facilities during construction; and off-site distribution warehouses.

The separate cost estimation of auxiliary/support facilities item by item is a very time consuming and difficult task. However, in certain cases, the capital cost for facilities such as utility and storage facilities can be more accurately estimated on the basis of their capacity and type.

Many auxiliary/support facilities are complex units; in their own way, they can be as complex as the primary production units they support. An estimate starting with item by item equipment design could be as time consuming as the primary plant estimate itself. Fortunately, with available cost correlations, the job of estimating costs associated with steam generating plants, steam-electric generation plants, cooling towers, and ammonia and phosphoric acid storage facilities separately becomes relatively straightforward.

Table 21.4. Ratio Factors for Estimating Auxiliary/Support Facilities Cost

	Grass-Roots Plant	Battery-Limits Addition to Existing Site
Utility facilities (U)		
% of B/L cost		
Low	10	3
Average	20-30	6-14
High	50	30
Storage facilities (S)		
% of B/L cost		
Low Raw material by pipeline, little warehouse space	5	0
Average	15-20	2-6
High	50	20
General service facilities (G)		
% of (B/L + U + S)		
Low	5	0
Average	10-16	2-6
High	25	15

Site Expenses and Preproduction Expenses – Fixed investment expenses also include **site expenses and preproduction expenses**. Site expenses can include the cost of land, site preparation, civil works, engineering and design costs, project design costs, and insurance and taxes related to civil works. Preproduction expenses may include the cost of previous studies, preliminary costs for issuing capital, project and site management, preproduction marketing costs, preproduction implementation costs, personnel recruitment and training, administration overheads, startup and commissioning expenses, and interest accrued during construction. These costs are usually capitalized into the fixed investment cost.

21.2.2 Estimating Working Capital

Estimates of working capital requirements fall into four areas: inventories, accounts receivable, cash in hand, and current liabilities. To estimate these, it is necessary to consider the different production stages in which materials can be found, which are (1) raw materials paid for but not received (a portion of current assets); (2) raw materials on hand but not paid for (a portion of current liabilities); (3) materials in process; (4) finished products in store whether on-site or off-site; and (5) finished products delivered to customers but not yet paid for (accounts receivable). The calculation of the amounts of each of these material inventories depends on such factors as distance from raw material suppliers, types of contracts for raw material purchases, raw material purchase financing methods, quantity discounts and lot sizes available for raw materials, available modes of transportation, cost of storage facilities, plant size and capacity, seasonality of sales volumes, marketing system, and customer credit policies.

In general terms, storage time for raw materials can range from 10 to 90 days, although natural gas supplies from pipelines incur no storage time. Once the total days of storage has been determined for each raw material, the total cost of the raw material is calculated by multiplying the unit cost of that raw material per tonne of finished product by the daily plant production rate and by the days of storage estimated.

The cost of finished product in bulk storage depends on the nature of the material (some materials need curing time before bagging) and on the capacity of the plant. A bulk storage time of about 5 to 20 days is usually assumed. The cost of this inventory is calculated by multiplying the unit production cost of finished fertilizer, excluding bags and bagging, by the daily production rate and by the days of storage estimated.

The size of finished bagged product inventory depends on the capacity of the plant and the marketing system used. An average storage time of 30 days can be used to estimate its total inventory cost, multiplying the unit production cost, including bags and bagging, by the daily production rate and by the days of storage estimated.

The cost of in-process materials is usually small compared to the cost of finished products in inventory. Adding one extra day to the bulk storage estimate is usually sufficient to estimate this cost. When intermediate products such as ammonia, nitric acid, or phosphoric acid are produced for later processing, 5 to 10 days production requirements are usually to be kept in storage.

The cost of spare parts inventory can be estimated at between 2% and 4% of the total fixed investment cost.

Accounts receivable may vary from 25 to 35 days of average daily sales revenues in well-managed domestic marketing systems, but export sales, with long delivery times, may require an allowance of 45 to 60 days for accounts receivable. Many state-owned fertilizer factories operate on a cash-only sales basis, and accounts receivable are not applicable.

Cash-in-hand is often estimated at 5% of the total working capital as calculated above. The calculation of total working capital requirements is dependent on a calculation of production costs.

21.3 The Structure of Production Costs

Production Cost or manufacturing cost is the sum of all of the costs required to make a product. It can usually be broken down into variable costs and fixed costs.

21.3.1 Variable Costs

Variable costs increase with production rate. These costs are computed on a per-unit (usually tonne)-of-product basis. Common variable costs include those of raw materials, chemicals, and catalysts; utilities; and contract labor.

Raw Materials, Chemicals, and Catalysts are usually the most important and largest component of variable cost items. Care should be exercised in calculation. Costs of these should include delivery costs and losses in storage and inefficiencies of the process. The different available supply sources, material specifications, lot quantities, and freight mode should be considered. Estimated raw material requirements for different fertilizer processes are shown in Table 21.5. Operating sup-

Table 21.5. Raw Material Requirements for Selected Fertilizers

Product and Process	Feedstock	Ammonia	Nitric Acid	Carbon Dioxide	Limestone	Sulfur	Phosphate Rock 32% P_2O_5	Sulfuric Acid 100%	Phosphoric Acid 100% P_2O_5
	(Gcal/t)	(t/tonne of product)							
Ammonia									
Natural gas	5.1								
Naptha	5.8								
Fuel oil	7.6								
Coal	9.3								
Ammonium nitrate, prilled		0.210	0.773						
Ammonium sulfate, crystallization		0.258						0.744	
Calcium ammonium nitrate, prilled		0.160	0.590		0.260				
Diammonium phosphate, slurry granulation		0.230							0.470
Monoammonium phosphate, slurry granulation		0.540							0.140
Nitric acid (60% HNO_3) high pressure		0.287							
Phosphoric acid (54% P_2O_5), dihydrate							3.400		
Single superphosphate, run-of-pile							0.626	0.363	
Single superphosphate, granular							0.626	0.363	
Sulfuric acid (93% H_2SO_4) double contact, double absorption						0.340	2.780		
Triple superphosphate, run-of-pile							0.400	0.340	
Triple superphosphate, granular							0.400	0.340	
Urea, prilled		0.580		0.770					

plies can be estimated at about 1% of raw material costs for most processes.

Utilities include electricity, steam, process fuel, process water, boiler feedwater, cooling water, deionized water, compressed air, instrument air, refrigeration, inert gas, and effluent treatment. The unit use is dependent on the process technology, and the cost is site dependent. For each utility, unit use and unit cost should be recorded. The estimated use of utilities for different fertilizer processes is shown in Table 21.6. Some offsite utilities such as electricity are often priced with a fixed cost component and a variable cost component. The fixed and variable portions need to be calculated separately to provide an average variable cost per unit of production for a given annual production.

Care should be taken to avoid double consideration of utilities. For instance, electricity included in the cost of producing steam should not be included as electricity for the process. For utility generation within a process (e.g., steam in sulfuric acid production) a credit should be given to the production cost at the rate it would cost to produce or purchase the utility.

Contract Labor is a variable cost because when production ends the contracted labor is no longer needed. An example could be the bagging operation when it is not performed by plant operators. Bags are also a variable cost.

21.3.2 Fixed Costs

Fixed costs are not readily influenced by the production rate. These costs are usually computed on an annual basis and then allocated to products. The major categories of fixed costs are discussed as follows.

Depreciation is an accounting method used to distribute the initial investment costs of productive fixed assets, except land, over the lifetimes of the assets, which are usually considered as standard financial lifetimes. Depreciation costs are calculated on the basis of the original value of fixed investments, using rates for either straight line, declining balance or accelerated deprecia-

Table 21.6. Utility, Catalyst, and Chemical Requirements for Selected Fertilizers

Product and Process	Electricity	Steam	Fuel	Process Water	Cooling Water Circulation	Pond Water	Boiler Feed Water	Catalysts, Chemicals, and Supplies, 1986
	(kWh/t)	(t/t)	(Gcal/t)	(t/t)				(US $/t)
Ammonia								
Natural gas	35	Self	1.9		166		2.3	3.0
Naptha	50	Self	2.0		166		2.8	3.5
Fuel oil	50	Self	1.4		248		1.3	2.0
Coal	150	Self	–		234		2.1	2.0
Ammonium nitrate, prilled	20	0.20			8			2.5
Ammonium sulfate, crystallization	36			50.0				1.5
Calcium ammonium nitrate, prilled	20	0.20			8			2.5
Diammonium phosphate, slurry granulation	40	0.07	80			43.00		1.0
Granular NPK, steam granulation	24	0.06	120			65.00		0.75
Monoammonium phosphate, slurry granulation	50	0.03	135			43.00		1.0
Nitric acid (60% HNO_3) high pressure	10	-0.04			87		8.5	2.5
Phosphoric acid (54% P_2O_5), dihydrate	150	2.50		7.5	38	130.00		1.6
Single superphosphate, run-of-pile	20					5.00		0.5
Single superphosphate, granular	35	0.055	100	0.085		15.00		0.75
Sulfuric acid (93% H_2SO_4) double contact, double absorption	35	-1.20		0.2	25		1.5	0.5
Triple superphosphate, run-of-pile	20					5.00		0.5
Triple superphosphate, granular	60	0.07	135			60.00		1.0
Urea, prilled	130	1.20			70			1.5

tion adopted by management and approved by tax authorities. Depreciation schedules should be constructed for the battery-limits plant and off-site buildings and structures, for equipment and machinery, and for office equipment. Annual depreciation rates allowed vary for each of these categories. Total annual depreciation costs need to be shown separately from overhead costs so that they can be used for calculation of both unit costs and operating profit and omitted from financial cash flow calculations.

Operating Labor and Supervision include the cost of salaries and wages, premiums, overtime, and benefits (medical insurance, meal allowances, holidays, vacations, reserve for retirement pensions, unemployment taxes, social security taxes). Detailed organization and manning tables need to be prepared including shift operations and specification of requirements for management and for professional, skilled, and unskilled workers. In some developing countries, the availability of professional and skilled workers may require extensive initial training (a pre-startup expense), and in all areas on-going training costs will be incurred as an overhead. Only the direct operating labor and supervision of plants, utilities, and site services are included in this category of fixed production costs. Generally, a good approximation of the required personnel is achieved if the number of actual operating positions is multiplied by a factor of 4.5 for the 40-hour workweek and 3.8 for the 48-hour workweek. These calculations result in the number of operators to cover plant operation on a three-shift-per-day basis, vacations, sickness, and a personnel turnover of 10% per year.

Maintenance Costs consist of the costs for material, craft labor, supervision, and scheduling (often including central machine shops). The relative incidence of these components in the total cost of maintenance is about 50%, 40%, and 10%, respectively. Before a plant is built, the maintenance cost can be estimated by relating maintenance to the capital investment in the battery-limits plant and in the other facilities. The percentage to use for maintenance should be determined for particular plants depending on the process and factors such as materials of construction and environment. In general terms, annual maintenance costs can be estimated at a minimum of approximately 4% of fixed investment cost. For corrosive processes, or those with extensive instrumentation, this figure may be as high as 7% to 10%. In addition, the inventory of spare parts will form part of the working capital requirements, and depreciation of specialized maintenance equipment is included in the depreciation schedule for equipment.

Administration Expenses and Supervision are the costs that are not chargeable to a particular production or maintenance operation. These costs include administration, management, laboratory, accounting, distribution, and marketing expenses for salaries, wages, and benefits, along with annual operating costs. These expenses can equal the cost of operating labor and supervision.

Insurance and Taxes together typically account for 1%-2.5% of the Total Installed Cost.

It is now possible to calculate unit costs of conversion for comparison with sales price per unit. For a single product, project unit costs are simply calculated by dividing total annual production costs by the number of units produced. Unit costs therefore reflect capacity utilization, and this is a critical factor in calculating unit costs. For multiple-product projects without any historical data on which to base fixed cost allocations, it is generally better to only calculate the contribution per unit (sales revenue less variable cost) to covering fixed costs and profit.

21.3.3 Effect of Capacity Utilization

One of the most important factors affecting production cost is the capacity utilization of the plant. Consider a product that has a cost of $150/tonne composed of $75 for variable cost and $75 for fixed cost, when a plant is operating at design capacity, 330 days a year. This may be considered 100% capacity utilization for plants that have outages of 35 days per year for scheduled maintenance. Capacity utilization can be lower or higher than 100%. Lower capacity utilization can be due to operational problems or soft demand for the product. Higher capacity utilization can be achieved by operating more days per year or by operating at rates above design capacity. Variable production costs per unit do not change, but fixed production costs per unit fall as capacity utilization increases, as illustrated in Table 21.7.

21.4 Financial Analysis

Investment has been defined as a long-term commitment of economic resources made with the objective of producing and obtaining net gains in the future. Conventional methods used in comparing annual net profit with capital invested do not take account of the time value of money or risk associated with a project investment. Commercial profitability analysis relies on the use of discounted cash flows to account for time value of money and risk in assessing the comparative profitability of investments. Financial analysis should ensure that the decisionmakers' strategic and profit objectives are fulfilled within the confidence levels of a feasibility study and that identification is made of (1) the most attractive alternative, (2) the critical variables, (3) the flow of financial resources during investment, startup, and operational phases, and (4) the lowest cost financial

Table 21.7 Impact of Capacity Utilization on Average Unit Costs

Capacity Utilization (%)	Variable Cost	Fixed Cost	Average Total Unit Cost
	(US \$/tonne)		
110	75.00	68.18	143.18
100	75.00	75.00	150.00
85	75.00	88.24	163.24
70	75.00	107.14	182.14
60	75.00	125.00	200.00

Assuming that the product price is US \$170/tonne, the production would become nonviable at about 79% capacity utilization.

resources and their most effective use. These objectives are all interrelated.

The **planning horizon** for a project is determined by its economic life, which in turn is determined by factors such as duration of demand, raw material supply, and equipment life and by the rate of technical progress, industry life-cycle, and opportunities for alternative investment. A 15-year planning horizon is commonly used for substantial investments in fertilizer production projects. Construction of a large fertilizer complex may take 2 to 4 years before commissioning. During this time, annual capital investments are made as construction proceeds, and these have to be financed. Usually the funds to pay for these costs are borrowed and interest charges incurred. These **interest charges during construction** are considered part of the capital investment.

The **pricing** of inputs to and outputs from a project is also an important consideration. Prices can be defined as market or shadow prices, absolute or relative, and as current or constant prices. In financial analysis, market prices are used. Market prices are those present in the market irrespective of whether they are determined by supply and demand or set by the government. Current and constant prices differ over time as a result of inflation. Operational and financial cash flows are usually projected using constant prices in the national currency units and with separation of foreign and national currency flows. Under conditions of high inflation, it is preferable to make cash flow forecasts using current or nominal prices and then convert the nominal net cash flow back to a net cash flow in real terms. This is done because, under conditions of high inflation, depreciation is overstated and working capital is understated if all cash flow items are forecast in real terms. Also, for projects dependent on imported raw materials, these costs can be underestimated due to falling exchange rates under high-inflation conditions. When forecasts are made using current prices, anticipated inflation rates should be determined for major cost and revenue items, item by item.

Determing the price of a product which is not on the market can be achieved by utilizing price comparison with imported products on a nutrient basis. For multiple nutrient products, new product prices can be determined by calculating the price based on imported component materials. For example, the price of a new multinutrient product 4:25:8 can be determined as follows:

Imported urea price, US \$220/tonne =

nitrogen unit price, US \$478/tonne

Imported TSP price, US \$280/tonne =

P_2O_5 unit price, US \$608/tonne

Imported KCl price, US \$130/tonne =

K_2O unit price, US \$210/tonne

The assumed minimum price of the 4:25:8 product is calculated as: US \$478 * 0.04 + US \$608 * 0.25 + US \$210 * 0.08 = US \$188/tonne.

Risk and uncertainty have to be taken into account in financial analysis because returns on investments are related to future cash flows. Risk is present when probabilities of outcomes can be assigned on the basis of past performance; when risk probabilities have to be assigned subjectively, then uncertainty exists.

21.4.1 Flow of Financial Resources

From the estimates for fixed capital cost and working capital cost, a schedule of total investment costs can be prepared. Then the sources and costs of financing these investments must be examined in order to prepare a flow of financial resources statement and a debt servicing statement.

Cash flows for a project are either receipts (cash inflows) or payments (cash outflows). For the purposes of financial analysis it is necessary to distinguish between cash flows representing the operation of the project (operational cash flows) and financial cash flows that are related to the financing of an investment. These are defined in the schedule below:

Operational Cash Outflows	Operational Cash Inflows
Increase in fixed assets (investment)	Revenues from sale of fixed assets
	Recovery of salvage values at end of project
Increases in net working capital	Revenues from decreases in net working capital
Operating costs excluding depreciation and interest	Net sales revenues
Marketing expenses	
Production and distribution losses	Other income due to plant operation
Corporate (income) taxes	

Financial Cash Inflows	Financial Cash Outflows
Paid-in equity capital	Dividends paid
	Buying back of shares
Subsidies, grants	Repayments if required
Long- and medium-term loans	Interest paid on loans and other finance costs
	Amortization of loans
Short-term loans and bank overdrafts	Interest paid and repayment of short-term loans and overdrafts
Increase in accounts payable	Decrease in accounts payable

A distinction needs to be made between cash flow statements and financial accounting statements such as balance sheets and income (profit and loss account) statements. In cash flow statements, **expenditures** represent outflows of cash during a given time period, whereas **costs** in accounting statements are not related to an outflow of funds but represent the total expenditures required to produce a product or service during a given period, usually one year. The difference becomes clear when expenditures and costs are compared for raw materials and investment for a given period. Raw material expenditures are related to the purchase of raw materials during a year, but raw material costs reflect the use of raw materials in processing during the year. Investment expenditures are actual cash outflows at a particular point in time, but investment costs are accounted for by depreciating the investment expenditures over a certain period of years in order to apportion investment costs through annual depreciation charges. Depreciation costs are therefore not cash outflows but are a part of annual costs.

Annual debt-servicing costs, excluding amortization (i.e., just interest and finance charges), are also considered as costs, but these are part of the financial cash outflows and should not be considered as part of the operational cash outflows in financial analysis. However, both depreciation and interest costs affect the taxable income level and therefore tax payments and net after-tax income. It is therefore necessary to project annual income statements for the purposes of estimating tax payments prior to preparing a cash flow statement for either financial analysis or discounted cash flow analysis.

Revenues represent inflows of cash and are the opposite of expenditures. **Income** is generally defined as the remuneration received from sales of products or services and is considered **net income** after the related costs and direct taxes are deducted. Income may include interest received and extraordinary income (e.g. sale of assets), but for financial analysis purposes, income, excluding any that is not derived from the productive use of assets, is considered to be equal to revenue. Often simplification is adopted in financial analysis in respect to expenditures and revenues and costs and income, i.e., it is assumed that, on average, the differences between annual revenues and expenditures are the same as the differences between annual income and costs (annual net income) plus annual depreciation charges and finance charges. This simplification is applicable only if there are no significant changes in fixed and current assets.

Both operational and financial cash flows should be estimated on an annual basis for comparative financial analysis over the planning horizon. Financial analysis examines the profitability of an investment both prior to the financing and after financing, using cash flow concepts.

21.4.2 Project Financing

In opportunity and prefeasibility studies, financial analysis is conducted before considering the source of financing a project. However, during these stages the magnitude of capital required is established. How to finance this capital requirement has to be considered in the feasibility study stage.

In general terms, the initial fixed capital investment and the minimum net working capital are covered by a mix of equity and long-term loans and additional net working capital from short- and medium-term loans or from positive net cash flow (equity). Within this structure, various combinations and permutations need to be considered related to cost of finance, financial flexibility, debt service, and taxation. Consideration should also be given to leasing, supplier credits, and other sources of finance. In all cases, a balance has to be struck between equity and debt finance.

The cost of equity capital is determined by the opportunity cost of capital, the expected risks, and the expected benefits other than dividends for shareholders. Equity capital may have dividends related to earnings (ordinary or common shares) or only partially related to earnings (preference shares). Debt service includes both interest and amortization and is a fixed legally binding cost to a firm which has to be paid irrespective of whether the generation of cash is sufficient to meet the annual commitments. The determination of the optimal capital mix is therefore essential when a financing strategy is designed. Two systems of debt servicing are also available; periodic debt service with equal amortization payments plus gradually declining interest; and periodical debt service with constant payments (annuities). The first system requires less total financing cost, but the initial debt-service cost is high. The second system is preferable for a new firm because the initial debt-service cost is smaller even though the total finance costs are higher.

In determining the optimum finance mix, it is useful to examine certain **financial ratios** from the projected balance sheets, income statements, and cash flow statements. The **long-term debt/equity ratio** is an indicator of the financial project risk for both the equity and the loan capital. Because the long-term debt service is a legally binding commitment of a firm, the higher the debt in relation to the equity, the higher is the risk to both the firm and the lender. The ratio also indicates the extent to which the outstanding debt is covered by the assets. For an existing firm, the earned surplus and reserves must be added to the equity capital (net worth) to reflect the true debt equity or **long-term debt/net worth** ratio. A debt/equity ratio for large and medium sized projects is often 50:50, but this is by no means standard. Ratios of 67:33 or 75:25 or even higher can be seen in fertilizer companies in some countries. High debt/equity ratios reflect increases in shareholder leverage because the smaller the equity capital, the higher is the income per share unit. Equity owners therefore favor higher ratios. Generalizations cannot be made, and each case should be assessed on its own merits.

Current ratio is a liquidity measure computed by dividing the current assets by current liabilities; it measures short-term solvency or the ability of a firm to meet current liabilities. Because current assets include inventory that may or may not be convertible into immediate cash, the **quick ratio** is frequently used in addition to the current ratio. The quick ratio is calculated by dividing cash plus marketable securities and discounted receivables by current liabilities. Satisfactory values for these two ratios are 1.2-2.0 for current ratio and 1.0-1.2 for quick ratio.

Long-term debt-service coverage is defined as the ratio of cash generation to debt service, and acceptable ratios of 1.5-3.0 are normally considered sound. Annual net cash flows should always be more than sufficient to cover debt servicing by 1.5 to 3 times.

When financing sources and costs have been determined, then an annual schedule of the flow of financial resources and debt servicing can be prepared.

21.4.3 Cash Flow

The schedules for investment, flow of financial resources, debt servicing, and operational cash flow are combined to provide a cash flow for financial planning, which shows annual cash inflows and outflows including loan repayments and dividends and annual and cumulative cash balances. As is seen in Schedule 8, the total cash inflow includes funds, operational inflows, and other income. This final category includes scrap value, if any, of fixed assets at the end of the project. Total cash outflows include increases in fixed assets, preproduction expenses (net of interest paid), increases in current assets, operating costs excluding depreciation and interest, marketing costs, tax payments, interest payments, loan repayments, and dividends paid. Tax and dividend payments are normally paid in the year following the income year they relate to. This cash flow schedule shows whether the funding for a project is synchronized with funding demand and is then used to prepare the accounting statements and the discounted cash flow schedule.

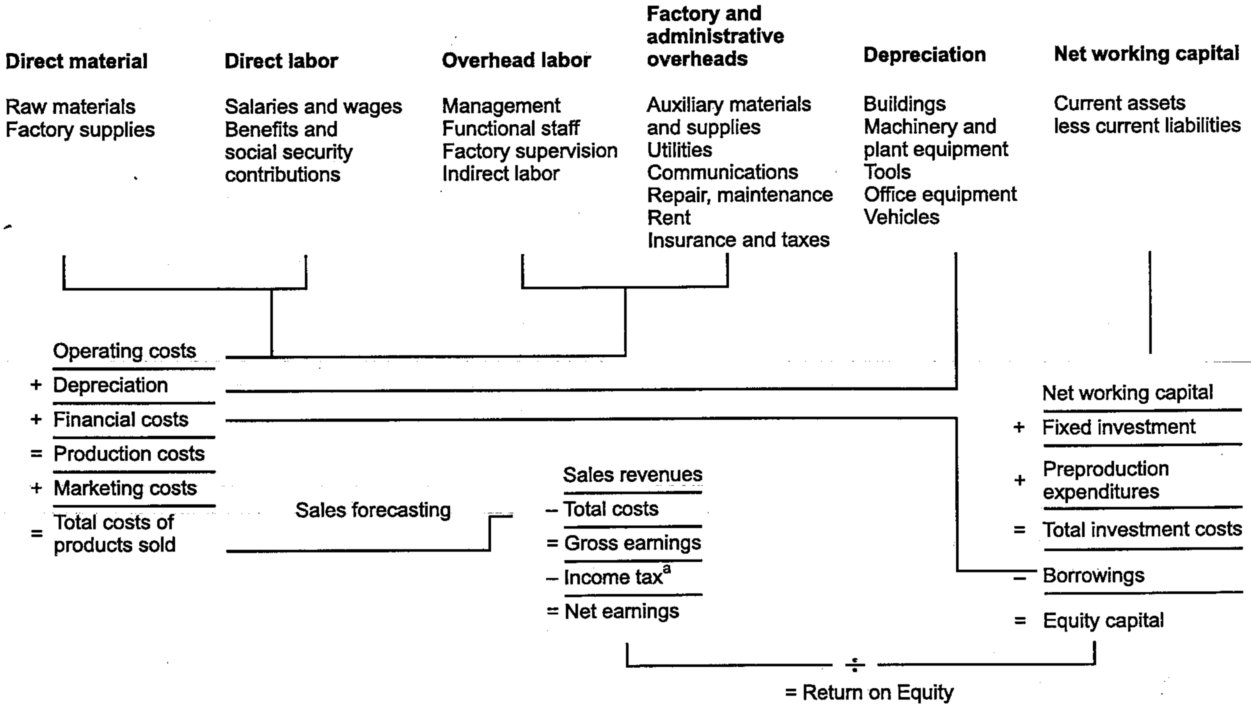
21.4.4 The Net Income Statement and the Balance Sheet Statement

The net income statement is used to compute the annual net income or deficit of a project. The statement differs from the cash flow schedule because it shows incomes and costs and not revenues and expenditures by period. The accrual concept is used in which income from operations is associated with the costs needed to produce the income during the same period. In financial analysis for feasibility studies, it is usually assumed that inventories are the same at the beginning and end of each year. The derivation of costs, revenues, and investments are shown in Figure 21.2. The income statement is related to the balance sheet statement as shown in Figure 21.3 such that the annual profit (or loss) increases (or reduces) the net worth of the company. The balance sheet statement shows the accumulated wealth of a company (assets) and how these assets are financed (liabilities). By definition both sides are equal.

The differences between the income statement and the cash flow statement are shown as follows:

A. Income Statement

1. Total income
2. Less variable costs
3. Less fixed costs including depreciation



a. Calculate income (corporate) tax as applicable.

Figure 21.2. Origin of Cost Items for Profitability Calculation (Return on Equity).

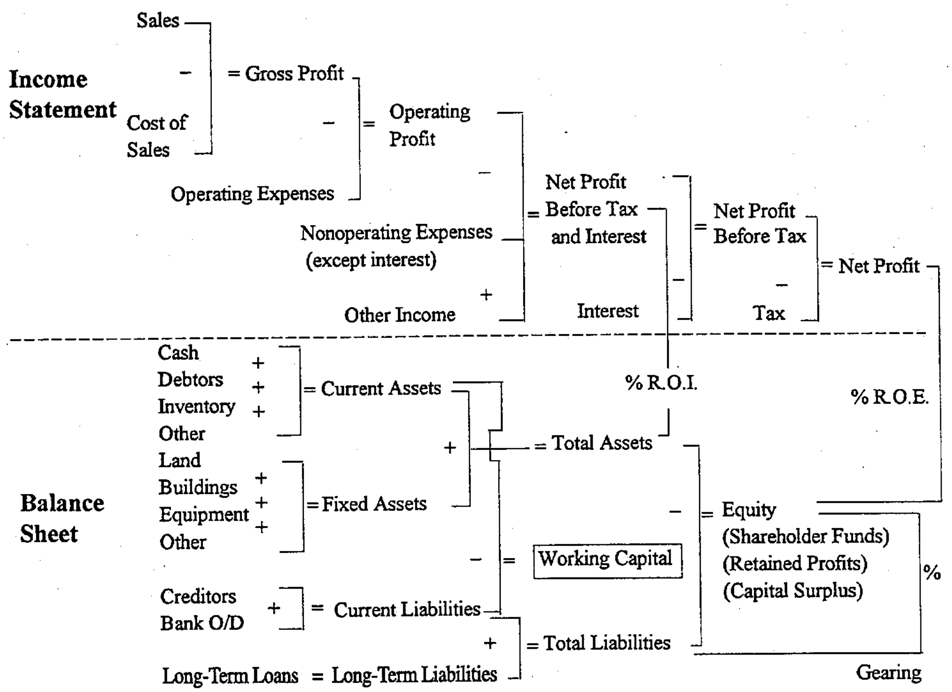


Figure 21.3. Relationship of the Income Statement to the Balance Sheet Statement.

4. Operational margin
5. Less working capital interest
6. Net profit before tax
7. Less income tax
8. Net profit after tax

B. Operational Cash Flow Statement

B(i) Cash Inflows

1. Net profit after tax
2. Working capital interest added back
3. Depreciation added back
4. Working capital released at end of project
5. Residual or scrap value of fixed plant investment

B(ii) Cash Outflows

1. Fixed capital investment
2. Working capital investment
3. Preproduction expenses net of interest

B(i) less B(ii) = Net Operational Cash Flow

Discounted cash flow analysis can be completed on the net operational cash flows for alternative competing investment projects for opportunity and prefeasibility studies.

21.4.5 Discounted Cash Flow Analysis

The basic assumption underlying the discounted cash flow analysis is that there is a time value and a risk value for money invested over time. For example, a given sum of money available now is worth more than an equal sum available in the future. The difference can be expressed as a percentage rate indicating the relative change for a year (or any other time period, if required). Consider that a project may obtain a certain amount of funds, F, which is required to be repaid after one year, including an agreed amount of interest, I, then the total sum to be repaid at the end of one year would be (F+I), where

$$F + I = F(1+r)$$

and r is defined as the interest rate in percentage per year divided by 100 (i.e., 12% equals .12). The nominal value of the total repayment is equal to the present value. Suppose now that CF_n is the nominal value of a future cash flow in the year n, and CF_p is the value at the present time (i.e., the present value) of this expected inflow or outflow, then, assuming that r is constant,

$$CF_p = CF_n / (1+_r)_n$$

or

$$CF_p = CF_n \ (1+_r)^{-n}$$

The future CF_n values are discounted over time to the present time. There are two main discounting methods used for the financial appraisal of investment projects: the net-present-value method (NPV) and the internal-rate-of-return method (IRR).

21.4.6 Net Present Value

The **Net Present Value** (NPV) of a project is defined as the value obtained by discounting, at a constant interest rate and separately for each year, the differences in cash inflow and outflow (i.e., the annual net cash flows [NCF]) throughout the life of the project. The annual NCFs are discounted to the point at which the project is supposed to start. The NPVs obtained for the years of project life are summed to provide a total NPV as follows:

$$NPV = NCF_0 + (NCF_1 \times a_1) + (NCF_2 \times a_2) + ... + (NCFn \times a_n)$$

$$\text{or } NPV = \sum_{n=0}^{n=j} \frac{NCF_n}{(1+r)^n}$$

where NCFn is the annual net cash flow of a project in the years n= 1,2,...,j, and a_n is the discount factor in the corresponding years, relating to the discount rate applied throughout the equation

$$a_n = (1+r)^{-n}$$

Discount factors (a_n) may be obtained from present value tables and computer software, including spreadsheets, that provide for these calculations. A simple example of NPV calculations at two discount rates is provided in Table 21.8.

The **discount rate** should be equal to the actual rate of interest on long-term loans in the capital market or the average interest rate (cost of capital) paid by the borrower. The discount rate should basically reflect the **opportunity cost of capital**, which corresponds to the rate of return an investor would obtain if the funds were invested elsewhere with a similar level of risk. The discount rate therefore represents the minimum rate of return acceptable to the investor. When comparing alternative investments with different perceived risks, the discount rate can be increased for the more risky project investment so that a comparison can be made between the alternatives.

If a computed NPV is positive, the profitability of the investment is above the cut-off or hurdle discount rate. If it is zero, the profitability is equal to the discount rate. If the NPV is negative, the profitability of the investment is below the discount rate and should be rejected.

Where a choice is to be made between competing alternative investments, the choice cannot be made entirely on the basis of the largest NPV because the NPVs only

Table 21.8. Example of Cash Flow Discounting

Year	Annual Cash Flow ($'000)	Discount Factor @ 18%	NPV ($'000)	Discount Factor @ 20%	NPV ($'000)
1	(3,291)	1.000	(3,291)	1.000	(3,291)
2	(5,127)	.847	(4,343)	.833	(4,271)
3	(88)	.718	(63)	.694	(61)
4	1,722	.609	1,049	.579	997
5	2,700	.516	1,393	.482	1,301
6	3,343	.437	1,461	.402	1,344
7	2,259	.370	836	.335	757
8	1,208	.314	339	.279	337
9	2,192	.266	583	.233	511
10	2,170	.225	488	.194	421
11	2,170	.191	414	.162	352
12	1,995	.162	323	.135	269
13	1,805	.137	247	.112	202
14	1,805	.116	209	.093	168
15	1,805	.099	177	.078	141
16	1,805	.084	152	.065	117
17	1,805	.071	128	.054	97
18	2,723	.060	163	.045	123
Accumulated total			265		(486)

Note: Figures in parentheses are negative.

Source: UNIDO, Manual for the Preparation of Industrial Feasibility Studies, 1991.

indicate the total net benefits of the investments. The efficiency of the alternative investments needs to be estimated by relating the positive NPVs to the present values of the alternative investments (PVI). This is calculated with the net-present-value ratio (NPVR), which provides a discounted rate of return.

$$\text{NPVR} = \frac{\text{NPV}}{\text{PVI}}$$

The NPV concept has substantial advantages compared with simple payback periods or annual rates of return because it accounts for the timing of cash flows over the whole project life and the NPVR can be considered as a calculated investment rate that the profit rate of the investment should at least reach. Some shortcomings include the difficulty in selecting the appropriate discount rate and the fact that the NPV does not show the exact profitability of the project. In addition the same NPV can be obtained from two entirely different cash flow arrays. It should therefore be used in conjunction with the IRR.

21.4.7 Internal Rate of Return

The **Internal Rate of Return** (IRR) is the discount rate at which the net present value of cash flows is equal to zero. Mathematically, it means that in the NPV equation one calculates the discount rate, r, at which the NPV equals zero. The calculation is made by an iterative process using discount tables or by a suitable computer program. In Table 21.7, the NPV is positive at an 18% discount rate and negative at a 20% discount rate. The IRR is therefore between 18% and 20% and can be calculated by interpolation.

The IRR can be considered as the annual net cash return produced on capital outstanding per period or as the highest rate at which a project could raise funds. An investment proposal may be accepted if the IRR is greater than the cut-off rate (i.e., the minimum acceptable interest rate for the invested capital). When competing alternative investments are being considered and the IRRs are above the cut-off rate, it is not necessarily the project with the highest IRR that should be selected. As with NPV, different cash flow arrays can produce identical IRRs; it is also possible for a project with a lower IRR to be preferable to a project that has a higher IRR but an undesirable cash flow structure. These ranking problems, and the situation with mutually exclusive projects, require that the use of IRR, NPV, and NPVR, must take account of the financial objectives and decision criteria of the investors.

Occasionally, one can come across a discounted cash flow analysis in which the annual net cash flows change from negative to positive, back to negative, and then revert to positive. When this occurs, Newnan's law of signs applies, which states that "there may be as many positive values for r as there are sign changes in the net cash flow." When this occurs, the problem may be overcome by discounting the negative net cash flows at nonzero time to zero time, using the appropriate discount factor, and adding these discounted values to the zero time investment.

Finally, in analyzing investment proposals, it is necessary to identify and evaluate project sensitivity to changes in major variables such as output prices, input prices, sales and production volumes, etc. Sensitivity analysis can assist in overcoming ranking problems in assessment.

21.5 Economic Analysis Structure

Financial analysis in real, present value terms is generally sufficient for commercial calculations and is essential prior to conducting an economic analysis in which net national benefits arising from a proposal are determined. In its most simplified form, economic analysis uses **net value added** as a proxy for national welfare. Net value added comprises two components: salaries and wages and social surplus. Social surplus is the portion of value added that is directed and distributed through taxes to the treasury; dividends to shareholders; interest on borrowed capital to financial institutions; rent; or allocations for the expansion, reserves, and social welfare funds of individual firms. Distortions in domestic prices are removed in economic analysis by using international equivalent prices – **border prices** – for traded goods and services and **shadow prices** for non-traded goods and services. These provide an absolute efficiency test and then relative efficiency tests are used to rank alternative projects under constraints of capital, foreign exchange, and skilled labor. The value added by a project is measured against the efficient use of the scarce production factor.

21.5.1 Shadow Prices

In a perfect market, the shadow price for any resource would be its market price; in the real world, market imperfections – caused, for example, by tariffs, quotas, and monopolies – distort prices so that true economic values are not represented by market prices. The estimation of border prices and shadow prices attempts to remove these distortions. A central issue in economic pricing is tradability of goods and services. The major categories related to tradability are as follows:

Tradable:	A good that would be imported or exported in the absence of trade barriers.
Traded:	A good that is actually traded.
Non-tradable:	A good whose real domestic cost of production together with its international transport cost is too high to permit export and too low to make import attractive.
Non-traded:	A tradable that is not traded because of the trade policies of the country but could be traded if the policies changed.

These definitions apply equally to services. How these categories impact on the valuation of shadow prices is discussed fully in the UNIDO Guidelines and summarized below [2].

A Guide to Shadow and Border Pricing

Type of Good or Service

	Type of Impact		
Type of Goods	Input	Output	Valuation
Domestic (nontraded)			
Production (supply)	More from local producers	Less by other local producers	Cost of production
Consumption (demand)	Less to other local users	More to other local users	Value to consumer
Foreign (traded)			
Exports (supply)	Less export	More export	Value of export(f.o.b.)
Imports (demand)	More import	Less import	Cost of import (c.i.f.)

Examples of non-tradables include electricity, water, maintenance cost, transportation, communications, buildings and land, and local services such as insurance, advertising, and legal services. Conversion factors are often used to convert domestic market prices of a non-tradable good into an economic border-equivalent shadow price. The standard conversion factor (SCF) is an average ratio of border to domestic market prices. In its simplest form it is the ratio of the two versions of a country's foreign trade turnover: one exclusive of import/export taxes and the other inclusive. Local market prices of non-tradables are multiplied by the SCF to produce an estimate of a good's border price on the world market.

The calculation of border prices for traded goods usually includes an adjustment to take account of domestic transportation to a project or to the project's primary market. For exports, the f.o.b. price is the total cost expended to produce, transport to the border, and prepare for transportation outside the country of origin. For imports, the c.i.f. price is the landed cost of an import including insurance but net of any additional domestic tariffs or other taxes and fees. It should also be adjusted for internal transport costs or savings from the port of entry to the market if these costs are significantly different from domestic factory-to-market costs, and it may also be adjusted for additional inventory cost required to cover delays or lumpiness in supply compared to domestic shipments.

Labor and land costs are also subject to adjustment although they are unlikely to impact greatly on fertilizer projects. The principles of shadow pricing used for goods apply equally to labor. A project has impacts on the rest of the economy when it hires labor. A project may take labor away from other users, it may stimulate the emergence of new workers, or it may cause the importation of workers. For the first type of impact the shadow price of labor is the willingness of other users to pay for this labor. The second type of impact is important in four areas:

Employment of previously unemployed workers
Improved productivity of underemployed workers
Urban employment of rural workers
Skilled employment of previously unskilled workers

Unemployed workers can be considered to have a minimum reservation wage rate equivalent to the value of 3 kilograms of grain per day; often, however, there are other factors to take into account, such as existing income from transfer payments, that increase the shadow price of unskilled unemployed workers. The cost of transforming an underemployed worker is the value of what he may have produced in his former employment plus the reservation wage. The cost of transforming a rural worker to an urban worker is the social cost of migration, which usually includes the cost of migration of additional family members. The social service costs of the migrants associated with producing an additional man-year of labor in an urban area need to be accounted for in the shadow price of labor for this circumstance. The cost of transforming an unskilled worker into a skilled worker is the cost of training, and this is usually accounted for in project costs. The importation of skilled labor when a project requires skilled managers, technicians and workers not available domestically leads to shadow prices equivalent to the wages they command. For further discussion on the shadow pricing of labor, readers are referred to [5] and [3].

The shadow price of **foreign exchange** needs to be applied when foreign exchange is deemed to be more valuable than indicated by the official exchange rate. The shadow price is applied only to those goods that were valued at border prices, since inputs and outputs shadow priced with reference to domestic consumer willingness to pay or cost of production already implicitly include a premium on foreign exchange. Border-priced shadow prices generally include all major inputs and outputs and any major non-traded inputs with a substantial foreign exchange component. For the determination of foreign exchange shadow prices, see [5]. Where a parallel foreign exchange market exists in a country, the market rate can often be considered to be the shadow exchange rate.

The adjustments illustrated in Schedule 11 to market prices afforded by shadow pricing enable the economic net present value and economic internal rate of return to be calculated from the adjusted financial analysis. This completes the first stage of economic acceptability analysis.

21.5.2 Distribution Impact

As stated previously, the net value added is a simple proxy for national welfare and comprises salaries and wages and social surplus. The distribution of the net value added should be considered as the gains and losses of individual groups within society. These can be assumed to be equal to the differences between shadow and market payments to each input or output in the case of physical resources or the distortion between price paid and value received in the case of financial transactions. Each gain is offset by an equal loss. For example, when a project pays workers a market rate that is higher than the economic rate the workers have a gain equal to the project loss. The groups over which the distribution income is measured can be aggregated or disaggregated to variable levels. UNIDO has suggested the following groups as being a reasonable compromise [2]:

Project
Other private business
Government
Workers
Consumers
External sector

For each group, the data required for the income-flow analysis derive from the adjustments made to move from market prices to shadow prices including exchange rate adjustments. The losses and gains for each group are summed to provide a net impact as shown in Schedule 12.

Further economic analysis dealing with the savings impact and income redistribution are beyond the scope of this outline.

21.6 Use of Computers for Financial and Economic Analysis

Today, process simulation/project evaluation/financial evaluation software is available that can be applied to a wide variety of projects in the chemical and petroleum industries. The most sophisticated evaluation systems contain built-in design systems, scheduling systems, and up-to-date knowledge bases of international cost and work-hour models. Software can work from a brief outline of a project's scope and automatically develop design details in the early stages of a project. Software packages available can produce detailed cost estimates within -5% to +14% of actual cost [6].

However, at present, there is no single software package that can (1) design the process system, (2) develop and evaluate project scope, and (3) develop the financial and economic analysis. Therefore it is common for several software programs to be used to develop and evaluate the same project.

Since 1982, UNIDO has developed COMFAR[1] from a model for financial analysis at the enterprise level into a complex system for financial and economic analysis of investment projects for use on personal computers. It features guiding the user through the data entry system by requesting exactly the input required for the computation of the system output as predefined by the user; assisting with the analysis by allowing a comparison with key data from similar investment projects; making entries in different currencies; and preparing economic cost-benefit analysis following different methodologies.

Use of spreadsheets is common and can be an effective way to evaluate information quickly and efficiently. Most spreadsheets have sophisticated financial functions; thus, in the hands of a skilled analyst, a spreadsheet can be an invaluable tool. Spreadsheets provide a high degree of flexibility, contain a large number of valuable time-saving functions, and can be used to organize and evaluate large quantities of data quickly. However, there are hazards in using spreadsheets. Common problems include improper setup of problems, defective functions, misunderstood functions, functions based on improper inputs, improper cross-referencing, and difficulty in interpreting the design approach used in another's spreadsheet.

Due to these kinds of problems, many spreadsheets have undetected errors. It is therefore important that spreadsheets used for sensitive tasks be well documented and reviewed. Spreadsheet users should incorporate checks and balances within spreadsheets to ensure that errors in design are eliminated.

21.7 Guidelines for Achieving Well-Established Projects

The most important factors in achieving well-established projects are having clear objectives, a defined scope, and a well-defined, systematic methodology for information collection and financial and economic analysis.

Objectives should be based on well-defined business strategies with regard to all aspects of marketing, production and supplies, financing, personnel, and management and organization.

The scope of the project must be clearly understood in order to prepare reliable forecasts on investment, production, and marketing costs.

A systematic methodology is required to allow decisionmakers to compare alternative projects. The UNIDO Guidelines provide checklists and schedules for each stage in opportunity, prefeasibility, and feasibility studies. These are summarized in the following sections, with examples of the main schedules required for financial analysis.

21.7.1 Feasibility Study

Having established the first two requirements, i.e., objectives and scope, the steps in a feasibility study are as follows:

1. Conduct market analysis and determine marketing concept, including demand and sales forecasts, competitor analysis, life cycle, marketing strategies, marketing costs, and prices received.

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[1] The UNIDO Computer Model for Feasibility Analysis and Reporting. User licenses may be obtained from the UNIDO Department of Industrial Operations, Feasibility Studies Branch.

2. Determine availability and cost of raw materials and supplies.
3. Justify location site and environmental considerations and costs related to site.
4. Consider engineering and technology related to production program and capacity (determined by the sales forecasts). Justify selected technology; quantify equipment requirements and costs.
5. Identify organization and management required and overhead costs.
6. Identify human resources required, skills, and costs.
7. Prepare a project implementation schedule and identify critical actions for timely implementation.
8. Prepare the financial analysis and investment appraisal.
9. Prepare the economic analysis, if required.

21.7.2 Schedules for Financial Analysis

All schedules prepared for a financial analysis should show both local and foreign costs and revenues with the foreign components converted to local currency at the chosen exchange rate.

Marketing:	(1)	Prepare a schedule of the projected sales program including, for both local and export markets, sales units, prices, and total revenues for each year.
	(2)	Prepare a schedule of projected fixed and variable marketing costs.
Raw Materials:	(1)	Prepare a schedule of projected costs of raw materials and supplies by year including variable and fixed cost components per unit and units consumed.
Site:	(1)	Prepare a schedule of site investment costs and environmental investment costs.
	(2)	Prepare a schedule of site and environmental annual operating costs.
Engineering:	(1)	Prepare a schedule of technology costs either as lump sum payments or royalties related to operating costs or sales revenues.
	(2)	Prepare a schedule of plant machinery and equipment investment costs.
	(3)	Prepare a schedule of civil engineering works investment costs
Manpower:	(1)	Prepare a manning table and a schedule of operating labor costs, maintenance labor costs, and administration, marketing, and management staff costs, separating wages and salaries from social overhead costs.
Overheads:	(1)	Prepare estimates of overhead costs including site overheads, administration overheads, a depreciation schedule, and financing cost overheads.
Production Costs:	(1)	Prepare a production cost schedule for each product.
Working Capital:	(1)	Prepare a working capital schedule derived from sales and production cost schedules.
Financial Analysis:	(1)	Summarize fixed and working capital investment as shown in schedule 1.
	(2)	Summarize annual costs of products sold as shown in schedule 2.
	(3)	Prepare a schedule of sources of finance as shown in schedule 3.
	(4)	Prepare a schedule of total financial flow as shown in schedule 4.
	(5)	Prepare a total debt service schedule as shown in schedule 5.
	(6)	Prepare a projected net income statement as shown in schedule 6.
	(7)	Prepare a projected balance sheet as shown in schedule 7
	(8)	Prepare a cash flow for financial planning as shown in schedule 8.
	(9)	Prepare a discounted cash flow schedule for total capital invested as shown in schedule 9.
	(10)	Prepare a schedule of discounted return on equity investment as shown in schedule 10.

The projections and math are only a small part of project appraisal. An adequate understanding of any project requires that all the information and data used be subjected to critical evaluation so that the appraiser is aware of the strengths and weaknesses of the inputs to the analysis.

Schedule 1 - Total Investment Cost

Investment Category	Total During Construction	Total During Production	Construction 1	Construction 2	Production 3
1. Total fixed investment	264.33		158.60	105.73	
2. Total pre-production					
Net of interest	38.36		23.02	15.34	
Interest accrued	22.47		5.34	17.13	
3. Total net working capital	16.83			3.37	13.46
Total Investment Cost	341.98		186.95	141.57	
Foreign share, %	40.00%				

Assumptions

1. 1,000-tpd ammonia/1,750-tpd urea plant; new site; developing location; Type I.
2. Operating 330 days per year.
3. Annual production 577,500 tonnes.
4. 90% capacity in year 1 all subsequent years 100% capacity.
5. Sales price $180.00/tonne.
6. Natural gas price $4.00/Gcal.
7. Working capital based on: (a) finished product inventory 30 days.
   (b) work in progress inventory 1 day.
   (c) factory supplies inventory 45 days.
   (d) catalysts and additives inventory 90 days.
   (e) accounts receivable 45 days.
   (f) accounts payable 30 days.

Schedule 2 - Annual Costs of Products Sold

					Production Years ($ Millions)														
	Units	Quantity	$/unit	$/tonne	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Process gas	Gcals	2.96	4.00	11.83	5.28	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86	5.86
Combustion gas	Gcals	1.10	4.00	4.41	1.97	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
Catalysts and additives	$/t		3.24	3.24	1.45	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
Inert gas	$/t		0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Boiler water	m3/t	0.64	0.20	0.13	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Cooling water	m3/t	121.80	0.02	2.44	1.09	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21	1.21
Electricity	kWh	150.00	0.05	7.50	3.35	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71
Effluent treatment	$/t		0.15	0.15	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Operating supplies	$/t		0.16	0.16	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Total Variable Costs				29.87	13.32	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79
Direct labor	workhrs/tonne	0.30	10.00	3.00	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49
Indirect labor	workhrs/tonne	0.30	10.00	3.00	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49
Maintenance			13.47	13.47	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67
Depreciation			40.81	40.81	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	1.79
Insurance and taxes			8.16	8.16	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04
Marketing costs			0.71	0.71	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Plant overheads			3.00	3.00	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49
Total Direct Costs				72.15	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	35.71	17.30
Total Production Cost				102.02	49.04	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	50.50	32.09

Depreciation based on (a) straight line over 15 years for battery limits investment.
(b) straight line over 22 years for off-sites investment.

Schedule 3 - Sources of Finance

	Year 1	Year 2	Year 3	Total	Terms
Equity Capital					
1. Equity local investor	50.10	37.94		88.04	First Payment year1 as lump sum, 12% dividend yield
2. Equity foreign investor	24.68	18.69		43.37	First Payment year1 as lump sum, 12% dividend yield
Loan Capital					
1. Equipment suppliers credit	70.00	70.00		140.00	Repayment starting in year 3, 10% annual interest,10 year amortization
2. Local loan	42.45	14.94		57.40	Repayment starting in year 3, 10% annual interest, 10 year amortization
3. Bank overdraft		0	5.5	5.5	Repayment starting in year 5, 15% annual interest, 5 year amortization
Total	186.95	141.57	5.50	334.03	

Schedule 4 - Total Financial Flow

	Construction		Production														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Sources	Total Disbursement																
Equity Capital Local	50.10	37.95															
Equity Capital Foreign	24.68	18.69															
Equipment Suppliers Credit	70.00	70.00															
Commercial Banks	42.45	14.94															
Bank Overdraft		0.00	5.50														
Accounts Payable		0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73
Total Financial Flow	187.23	142.31	6.23	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73

Schedule 5 - Total Debt Service

	Construction		Production														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Long Term Loan																	
Disbursements	42.45	14.94															
Repayments			5.74	5.74	5.74	5.74	5.74	5.74	5.74	5.74	5.74	5.74					
Debt balance at end of year	42.45	57.39	51.65	45.91	40.17	34.43	28.70	22.96	17.22	11.48	5.74	0.00					
Interest payable	2.12	5.42	6.03	5.39	4.76	4.13	3.50	2.87	2.24	1.61	0.98	0.34					
Equipment Suppliers Credit																	
Disbursements	70.00	70.00															
Repayments			14	14	14	14	14	14	14	14	14	14					
Debt balance at end of year	70.00	140.00	126	112	98	84	70	56	42	28	14	0					
Interest payable	3.50	10.5	9.8	11.9	10.5	9.1	7.7	6.3	4.9	3.5	2.1	0.7					
Short Term Loans																	
Bank overdraft																	
Disbursements		0.00	5.5														
Repayments				0.00	1.38	1.38	1.38	1.38									
Debt balance at end of year		0.00	5.5	5.50	4.13	2.75	1.38	0.00									
Interest payable		0.00	0.41	0.83	0.72	0.52	0.31	0.10									
Reduction in accounts payable				0	0	0	0	0									
Total Debt Service																	
Disbursements	112.45	84.94	5.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Repayments	0.00	0.00	19.74	19.74	21.11	21.11	21.11	21.11	19.74	19.74	19.74	19.74	0.00	0.00	0.00	0.00	0.00
Debt balance at end of year	112.45	197.39	183.15	163.41	142.30	121.18	100.07	78.96	59.22	39.48	19.74	0.00	0.00	0.00	0.00	0.00	0.00
Interest payable	5.62	15.92	16.24	18.12	15.99	13.75	11.51	9.27	7.14	5.11	3.08	1.04	0.00	0.00	0.00	0.00	0.00

Schedule 6 - Projected Net Income Statement

	Production														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14.	15
Sales Revenue	93.56	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95
Interest on securities	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Other income	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Income	93.56	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95
Less Variable Costs															
Material	13.32	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79	14.79
Personnel															
Marketing	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Other															
Total Variable Costs	13.42	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89	14.89
Variable Margin	80.14	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06	89.06
(In % of total income)	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%	86%
Less Fixed Costs															
Material	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67	6.67
Personnel	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97
Marketing	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26
Depreciation	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	20.20	1.79
Other Fixed Costs	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53	5.53
Total Fixed Costs	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	35.62	17.21
Operational Margin	44.52	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	53.44	71.85
(In % of total Income)	48%	51%	51%	51%	51%	51%	51%	51%	51%	51%	51%	51%	51%	51%	69%
Less Costs of Finance	16.24	18.12	15.99	13.75	11.51	9.27	7.14	5.11	3.08	1.04	0.00	0.00	0.00	0.00	0.00
Gross Profit	28.28	35.32	37.45	39.69	41.93	44.17	46.30	48.33	50.36	52.39	53.44	53.44	53.44	53.44	71.85
Less Allowances															
Taxable Profit	28.28	35.32	37.45	39.69	41.93	44.17	46.30	48.33	50.36	52.39	53.44	53.44	53.44	53.44	71.85
Tax	8.48	10.60	11.24	11.91	12.58	13.25	13.89	14.50	15.11	15.72	16.03	16.03	16.03	16.03	21.56
Net Profit	19.79	24.72	26.21	27.78	29.35	30.91	32.41	33.83	35.25	36.67	37.40	37.40	37.40	37.40	50.29
Dividends Payable	13.50	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77
Retained Profit	6.29	8.95	10.44	12.01	13.58	15.14	16.64	18.06	19.48	20.90	21.63	21.63	21.63	21.63	34.52
Ratios															
Gross Profit/Sales															
Net Profit After Tax/Sales	30%	34%	36%	38%	40%	42%	45%	46%	48%	50%	51%	51%	51%	51%	69%
Net Profit/Equity Capital	15%	19%	20%	21%	22%	24%	25%	26%	27%	28%	28%	28%	28%	28%	38%
Net Profit + Interest/Investment	11%	13%	13%	13%	13%	13%	12%	12%	12%	12%	12%	12%	12%	12%	16%

Schedule 7 - Projected Balance Sheet

	Construction		Production														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Total Current Assets																	
Inventory on materials and supplies		0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Work in progress		0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Finished products in stock		3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18
Accounts receivable		0.00	11.53	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82	12.82
Cash in hand		0.37	0.95	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Cash surplus	0.00	1.22	1.36	9.43	18.96	30.05	42.71	56.94	74.04	92.56	112.50	133.86	175.69	217.53	259.36	301.19	337.50
Securities																	
Total Current Assets	0.00	5.32	17.58	26.99	36.52	47.61	60.27	74.50	91.60	110.12	130.06	151.42	193.25	235.09	276.92	318.75	355.06
Fixed investment		158.60	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33	264.33
Construction in progress	158.60	105.73															
Pre-production expenditures	28.64	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90	59.90
Less accumulated depreciation			20.20	40.40	60.60	80.80	101.00	121.20	141.40	161.60	181.80	202.00	222.20	242.40	262.60	282.80	284.59
Net Fixed Assets	187.23	324.22	304.02	283.82	263.62	243.42	223.22	203.02	182.82	162.62	142.42	122.22	102.02	81.82	61.62	41.42	39.64
Accumulated losses brought forward																	
Loss in current year																	
Total Assets	187.23	329.55	321.60	310.81	300.14	291.04	283.50	277.52	274.42	272.74	272.48	273.64	295.28	316.91	338.54	360.18	394.70
Current Liabilities																	
Accounts payable		0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73
Bank overdraft		0.00	5.50	5.50	4.13	2.75	1.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Current Liabilities	0.00	0.73	6.23	6.23	4.86	3.48	2.11	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73	0.73
Total long-term debt	42.45	57.39	51.65	45.91	40.17	34.43	28.70	22.96	17.22	11.48	5.74	0.00	0.00	0.00	0.00	0.00	0.00
Suppliers credit	70.00	140.00	126.00	112.00	98.00	84.00	70.00	56.00	42.00	28.00	14.00	0.00	0.00	0.00	0.00	0.00	0.00
Total equity capital	74.78	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42	131.42
Reserves, retained profit brought forward			0.00	6.29	15.24	25.69	37.70	51.27	66.41	83.05	101.11	120.59	141.49	163.12	184.75	206.39	228.02
Dividends payable			13.50	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77
Retained profit			6.29	8.95	10.44	12.01	13.58	15.14	16.64	18.06	19.48	20.90	21.63	21.63	21.63	21.63	34.52
Net profit after tax			19.79	24.72	26.21	27.78	29.35	30.91	32.41	33.83	35.25	36.67	37.40	37.40	37.40	37.40	50.29
Total Liabilities	187.23	329.55	321.60	310.81	300.14	291.03	283.50	277.52	274.42	272.74	272.48	273.64	295.27	316.91	338.54	360.17	394.69
Check	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Ratios																	
Equity/total liabilities	40%	40%	41%	42%	44%	45%	46%	47%	48%	48%	48%	48%	45%	41%	39%	36%	33%
Long-term debt/net worth	1.50	1.50	1.35	1.15	0.94	0.75	0.58	0.43	0.30	0.18	0.08	0.00	0.00	0.00	0.00	0.00	0.00
Current assets/current liabilities			2.82	4.33	7.52	13.68	28.62	101.94	125.34	150.68	177.97	207.20	264.44	321.68	378.93	436.17	485.85

Schedule 8 - Cash Flow for Financial Planning

	Construction		Production														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1. Inflow Funds																	
Total Equity	74.78	56.64															
Total Long-Term Loans	112.45	84.94															
Total Short-Term Finance		0.73	5.50														
Total Funds Inflow	187.23	142.31	5.50														
2. Inflow Operations																	
Sales Revenue			93.56	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95
Interest on Securities																	
Other Income																	
Total Cash Inflow	187.23	142.31	99.06	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95
Increase in Fixed Assets																	
- Fixed Investments	158.60	105.73															
- Preproduction Expenses	23.02	15.34															
Increase in Current Assets		4.10	12.11	1.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Operating Costs			28.48	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95
Marketing Costs			0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Corporate Tax Paid			8.48	10.60	11.24	11.91	12.58	13.25	13.89	14.50	15.11	15.72	16.03	16.03	16.03	16.03	21.56
Interest Paid	5.62	15.92	16.24	18.12	15.99	13.75	11.51	9.27	7.14	5.11	3.08	1.04	0.00	0.00	0.00	0.00	0.00
Loan Repayments			19.74	19.74	21.11	21.11	21.11	21.11	19.74	19.74	19.74	19.74	0.00	0.00	0.00	0.00	0.00
Dividends Paid			13.50	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77	15.77
Total Cash Outflow	187.23	141.09	98.91	95.88	94.41	92.84	91.28	89.71	86.84	85.42	84.00	82.58	62.11	62.11	62.11	62.11	67.63
Surplus (Deficit)	0.00	1.22	0.14	8.07	9.54	11.11	12.67	14.24	17.11	18.53	19.95	21.37	41.84	41.84	41.84	41.84	36.32
Cumulative Cash Balance	0.00	1.22	1.36	9.44	18.98	30.08	42.75	56.99	74.10	92.63	112.58	133.95	175.79	217.64	259.48	301.32	337.64

Schedule 9 - Discounted Cash Flow Total Capital Invested

	Construction		Production															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Sales Revenue			93.56	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	
Interest on Securities																		
Other Income (Release of Working Capital)																		16.83
Total Cash Inflow			93.56	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	103.95	16.83
Increase in Fixed Assets																		
Fixed Investments	158.60	105.73																
Preproduction Expenses	23.02	15.34																
Increase in net Working Capital		3.37	12.11	1.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Operating Costs			28.48	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	29.95	
Marketing Costs			0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	
Corporate Tax Paid			8.48	10.60	11.24	11.91	12.58	13.25	13.89	14.50	15.11	15.72	16.03	16.03	16.03	16.03	21.56	
Total Cash Outflow	181.61	124.45	49.43	42.25	41.54	42.21	42.88	43.55	44.19	44.80	45.41	46.02	46.34	46.34	46.34	46.34	51.86	0.00
Net Cash Flow	-181.61	-124.45	44.12	61.70	62.41	61.74	61.07	60.40	59.76	59.15	58.54	57.93	57.61	57.61	57.61	57.61	52.09	16.83
Cumulative Net Cash Flow	-181.61	-306.06	-261.94	-200.23	-137.82	-76.08	-15.02	45.38	105.13	164.28	222.82	280.74	338.36	395.97	453.58	511.20	563.29	580.12
Net Present Value @15%	-181.61	-108.22	33.36	40.57	35.69	30.70	26.40	22.70	19.53	16.82	14.47	12.45	10.77	9.36	8.14	7.08	5.57	1.56
Cummulative Net Present Value	-181.61	-289.83	-256.47	-215.90	-180.21	-149.52	-123.12	-100.41	-80.88	-64.07	-49.60	-37.15	-26.38	-17.02	-8.88	-1.80	3.77	5.34
NET PRESENT VALUE @ 15%	5.34																	
INTERNAL RATE OF RETURN	15.33%																	

Schedule 10 - Discounted Return On Equity Capital Invested

	Construction		Production															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Cash Surplus (Deficit)	0.00	1.22	0.14	8.07	9.54	11.11	12.67	14.24	17.11	18.53	19.95	21.37	41.84	41.84	41.84	41.84	36.32	0.00
Dividends Paid	0	0	13.5	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	15.7708	0
TOTAL CASH INFLOW	0.00	1.22	13.64	23.85	25.31	26.88	28.44	30.01	32.88	34.30	35.72	37.14	57.61	57.61	57.61	57.61	52.09	0.00
Equity Capital Paid	74.78	56.64	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NET CASH RETURN	-74.78	-55.42	13.64	23.85	25.31	26.88	28.44	30.01	32.88	34.30	35.72	37.14	57.61	57.61	57.61	57.61	52.09	16.83
Cummulative Net Cash Return	-74.78	-130.206	-116.56	-92.72	-67.41	-40.53	-12.09	17.92	50.80	85.10	120.82	157.96	215.58	273.19	330.81	388.42	440.51	457.34
Net Present Value @ 15%	-74.78	-48.20	10.32	15.68	14.47	13.36	12.30	11.28	10.75	9.75	8.83	7.98	10.77	9.36	8.14	7.08	5.57	1.56
Cummulative Net Present Value	-74.78	-122.979	-112.66	-96.98	-82.51	-69.15	-56.85	-45.57	-34.82	-25.07	-16.24	-8.26	2.51	11.87	20.01	27.09	32.66	34.22
NET PRESENT VALUE @ 15%	34.23																	
INTERNAL RATE OF RETURN ON EQUITY	18.84%																	

Schedule 11 - Adjustment to Cash Flow for Economic Analysis

Item	Financial NPV @15% $M	Economic Price Adjustment %	Economic Adjusted NPV @15% $M	Exchange Rate Adjustment			Exchange Rate NPV @15% $M	Net Project Adjustment $M
				Content %	Premium %	Weighted Premium %		
Net Cash Flow--Real	5.34		-115.96		10%		54.48	-56.14
Operating Sources of Funds	456.40		-129.08		10%		55.99	383.31
Operating Profit								
- Sales Value	522.26	-20%	-104.45	100%	10%	10%	52.23	52.23
- Costs								
- Imported Materials	0.41	-20%	-0.08	100%	10%	10%	0.04	-0.04
- Domestic Materials	73.67	-15%	-11.05	30%	10%	3%	2.21	-8.84
- Operating Expenses								
- Unskilled labor	0.76	-50%	-0.38	0%	10%	0%	0.00	-0.38
Operating Use of Funds								
- Current Assets								
- Inventories	12.98	-20%	-2.60	55%	10%	6%	0.71	-1.88
- Fixed Assets								
- Land and Buildings	91.94	-10%	-9.19	0%	10%	0%	0.00	-9.19
- Equipment	13.34	-10%	-1.33	60%	10%	6%	0.80	-0.53
Net Cash Flow--Financial								
Sources--Equity	124.03			39%	10%	4%	4.84	4.84
Uses--Interest	72.86	35%	25.50	70%	10%	7%	5.10	30.60
- Taxes	64.07	-100%	-64.07	0%	10%	0%	0.00	-64.07
- Dividends	90.24	-100%	-90.24	39%	10%	4%	3.52	-86.72

Notes:

1. Economic price adjustments used are hypothetical but typical.
2. Exchange rate adjustments based on a 10% over-valued exchange rate.

Schedule 12 - Income Flow Analysis

Item	Project Adjustment	Other Private Business	Government	Workers	Consumers	External
Net Cash Flow--Real						
Operating Sources of Funds						
Operating Profit						
Sales Value	52.23				-52.23	
Costs						
Imported Materials	-0.04		-0.04			
Domestic Materials	-8.84	8.84				
Operating Expenses						
Unskilled Labor	-0.38			0.38		
Operating Use of Funds						
Current Assets						
Inventories	-1.88	1.88				
Fixed Assets						
Land and Buildings	-9.19	4.60		4.60		
Equipment	-0.53	0.27		0.27		
Net Cash Flow--Financial						
Sources--Equity	4.84					-4.84
Uses - Interest	30.60		-12.24			-18.36
- Taxes	-64.07		64.07			
- Dividends	-86.72		-3.52			90.24
Net Distribution Impact	-84.00	15.59	48.27	5.24	-52.23	67.04

21.8 References

1. UNIDO. 1978. Manual for the Preparation of Industrial Feasibility Studies, 1st Edition.
2. UNIDO. 1991. Manual for the Preparation of Industrial Feasibility Studies, 2nd Edition.
3. Duvigneau, J. Christian, and Prasad, Ranga N. 1984. Guidelines for Calculating Financial and Economic Rates of Return for DCF Projects, The World Bank Technical Paper Number 33.
4. United Nations, 1989, Guidelines for Project Evaluation, [Prepared by P. Dasgapta, S. Marglin and A Sen], Sales No. 72.11.B.11.
5. UNIDO. 1986. Guide to Practical Project Appraisal – Social Benefit-Cost Analysis in Developing Countries.
6. Stienberger, Robert L. 1994. "Reengineering Investment," Chemical Engineering, October 1994, McGraw Hill Inc.

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Chapter 22. Challenges Facing the Fertilizer Industry

22.1 Introduction

As a result of political and economic reforms in the formerly centrally planned economies, structural adjustment programs in the developing countries, and grain surpluses in the industrialized countries, the fertilizer industry is facing many challenges. These challenges include, but are not limited to, sustainable growth in fertilizer use and supply, management of environmental impacts associated with fertilizer use, especially nonpoint pollution, restructuring and rehabilitation of the fertilizer sectors and the development of competitive markets systems in transition economies (Eastern Europe and former U.S.S.R.), and policy and organizational reforms in developing countries. Some of these challenges, and strategies to deal with them, are analyzed in this chapter.

22.2 Resolution of Macroeconomic Contradictions

The use of fertilizers and other agricultural inputs is essential in any region of the world and, in particular, in developing countries. Only agricultural inputs can help in meeting the food needs of the world's growing population. The principle of nutrient balance is an objective law of nature; therefore, whatever is taken from soil must be replaced to protect the environment and increase food production. The concept that healthy food can only be produced using organic fertilizers is not economically viable worldwide and also not theoretically true. During the next century it will be necessary to cope with the most urgent needs of the poor populations worldwide. Inorganic fertilizer is one of the materials required to resolve the food problems of the poor. The safe and judicious application of fertilizers may also produce healthy food of adequate quantities [1].

22.2.1 National Income and Crop Prices

Food prices in the developing countries are still low and, in particular, are those of staple foods such as rice, cassava, maize, and wheat. Because most of the population has a low income, they cannot afford expensive food. On the other hand, poverty is induced by a large proportion of the agricultural population or population unemployed outside the agricultural sector. Most small farmers cannot produce efficiently enough; therefore, to keep food prices low the Government is forced to keep farmers' income as low as possible. However, agricultural restructuring in many countries to produce food efficiently, which ensures on the one hand low prices and on the other hand an adequately high income of a limited number of farmers (e.g., 5%-7% of the total labor force), requires the creation of a large number of industrial and service posts, implementation of a large-scale program of housing construction, and overall development of infrastructure. Otherwise, small farmers will become a potentially large unemployed labor force, which cannot be accepted by any government. Following this structural deficiency small farmers and the overall agricultural infrastructure cannot afford to purchase adequate amounts of agricultural inputs such as fertilizers. More efficient farmers are not using adequate amounts of fertilizers because of the low benefit:cost ratio. Cheap prices for crops and feasible production prices of fertilizers are generally not producing an incentive for farmers to use fertilizers. Consequently, crop yields and incomes are low, and the vicious cycle of poverty and food deficits begins again.

International development agencies are encouraging the development and implementation of policies that promote the efficient development of the fertilizer and agricultural sectors. Policies can be developed that promote privatization of fertilizer sectors. Thus, a favorable environment can be established so that the private sector can assume the responsibility for the fertilizer and agricultural sector development. Only good macroeconomic management can resolve the problems of the fertilizer sector, which is imperative for sustainable development. Some parameters of macroeconomic management will be discussed.

22.2.2 Subsidies

It has been proven that a favorable fertilizer:crop price ratio stimulates food production and high returns. Therefore, if crop prices cannot be raised, the only solution is to lower fertilizer prices. This is accomplished by applying fertilizer subsidies. The most common forms of subsidies are:

- Direct fertilizer price subsidy.
- Storage and transportation subsidy.
- Purchase credit subsidy.

An alternative to fertilizer price subsidies is a crop price support. Regardless of the form of subsidy applied, it requires a large-scale managerial effort, clear and transparent administrative procedures, precise contracting/accounting principles, and budgetary financial resources. Hence, input subsidies are preferable to output subsidies.

Once applied subsidies have a great impact on the country's overall economy; this impact has positive and negative elements, examples of which are given in Table 22.1.

Entering any subsidy scheme should be handled carefully; macroeconomic models should be used to simulate outcomes and to evaluate benefits from alternative investments. Each government should be aware that entering a subsidy scheme is difficult and requires many regulations to ensure its success. Hence, reliance on subsidies should be minimal.

Table 22.1. Macroeconomic Impact of Fertilizer Subsidies

Positive Impact	Negative Impact
Expansion of fertilizer use	Waste of fertilizers
Increased demand for other agri-inputs	Cost to the treasury
Increased productivity	Production surplus lowering crop prices
Higher land value	Mislocation of resources

22.3 Fertilizer Production Capacity and Demand

Establishment of a fertilizer factory should be considered only when local or regional consumption at the time of the startup will reach the level of the minimum economic installation capacity, allowing for 10%-15% of imports. Operation of the factory at 85% capacity is conditional to its competitiveness. However, the problem of capacity utilization represents a contradiction: the fertilizer plant should be operated continuously throughout the year but fertilizer use is concentrated in two or three periods of the year. Fertilizers are used in a relatively short period of time. This poses problems of storage capacity, distribution networks, and the financing of the stored fertilizers. In fact, the working capital necessary to cope with this situation is significantly higher than that in other branches of industries where demand correlates well with production. This additional cost would generate a price increase; however, if the technology is up to date and operation efficient, local fertilizer prices may remain competitive with those of imported products, which must incur the high cost of transportation and loading/unloading operations and port demurrages. However, over the market constraints of capacity utilization and satisfying demand at competitive prices, there are internal reasons for undercapacity operation. These internal reasons are listed in Table 22.2.

Full capacity utilization would be the priority in any program of restructuring the fertilizer industry. As has been stated many times in this manual, fertilizer demand

Table 22.2. Internal Reasons for Undercapacity Operation of a Fertilizer Plant

Undercapacity Caused by	Reason for the Cause
Faulty plant design	Wrong design data Inexperienced engineering company Unfair contractor/supplier
Lack of quality maintenance	Lack of spare parts because of exchange regulations or lack of funds Untrained personnel
Inadequately trained operation personnel	Late and/or inadequate training Large personnel turnover
Infrastructural deficiencies	Unstable supply of electrical energy Water deficit or inadequate quality Transportation bottlenecks
Irregular supply of raw materials	Lack of foreign exchange Transportation bottlenecks

is driven by the benefit:cost ratio. In free market conditions only obvious profits can motivate farmers to increase fertilizer use. Therefore, macroeconomic governmental policies should take part of the burden and risk from farmers, especially in countries where farmers cannot pay cash for agricultural inputs. In more developed countries, it is necessary to create convenient credit schemes for farmers to purchase inputs and systems for marketing outputs. Although the benefit:cost ratio is fundamental for increased food production, professional services are equally important to achieve a balance in fertilizer use. The availability of soil analyses; advisory services on crop selection; and the proper use of fertilizers, pesticides, and other inputs are necessary conditions to increase fertilizer demand. By conducting demonstrations on local and regional fields, the extension service can efficiently prove the potential of fertilizer use. Although this requires budgetary inputs, this input is much lower than extensive subsidies. The combination of the supply-side factors and benefit:cost-driven demand may ensure the best use of natural (mineral) resources and manpower to efficiently produce food sufficient for a country's population.

22.4 Transformation From Public to Private [2]

Fertilizer industries in developing countries have been established by the governments as different forms of parastatal enterprises, either fully administered by the respective ministries of industry or economy or public shareholding companies with the majority of the shares owned by the Treasury or other constitutional state owner. Establishment of the fertilizer industry by the state has created the economic climate in which this industry has been operating. Under such systems, the following elements of the operation have been regulated:

- **Fertilizer Prices** – The required introduction of custom duties and internal subsidies to motivate farmers to increase fertilizer use has allowed the country governments to control fertilizer prices.
- **Distribution and Marketing System** – To control subsidies, to ensure continuous production and storage of fertilizers, and to ensure subsidized credit for farm inputs, governments have taken over the entire distribution system.
- **Fertilizer Production** – To encourage investment in fertilizer production, parastatals or state-owned enterprises (SOEs) have been created.

The lack of market forces impacting the production and distribution of fertilizer and other agricultural inputs has led initially to undesirable and economically faulty procedures and facts, including the following:

- Capacities were not fully utilized, and sometimes lengthy periods of production downtimes were noted.
- Costs of fertilizer production were not reduced.
- Any economic actions taken by plant management that led to cost reductions resulted in increases in the state budget. This demoralized the staff, consumed financial resources needed for maintenance, restructuring, and modernization of the installations, and increased fiscal burdens.
- Overstaffing.
- Limited management autonomy and motivation.

Therefore, many governments prepared programs for restructuring the fertilizer industry. The common action was the establishment of shareholding companies with Boards composed of bank representatives, ministries, and political parties. Shares were controlled by the local Treasury (or Ministry of Finance/Economy). The Board nominated directors of the company, who were responsible for the factory's operation and product sales. In countries where these actions were accompanied by the deregulation of foreign trade and introduction of the free market system of foreign exchange, public sector fertilizer companies began to be privatized. As the revamping process began, unprofitable units were closed, capacity utilization was improved, and production costs were reduced.

Next, deregulation of fertilizer marketing and trade liberalization motivated public companies to further reduce production costs. A new network of private dealers and traders was established to compete with the state system. In several countries where divestiture and subsidy removal has been immediate, short-term fertilizer use and production declined significantly; therefore, the whole system requires time for adjustment and achievement of a new balance.

The third step is the privatization of fertilizer companies. There are few examples of full privatization of fertilizer companies, e.g., when private concerns take over a company from the government. The basic difficulty is that the fertilizer subsector is very vulnerable to changes in international markets (products and raw materials) and very much depends on local government policies. Therefore, the risk of purchasing a fertilizer company is high, and the private owner is constrained to obtain an adequate amount of money to pay for the assets. The government is interested in selling its assets at the highest possible price. Therefore, a very detailed assessment is necessary to consider long-term government incomes from value-added taxes and taxes of the operational fertilizer factory on the one hand, and on the other hand the potential earning capacity of an installation and the investor's gains from possible restructuring of hardware and introduction of new technology and products. Open market auctions may provide true market values and lessen the political pressure on the government agency that is responsible for privatization.

The closure of a fertilizer plant should be considered only as an extreme case, when the costs of continuing production are higher than the cost of imported material, and other opportunities for investment show greater profitability.

22.5 Establishment of New Facilities

In the short-term a global surplus of capacities is observed; however, the capacities of Central and East European countries and the former Soviet Union (FSU), which may not be operating in the future, are playing a substantial role in this surplus. Asia and Latin America show capacity deficits, and in the coming years, worldscale fertilizer plants should be put under construction. The overall investment costs of about US $18-22 x 10^9 in 5-8 years and the necessary financial instrument would be available because it is a small part of annual world investment. Therefore, the constraints to the implementation of investment programs in the fertilizer industry should be considered.

22.5.1 Technology

Although fertilizer production technologies are considered established and they were not a priority of research programs during the past 20 years, a variety of new processes of fertilizer production were developed that should meet the demand. A detailed review of these technologies has been made in the respective chapters. The attention of decisionmakers is drawn to the following facts.

- The yields of products from raw materials are very high; even in the most energy-consuming ammonia process, methane consumption reached 75% yield. Other intermediates and fertilizer processes reached yields of 98%-99.5%.
- The environmental impact of large-scale fertilizer plants when introducing the necessary treatment schemes has been reduced to acceptable levels.
- The market of technology is diversified. Professional capabilities have been established in many developing countries where engineering organizations can meet world competition on the quality and schedules of the design and procurement of fertilizer installations. More and more equipment could be constructed in developing countries at competitive prices.
- New technologies have reduced the minimum economic size of fertilizer installations; this would reduce worldwide transportation costs of fertilizers in the future and at new production sites.
- New alloys and polymers used in equipment construction have increased the reliability of the operation and reduced maintenance.
- The methodology of preventive maintenance has been developed for the purpose of operating fertilizer plants. It may reduce unexpected downtimes of installations and increase overall annual operation time.

The transfer of adequate technology is no longer a constraint of fertilizer industry development. Some countries coordinate financial credit and the purchase of the technology using a local licenser. These proposals must be dealt with carefully because the technology offered may not meet competitive standards, and its deficiencies would negatively influence the position of the fertilizer producer later. However, the internationalization of the banking system reduces the need for such arrangements.

22.5.2 Financing (Investment and Working Capital)

22.5.2.1 Financing the Construction of the Fertilizer Plant—The financing scheme of fertilizer plant construction poses serious problems. In developing countries few private investors can afford construction of a fertilizer plant. Because the minimum investment cost of an NPK fertilizer complex or an ammonia-urea complex can amount to US $350-$500 million, the following obstacles appear:

- The amount of equity considered safe for any investment is about 30% of the total value (debt:equity ratio = 2.1). Therefore, an investor should collect about US $100 million in assets. If this is possible, the other investing opportunities are more profitable (e.g., in beer production and the plastic industry), and the risk of investing in a fertilizer project would transfer the capital to other projects.
- The remaining debt should be covered by convenient credit facilities (e.g., suppliers' credit). This credit covers only 85% of the delivery cost and must be paid in 6-8 years after the startup of the installation or grace period. An insurance premium is added to the credit cost. The rate of interest may be preferential in case a suppliers' country has such an export promotion scheme. However, it is doubtful that international banks, even under supplier's credit facilities, would provide US $150-300 million to the small private investor in a developing country. In any case the

national bank guarantees of the buyer's country should be issued. Such an arrangement would be possible in very few developing countries.

- All local civil works and other infrastructural costs should be financed locally. In only a few developing countries could local banks finance part of a construction project in the amount of US $100-200 million, with a small local investment group as the debtor.

  The total costs including interest at unfavorable conditions (delay in construction and high rate of interest of local credit) may easily double the fixed investment costs.

- Since the loans are guaranteed by the government (Central Bank or Treasury), there is a practice to relend the loan to an investing group at local interest rates, which are much higher than that approved by the supplier's foreign bank. The difference goes to the budget through the taxed profits of the local investment bank. This practice may raise the investment cost over the level of minimum feasibility.

  Therefore, establishment of the fertilizer complex by a local private investment group may be an exception, especially in Africa. A joint venture with a serious international investment group would require involvement of the government for the purpose of stable agricultural policies ensuring demand after the establishment of the plant.

  When large-scale investment in fertilizers is considered in developing countries, especially in Africa, government involvement may be necessary in those countries where the fertilizer sector development is in its infancy. However, this involvement and guarantees must be given without seriously influencing the investment process and management autonomy. Therefore, the establishment of a public shareholding company to carry out the whole investment procedure and construction of the fertilizer plant should be considered only as a last resort. After startup of the factory, shares could be sold on the stock exchange, leading to the privatization of the company. Implementation of this alternative requires devoted and professionally capable local staff and a liberal exchange control policy.

  The exchange control policies present an additional difficulty in the establishment of the fertilizer plant. The design and construction schedules obviously should be tight to reduce interest charges as much as possible. This requires a flexible policy regarding signing of the contracts and issuing payments. If the Central Bank exercises total control over the exchange in release of foreign payments, the management of a large-scale investment project is very difficult and inefficient.

22.5.2.2 Working Capital – Another element of total investment cost is the working capital. Considering the seasonal consumption of fertilizers, delayed payments may be accrued only in 4-8 months on average throughout the year from the production time. This increases the usual value of working capital from 9%-11% to 30%-40% of the sales value. Depending on the prevailing interest rate of the local financial market, this may increase the farm-gate price of fertilizers by 8%-10%. The banking sector should ensure that the production and marketing operations are not hampered by the paucity of working capital.

22.5.3 Project in Trouble

Any industrial investment has its own procedure that leads to a successful project. A fertilizer project also has its systemic implications. If these are not considered in planning the project implementation and the adequate instruments to abate investment distortions are not prepared, then ad-hoc measures may not avoid the losses.

22.5.3.1 Inadequate Credit Schemes – A typical problem in the credit scheme is a down payment. In almost all suppliers' contracts, the insurer requires that 15% of the contract value should be paid as a down payment upon validation of the contract. This can be paid from the equity if available in cash. However, the equity in developing countries is usually in assets and obligations; therefore, cash is not available. The investor must arrange for another loan at international financing institutions. Negotiations of this loan, depending on bank guarantees, may delay implementation of the suppliers' contract over the price validity term, and contract renegotiations would begin again. Therefore, arrangements for the down payment should be made concurrently with the main suppliers' contract and involve the financing institution in assessing the project's feasibility.

Another inadequacy of the credit scheme is a nonoptimal repayment schedule. It is not true that the longer the grace period and delay in repayment of the debt, the better is the financial position of the project. Each credit scheme has its optimum, and the optimization factor should be the project liquidity or earliest possible date of net profitability. Computer models are available to simulate credit conditions at different assumptions of the sales and price risks. The investor should use these models before beginning negotiations of the credit arrangements. Considering the project's risks after the optimal scheme is negotiated, a refinancing scheme should be included in the financial agreement.

22.5.3.2 Price Distortions and Debt Repayment Difficulties – Lack of stable industrial policies in the promotion of locally produced fertilizers may result in difficulties in plant operation when fertilizer prices on the international market are dropping. During recession periods many companies have sold their products for the cost of the raw materials, utilities, and labor; this practice will undermine local production even if it is carried out in a normally competitive way. Obviously, a local company should adjust its prices, but then profits will be reduced and repayment of the debt will be in danger. Then, only policy instruments, such as antidumping judgments and penalty custom duties, may save the company. Therefore, the government should continuously watch the international fertilizer situation to avoid disruption of the business and loss of incurred investments.

22.5.4 Marketing and Distribution

Marketing and distribution networks should exist long before the local fertilizer factory is established. The government's role to ensure regulatory frameworks is vital to avoid high costs of the distribution system. Distribution and marketing costs may equal production costs, and measures should be taken to maintain them at the lowest possible level. In fact, there is a contradiction between the requirements of the efficiency of fertilizer use by farmers and a low-cost distribution system. A distribution network that supplies farmers with fertilizers on time and of the required quality, with necessary advisory services requires large quantities of fixed and working capital. Returns are realized through the increased crop production yields even at fertilization rates below the economic optimum. However, establishment of such a system throughout the country is difficult, logistically and financially. Government involvement is necessary to provide assistance in establishing local storage and providing transportation. This system may be established by a parastatal organization, which can be privatized later. Another possibility requires the establishment of a package of policies for a private investor: satisfactory credit facilities, special repayment schedules, and fiscal privileges. All measures should consider only one goal: low distribution costs at realistic returns on capital investment. The regulatory framework should be established to promote competition and restrict monopoly practices. Farmers should be encouraged to develop viable cooperative networks.

22.6 Potential for Reducing Fertilizer Costs

Fertilizer production costs are always specific to a given factory. However, to show the possible trends in the fertilizer production costs, the cost trends in major elements are discussed [4] .

22.6.1 Raw Materials

As has been discussed the opportunities to lower costs of the raw materials are limited. Current technologies have achieved a high level of raw material utilization and high reaction yields. Technology to convert byproduct phosphogypsum into a salable product could bring a substantial discount (if no additional costs). Natural gas prices are stable or rising, and a reversal of the trend is not likely. Phosphate rock prices are relatively stable, and resources at these prices are limited to existing mining operations. Therefore, with the exhaustion of operational reserves, prices of phosphate rock should increase.

22.6.2 Investment Costs

According to the U.S. chemical engineering plant cost index [4], during the past 25 years the unit investment cost of fertilizer plants has risen by a factor of 3, with only a 1.5-2.0 times increase in fertilizer prices. Therefore, a decrease in depreciation cost is not likely for new plants. New developments in ammonia technology may keep unit investment costs stable for a period of time; therefore, present investment decisions in the fertilizer industry may be beneficial to the investor in comparison with delayed construction.

22.6.3 Other Cost Elements

Labor and utility costs are a small part of total costs for basic fertilizer producers. Newer sulfuric/phosphoric acid plants are net exporters of energy. In solid fertilizer production the heat of acid neutralization may be used to save energy in the granulation/drying operations. Therefore, it is difficult to expect any substantial change in this already marginal cost. Financial costs may increase, depending on interest rates and the storage period of products and sales costs in which the growing component of fertilizer marketing should be considered. The overhead costs also include local taxes, rents, research and development expenditures, maintenance costs, and management costs. This element in fertilizer cost calculation is relatively low. There are branches of industries where this cost reached 25%-30% of production costs. Therefore, there is little opportunity to decrease the cost of this element.

22.6.4 Expected Price Changes

Following the logic of the previous analysis, it is not likely that the cost of fertilizer production can be drastically reduced. Price fluctuations relate to changes in temporary demand, and are not linked with changes in cost of production. In times of depression the producers are charging only variable costs, labor and some elements of the sales and financial costs, expecting a cyclic increase in prices and then possibly to recover the permanent costs and profits. Modern installations that are nearly depreciated but well maintained are especially privileged in this situation.

22.6.5 Biological Fixation of Nitrogen

A large part of the supply of nitrogen already comes from biological fixation of nitrogen from air and soil. Extensive research has been carried out for more than 20 years [5] to develop genetic varieties of basic crops that can fix nitrogen directly from the air. The successes are limited to a few species; however, even in the case of success in this field, the testing of the environmental impacts and reproduction of the new species and their distribution worldwide may take considerable time.

One can also expect studies to continue on the enzymatic fixation of nitrogen. The simple reaction of nitrogen and water can produce ammonia in the enzymatic process. However, efficient bacterial species must be developed through genetic manipulation to produce these enzymes. Installations including bacterial processes are generally quite large and require a large-scale investment. Therefore, the simplicity of the enzymatic process of ammonia synthesis would likely be offset by the cost of production of enzymes.

Therefore, the production of nitrogen fertilizer by present means may continue for a long period.

22.6.6 An Alternate Supply of Other Mineral Nutrients

Other than nitrogen, which could be naturally supplied from the air, the remaining nutrients must be regularly supplied through fertilization. There are numerous detailed research results, which describe the extraction of nutrients by crops [6]. Artificial fertilization and partial recycling of crop residues are the only solutions supporting soil fertility. This is valid for such elements as Ca, Mg, K, and the micronutrients (Fe, Cu, Mn, Co, etc.). These elements must be supplied in soluble form, or conditions must be created for their solubility in the soil.

22.6.6.1 Enzymatic Phosphoric Solubility – In the 1980s Canadian scientists [7] discovered that some kinds of naturally occurring fungi in the soil are able to solubilize the phosphate salts normally unavailable to plants. In a radical way this may influence development programs of the phosphatic industry. Many studies on the use of fertilizers have shown that up to 70% of the soluble phosphate applied by the farmer can become adsorbed onto clay soils and organic matter and become bound to the soil and therefore not readily available to the plants. One of the naturally occurring microorganisms (Fungus Penicilinum Bilaji) has the ability to solubilize phosphate in the soil. Research has shown that this microorganism can reduce the amount of commercial phosphate required by up to 50% by solubilizing both mineral and organic phosphate while maintaining crop yields. It may be also expected that microorganisms can make phosphorus directly available from phosphate rock, which would lead to a substantial saving in investment, especially in countries with phosphate rock resources but with no possibility of establishing a feasible phosphatic fertilizer plant. An additional effect, the large development of roots, contributes to efficient plant growth even in less favorable weather conditions. However, FAO has been reluctant to undertake any confirmation tests, and tests conducted by IFDC have not been convincing. Finally, the developing company has been purchased by a large multinational company, and since that time no additional information has become available on the product and process development.

In summary, it appears that opportunities for reducing fertilizer production costs via new technologies are limited. However, recent consolidations have resulted in a few closures of high cost plants, and have contributed to increased operating rates for the lower cost producers. This has reduced costs and has increased the percentage of fertilizer intermediates and finished products which enter world trade. Importers have entered into joint ventures with firms in energy (primarily natural gas-rich countries) or with firms which have access to phosphate or potash reserves. This also contributes to reduced costs.

Major opportunities exist for reducing the total fertilizer costs per unit of agricultural output by increasing the efficiency of fertilizer distribution systems and by increasing the efficiency of on-farm use.

22.7 General Conclusions

The consumption of fertilizer and, thus, increasing yields of crops are primarily dependent on the benefit:cost ratio and government policies reducing the farmers' risks. Establishment of these policies is difficult and requires detailed research and preparation of a decisionmaking computerized model in every country. Only when stable agricultural policies are established and fertilizer consumption approaches the minimum capacity level is it reasonable to consider establishment of a fertilizer plant. Grain overproduction in industrialized countries and the problems with agricultural and export subsidies have slowly decreased the consumption of fertilizer in many countries with intensive agriculture, leaving free capacities to supply the international market. On the other hand, solution of the worldwide food supply problem requires increases in fertilizer use. Technologies have been improved and new concepts implemented to produce high yields and better financial efficiency. Therefore, the construction of national fertilizer plants in the next decade will be necessary to cover the growing demand of local markets. Obviously some countries that are endowed with raw materials can consider establishing a fertilizer industry (in particular, a phosphate fertilizer industry) as an export-oriented industry.

Experience has shown that the fertilizer industry has been started as a public sector or mixed public/private venture. The price cycles and over-capacities for many years have reduced interest of financial and international development organizations in the continuous improvement of the market situation; technical assistance in the fertilizer industry has been practically abandoned by UNIDO and the World Bank. A decision to establish a fertilizer plant requires an extensive programming and planning effort from government decisionmakers regardless of the future owner of the fertilizer plant. Credible demand assessment, implementation of complex agricultural policies, selection of the plant's location, raw material supply identification, technology preselection and identification of financing sources, and preparation of the necessary guarantees are the challenges that the governments must meet in the industrialization of agriculture. International organizations should reinstate their fertilizer programs and support actions of the developing-country governments intending to consider construction of fertilizer plants or revamping of the existing industry. Both the country governments and international organizations should create an enabling policy environment to promote investment in fertilizer production and distribution. In this context, joint ventures between developed and developing countries (North-South collaboration) and among developing countries (South-South cooperation) should be developed.

22.8 References

1. "Perceived Global and Regional Issues." 1993. Fertilizer Industry/World Bank Roundtable Meeting, 9-13 September. World Bank Report.
2. Gregory, D. I. 1994. "Issues in Privatization of Public-Sector Fertilizer Production Units and Market Liberalization," IFDC, Muscle Shoals, AL, U.S.A. (unpublished).
3. SRI International 1989. PEP Yearbook.
4. *Chemical Engineering*. 1995. December.
5. Aziz, Zahid. 1994. Development and Transfer of Technology Series No. 17. UNIDO draft publication, p. 47.
6. Tandon, H.L.S. 1993. "Assessment of Soil Nutrient Depletion," Proceedings of the Regional FADINAP Seminar on Fertilization and the Environment. Chiang Mai, Thailand, 7-11 September 1992, United Nations ST/ESCAP/1256.
7. Kucey, R.M.N. 1990. Agriculture Canada, Research Branch, private communication.

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