Fertilizer Technology

20
23

Perpared By:

Nour
Khraisat

Dr:

Yousef
Mubarak

FERTILIZERS TECHNOLOGY

CHEM 0905554

Second Semester 22/23

CHAPTER 1

INTRODUCTION TO FERTILIZERS TECHNOLOGY

→ liquid fertilizers. (plastic or metal)

4 : 3 : 3 ←

N P2O5 K2O

pure liquid (not suspension)

⇒ single fertilizer contain only one compound.

→ Solid fertilizers

⊛ كل نبتة لها متطلبات معينة وتختلف من نبتة لأخرى.

*fertilizers → organic such as, foodwaste.
→ inorganic

→ primary fertilizers
1) Nitrogen 2) phosphorus 3) pottasi
↳ All plants needs them
why primary?
↳ plants needs them in the Largest amounts compared to the others.

INTRODUCTION

- Fertilizers are formulations which may contain nitrogen, phosphorus and potassium compounds added to soil to improve plants' growth and yield.
- First used by ancient farmers, fertilizer technology developed significantly as the chemical needs of growing plants were discovered.
- Modern synthetic fertilizers are composed mainly of the following compounds:

تصنف الاسمدة بناءً على ما تحتوي من primary fertilizer

1. Nitrogen.
2. Phosphorous.
3. Potassium.
4. Secondary nutrients added.

(1–3) → single

⊛ single primary nutrient exsist ⇒ straight fertilizer
such as 1) KCl 2) NH_3 3) urea 4) phosphoric Acid.
chlorine → may be secondery or trace.

⊛ if it contains two primary nutrient ⇒ mixed fertilizer.
Such as ⇒ 1) monoAmmonium phosphate 2) mono pottasium phosphate
3) pottasium Nitrate.

⇒ fertilizers in both types
Sometimes it may contains some of trace elements or coated by sulfur.

FERTILIZERS SOLUBILITY

→ most important specification

- Fertilizer compounds must be soluble in water so they can be absorbed by the root hair cells:
  - ✓ Ammonium ions, NH_4^+, and nitrate ions, NO_3^-, are sources of soluble nitrogen
    → it's more preferable for plants. (Absorption is faster)
  - ✓ Phosphate ions, PO_4^{3-}, are a source of soluble phosphorus ⇒ but in markets we found phosphorus as P_2O_5
  - ✓ All common potassium compounds dissolve in water to produce potassium ions, K^+

→ if it's not soluble in water? → we may add filler to make the fertilizer exsist as granules by adding very fine particles of diAmmonium salfate other wise it's gonna be exsists as chunks.

if diammonium sulfate → not Available? add some sands ↓ only for putting the fertilizer directly on the soil

what's the problem? → they are insoluble in water ↓ not for drip irrigation

↳ لأنه هاي الحبيبات رح تسكّر ال nozzed تبع الرش وهاد 2 نستفيد.

SOIL HEALTH

- Fertilizers play an important role for soil health:
  - ✓ They supplement the natural supply of soil nutrients. → may be Natural regons such as <u>rain</u> (Almost leaching)
  - ✓ Build up soil fertility.
  - ✓ Compensate for nutrients taken by harvested crops or lost to other factors which locally-specific nutrient use management can mitigate.
  - ✓ Fertilizers also help build carbon sinks in agricultural soils.

nutrients consumption in Soil:-

→ metabolism in plants
produces carbon
So to avoid carbon accumulation
we must add fertilizers to make the Balance

NON-MINERAL NUTRIENTS ⇒ not primary but essential and without them The photosynthesis will not accomplish as it should.

1. Hydrogen (H) ⇒ available in H_2O
2. Oxygen (O) ⇒ available in the atmosphere
3. Carbon (C). ⇒ available in the atmosphere ⊕ in the soil

← carbon is available in the largest amounts in the roots of the plant.

- These nutrients are found in the air and water.
- In a process called photosynthesis, plants use energy from the sun to change carbon dioxide (CO_2 - carbon and oxygen) and water (H_2O- hydrogen and oxygen) into starches and sugars.
- These starches and sugars are the plant's food.

MINERAL NUTRIENTS

<table>
<tr><th colspan="2">Macronutrients ⇒ large quantities.</th></tr>
<tr><th>Primary Nutrients</th><th>Secondary Nutrients</th></tr>
<tr><td>1. Nitrogen (N)
2. Phosphorus (P)
3. Potassium (K)
⇒ mostly causes the defeciency in the plants
▪ These major nutrients usually are lacking from the soil because plants use large amounts for their growth and survival.</td><td>1. Calcium (Ca)
2. Magnesium (Mg)
3. Sulfur (S)
▪ There are usually enough of these nutrients in the soil, so fertilization is not always needed.</td></tr>
</table>

MINERAL NUTRIENTS

Micronutrients

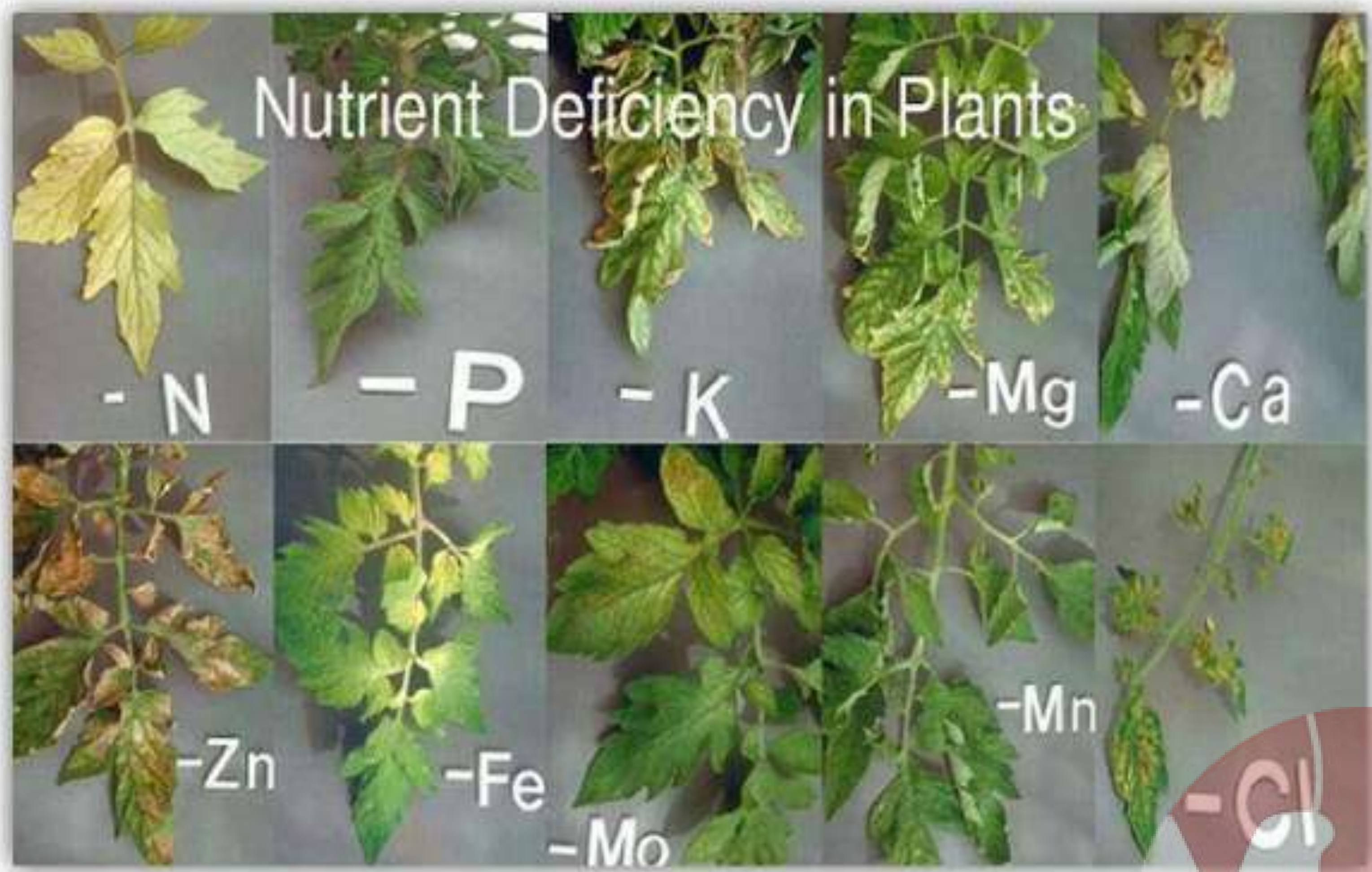
1. Boron (B)
2. Copper (Cu)
3. Iron (Fe)
4. Chloride (Cl)
5. Manganese (Mn)
6. Molybdenum (Mo)
7. Zinc (Zn)
8. Cobalt (Co)
9. Nickel (Ni)

→ All Summation = 1%

- Micronutrients are those elements essential for plant growth which are needed in only very small (micro) quantities. ⇒ usually ⇒ chelated very porus ⊕ weak.] → to be easily dissolved in water.
- These elements are sometimes called minor elements or trace elements.

Cost ⇒ expensive / usually we use them when there is defeciency in the soil

Ⓐ defeciency ⇒ not in enough amount.



NITROGEN (N)

- Nitrogen is a part of all living cells and is a necessary part of all proteins, enzymes, and metabolic processes involved in the synthesis and transfer of energy.
- Nitrogen is a part of chlorophyll, the green pigment of the plant that is responsible for photosynthesis.
- Helps plants with rapid growth, increasing seed and fruit production and improving the quality of leaf and forage crops.
- Nitrogen often comes from fertilizer application and from the air.

NITROGEN DEFICIENCY

Symptoms

- The whole plant looks pale to yellowish green.
- Early senescence of older leaves.
- Increased root growth and stunted shoot growth result in a low shoot/root ratio.

PHOSPHORUS (P)

- Phosphorus (P) is an essential part of the process of photosynthesis.
- Involved in the formation of all oils, sugars, starches, etc.
- Helps with the transformation of solar energy into chemical energy; proper plant maturation; withstanding stress.
- Effects rapid growth.
- Encourages blooming and root growth.
- Phosphorus often comes from fertilizer, and superphosphate.

PHOSPHORUS DEFICIENCY

- Phosphorus deficiency tends to inhibit or prevent shoot growth.
- Leaves turn dark, dull, blue-green, and may become pale in severe deficiency.
- Reddish, reddish-violet, or violet color develops from increased anthocyanin synthesis.
- Symptoms appear first on older parts of the plant

POTASSIUM (K)

- Potassium is absorbed by plants in larger amounts than any other mineral element except nitrogen and, in some cases, calcium.
- Helps in the building of protein, photosynthesis, fruit quality and reduction of diseases.
- Potassium is supplied to plants by soil minerals, organic materials, and fertilizer.

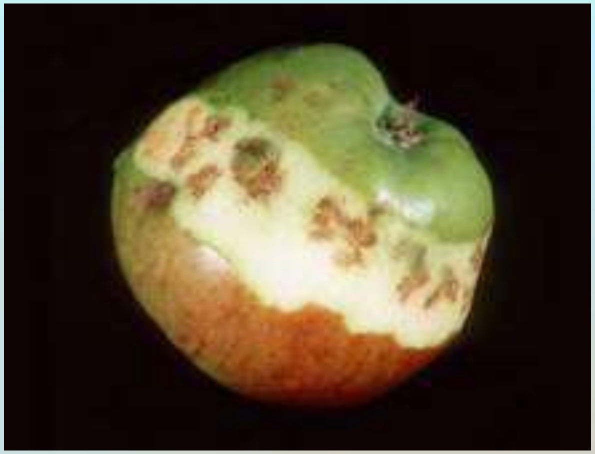
POTASSIUM DEFICIENCY

- Symptoms of potassium deficiency appear on the lower portion of the plant first with chlorosis (yellowing) at the leaf margins followed by necrosis (death).
- Potassium deficiency can be caused by soil pH, extreme liming or calcium rich areas of fields, lack of soil oxygen or true soil deficiency

CALCIUM (Ca)

- Calcium, an essential part of plant cell wall structure, provides for normal transport and retention of other elements as well as strength in the plant.
- It is also thought to counteract the effect of alkali salts and organic acids within a plant.
- Sources of calcium are dolomitic lime, gypsum, and superphosphate.

CALCIUM DEFICIENCY



- Symptoms of calcium deficiency first appear on younger leaves and tissues, growth is inhibited, and plants have a bushy appearance.

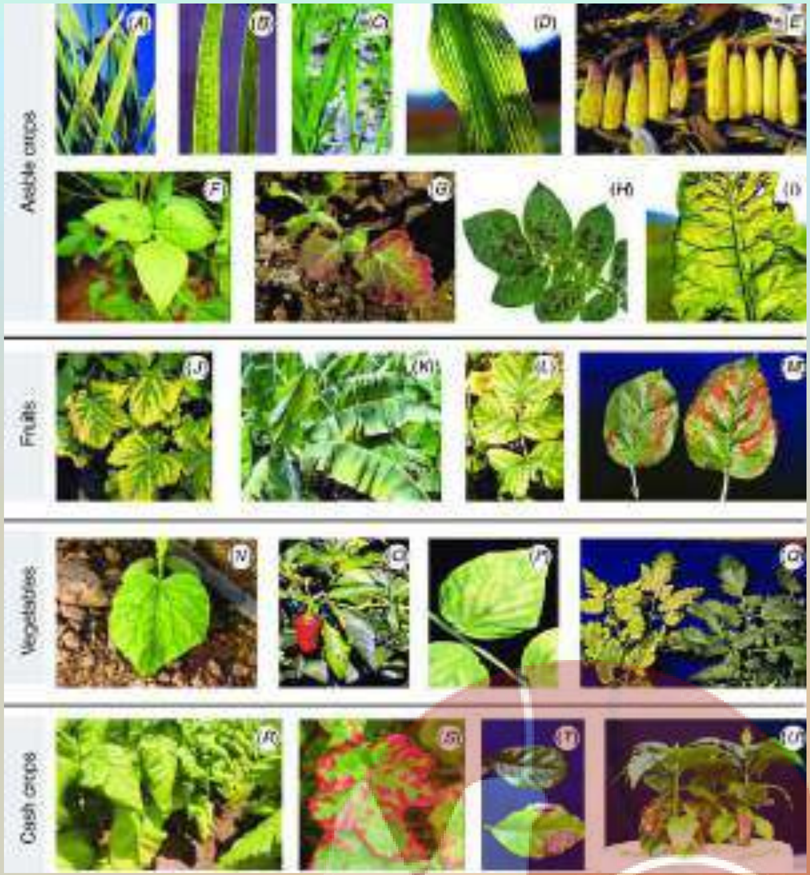
- The youngest leaves are usually small and misshapen with brown chlorotic spots developing along the margins, which spread to eventually unite in the center of the leaves

MAGNESIUM (Mg)

- Magnesium is part of the chlorophyll in all green plants and essential for photosynthesis.
- It also helps activate many plant enzymes needed for growth.
- Soil minerals, organic material, fertilizers, and dolomitic limestone are sources of magnesium for plants.

MAGNESIUM DEFICIENCY

- Magnesium is highly mobile in the plant and deficiency symptoms first appear on the lower leaves.



- Symptoms are more severe on the lower leaves because magnesium is moved to the new growth.
- Deficiency symptoms consist of interveinal chlorosis (leaf veins stay green while the regions between them turn yellow)

SULFUR (S)

- Essential plant food for production of protein.
- Promotes activity and development of enzymes and vitamins.
- Helps in chlorophyll formation.
- Improves root growth and seed production.
- Helps with vigorous plant growth and resistance to cold.
- Sulfur may be supplied to the soil from rainwater. It is also added in some fertilizers as an impurity, especially the lower grade fertilizers. The use of gypsum also increases soil sulfur levels.

SULFUR DEFICIENCY

- A sulfur deficient plant will experience yellowing or pale green coloring throughout the plant.
- Younger leaves suffer from chlorosis with their tips becoming necrotic.
- Overall plant development and growth will be stunted without enough sulfur in the soil

BORON (B) AND COPPER (Cu)

Boron (B)

- Helps in the use of nutrients and regulates other nutrients.
- Aids production of sugar and carbohydrates.
- Essential for seed and fruit development.
- Sources of boron are organic matter and borax.

Copper (Cu)

- Important for reproductive growth.
- Aids in root metabolism and helps in the utilization of proteins.

BORON DEFICIENCY

- Boron deficiency is a common deficiency of the micronutrient boron in plants. …
- Boron deficiency affects vegetative and reproductive growth of plants, resulting in inhibition of cell expansion, death of meristem, and reduced fertility.
- Plants contain boron both in a water-soluble and insoluble form.

COPPER DEFICIENCY

- Copper is immobile, meaning its deficiency symptoms occur in the newer leaves.
- Symptoms vary depending on the crop.
- Typically, the symptoms start as cupping and a slight chlorosis of either the whole leaf or between the veins of the new leaves

CHLORIDE (Cl) IRON (Fe) and MOLYBDENUM (Mo)

Chloride (Cl)

- Aids plant metabolism.
- Chloride is found in the soil.

Iron (Fe)

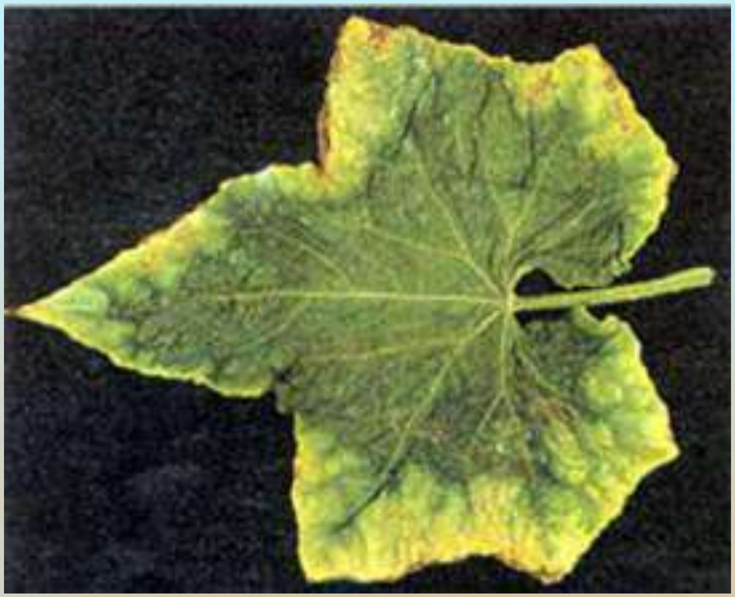
- Essential for formation of chlorophyll.
- Sources of iron are the soil, iron sulfate, iron chelate.

Molybdenum (Mo)

- Helps in the use of nitrogen.
- Soil is a source of molybdenum.

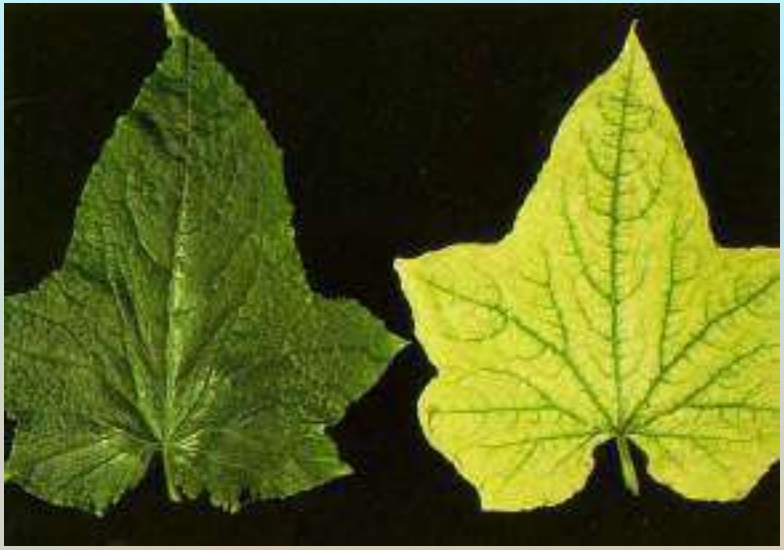
CHLORIDE DEFICIENCY

- Chloride deficiency can occur if there is consistently less than 2 ppm chloride in the growing medium and the symptoms appear as chlorotic blotches with necrotic spots located between the veins or on the margins of the younger leaves.
- In advanced cases, chloride deficiency could cause plant wilting



IRON DEFICIENCY

- The symptoms of iron deficiency appear on the youngest, newest leaves.
- The area between the leaf veins becomes pale yellow or white (this is called interveinal chlorosis).
- Usually, no noticeable physical deformity occurs, but in severe cases the youngest leaves may be entirely white and stunted



MANGANESE (Mn) and ZINC (Zn)

<u>Manganese (Mn)</u>

- Functions with enzyme systems involved in breakdown of carbohydrates, and nitrogen metabolism.
- Soil is a source of manganese.

<u>Zinc (Zn)</u>

- Essential for the transformation of carbohydrates.
- Regulates consumption of sugars.
- Part of the enzyme systems which regulate plant growth.
- Sources of zinc are soil, zinc oxide, zinc sulfate, zinc chelate.

MANGANESE DEFICIENCY

- Manganese deficiency symptoms, which often look like those of iron deficiency, appear as interveinal chlorosis (yellow leaves with green veins) on the young leaves, and sometimes tan, sunken spots that appear in the chlorotic areas between the veins.
- Plant growth may also be reduced and stunted

ZINC DEFICIENCY

- Zinc deficiency causes a type of leaf discoloration called chlorosis, which causes the tissue between the veins to turn yellow while the veins remain green.
- Chlorosis in zinc deficiency usually affects the base of the leaf near the stem

FERTILIZERS

Organic

- Carbonaceous materials mainly of vegetable and/or animal origin added to the soil specifically for the nutrition of plants.

↳still exsist but not in suffecient amounts.

Inorganic (chemical fertilizer)

- A term used by the International Organization for Standardization (IOS) 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.

INORGANIC FERTILIZERS

Straight Fertilizer

Single + primary fertilizer.

- A qualification generally given to a nitrogenous, phosphatic, or potassic fertilizer having a declarable content of only one of the primary plant nutrients.

⊛ Compound Fertilizer

- A fertilizer that has a declarable content of at least two of the plant nutrients nitrogen, phosphorous, and potassium, obtained by chemically or by blending, or both.

⊛ Mixed Fertilizer (physical Blending)

- The term applied to a fertilizer that is a physical mixture of two or more of the straight fertilizer. Mixed fertilizer may be powdered or granulated.

INORGANIC FERTILIZERS (Continue …)

Blended Fertilizer

→ no Liquid.

- A fertilizer, obtained by dry mixing, that has a declarable content of at least two of the plant nutrients nitrogen, phosphorus, and potassium.

during nutrelisation
to get completed one
they do it normally
in the reactor but in partial to get the
diammonium phosphate
because the product
is very viscous

Granular Fertilizer

- Solid material that is formed into particles of a predetermined mean size.

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.

Slow-release Fertilizer partial Solubility

- 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.

ذكرناه مع الوقت .

Conditioned Fertilizer additives not nutrient
Such as some additives to prevent caking

- Fertilizer treated with an additive to improve physical condition or prevent caking.

Solution Fertilizer

- Liquid fertilizer free of solid particles

Suspension > Solid > liquid fertilizers that contains the highest amount of the nutrients.
NPK
28:28:28

Suspension Fertilizer

- A two-phase fertilizer in which solid particles are maintained in suspension in the aqueous phase.

Powder Fertilizer

- A solid substance in the form of very fine particles.

FERTILIZER SPECIFICATIONS

A well written fertilizer specification should include the following elements in details:

1. Nutrient contents and concentrations.
2. Nutrient chemical composition.
3. Moisture content. → for the customer
4. Physical condition ⇒ بمرجع العبارة
5. Particle size distribution. → Caking -- etc
6. Solubility. → very important.
7. Conditioner.
8. Packaging details.
9. Penalties or discount for deviation from stated values.

Crystalline
↳ No impurities
more expensive

COMMON FERTILIZER

Abbreviation	Name	Grade
AN	Ammonium Nitrate explosive	33-34% N
AS	Ammonium Sulfate least expensive due to Ammonia.	21% N
KNO_3	Potassium Nitrate	13% N, 46% K_2O
CN	Calcium Nitrate	15% N
DAP	Diammonium Phosphate } نسب توزيع ال Nutriats.	18-46-0
MAP	Monoammonium Phosphate	11-55-0 to 12-61-0
KCl	Potassium Chloride	60-62% K_2O
TSP	Triple Superphosphate not purified.	44-48% P_2O_5
SOP	Potassium Sulfate → main source for (K)	50% K_2O
	Urea → Ammonia most common used	45-46% N

↳ Not in jordan
required Natural gas.

Fine particles fertizers
↳ contains Larger amount
of impurities.

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.
- A fertilizer product with a grade of 18-46-0 is guaranteed by the manufacturer to have 18% N and 46% P_2O_5.

CONVERSION FACTORS

$\rightarrow \frac{Mw \text{ of } P}{Mw \text{ of } P_2O_5}$

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

FERTILIZERS TECHNOLOGY

CHEM 0905554

First Semester 21/22

⊛ قديش العالم استفاد + كم أنتج
من الأسمدة

CHAPTER 2
HISTORY OF FERTILIZERS

⊛ مشكلة إنّه توزيع السكان غير
منتظم بالعالم.

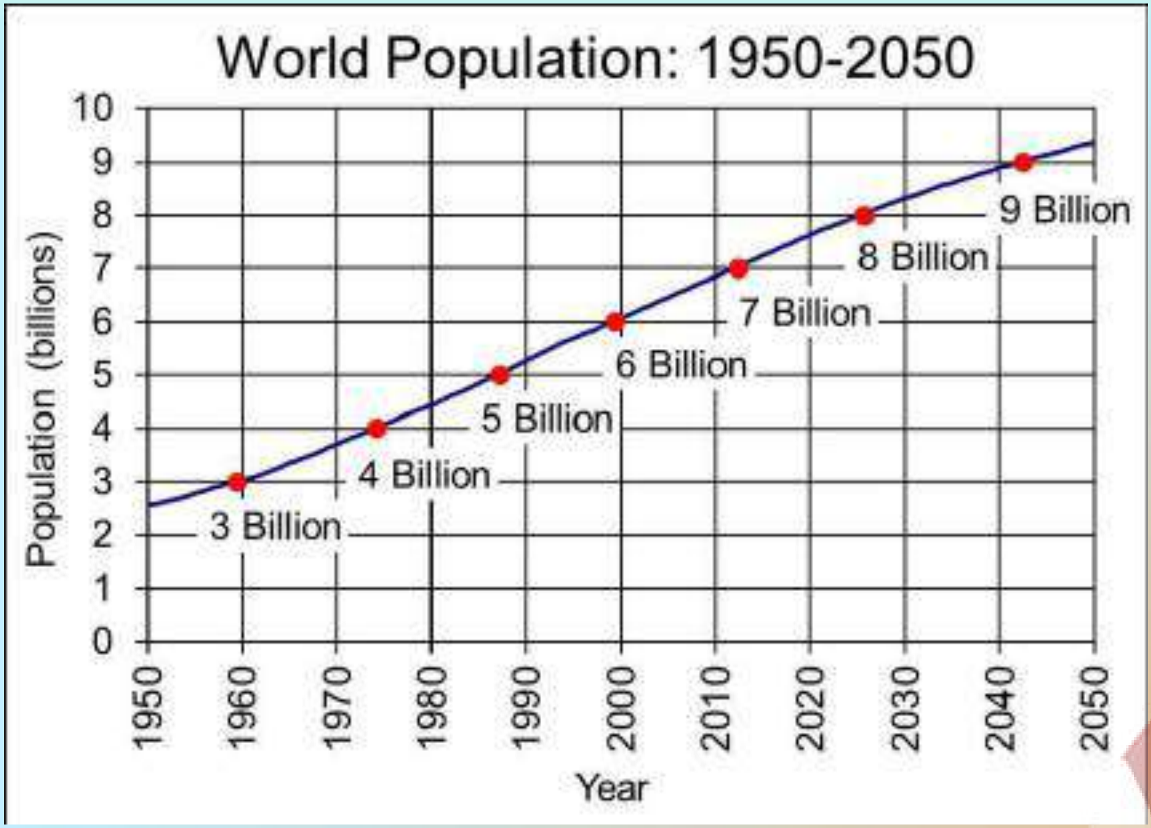
INTRODUCTION

- 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.
- 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 failure to maintain soil nutrients has led to the downfall of many ancient societies.

-problems :-

1) not all lands are suited for agriculture purposes such as farming → apply enough amount of fertilizers

WORLD POPULATION

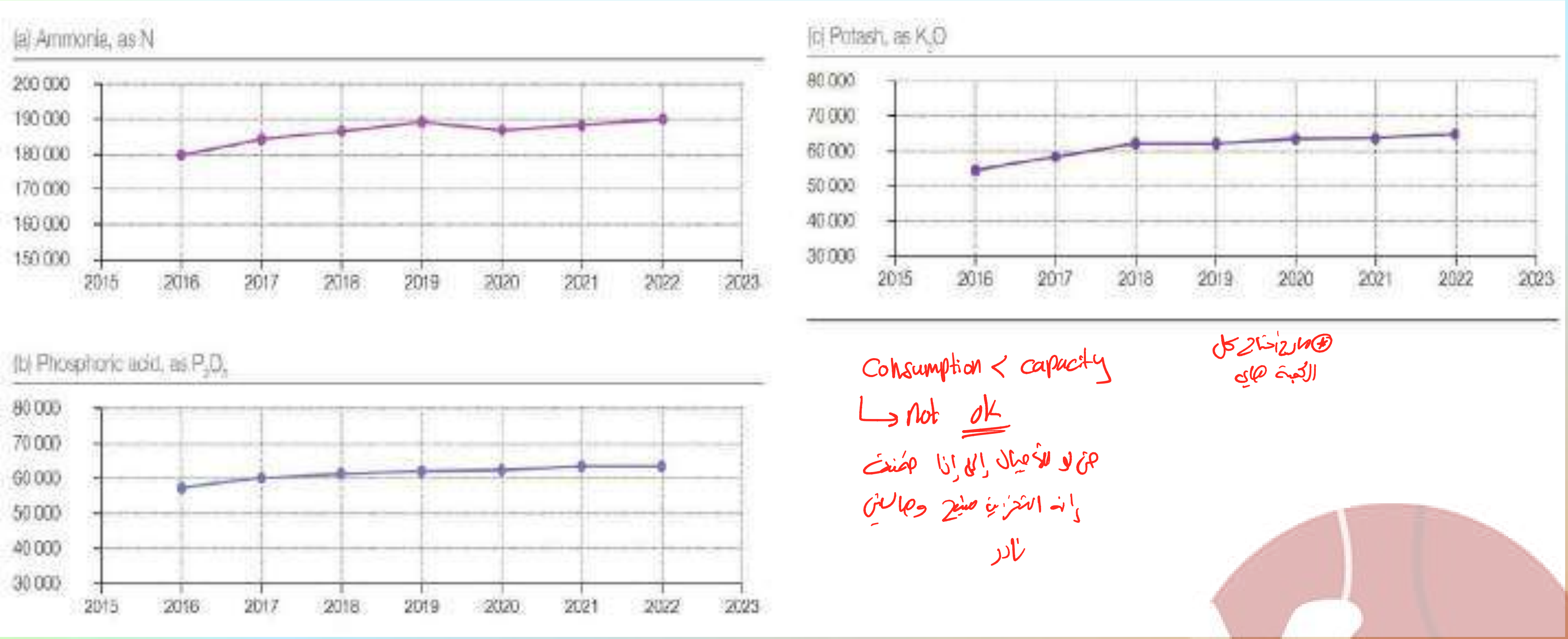


Soil fertility

Crop	Yield (t/ha)	N	P_2O_5	K_2O	S
		(kg/ha)			
Rice	6	100	50	160	10
Wheat	6	170	75	175	30
Maize	6	120	50	120	25
White Potato	40	175	80	310	20
Banana	40	250	60	1000	15
Cotton	1	120	45	90	20

← القدرة الانتاجية العالمية

WORLD CAPACITY FOR PRODUCTION (thousand tonnes)



Consumption < capacity
↳ not ok

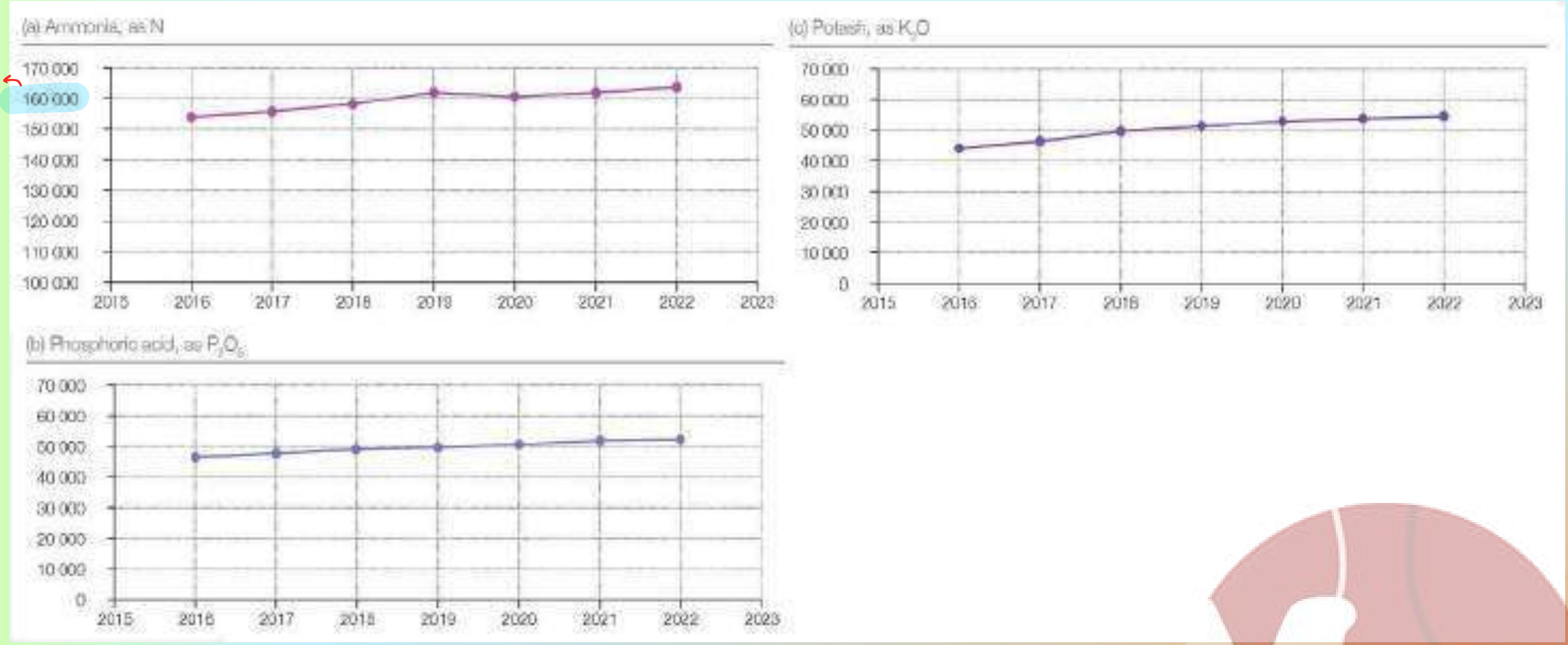
من لو الأحيان إلي إنا مصنع
لأنه التخزين صعب وماليش
نادر

⊕ مارح انتج كل
الكمية هاي

تقديرية جد بنتج

WORLD SUPPLY (Thousand tonnes)

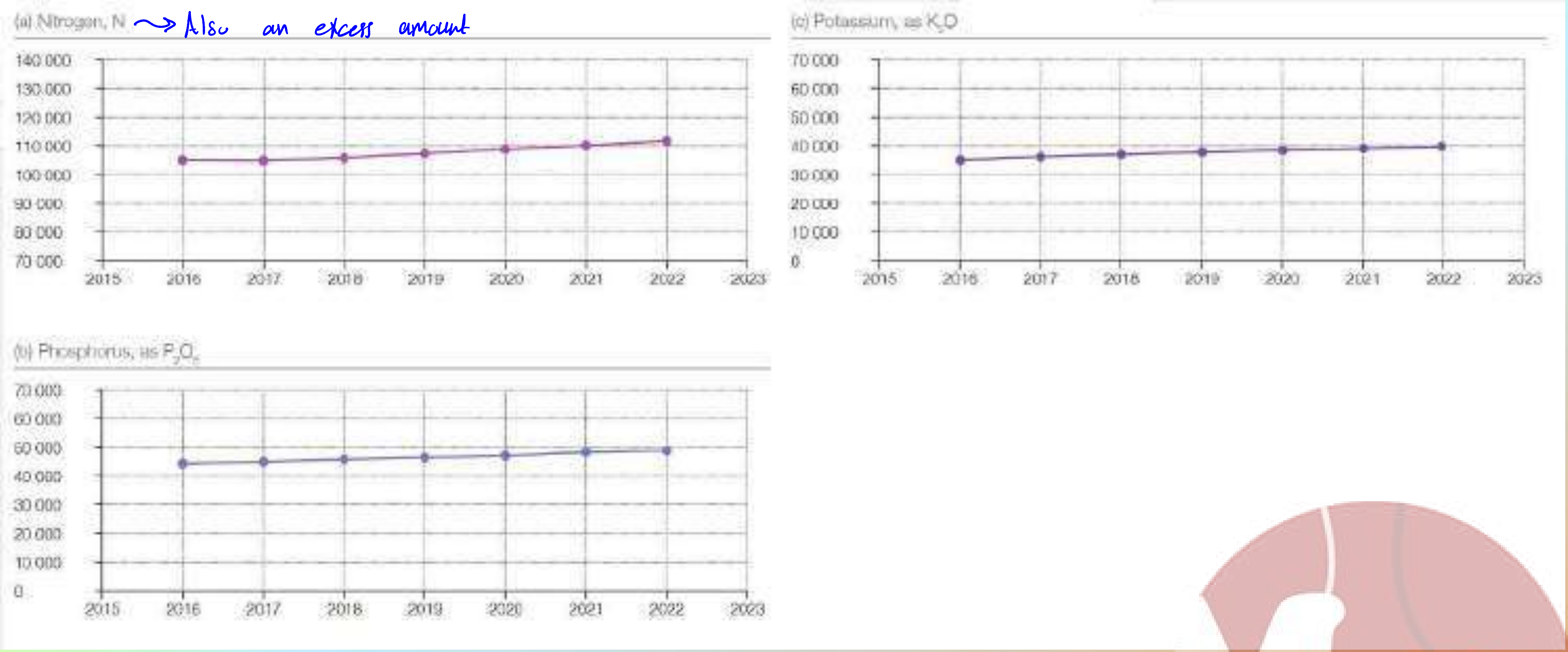
أقل من capacity عشان تخزين



-capacity

→ consumption

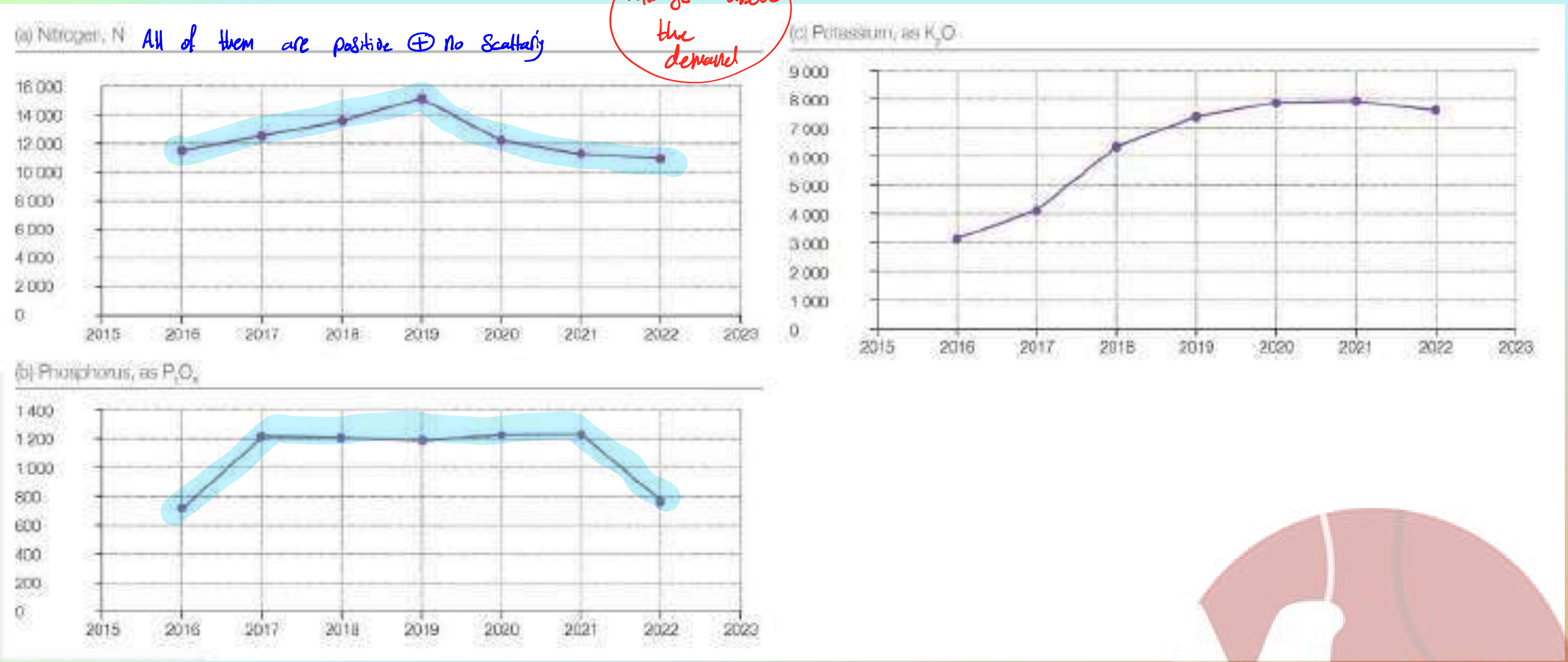
WORLD DEMAND (Thousand tonnes)



→ Also an excess amount

difference between capacity + supply → Balanced
↓
Are we in the safe side? → لازم يكون في احتياط → للطوارئ

POTENTIAL WORLD BALANCE (Thousand tonnes)



(a) Nitrogen, N

All of them are positive ⊕ no scattering

Always above the demand

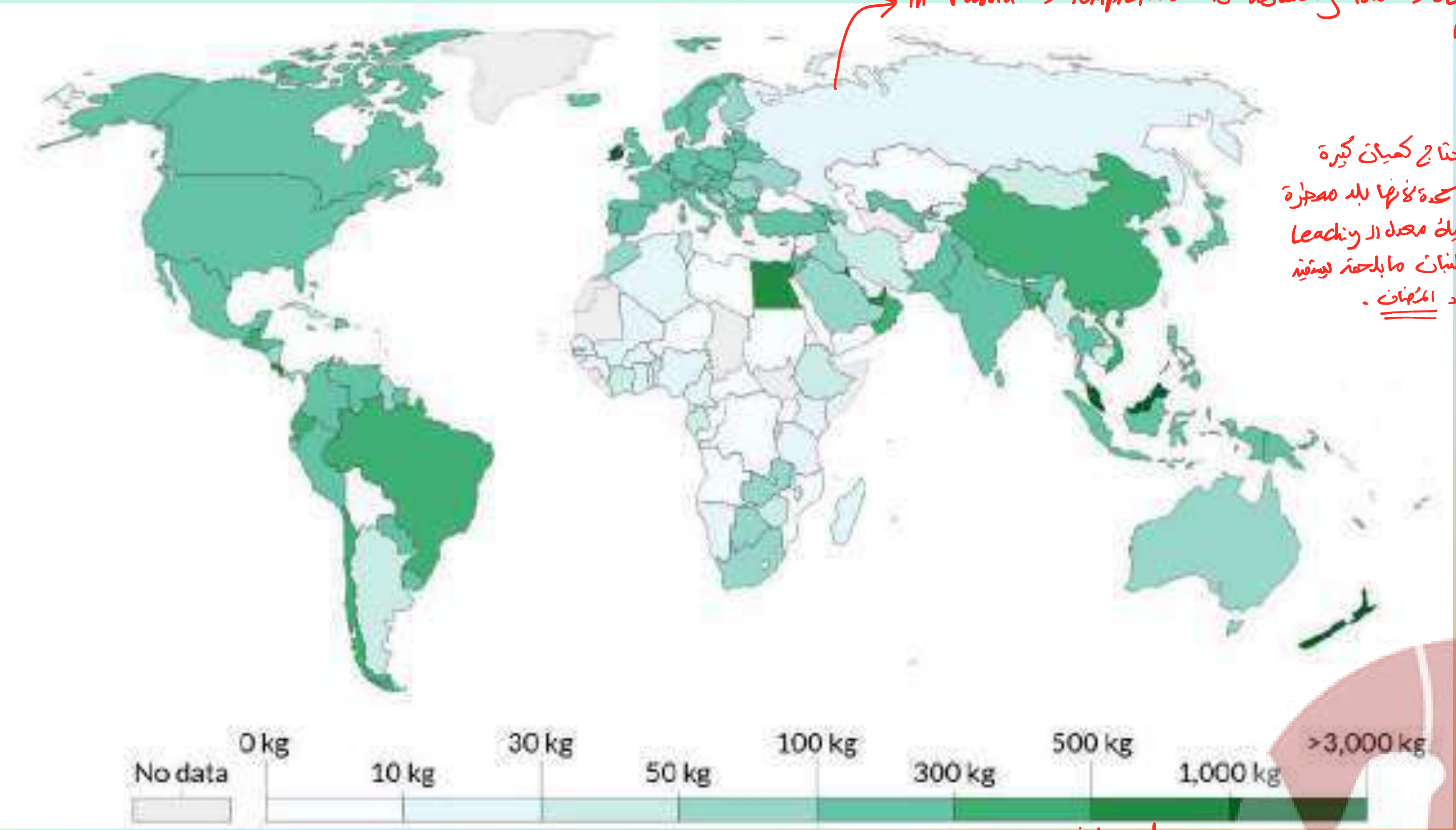
(b) Phosphorus, as P_2O_5

(c) Potassium, as K_2O

Policy

FERTILIZER USE PER HECTARE

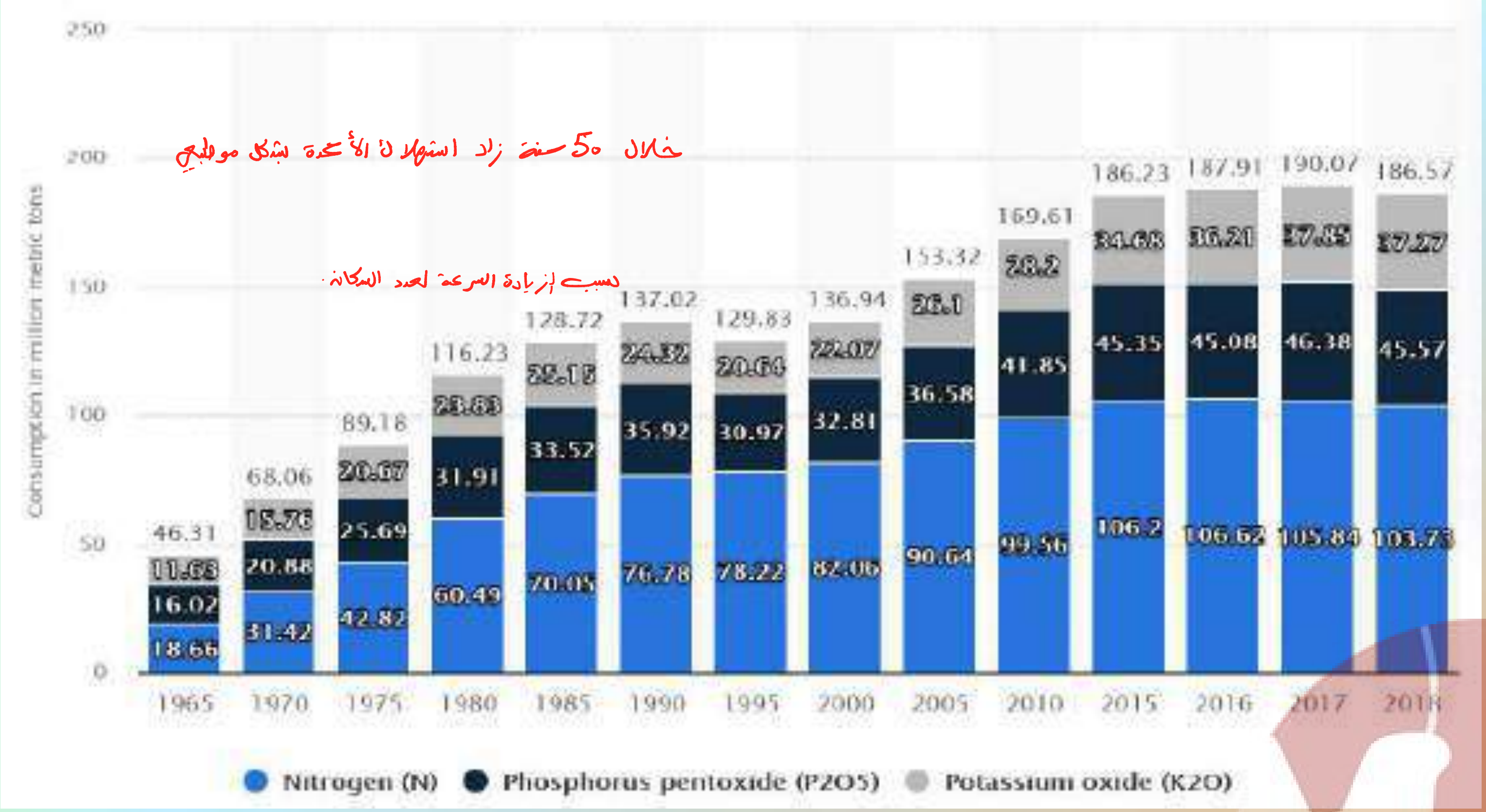
in russia → temprature is usually low → decrease the rate of Leaching



⊛ لذا نحتاج كميات كبيرة
من الأسمدة لأنها بلد ممطرة
عادةً فهيك معدل الـ Leaching
بزيد فالنبات مابلحق يستفيد
من السماد المضاف .

irland → rainy → leaching

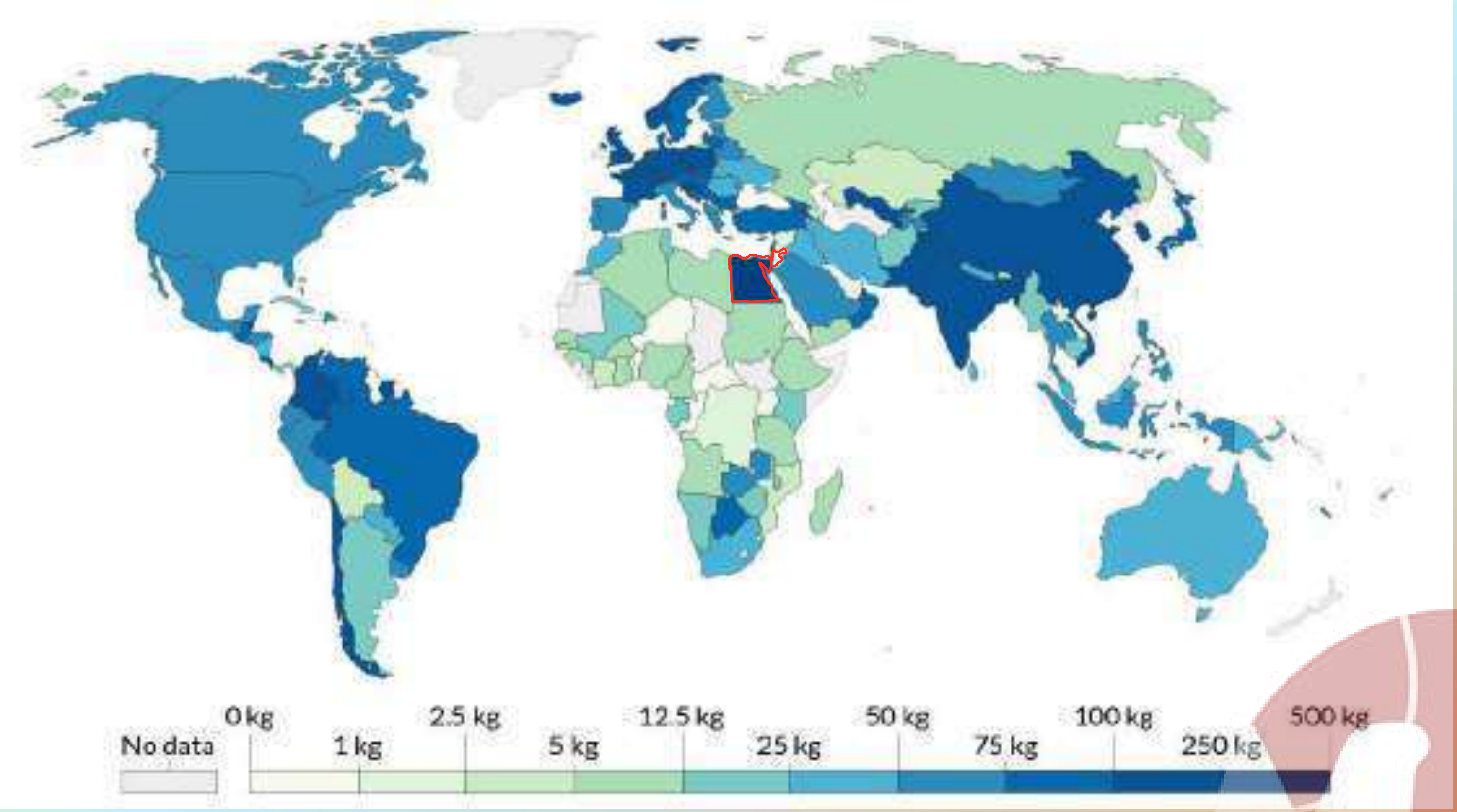
GLOBAL CONSUMPTION OF AGRICULTURAL FERTILIZER



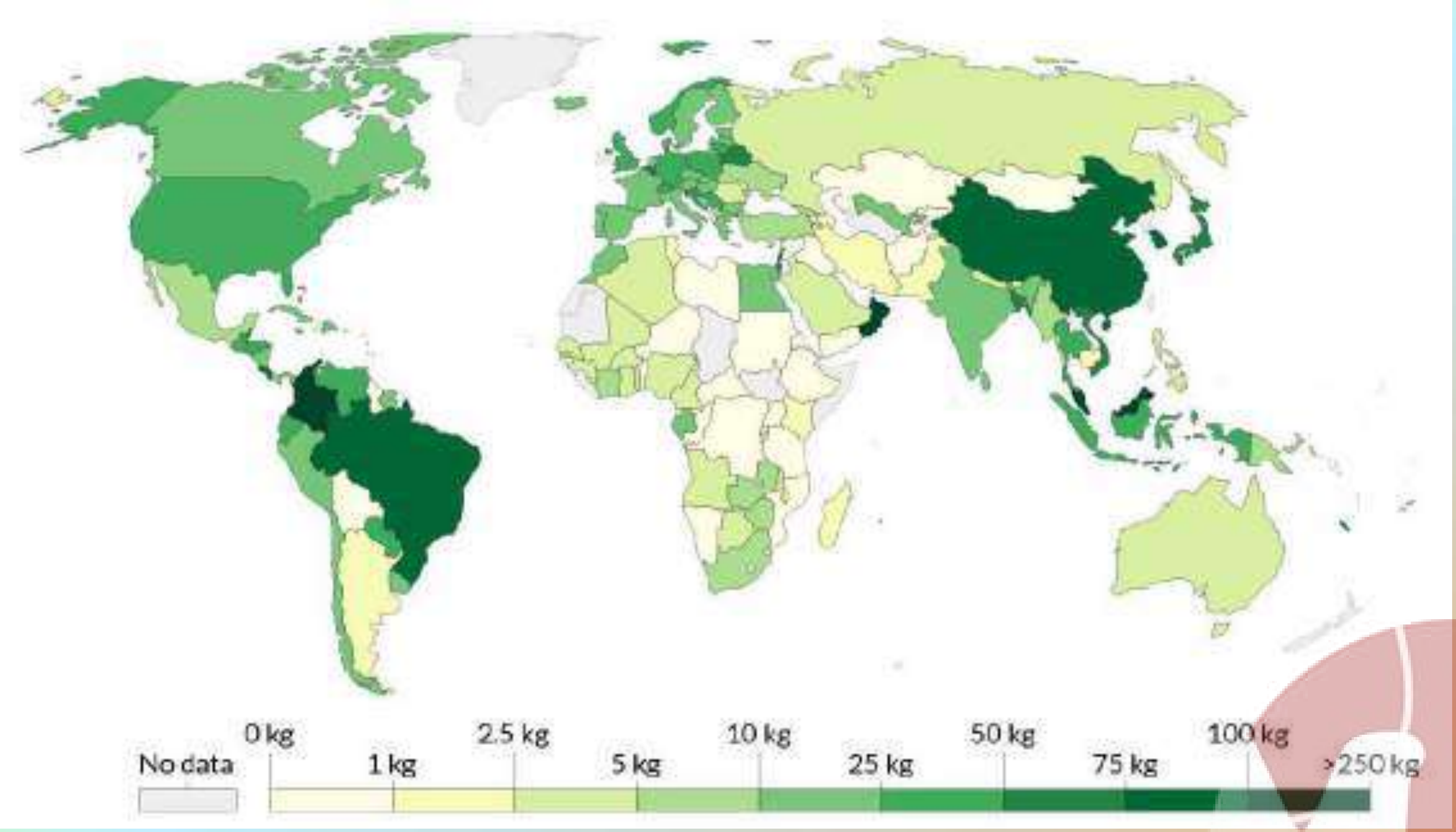
خلال 50 سنة زاد استهلاك الأسمدة بشكل ملحوظ

بسبب الزيادة السريعة لعدد السكان.

NITROGEN FERTILIZERS USE PER HECTARE

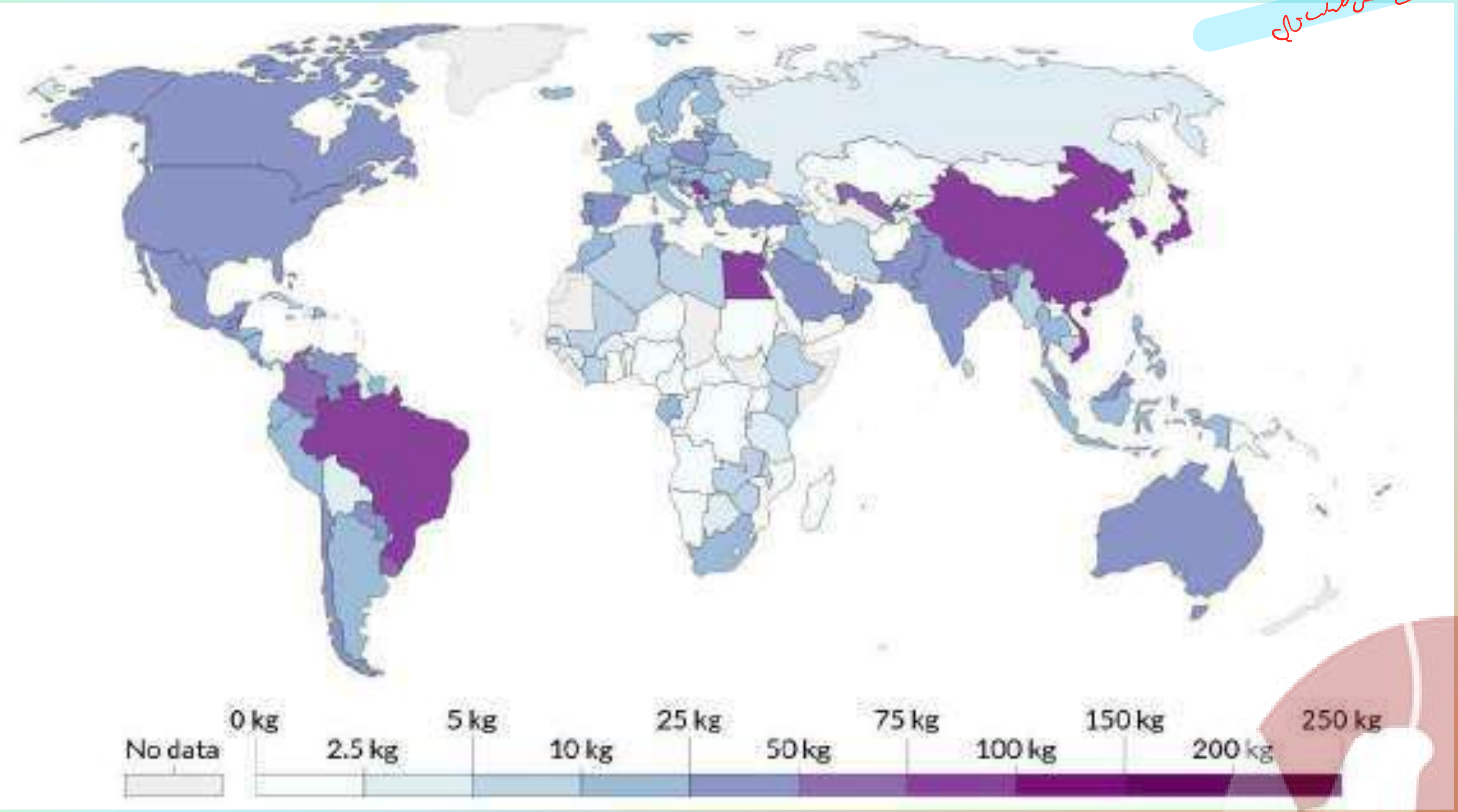


POTASH FERTILIZERS USE PER HECTARE

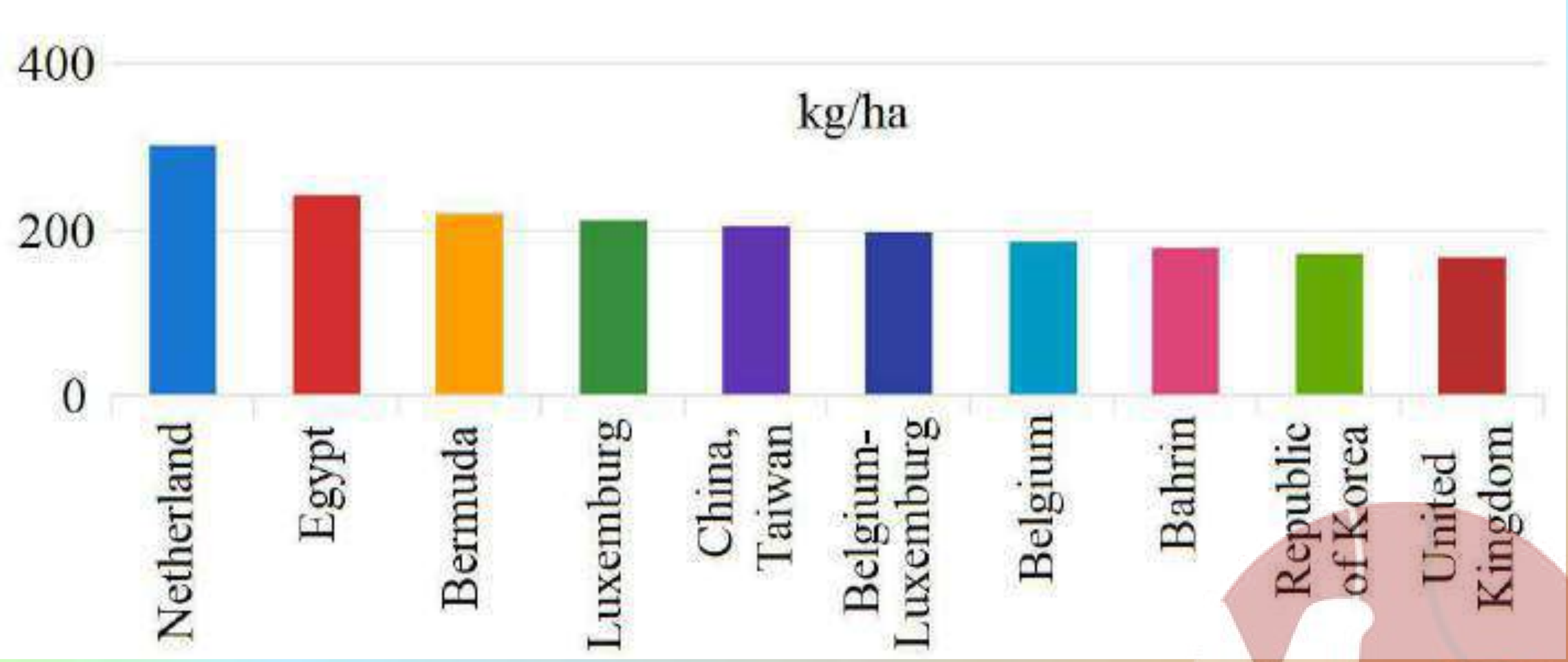


PHOSPHATE FERTILIZERS USE PER HECTARE

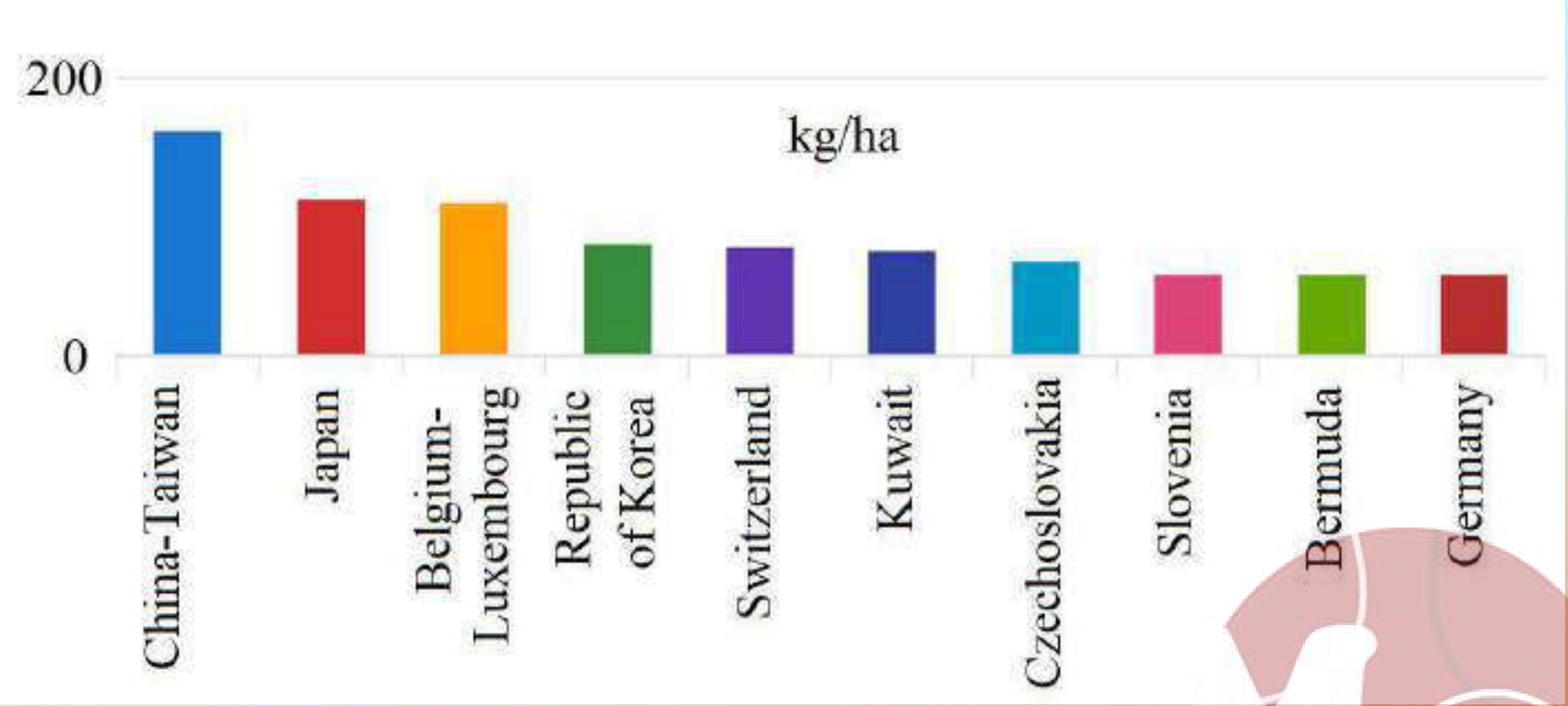
توزيع مش منطقي



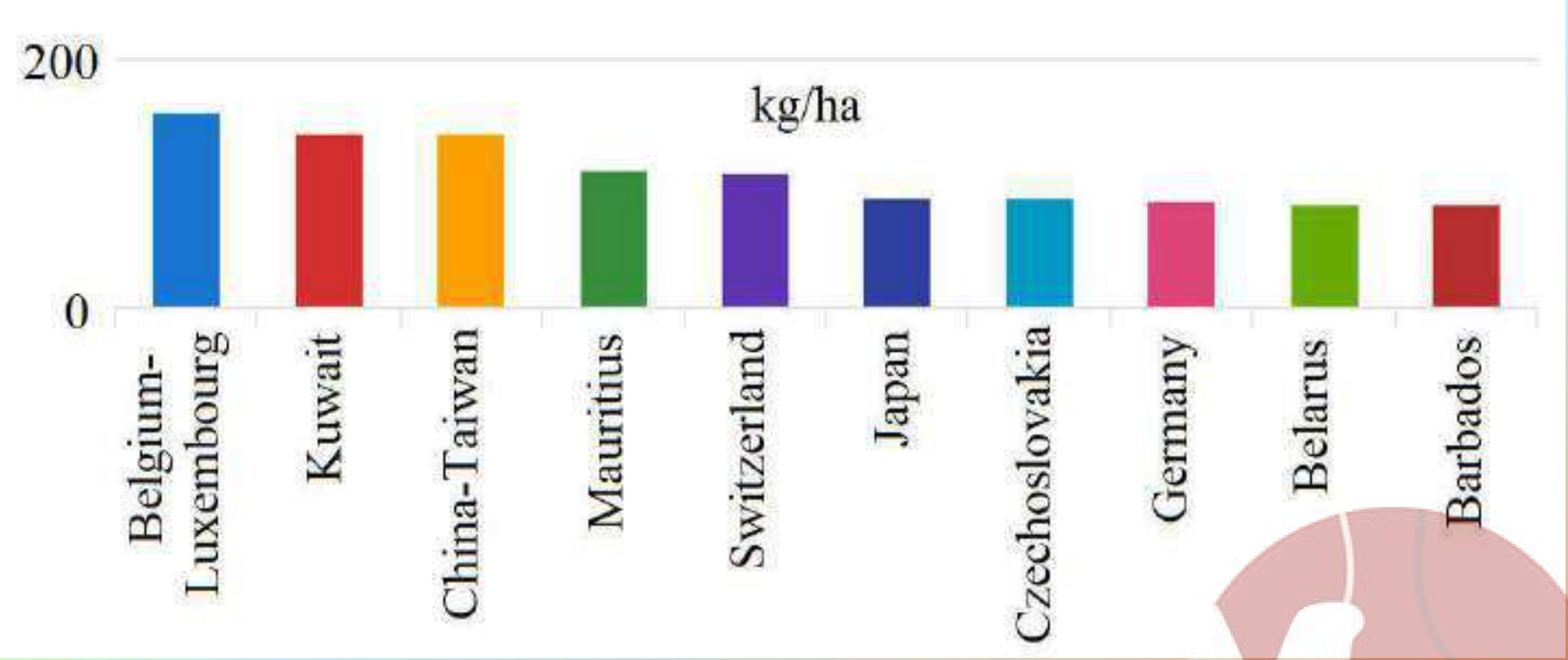
WORLD NITROGEN CONSUMPTION BY COUNTRY



WORLD PHOSPHATE CONSUMPTION BY COUNTRY

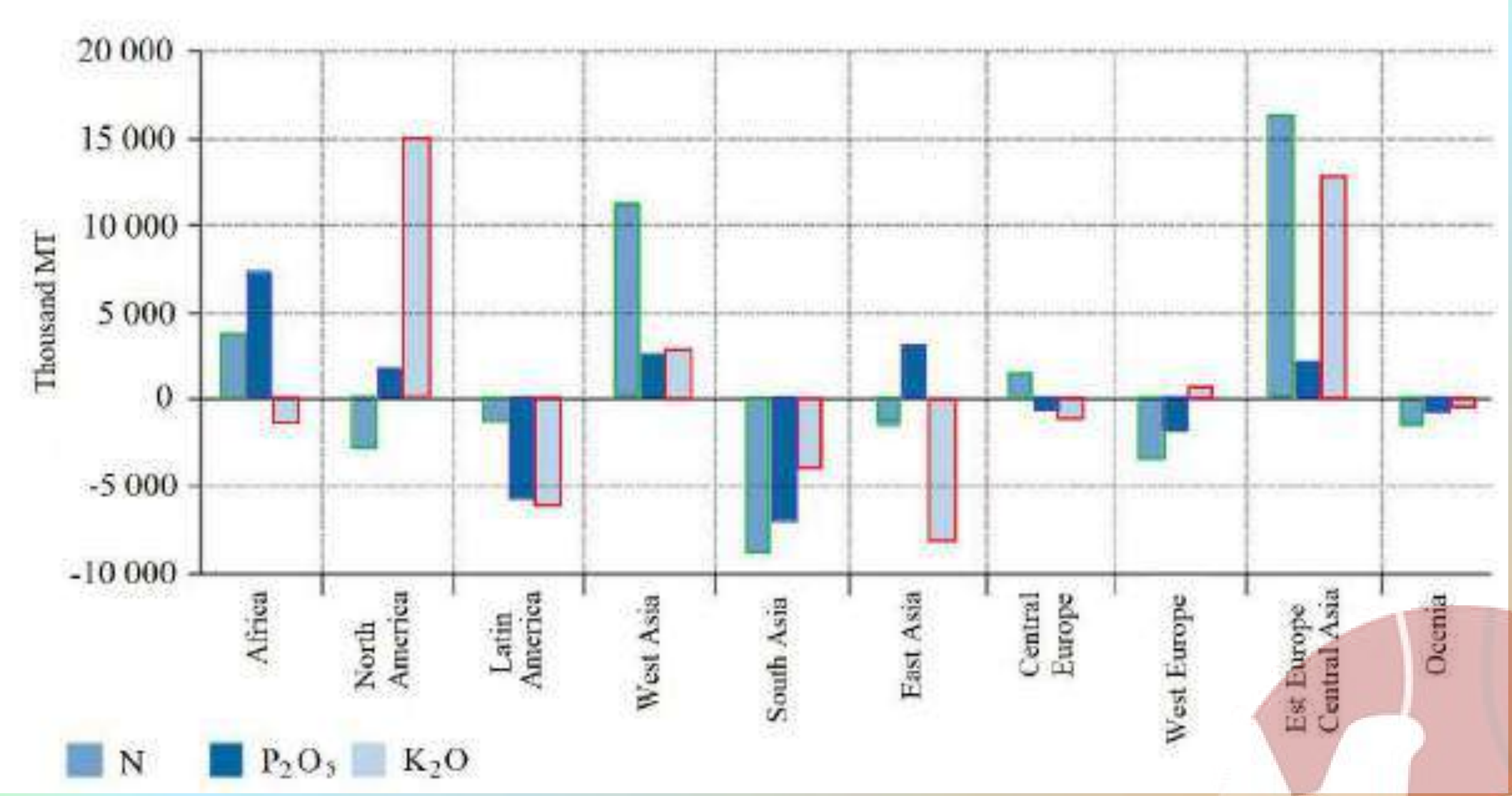


WORLD POTASH CONSUMPTION BY COUNTRY

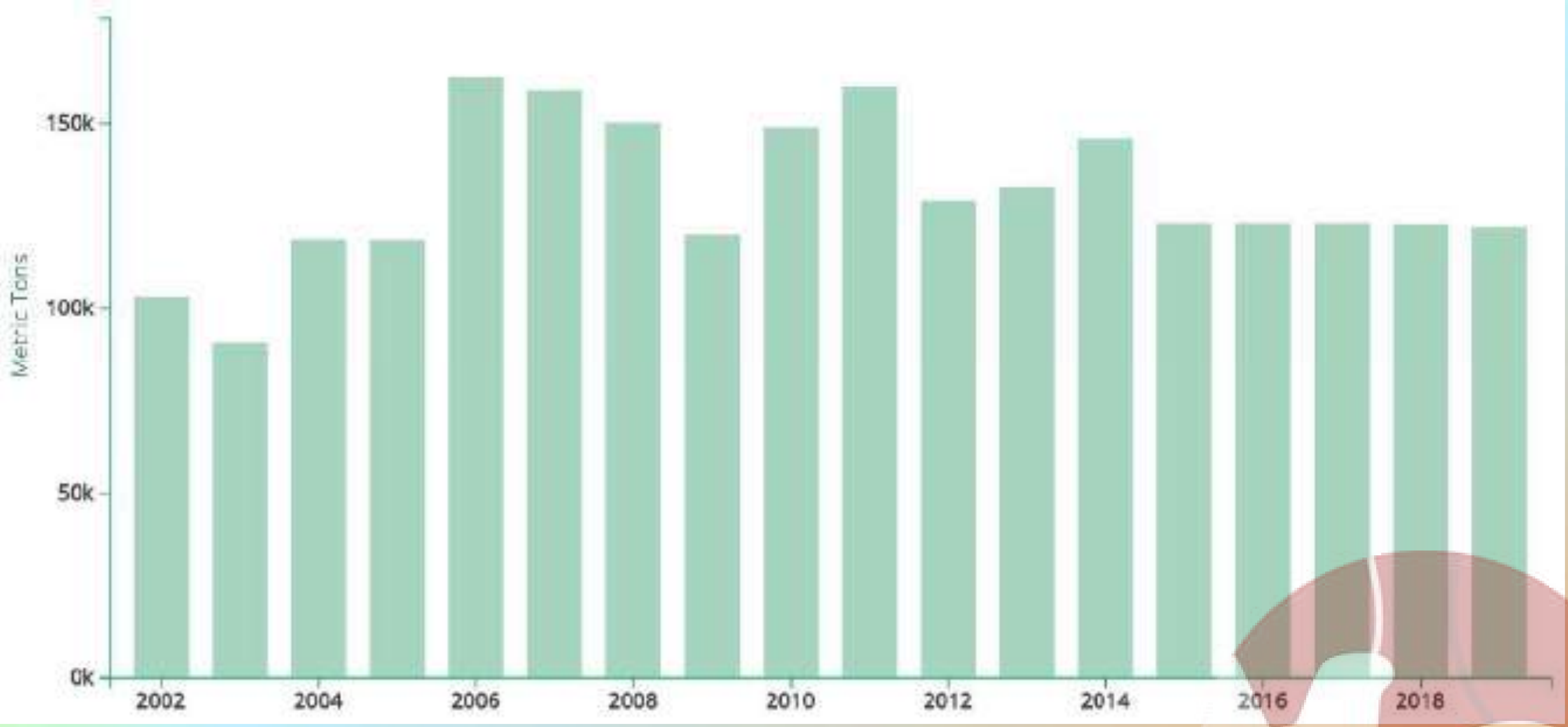


مو مشكلة، بس بنفس الوقت في Balance
حسب احتياج الدول وشو عندها فائض
بتتم الاتفاقيات.

NUTRIENT BALANCES FOR THE WORLD



JORDAN - NITROGEN FERTILIZER PRODUCTION



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.

PHOSPHATE ROCKS DEPOSITS

- Early sources of phosphate rock were small deposits in England, Ireland, Spain, France, Germany and USA.
- Most of these deposits are no longer mined because of their low grade.
- Present supplies are mainly from other areas of the USA, Russia, Morocco.
- Smaller outputs from Egypt, Tunisia, Algeria, Brazil, South Africa, Togo, Jordan, Senegal, and the Pacific Island.
- Jordan’s proven reserves of phosphates stand at 1.5 billion tons, enough to last for the foreseeable future.

PHOSPHATE ROCKS soft rocks.

→ these particles are coarse for diammonium phosphate process

⊛ لازم أطحنها عشان أقدر استخدمها ☺

SUPERPHOSPHATE

- In about 1840 treatment of phosphate rock with sulfuric acid yielded an affective phosphate fertilizer, which was called superphosphate. → made from digestion with sulfuric acid + granulation

  → single

- The first successful commercial superphosphate production was started in England in 1842.

  → After discovering phosphoric acid ⊕ rock → more $\boxed{P_2O_5}$

- The history of production of concentrated or triple superphosphate is associated with the production of phosphoric acid.

  ⊛ Both of them are reacted from ---

- The first known commercial production occurred in the 1870s in Germany.
- Triple superphosphate did not become an important fertilizer until the 1950s.

SINGLE ANS TRIPLE SUPERPHOSPHATE

Single Superphosphate

Triple Superphosphate

- The key difference between single superphosphate and triple superphosphate is that single superphosphate is produced from phosphate rock and sulfuric acid, whereas triple superphosphate is produced from phosphate rock and phosphoric acid.

Nowadays ⇒ super + triple are no loger using

AMMONIUM PHOSPHATE

reaction of $H_3PO_4 + NH_3$] → produced Mono + di

- Development of nitro phosphate fertilizer was started in Europe in the 1930s.
- 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.
- Several processes were developed, and subsequent improvements have added to their efficiency and improved the quality of the product.

MONO AND DIAMMONIUM PHOSPHATE

main differance
↳ accordig to their Solubility

● impure

Granular MAP

←

Granular DAP

→

Soluble

Crystalline MAP

←

Crystalline DAP

→

مشكلتها بال Handling ⇐ درجة الحرارة

NITROGEN FERTILIZERS

- Nitrogen content in natural gas varies depending on the gas reservoirs.
- The nitrogen content in coal varies with rank reaching a maximum at approximately 85 wt% carbon content. This nitrogen is present virtually exclusively as organic nitrogen and typical nitrogen contents vary from 0.7 to 2.0 wt%.

dominant raw material
→ crude oil + Natural gas

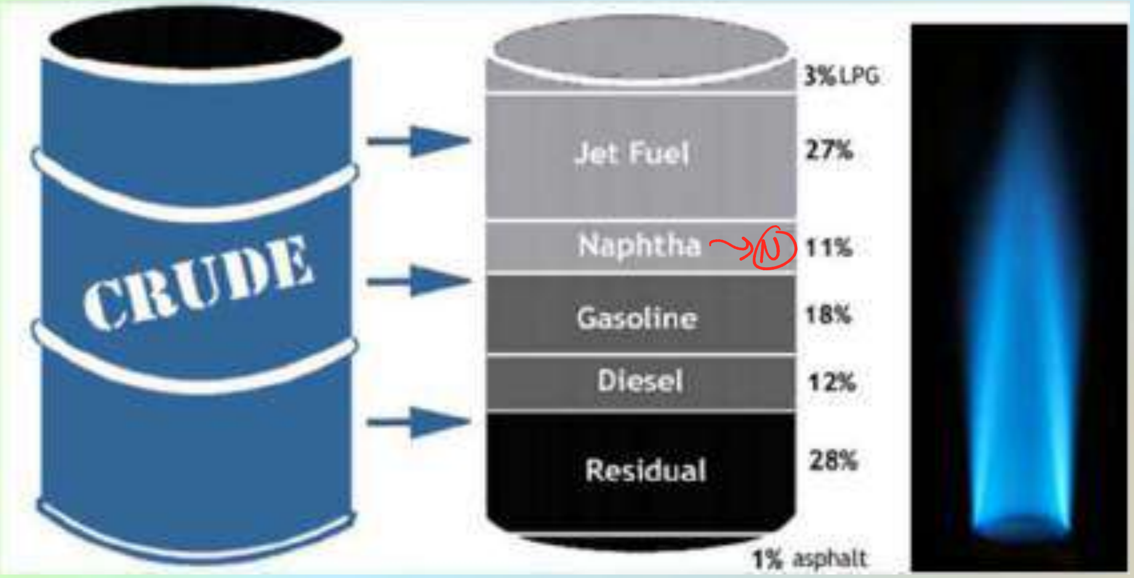
- Half of the nitrogen exist in coal is evolved as ammonia in byproduct coke ovens.
- Starting in the latter part of the 19th century, nitrogen became an increasing source of fertilizer nitrogen.

Storage of NH_3
by metal tank
⊕ thickness isolation

- Most of it was in the form of ammonium sulfate.

→ cheap + old.
drawback
→ Low content of Nitrogen 21%.
as single fertilizer

NITROGEN RESOURCES



HISTORY OF AMMONIA

- 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 1.
- 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 the 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.

HISTORY OF AMMONIA (Continue ..)

- 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.

OTHER NITROGEN FERTILIZERS

- At first the final products- ammonium sulfate, calcium nitrate, sodium nitrate were all low- analysis materials (15 to 21% N).

even if % of N
in it is less
than the source of NH_3

- Ammonium nitrate (34% N) began to be an important fertilizer material in the 1940s.

domint Source for Ⓝ

- 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, is popular in the USA, Canada, and Australia.

OTHER NITROGEN FERTILIZERS

- Nitric Acid

Ammonium Nitrate

explosive material hard to deal with

Potassium Nitrate

Ammonium Sulfate

Diammonium Phosphate

POTASH FERTILIZERS

Pot ash

- Early sources of potash were wood ashes, sugar beet wastes, and saltpeter. → مو كمية كبيرة
- → but now in canada
  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.
  → They need further processing.
- The development of refining methods gradually increased the grade of commercial products.

The first source of k

POTASSIUM CHLORIDE

↳ ⊝ Contains high amounts of cl

- High-grade potassium chloride (60-62% K_2O) is now the main product.

used in jordan ← [illegible]

- Potassium sulfate, and potassium nitrate are the principal non-chloride 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 France, Spain, Russia, USA, Canada, and Dead Sea.

ARAB POTASH COMPANY

FERTILIZERS TECHNOLOGY

CHEM 0905554

Spring Semester 22/23

CHAPTER 4

POTASH

INTRODUCTION

→ only organic wastes

- The term potash comes from the English : pot ash, which means ashes pot.
- Two centuries ago, potash was extracted from wood ash in large iron pots.
- First potash mine opened in Germany in the mid- 19th century, now potash comes mainly from potash mines of Saskatchewan (Canada) and Urals (Belarus and Russia).

⊛ في ألمانيا تسكّر المنجم لأنه خلّص
مخزونه البوتاسيوم + low quality

- Virtually all of the economic sources of potassium occur in sedimentary salt beds remaining after the evaporation of ancient seas and lakes.

potash → ores → sedimentry or ignious
potash → Brine

→ نتيجة جريان البحار
- ارتطامها بالصخور
وجفت مع الوقت
وبتكون البوتاس عن
الصخور ورح تتفاعل

potash ores in accepted concentration cannot be found on the surface

INTRODUCTION

- World reserves of such potassium-bearing deposits are immense, and they total about 250 billion tons of K_2O, of which 9.4 billion tons are considered commercially exploitable.

هدول إنّو بحتووا على نسب عالية من البوتاس

والّي بنقدر نحصلها [extraction] بالتكنولوجيا الحالية

- With current global consumption of about 25 million tons of K_2O annually both economical reserves and total resources are sufficient to satisfy world demand for centuries.

(*) even in Brines
the water is not
well mixed

Sedimentery

- Today, potash deposits are found buried at a depth of 500 to 1 000 meters underground.

- At least 95 percent of world production of potassium fertilizers is in the form of potassium chloride.

حيث 95% مكوّنة KCl
لأنّه KCl يتواجد بالطبيعة
بينما الباقي صناعات التحويلية

INTRODUCTION

1) سهولة الانتاج
2) Solubility
3) اكالة
4) less requirments
5) ارخص
6) less energy input

- Potassium sulfate is the next most important source followed by much smaller quantities of specialty materials such as potassium magnesium sulfate, potassium nitrate, potassium thiosulfate, potassium polysulfide, potassium carbonate and potassium bicarbonate.
- Potash is used to 95% by agriculture, the rest is used for detergents, soaps and glass.
- Potash Corp. of Saskatchewan Inc. , the world's largest potash producer, producing 90% of Canada’s total output and about one quarter of the world’s supplies.

ⓐ بسبب الأزمة المالية العالمية ووقّف الركان الحالية
لصناعة البوتاس ، صاروا يصنّعوا البوتاس بالـ maximum capacity
و بخزنوها لا حقاً لحد ما صارت الأسواق بحاجة للبوتاس
عشانه يتحكم بالسعر.

INTRODUCTION

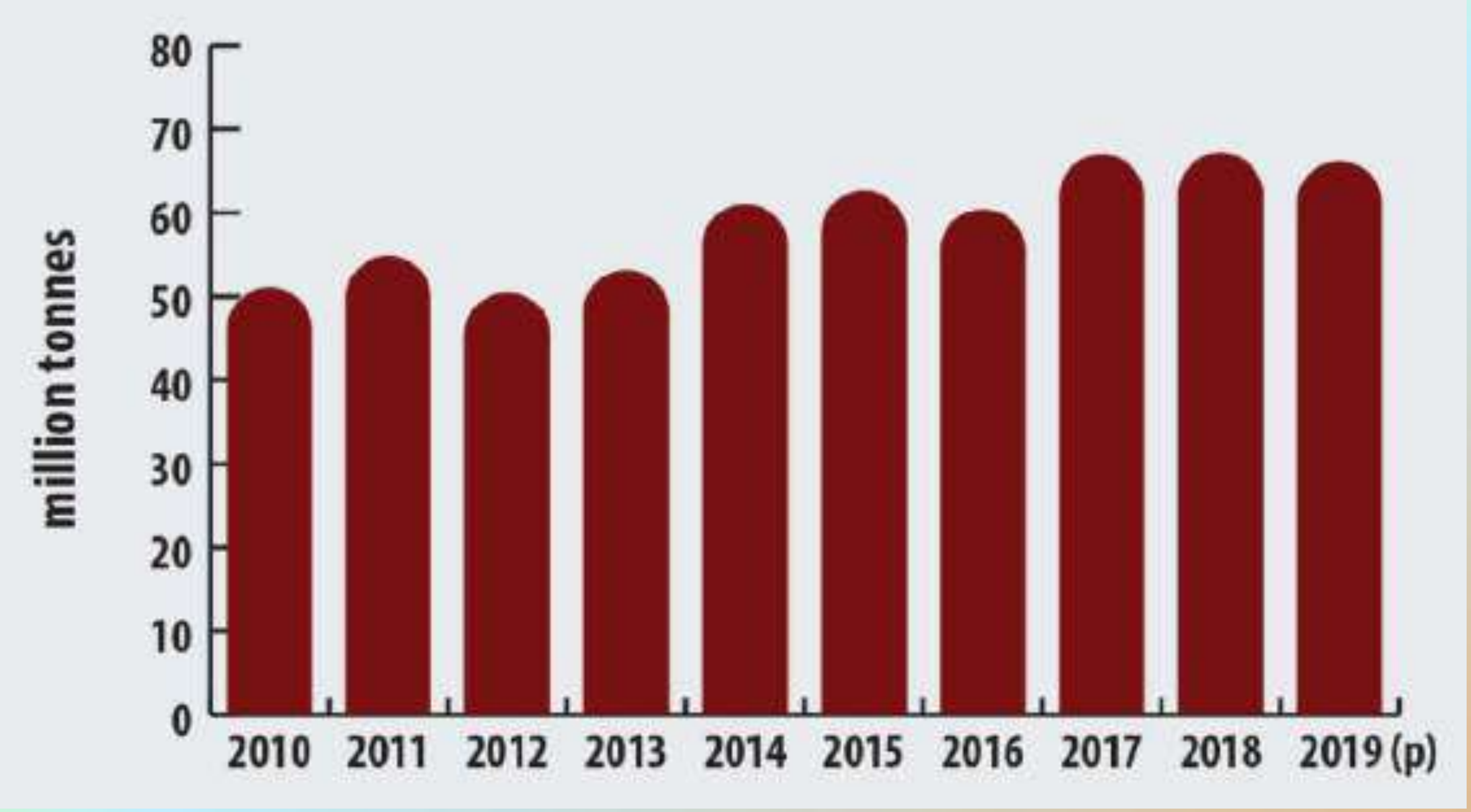
- Saskatchewan cut production by 3.5 million MT in January 2009 in response to decreased demand.
- There are at present over 45 operations producing KCl in 12 countries.
- The worlds total potash output was 62.2 Mt KCl in 2019.
- The global KCl producers operated at 85% of production capacity in 2007.

→ many countries but not All of them , becaușe it depends on 1) Nature of the soil 2) the fertility of the soil 3) types of crops. 4) rate of Fairy 5) temperature

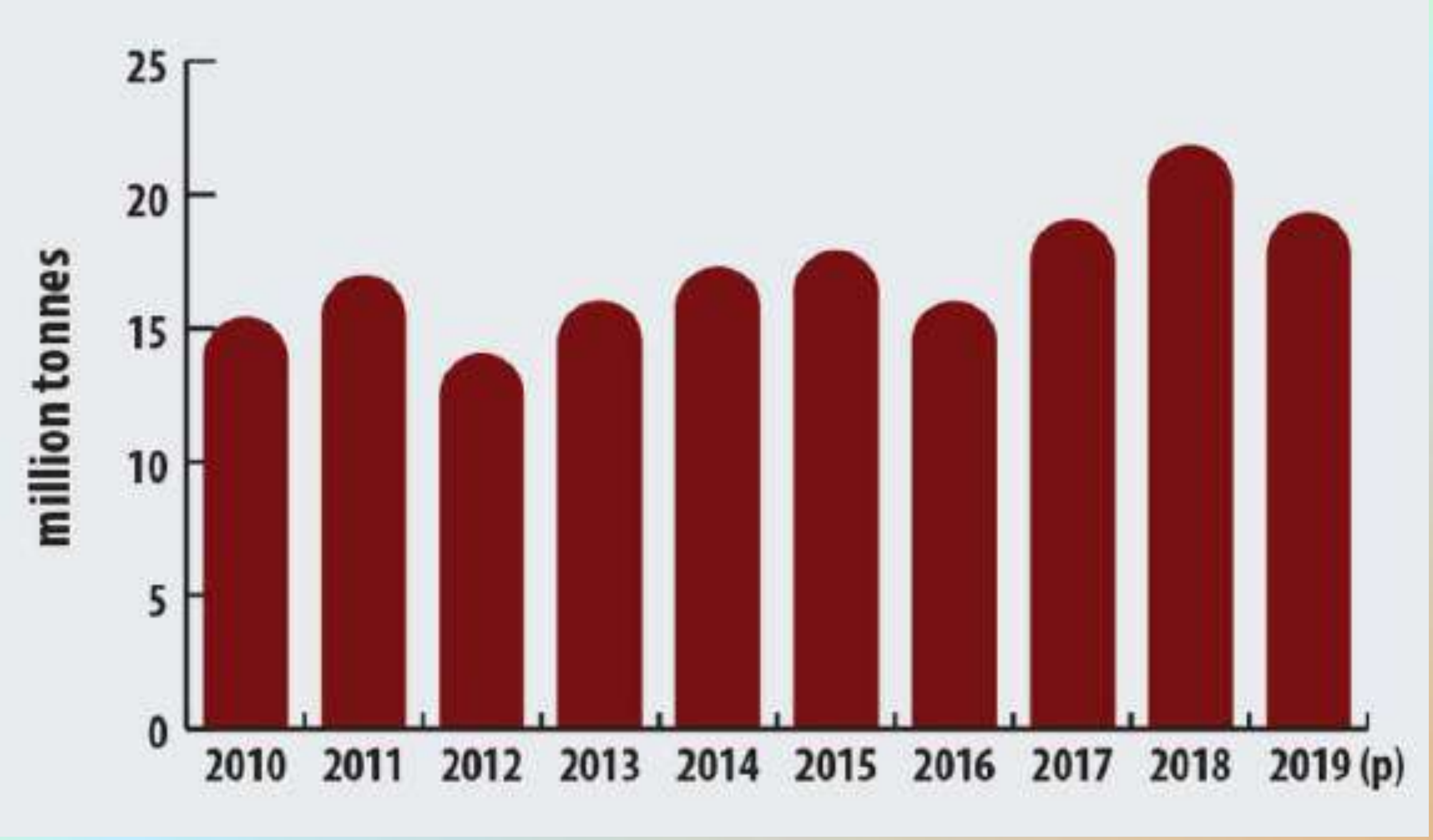
- The world has many consumers (over 150 nations) but very few producers.
- Canada, Russia and Belarus account for approximately 80% of output.
- Potash ore bodies in Saskatchewan are the world's largest, richest and most economical to mine.

WORLD PRODUCTION OF POTASH (POTASSIUM CHLORIDE)

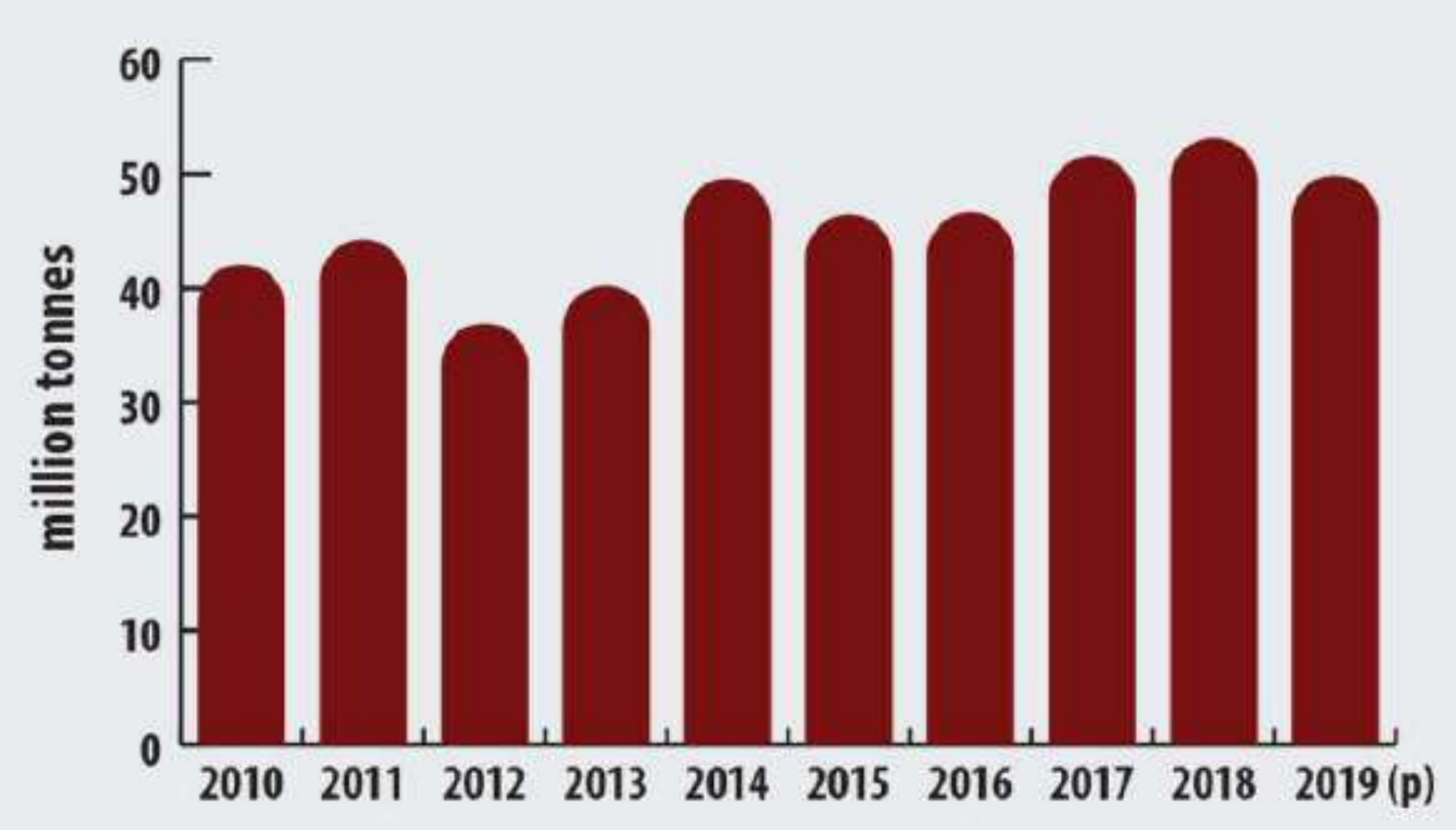
اعتمادية الانتاج تعتمد على معدل هطول الأمطار



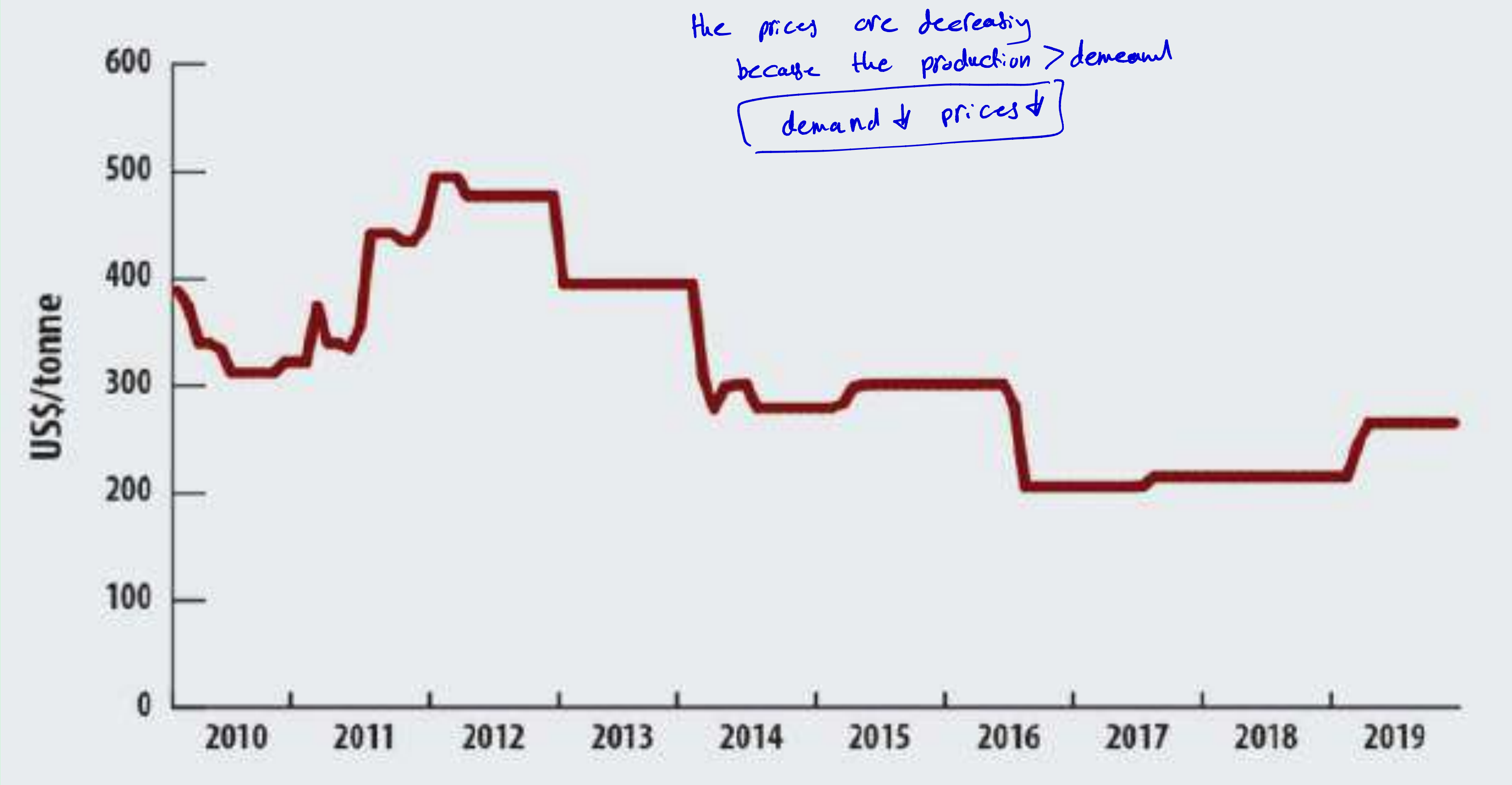
CANADIAN EXPORTS OF POTASH (POTASSIUM CHLORIDE)



WORLD EXPORTS OF POTASH (POTASSIUM CHLORIDE)



POTASSIUM CHLORIDE PRICES



the prices are decreasing
because the production > demand

demand ↓ prices ↓

SALT CONCENTRATION IN DIFFERENT WATER SURFACES

Water surface	Total concentration of salts (g/L)
Atlantic Ocean	34.00 – 37.30
Mediterranean Sea	36.00 – 39.50
Read Sea	38.00 – 42.00
Black Sea	18.00
Baltic Sea	6.00 – 11.00
Dead Sea	262.00 – 270.31 ٦ أضعاف أكبر من أي محيط أو بحر.

IONIC CONCENTRATION IN DIFFERENT WATER SURFACES

- The concentration of Potassium (K) in the Dead Sea water is 20 times more than that in the Atlantic Ocean and that of Magnesium (Mg) is 34 times more and that of Calcium (Ca) is 42 times more, but that of Bromine (Br) is about 90 times more.
- Yet the concentration of Sodium chloride (NaCl) in the different water areas is about 77% of the total mineral content whereas it is only about 25-30% in the Dead Sea.

نتيجة هالشي بخلّي فصل KCl بال Brine أسهل

Water surface	Na^{+1}	K^{+1}	Ca^{+2}	Mg^{+2}	Cl^{-1}	Br^{-1}	HCO_3^-
Atlantic Ocean	10.770	0.40	0.412	1.300	19.350	0.06	0.04
Black Sea	5.110	0.40	0.250	0.650	9.630	-	0.08
Dead Sea	39.160	7.96	17.130	43.350	22.750	5.36	0.08
River Jordan	0.224	0.03	0.129	0.095	0.762	0.00	0.18

TYPICAL DEAD SEA SALT MINERAL CONTENT

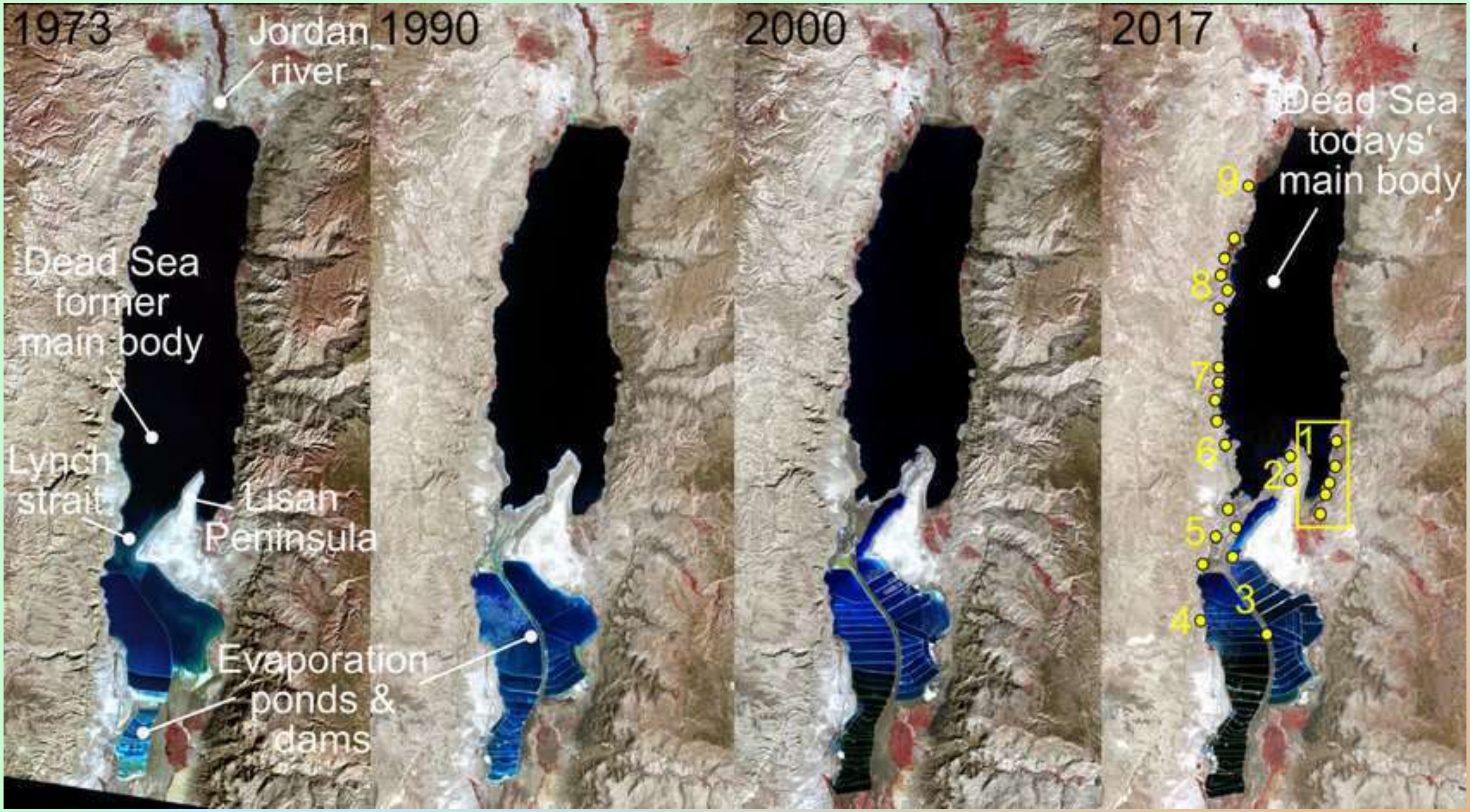
	g/liter
Mg^{+2}	33 - 41
Ca^{+2}	14 – 17
Na^{+2}	32 – 40
Ratio of Na/K	5.5 in Dead sea 60 in the oceans
K^{+}	6 - 7.5
Cl^{-}	173 – 217
Br^{-}	4 – 5
SO_4^{-2}	0.65 - 0.8
Density	1.18 - 1.215

مساحة ال ponds كبيرة وعددهم كثير

عشان أزوّد ال rate of evaporation يلّي

أصلًا بياخذ وقت طويل عشان أقدر أرسّب ال carnalite.

SATELLITE IMAGES OF THE DEAD SEA



DEAD SEA RESOURCES

	1975	2019
Total area (Km^2)	1000	605
Total volume (Km^3)	150	114
Max depth (m)	350	304
Evaporation rate (T/y)	1.7×10^9 (1% of V)	
Water source	65% Jordan river	0 - 10%
	20% local rivers ↓ mainly	50%
	5% rain	10%
	10% flooding	30%

DEAD SEA SINKHOLES

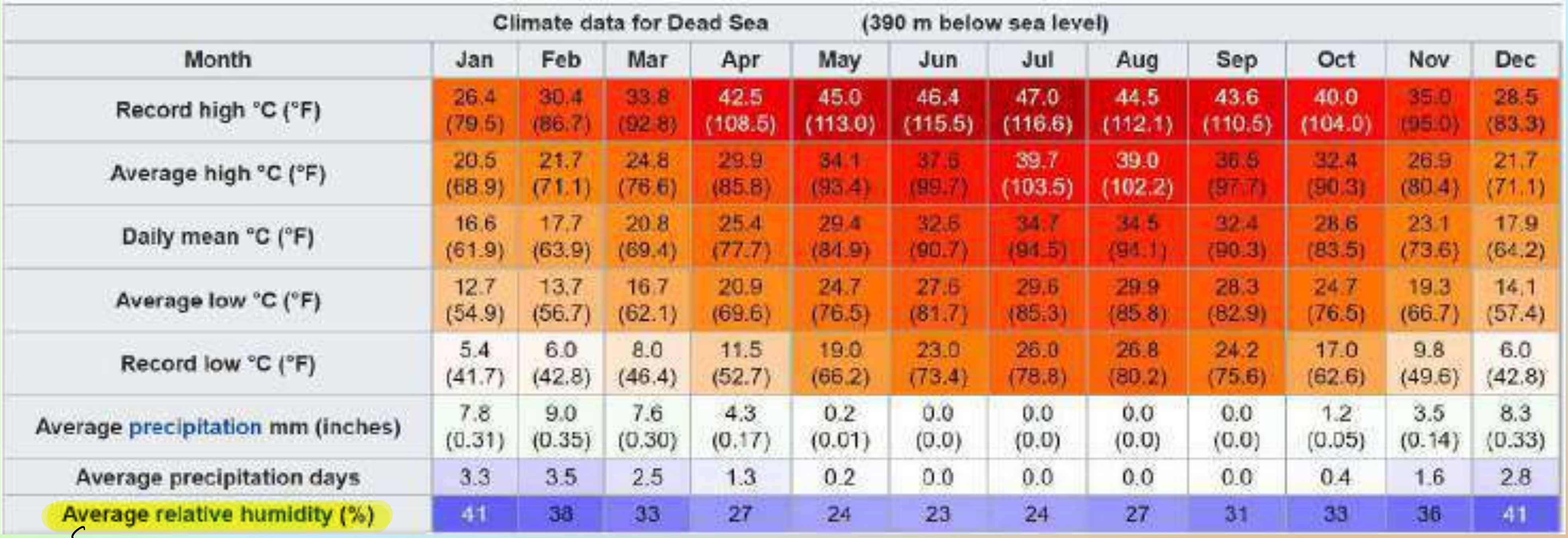
- The Dead Sea region has roughly 7000 sinkholes and will have double that number, 14,000, in the next few years.
- The sinkholes in the Dead Sea region have been proven to be the result of man-made dams and industrial activity which decreased the water volume in the Jordan River and, as a result, the volume of water currently in the Dead Sea.

TYPICAL DEAD SEA SALT MINERAL CONTENT

- When compared with other oceans and seas, the DS is more abundant in many elements, including chloride (212.4 g/l), magnesium (40.65 g/l), sodium (39.15 g/l), calcium (16.86 g/l), potassium (7.26 g/l), and bromide (5.12 g/l). Conversely, it has a lower concentration of sulfate (0.47 g/l), and bicarbonate (0.22 g/l).
- Heavy metals comprise a well-known group of inorganic chemical hazards. Furthermore, it was proved that chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), mercury (Hg), nickel (Ni), and arsenic (As) are usually found at contaminated areas.

من الأمور الأساسية إللي قامت عليها صناعة البوتاس بالبحر الميتة هو المناخ.

CLIMATE CONDITIONS AROUND THE DEAD SEA



Climate data for Dead Sea (390 m below sea level)

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Record high °C (°F)	26.4 (79.5)	30.4 (86.7)	33.8 (92.8)	42.5 (108.5)	45.0 (113.0)	46.4 (115.5)	47.0 (116.6)	44.5 (112.1)	43.6 (110.5)	40.0 (104.0)	35.0 (95.0)	28.5 (83.3)
Average high °C (°F)	20.5 (68.9)	21.7 (71.1)	24.8 (76.6)	29.9 (85.8)	34.1 (93.4)	37.5 (99.7)	39.7 (103.5)	39.0 (102.2)	36.5 (97.7)	32.4 (90.3)	26.9 (80.4)	21.7 (71.1)
Daily mean °C (°F)	16.6 (61.9)	17.7 (63.9)	20.8 (69.4)	25.4 (77.7)	29.4 (84.9)	32.6 (90.7)	34.7 (94.5)	34.5 (94.1)	32.4 (90.3)	28.6 (83.5)	23.1 (73.6)	17.9 (64.2)
Average low °C (°F)	12.7 (54.9)	13.7 (56.7)	16.7 (62.1)	20.9 (69.6)	24.7 (76.5)	27.6 (81.7)	29.6 (85.3)	29.9 (85.8)	28.3 (82.9)	24.7 (76.5)	19.3 (66.7)	14.1 (57.4)
Record low °C (°F)	5.4 (41.7)	6.0 (42.8)	8.0 (46.4)	11.5 (52.7)	19.0 (66.2)	23.0 (73.4)	26.0 (78.8)	26.8 (80.2)	24.2 (75.6)	17.0 (62.6)	9.8 (49.6)	6.0 (42.8)
Average precipitation mm (inches)	7.8 (0.31)	9.0 (0.35)	7.6 (0.30)	4.3 (0.17)	0.2 (0.01)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1.2 (0.05)	3.5 (0.14)	8.3 (0.33)
Average precipitation days	3.3	3.5	2.5	1.3	0.2	0.0	0.0	0.0	0.0	0.4	1.6	2.8
Average relative humidity (%)	41	38	33	27	24	23	24	27	31	33	36	41

→ As humidity ↑
rate of evaporation ↓

CLIMATE CONDITIONS AROUND THE DEAD SEA

- Air temperature in the Dead Sea district reaches 29 - 39 ° C in summer and it exceed 40 ° C in certain years.
- Therefore, the water is exposed to an intensive evaporation process, which leads to the existence of salty sediments on shores similar in different shapes to coral ones.
- The average temperature over the period from November to April is 22 - 29 ° C and over the period from May to September and October is 32 - 37 ° C and in June July is 38 - 39 ° C.
- The humidity level is low 27% in summer and 38% in winter.
- The atmospheric pressure is 800 - 810 mm Hg; while the oxygen concentration in the atmosphere of the Dead Sea is 15% more than of the Atlantic Ocean.

DEAD SEA DISAPPEARANCE

- Nowadays, the Dead Sea is intensively exploited.
- In addition to the many medical and tourist facilities on its shores there is a group of productive industries to produce minerals, which are used in chemical fertilizers industry.
- Such an intensive exploitation of water and minerals of the Dead Sea began to affect the existence of the Dead Sea itself.
- The river of Jordan after being diverted, it does not provide enough water to the Dead Sea.
- The low level of rainfall and the construction of damps add more to the problem of water evaporation.

DEAD SEA DISAPPEARANCE

- If the decrease on sea level continues, this decrease is expected to increase within few coming years due to the environmental unbalance around the Dead Sea because of the mentioned reasons.
- The step-by-step disappearance of the Dead Sea will lead to an environmental catastrophe affecting the region around and no one will be able to predict the negative effects of such a catastrophe.

DEAD SEA FACTORIES

- The Dead Sea brine typically contains 11.5 g/l KCl.

→compounds not elements

- The concentration of other salts is $MgCl_2$ 130 g/l NaCl 87g/l $CaCl_2$ 37 g/l MgBr 5 g/l.
- This concentration encouraged investors to establish different factories on both sides.
- These factories are trying to increase the KCl productive capacity annually. In recent years, new industries such as the Magnesium producing industry, an expensive substance, and the Bromine have been inaugurated.
- These industries utilize solar evaporation systems to extract salts whereby seawater is pumped to special salt ponds that occupy large areas of land extending to more than 120 km^2 only on the Jordanian side.

- In Jordan to produce KCl from dead sea brine, the first step is to concentrate the Dead Sea brine naturally in large ponds, there are 3 types of ponds: salt, precarnallite, and carnallite ponds.

الهدف عشانه يوصل تركيز الملح لحد معيّن عشانه يدخلوا ل carnalite ponds.

- These ponds are working in series, NaCl is precipitated in the first step then the solution is transported to other ponds where the carnallite ($KCl\ MgCl_2.6H_2O$), which is the key product is crystallized and precipitated, after which the remaining solution is returned to the sea.

* هسا ملّاحات ال NaCl مايتم جمعها والهدف منها بس عشانه أرسّب أكبر كمية منه.
د المتوقع إنه دائم مابدء صعودها ← لأنه برتفع منسوب الميّ فيها
فبتم رفع حواف الملّاحة أكثر عشانه تستوعب كمية أكبر.

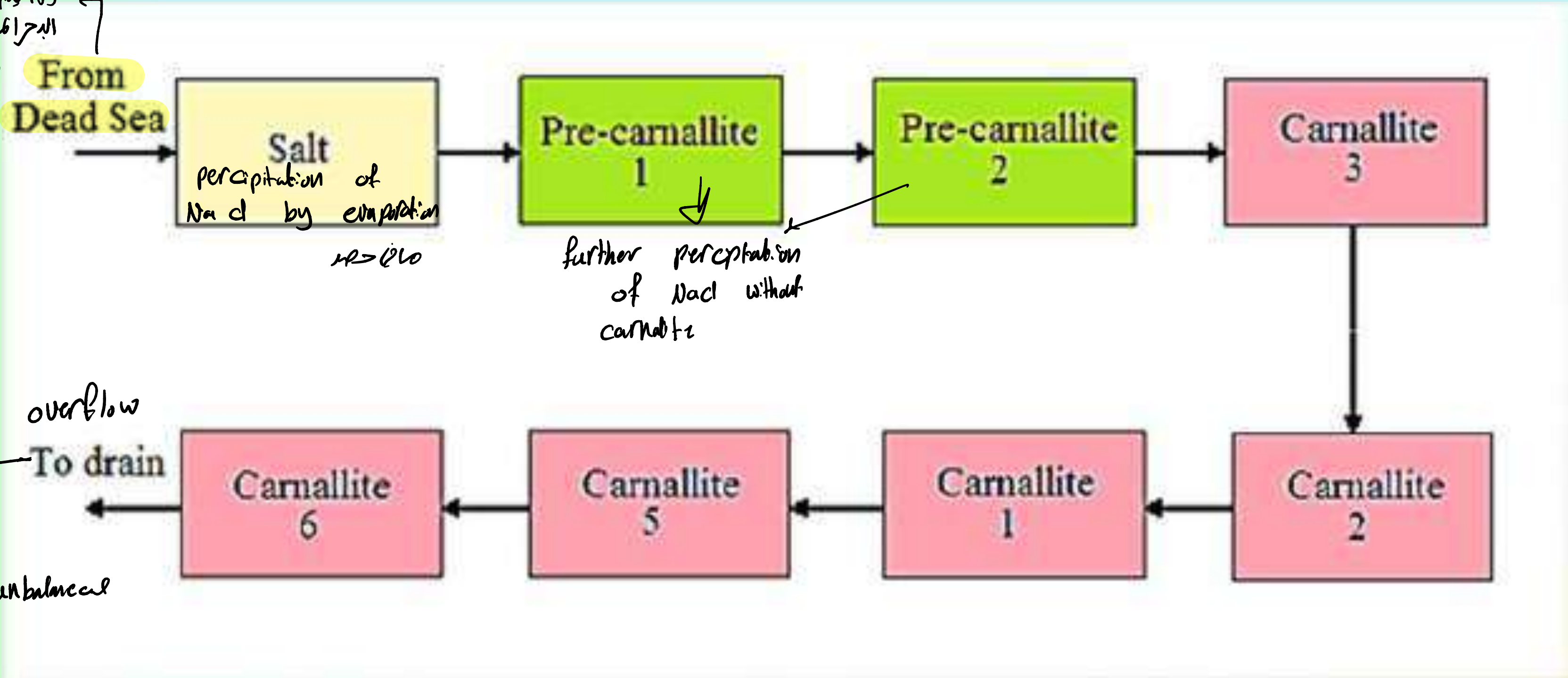
هل اتكوّن ال carnalite ولا لا.

* walls of ponds made from salts

Based on concentration of carnalite the transfer from precarnalite to carnalite ponds

+ ملّاحات ال precarnalite مايتم جمعها

DEAD SEA EVAPORATION PONDS



هون يتم سحب من مياه البحر الميت بالأول ومو من السطح ← على عمق معينة

percipitation of Na cl by evaporation

ملح صخر

further percptation of Nacl without carnalite

overflow

to the dead sea

over flow is unbalanced water

the mechanism of salt ponds

SALT PONDS

→ based on the solubility of salts in water

- At 30ºC sodium chloride has a solubility of approximately 36.09 g/100 g H_2O
- Maximum solubility of potassium chloride, KCl, at 30 ° C is 37.2 g/100 g H_2O.
- At 40 ºC the solubilities are 36.37 and 40.1 g/100 g H_2O, respectively.
- As temperature increases, its solubility increases as well.
- Dead sea brine is pumped from the Dead sea to the first NaCl pond.
- There are 4 pumps with a capacity of 4m³/sec.
- About 1×10⁶ m³ of Dead Sea brine is pumped to the salt pond.
- There are 2 pipelines with a diameter of 1.6 m and a length of 900 m.

→ to decrease energy input

↳ then by gravity → 1.5 km

هون عند درجات حرارة قليلة
بنلاحظ إنه الذائبية تبعت
NaCl ال KCl
كثير قريبة
لهيك بلزم أنا أضل أشتغل
على حرارة عالية عشان
الفصل يصير أحسن

⊕ مو كل يوم بس لما يكون
محتاج المزيد من الملح

SALT PONDS

→ largest amount of water in NaCl pond

- These 2 pipelines deliver the Dead Sea brine to a 10.6 km canal which is connected to the salt pond at its end.
- Large solar ponds, in series (100 km^2 total area) serve to evaporate water and settle NaCl.
- Dead Sea brine enters the salt pond with a percentage of water of 74.7 %.

الهدف

- As a result of water evaporation, the percentage of water reduces to 70%.

Then → from precipitation of NaCl → carnalite

بعرف النقل قديش عندي ملح ←

- The level of the brine in the salt pond is kept approximately 1 m.
- As a result of the continuous evaporation more and more NaCl will be precipitated and so, it is necessary to increase the height of the pond's walls after years.

⊛ product from this NaCl pond

بياخدوه لحساب وغايات أخرى غير التصنيع مثل

صنع أرضيات لملاحات الـ carnalite.

PRE-CARNALLITE PONDS

- There are 2 pre-carnallite ponds, the first one has an area of 4.5 km^2 and the second has an area of 2.5 km^2.

→ to get maximum of carnalite → I have to increase the concentration of it by increasing the rate of evaporation in pre carnalite pond

← المساحة أصغر من مساحة ال NaCl pond

عشان نضل قادرين نراقب متى رح يوصل التركيز لل carnalite

- The main purpose of the first one is the continuation of concentrating the brine and precipitation of NaCl.
- The brine flows from the first to the second pond by gravity, where the percentage of water within the brine reduced further to 68%.
- At this percentage, the carnallite will start to precipitate.

↓ mixture of $MgCl_2 + KCl + NaCl$.

PRE-CARNALLITE PONDS

second pre pond

- The percentage of the KCl will increased from 1.1% for Dead Sea brine to 1.8% at the second pre-carnallite pond.

(*) هلا أنا بدي أوصل تركيز ال Brine لـ 68% عشانه أقدر أحطه لل [Carnalite ponds]

عن طريقة ملاحات ال pre carnalite ذو المساحات الأصغر عشانه أقل مصاريف على الأمور.

- The carnallite point is an important point and needs more attention and control.
- Samples should be taken on a daily basis from the second pre-carnallite pond to check if the brine reaches the carnallite point.
- It will not be profitable if carnallite is allowed to precipitate in this pond.

CARNALLITE PONDS

- There are 5 carnallite ponds with an area of 22.5 km^2 .
- The main function of these ponds is to precipitate the carnallite ($KCl.MgCl_2.6H_2O$).
- As a result of the evaporation process, the carnallite will precipitate and this process will continue till the height of the carnallite reaches 35 to 50 cm.

لو أقل من هيك رح تاخذ من NaCl

- After precipitation, the carnallite will be harvested and pumped to the plant.

CARNALLITE PONDS

- Since the harvesting of the carnallite is carried out using very heavy machines, a solid ground is prepared before the actual operation is started.
- NaCl is used as a mattress for the carnallite ponds with a thickness of 20 to 40 cm.
- The height of the brine in the carnallite ponds is kept at 1 to 2 m.
- The height of the walls in the carnallite ponds remains constant.
- .

FACTORS AFFECTING THE CARNALLITE PRECIPITATION

[illegible]

1. **Wind speed.** ⇒ wind speed ↑ rate of evaporation ↑
   because the driving force ↑
2. **Temperature.** ⇒ T ↑ rate of evaporation
   but T ↑ solubility ↑
   → must be in some range
   (processing window)
3. **Relative humidity.** ⇒ H ↓ rate of evaporation ↑
   driving force ↑

- Increasing the wind speed and the temperature will increase the evaporation rate.
- In the meantime, increasing the temperature will increase the solubility of the salts specially the carnallite.

FLOATING-TRACK HARVESTERS

- The harvesters used in the Arab Potash company are specially designed to be used by the company.
- They consist of the following:

1. The cutting head.
2. Moving system.
3. Pumping system.
4. Control room.

- Length: 26 m, width: 9 m, and weight: 270 Ton

flexible + float. pipeline

air balls

عشان يعوم ال pipe على السطح.

cutting head of the harvester

collects → Brine
→ slurry
→ solids

- The precipitated salt is harvested by harvesting machines, which float on the pond's surface.

→ during suction process there is no filtration process → to make suction easier

- The carnallite slurry (20% - 25% solids) is cyclone to reduce the water content and pumped at 30 to 40% solids to the processing plant.
- The carnallite in the slurry contains 85% carnallite and 15% NaCl.
- Some seasonal rainfall in summer leads to diluting the solution in the ponds leading to a change in water solution-crystal phase equilibrium, as well to slow the crystallization process where the formed crystals may begin to dissolve in the solution again.
- The solution may stay for a long period of time in these ponds, which leads to mushroom-type sediments covering the ponds bottom and appearing on the surface.

KCl PLANT

- The building and construction of the buildings and equipment started in 1980.
- The plant started production on 18/3/1982.
- To produce KCl from the carnallite, the following steps are used:

1- Treatment of carnallite.

↳ separation of NaCl, $MgCl_2$, water.

2- Treatment of sylvinite.

3- Crystallization of KCl.

4- Drying.

5- Screening.

6- Store and transport.

CARNALLITE TREATMENT

- The pumped carnallite slurry is stored in 3 large storage tanks each with a 5000 m^3 capacity.

very important

- Continuous agitation is required to prevent precipitation of solid materials at the bottom of the storage tank. → cylinder

ellipse or conical

to prevent the solid from settling.

- The first step is to separate the solid materials from the liquid which carried out using 11 centrifuges. → physical separation by centrifugal force ↑ of this force ↑ separation ↑

لما تلف ال Drum ال

particles تلتصق ال

على الجدران وبنزل الأرض لحال.

⟹ Also the output liquid contains very fine particles (even if the centrifgues are effecient enough)

- The liquid flows out of these centrifuges is sent to one of the 3 carnallite thickeners. → conical

→ further separation by differance of ρ + time ⊕ slow agitation

- The main function of the thickener is to collect any solid materials remain in the liquid after centrifugation.

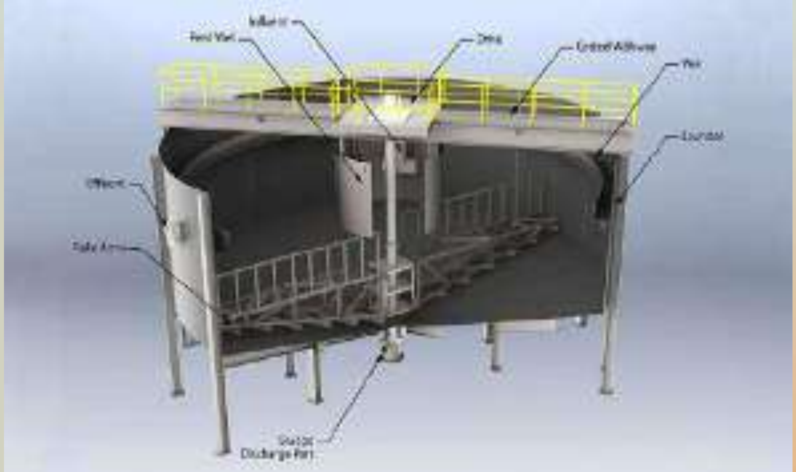
CARNALLITE TREATMENT

- The solid materials will be collected at the bottom of the thickener.

هاد إلّي بدي إياه.
بدي أحصل عل أكبر كمية ممكنة من ال solids

- An arm at the bottom of the thickener moves with a continuous slow speed will prevent the solid material from precipitation.
- The collected solid materials from both the centrifuges and the thickeners will be sent to the carnallite beneficiation tanks.

overflow ⇒ unwanted liquid



⊕ I want from these solids that we collected from thickner ± centrifuge ($NaCl + KCl + MgCl_2$)

⇓

Silvinite ($NaCl + KCl$) → carnalite beneficeation

كيف بدي أفصل ال $MgCl_2$ عنهم ؟

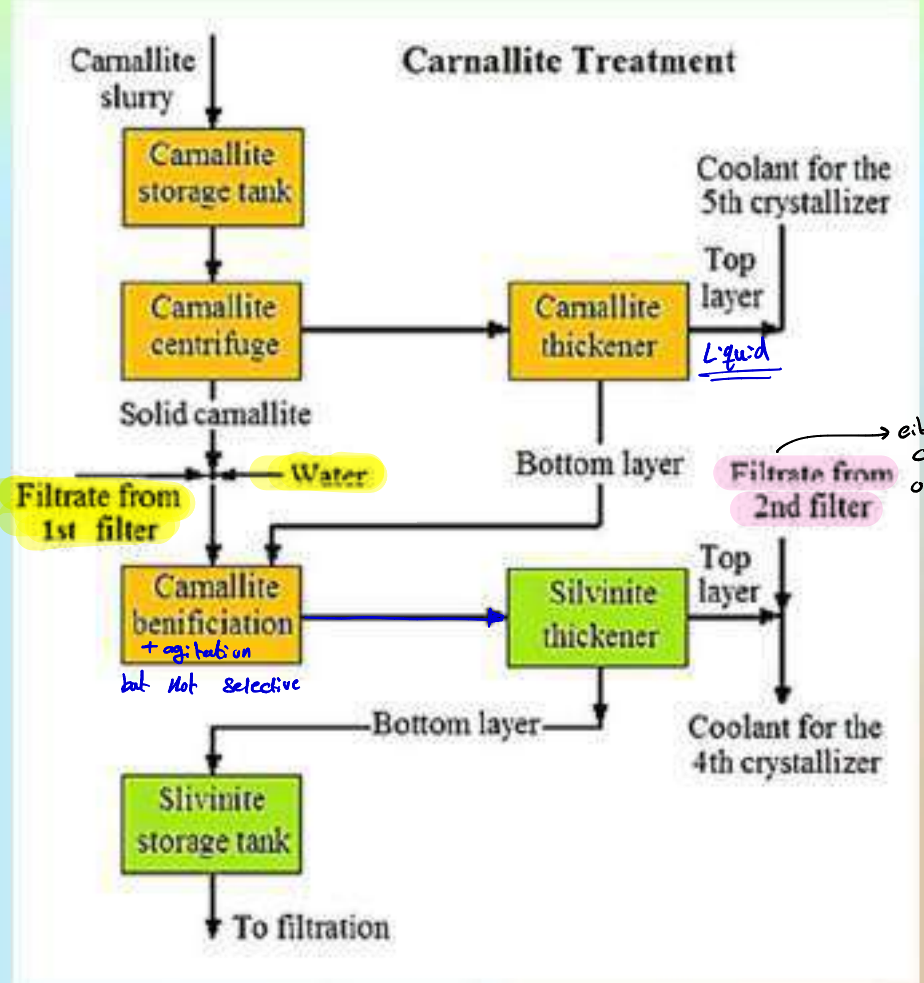
عن طريق إضافة المزيد من المي (fresh water)

عشان $MgCl_2$ بذوب أكثر من KCl و $NaCl$

this step is not selective around 8 to 9% of KCl will dissolve also

→ return this liquor to carnalite ponds

Carnallite Treatment



Carnallite slurry

Carnallite storage tank

Carnallite centrifuge

Carnallite thickener

Top layer

Liquid

Coolant for the 5th crystallizer

Solid carnallite

Bottom layer

Water

Filtrate from 1st filter

Carnallite benificiation

+ agitation

but not selective

Silvinite thickener

Top layer

Filtrate from 2nd filter

→ either coolant or ponds

Coolant for the 4th crystallizer

Bottom layer

Slivinite storage tank

To filtration

Main idea in this process is the solubility differance

⊛ إذا كانت المادة يلي ما بدي إياها ذائبيتها أعلى من إللي بدي إياه

← رح أذوبها

⊛ لو قلّ ← رح أرسبها

⊛ الخطوة الثانية عنا Kcl + Nacl

رح أذوّب Kcl عشان أرسب Nacl

SYLVINITE TREATMENT

→ Separation of Nacl and Kcl

- Fresh water is added to the beneficiation tanks to separate the potassium chloride from magnesium chloride.
- Magnesium chloride will dissolve in addition to small amount of potassium chloride (3 to 4 %). 72.7 g/100 ml water @ 100 °C.
- Most of the potassium chloride remains in its solid phase as well as sodium chloride.
- Potassium chloride and sodium chloride in a solid form known as Sylvinite.

SYLVINITE TREATMENT

- Sylvinite can be found in nature in some countries and is used as a raw material for potash.
- Fresh water is added with a constant ratio of 425 g/1 kg solid
- Usually, it takes 90 minutes to dissolve the carnallite in the beneficiation tanks.
- The exit from the beneficiation tanks flows to the sylvinite thickeners.

  → very fine particles of Nacl.
- Two layers are formed in the sylvinite thickener; the bottom layer which contains most of the solid materials and the top layer contains the saturated solution of magnesium chloride.

SYLVINITE TREATMENT

- The saturated solution ($MgCl_2$) is sent to the ponds because it contains 3 to 4% KCl.
- The bottom layer which contains 30% sylvinite is pumped to sylvinite storage tank.
- Three steps are carried out for sylvinite treatment:

1. Filtration. ⇒ because the input is slurry (contains high amount of water) + easy to pumping
2. Hot leaching. ⇒ why ? to increase the solubility of Kcl
3. Removal of NaCl.

SYLVINITE FILTRATION

- The sylvinite slurry is pumped from the storage tanks to 2 filtration units.
- These filters are belts made from rubber covered with special cloth and operates under vacuum.

→ to decrease the solubility
⊕ decrease residance time
عشان أمنع تبلور NaCl ←

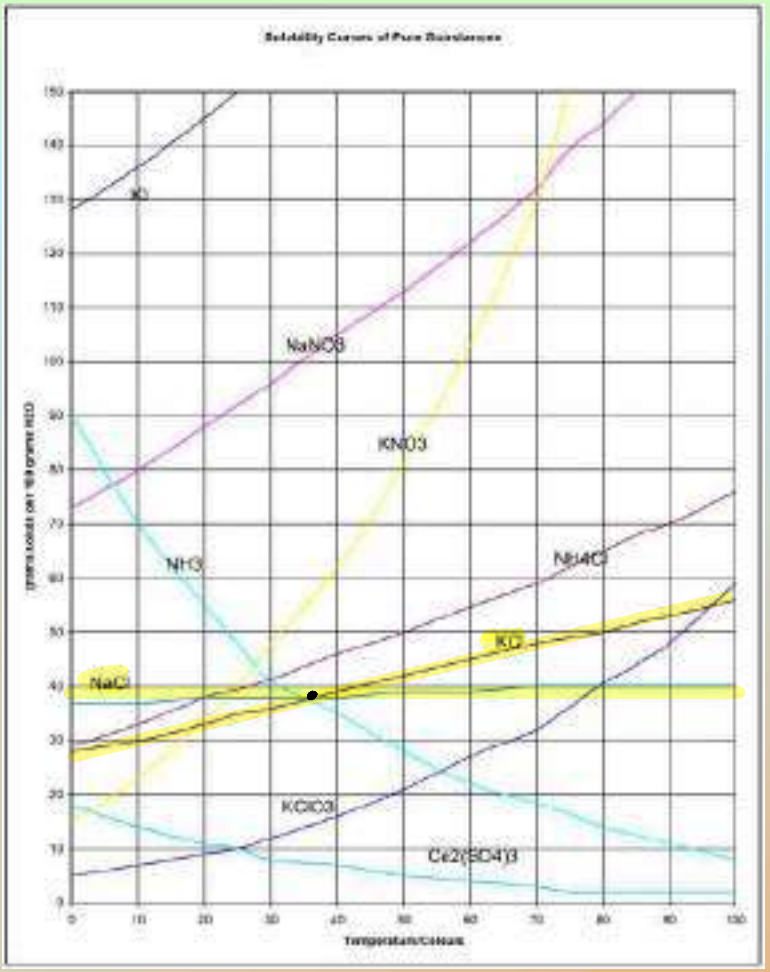
- The filtrate is collected in tanks and used in other processes.
- The cake (sylvinite) which contains 45 – 55 % KCl is transferred to the hot leaching step using belt conveyor.

HOT LEACHING

- The main purpose of this step is to separate the KCl from NaCl by dissolving the KCl in a saturated solution at 104°C.
- The saturated solution at this temperature will only dissolve KCl while the NaCl remains in its solid phase.
- The process is carried out in two stages, in the first stage and after dissolving the KCl, the solution is sent to the hot thickener where the KCl rich solution is collected in the top layer.

limitation by adding water

→ over flow ⇒ KCl



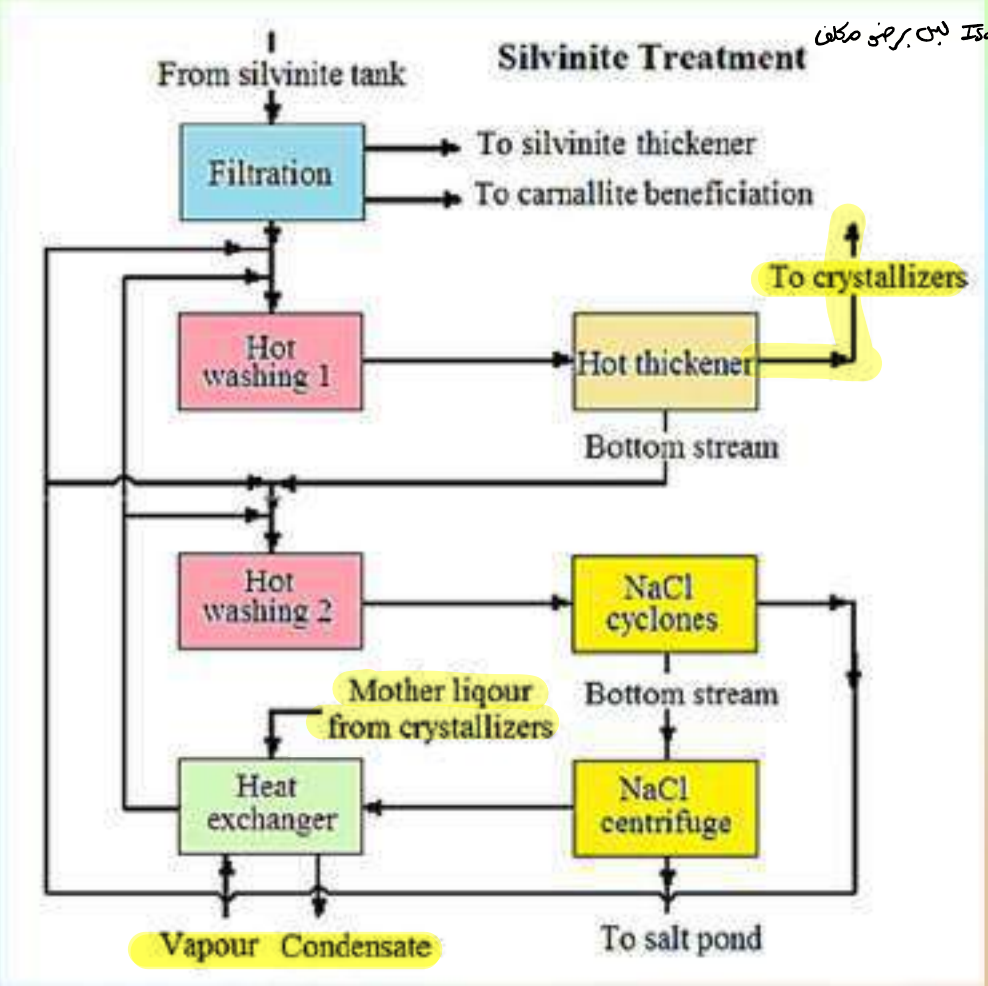
⊛ من الرسم بنلاحظ إنه عند درجات حرارة عالية ذائبية KCl > ذائبية NaCl

الهيك بنعمل hot leaching طب برضو رح يذوب NaCl شو أعمل عشانه ما أخليه يذوب ؟

المَيّ رح أضبطها رح أضيفها على دفعات مو excess عشانه أخلّي الأفضلية للـ KCl .

(*) for crystallisation process

رح يكون المحلول على درجة حرارة 104°C رح أبرده عشان أوصل
لل saturation وأفصل ال KCl
بس كلما أنزل الحرارة ال recovery ↑ بنفس الوقت رح يكون
مكلف لأنه أحل شي ممكن أضيف مواد تنزل ال freezing point
الميّ وهاد مو بلاش كمان، أو أستخدم Isopropane بس برضو مكلف
شو الحل؟ لازم أعمل optimisation



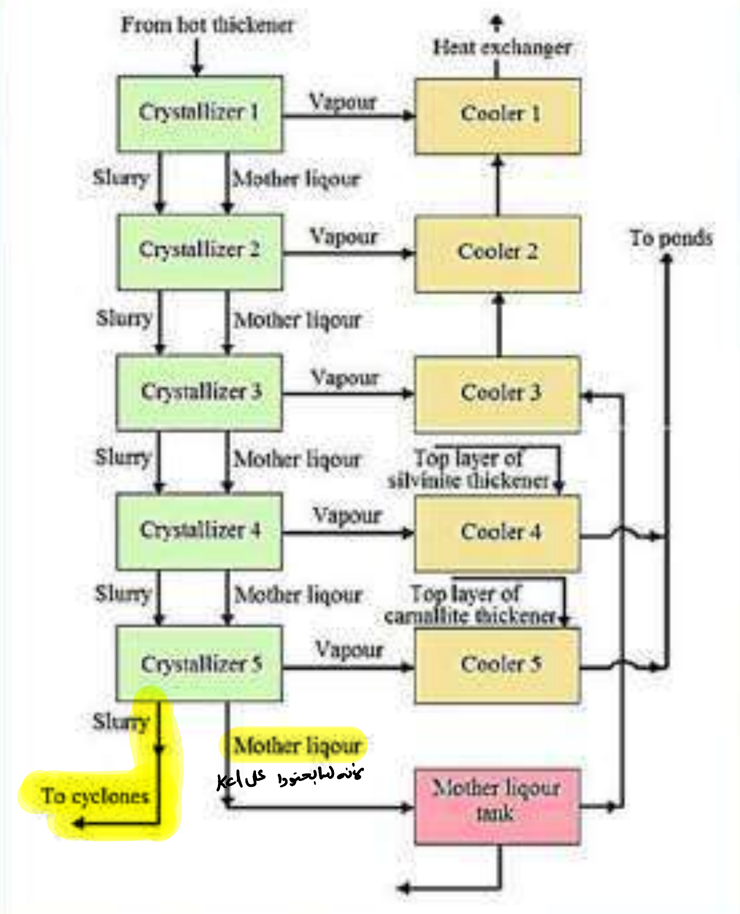
KCl CRYSTALLIZATION

→ two phase solid + liquid
at certain T & concentration

- The KCl saturated solution is pumped to the crystallizers to crystallize the potassium chloride.
- There are 5 crystallizers work in series.
- There are 2 streams exit from each crystallizer, the first one exit from the bottom of the crystallizer and contains the crystals formed and the second stream exits from the top layer of the slurry which contains not more than 1wt% KCl.

  ↳ very fine particles
- The KCl crystals formed as a result of cooling the saturated solution.

Crystallization Unit



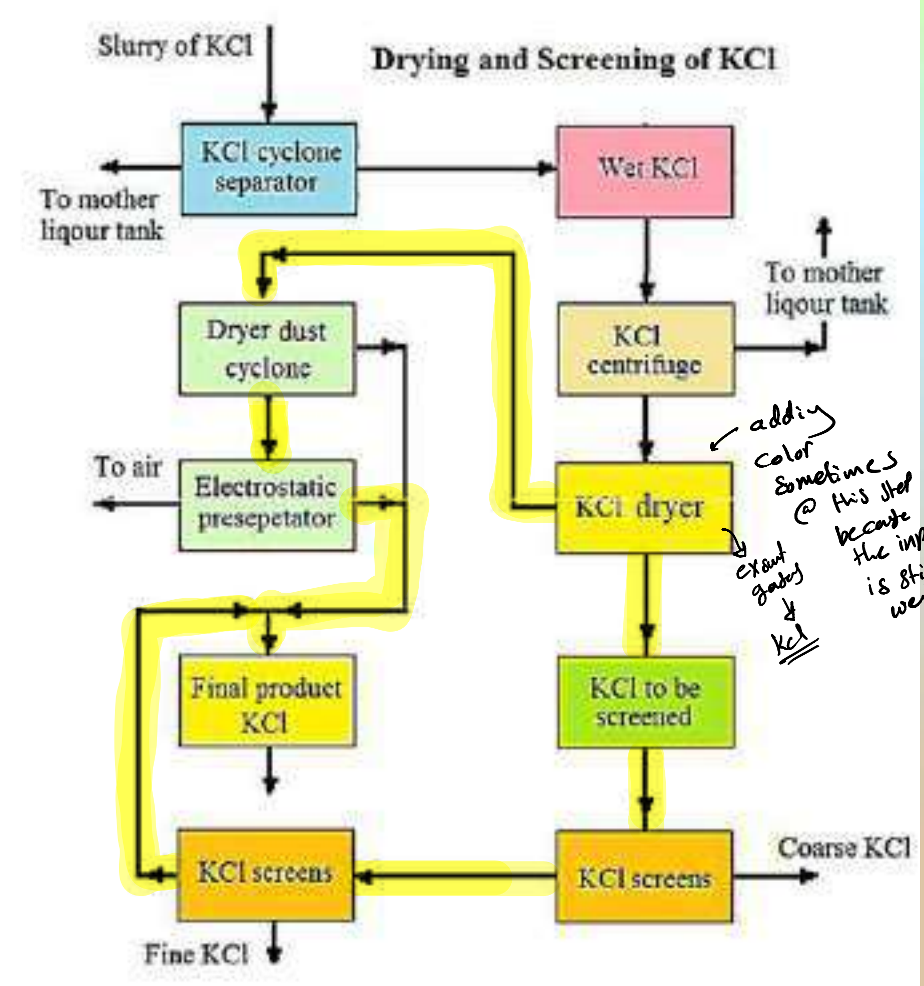
كانه لسا بحتوا كل KCl

- It is necessary to keep the amount of water within the crystallizer at a point which will not allow NaCl to crystallize.

ما بقدر أكثر من هيك لأنه لو اشتغلت
على حرارة أقل ← cost ↑
و لو أعلى ← رح يتبلور Nacl .

yield

- The discharge from the 5th crystallizer contains 15 to 25 % KCl crystals.
- Crystallizer discharge slurry is cycloned to remove part of the liquid present with the KCl crystals.
- 3 centrifuges are used to get rid of most of the liquid before KCl crystals are fed to the rotary dryer using a belt conveyor.
- KCl crystals exit the rotary dryer with at most 0.1% moisture content.
- The dried potassium chloride product passes through screens to be separated into two fractions, standard, and fines, according to the required size specifications.



adding color sometimes @ this step because the input is still wet

exaust gases
↓
KCl

BY-PRODUCTS OF KCl INDUSTRY

1. Solid material, sodium chloride (NaCl).
2. Final solution that contains:

   $MgCl_2$, $MgBr_2$, and $CaCl_2$

➢ **Future plans to produce:**

1. Bromine: used to produce chemical compounds for industrial and agricultural purposes, calcium bromide and sodium bromide.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

main raw material.

ممكن انتاج
أو نشتريه

BY-PRODUCTS OF KCl INDUSTRY

2. Sodium carbonate: used mainly in glass industry, papers, water treatment, detergents.

$$2NaCl + CaCO_3 \xrightarrow{NH_3} Na_2CO_3 + CaCl_2$$

3. Magnesium Oxide: used in thermal bricks industry where this can be used as a lining for furnaces.

$$MgCl_2 + H_2O \xrightarrow{heat} MgO + 2HCl$$ (digestion)

4. Sodium hydroxide:

$$2NaCl + 2H_2O \xrightarrow{} 2NaOH + Cl_2 + H_2$$

5. KoH from Kcl

BENEFICIATION AND PROCESSING OF POTASH ORES

concentrate the Kcl

- Four basic beneficiation techniques have been applied in the potash industry:

  1. Flotation ⇒ عن طريقة الأيونة إضافة مادة
     بتأين المادة على سطحها
     و بتطلع الرغوة.
  2. Heavy Media Separation
  3. Electrostatic Separation
  4. Thermal Dissolution Crystallization

- Most potash processing plants practice a combination of beneficiation techniques.

→Ball mill
في جوا Baffles عشان يقدر يحمل ال Balls
عشان يوقع كسقوط حر ← impact
↳mainly

floatation ↓

عشان آخذ impact عالي ال Drum تكون كبيرة عشان
يصير سقوط حر من مسافة أعلى.

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. ⇒using ball mill
- A prime consideration in crushing and grinding is that a minimum number of fines be produced.
- Any fines produced by grinding must be processed by more costly methods.

→we don't want very fine
particle → high cost
and @ the same time
it's not for floatation
↳material
of interest
(KCl)

I want to find reagent
that make sure to
float KCl
⊕ if the KCl hydrophobic → if it's
or not?! so by air

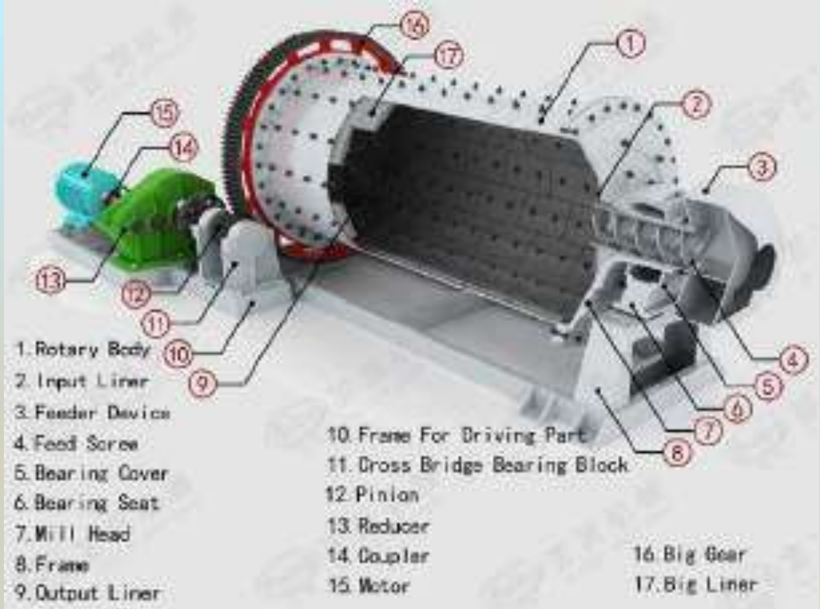
very fine particles
in floatation
1) cost
2) frother or collector
↳as particle size ↓
consumption of collector ↑
so ⇒ the accepted
particle size

وزنة الكرات داخل ال (Ball mill)
كبير عشان ما يكسروا بعض.

CRUSHING AND GRINDING

- 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.

↳ before ball mill.



⊕ Before floatation
1) crushing
2) grinding
3) disliming.

DESLIMING

↳ There is distribution of ball mill
as fine particles ↑ → more floating consumption → Also there is contamination

- Fine particles, both ore minerals and insoluble, are always removed to the greatest extent possible before the potash separation step.

عشان هيك رح أدخل على cyclones
عشان أشيل ال fine particles رح تلزق
بالحيط ورح تضل معلقة وأكثر رح ينزل لتحت.

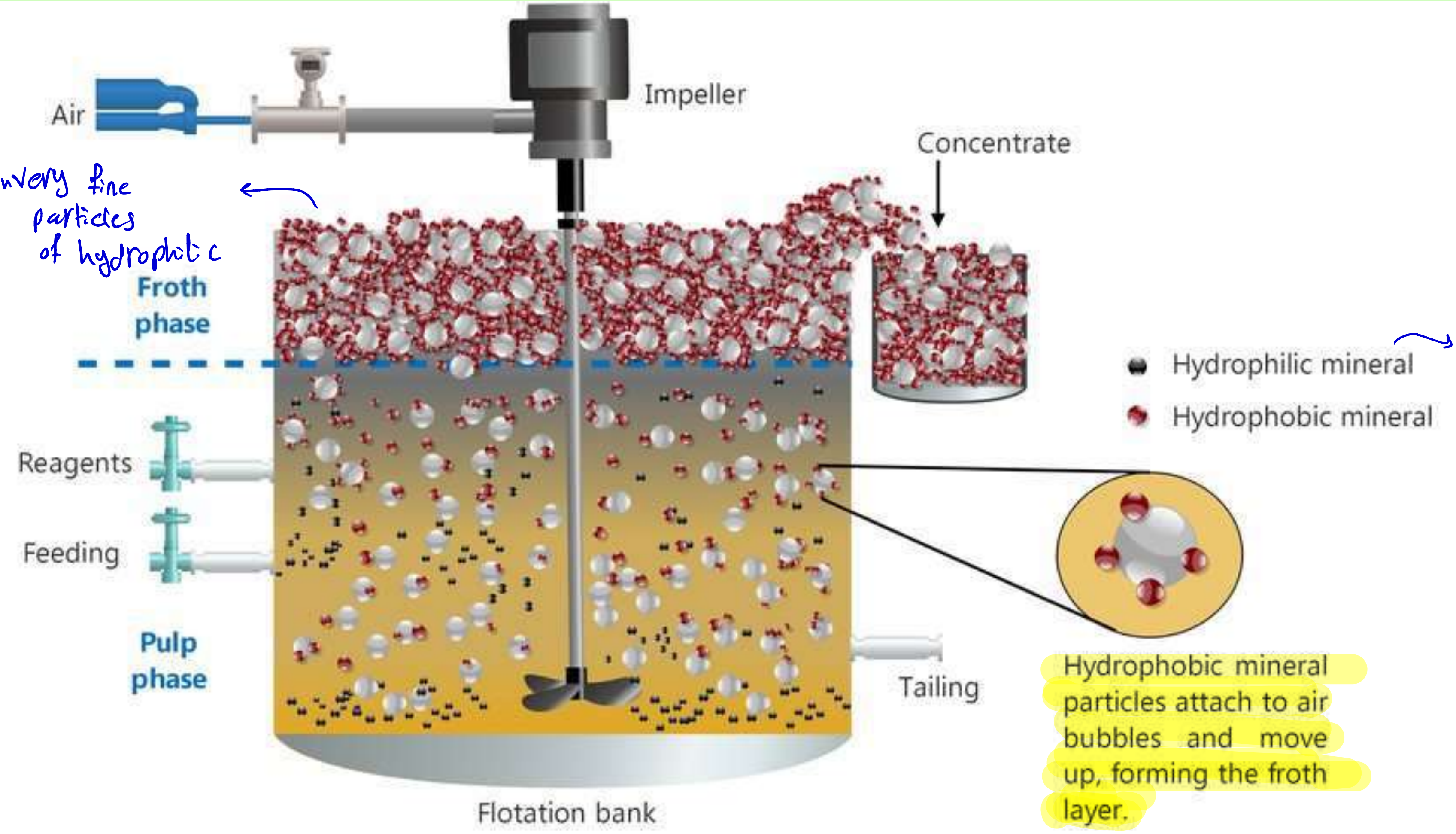
- In flotation, fine particles with high surface areas tend to adsorb excessive quantities of flotation reagents.
- Excessive amounts of fines can significantly raise reagent costs and cause contamination of the product.
- Most plants deslime by using one or more stages of cyclones and hydro separators.

FLOTATION

→ used in metal extraction

- 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 attach themselves to the air bubbles and float to the surface where they can be removed.

it may contain very fine particles of hydrophilic



رح ينزل تحت

Hydrophobic mineral particles attach to air bubbles and move up, forming the froth layer.

FLOTATION

- 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.
- 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.
- Another category of reagents that is commonly used is known as frothier.

HEAVY MEDIA SEPARATION

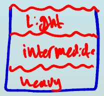
Based on
density of
the material.

- The process utilizes the difference in specific gravity of sylvite (KCl) and halite (NaCl).
- Halite is the denser mineral (specific gravity 2.13 versus 1.9 for sylvite).

with accept
particle
size

المحلول لازم يكون كثافته بالوسط عشان يقدر يفصل الخفيف عن الثقيل

- 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 slurred to create an artificial heavy medium at the specific gravity required for separation.

→ not larger than this because the weight of the particles will be > the media

- After separation, the magnetite or ferrosilicon is recovered by magnetic separation and recirculated to the system.

⇒ Not effected.

industrially
→ not pure output.

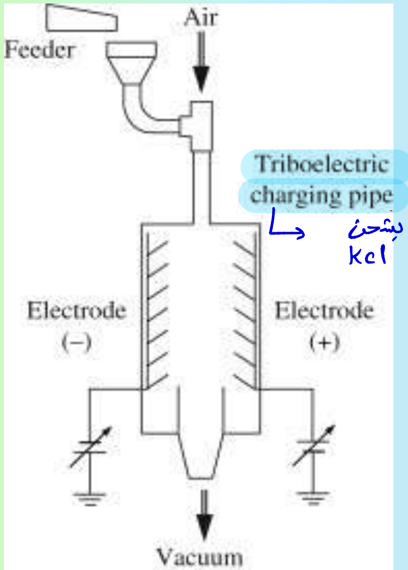
ELECTROSTATIC SEPARATION

بشحنوا ال particles
بشحنات معينة

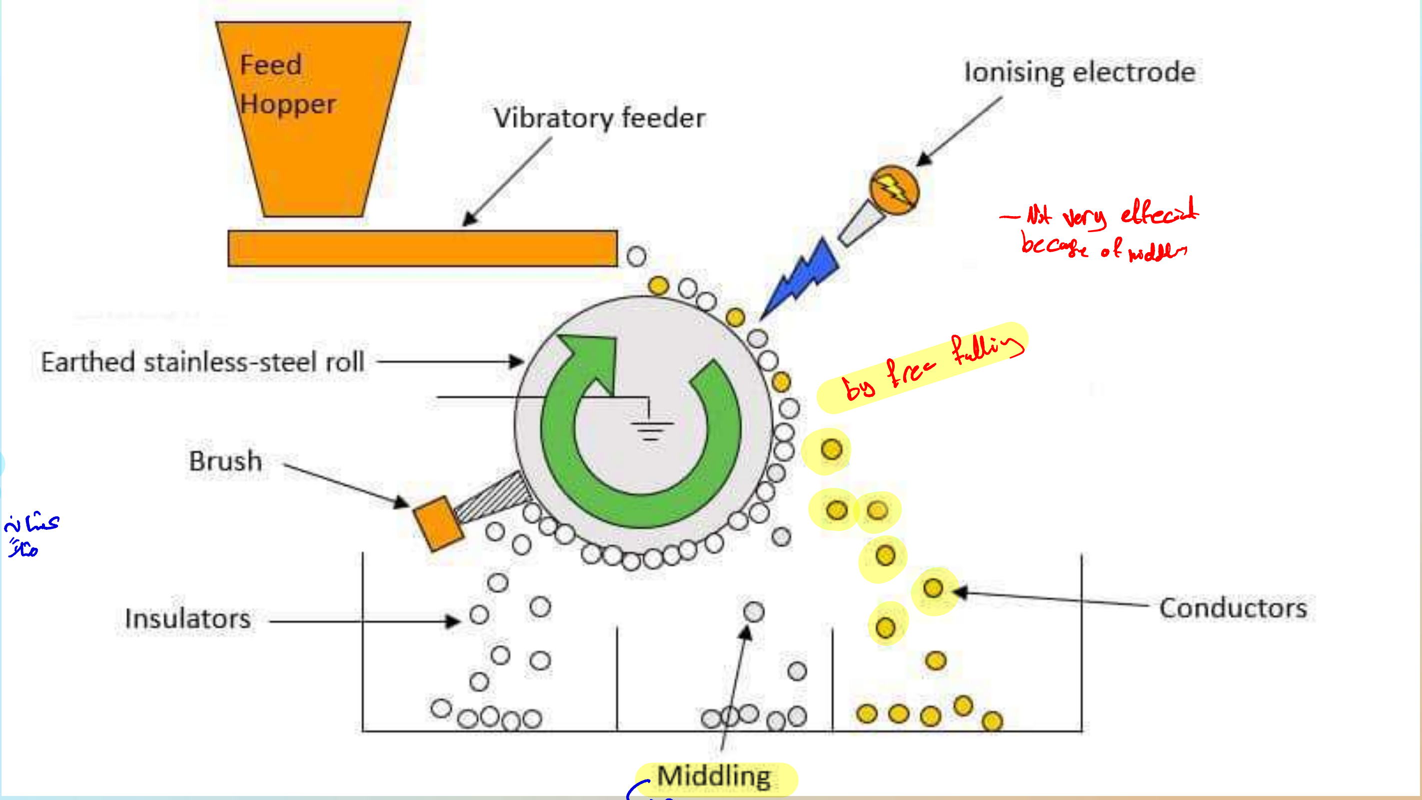
- Electrostatic separation is a dry technique in which a mixture of minerals may be differentiated according to their electrical conductivity.
- For potash minerals, which are not naturally conductive, the separation must be preceded by a conditioning step that induces the minerals to carry electrostatic charges of different magnitudes and different polarities.
- For potash, fractional or triboelectric charging is used; the charges are induced through repeated physical contact between the different minerals.

→ Not effecient

ELECTROSTATIC SEPARATION



عشانه يشحن KCl مثلاً



— Not very effecient because of middlers

by free falling

Middling → recycle.

بكونه ما انشحن أو صار
في مشكلة خلّته مايفصل.

ELECTROSTATIC SEPARATION

- 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: product, residue, and middling.
- The middling, after further grinding, are recycled to the conditioning stage.


SUNY GROUP

THERMAL DISSOLUTION-CRYSTALLIZATION

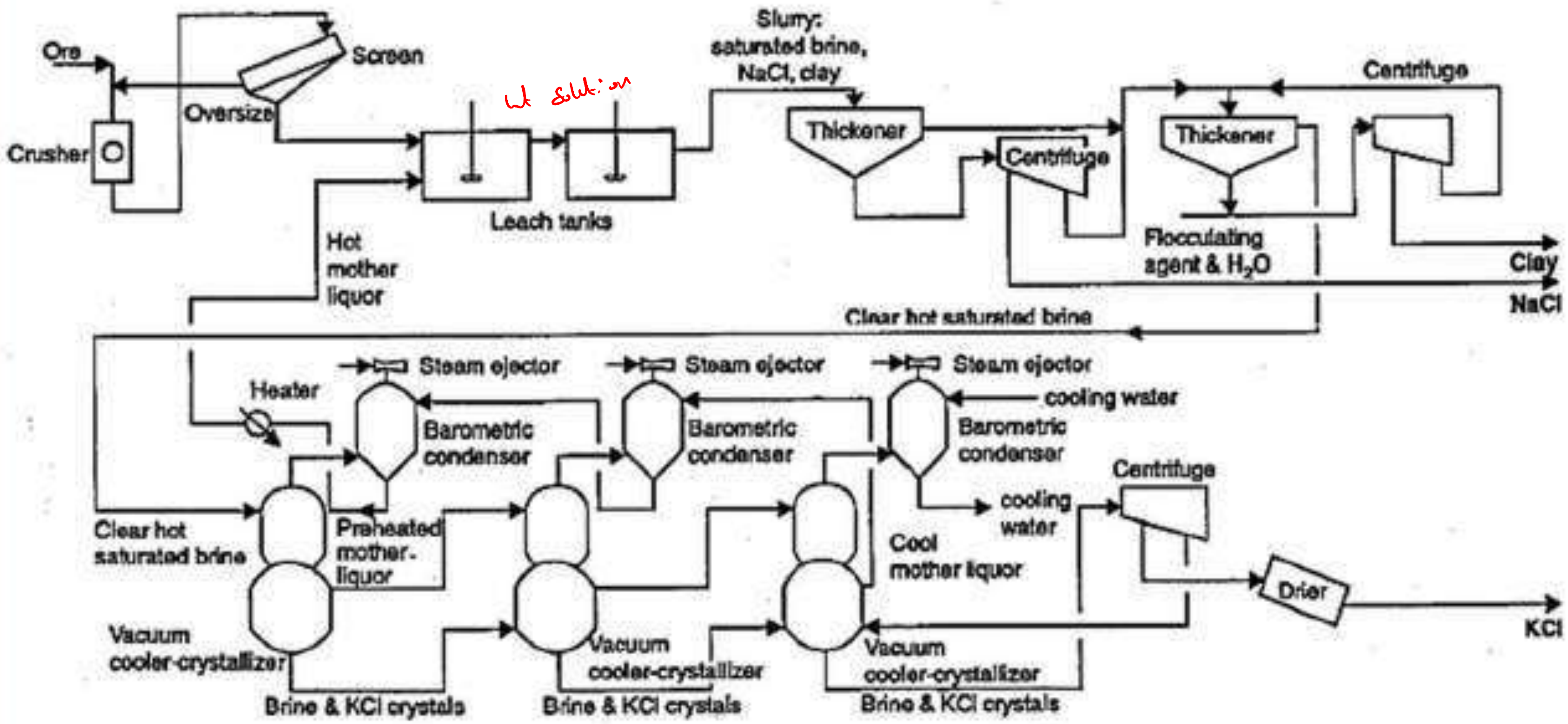
→ Based on solubility different

- 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.

→ after crystallization

1) Drying

2) Sieving.


Ore
Screen
Oversize
Crusher
wt solution
Leach tanks
Hot mother liquor
Slurry: saturated brine, NaCl, clay
Thickener
Centrifuge
Thickener
Centrifuge
Flocculating agent & H_2O
Clay
NaCl
Clear hot saturated brine
Steam ejector
Steam ejector
Steam ejector
cooling water
Heater
Barometric condenser
Barometric condenser
Barometric condenser
Clear hot saturated brine
Preheated mother-liquor
Cool mother liquor
cooling water
Centrifuge
Drier
KCl
Vacuum cooler-crystallizer
Vacuum cooler-crystallizer
Vacuum cooler-crystallizer
Brine & KCl crystals
Brine & KCl crystals
Brine & KCl crystals

FERTILIZERS TECHNOLOGY

CHEM 0905554

First Semester 21/22

CHAPTER 5

SULFURIC ACID MANUFACTURING

عشان أنتج ال DAP لازم أنتج ال phosphoric Acid عن طريق H_2SO_4

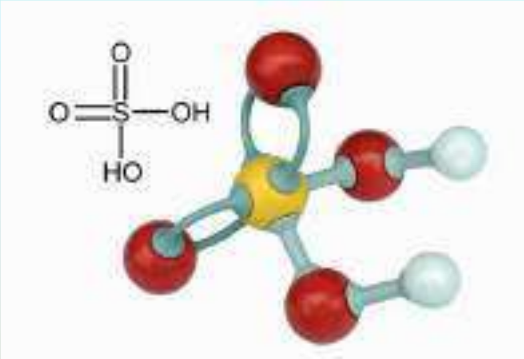
⊛ Most of H_2SO_4 production in Jordan consumed locally.

عشانه أقدر أنتج ال H_2SO_4 98% لازم أخلط SO_3 مع ال H_2O مو SO_2.

INTRODUCTION

H_2SO_4 reaction depends on
on
1) Sulfer $+ O_2 \rightarrow SO_2$ Combustion of Sulfur
2) $SO_2 \xrightarrow{catalyst} SO_3$ Conversion of $SO_2 \rightarrow SO_3$ Selection of catalyst depends on its surface

- One of the oldest industrially applied processes.
- Discovered by a Persian physician and alchemist Ibn Zakariya Al-Razi in the 19th century. he discovered sulfaric Acid by accedent.
- Saltpeter and sulfur were mixed in a glass container and burned in a moist atmosphere. Acid was collected from the condensed vapors. fume by showering
- In England, 1746, the lead chamber reactor was invented. This invention allowed for higher production rates (<78%).



⊛ main units in Sulfuric Acid manufacturing:

1) furnace → to produce SO_2 by combustion of sulfur.

2) catalytic bed convertor
$SO_2 \longrightarrow SO_3$

3) Absorbers.

INTRODUCTION

- In England, 1831, a patent described the oxidation of sulfur dioxide over a platinum catalyst, the Contact Process.
- This process increased yields of reaction from 70 to above 95%.
- In 1913, BASF was granted a patent for the use of vanadium pentoxide (V_2O_5) as a catalyst for the Contact Process.
- By the 1930's, vanadium pentoxide (V_2O_5) was becoming the dominate catalyst used because of insensitivities to poisons and lower cost. → it's the catalyst used to convert ($SO_2 \longrightarrow SO_3$) → with conversion $\boxed{99.9\%}$
- In 1960 a patent application was filed by Bayer using the so-called double-catalyst process (double absorption).

FORMS OF SULFURIC ACID

- Although 100% sulfuric acid can be made, this loses SO_3 at the boiling point to produce 98.3% acid. → for more stability in storage.

→ 2% of H_2O

- The 98% grade is also more stable for storage, making it the usual form for "concentrated" sulfuric acid.

- Other concentrations of sulfuric acid are used for different purposes:
  - ✓ 10%, dilute sulfuric acid for laboratory use (pH 1)
  - ✓ 33.5%, battery acid (used in lead-acid batteries) (pH 0.5)
  - ✓ 62.18%, chamber or fertilizer acid (pH about 0.4) → why? 1) prevention of corrosivity of the equipment 2) stable
  - ✓ 77.67%, tower or Glover acid (pH about 0.25)
  - ✓ 98%, concentrated (pH about 0.1) → in labs

SULFURIC ACID USES

- Sulfuric acid is a dense clear liquid.

↳ Almost colorless (yellowish some times)

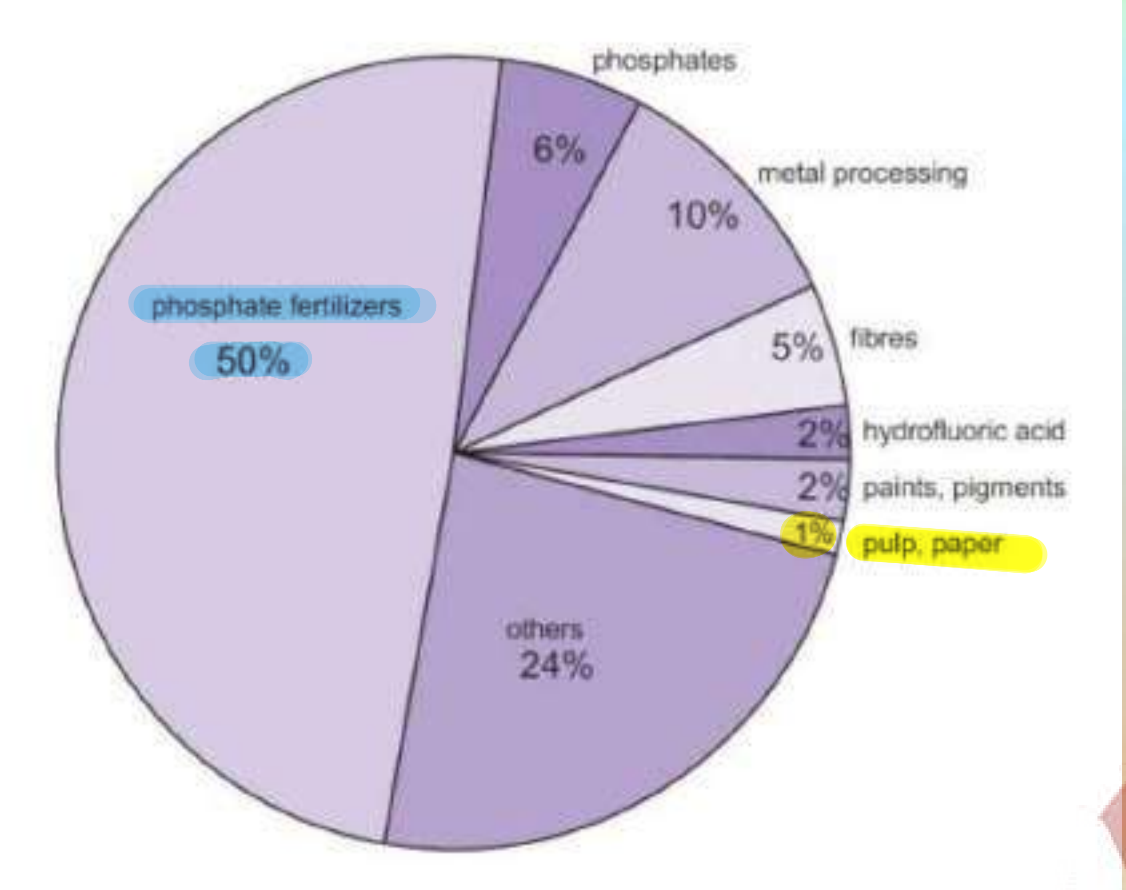
$\rho_{H_2SO_4} > \rho_w$

- It is used for:

1. Making fertilizers.
2. Organic chemical industry.
3. Leaching metallic ores. Such as extraction of metal from it's ore such as copper.
4. Refining petroleum as a catalyst.
5. Production of TiO_2 consumes large quantities. → glass, filler, paints ↓ مادة مُبيضة

- Worldwide, over 250 million tones of sulfuric acid are consumed per year.

SULFURIC ACID USES



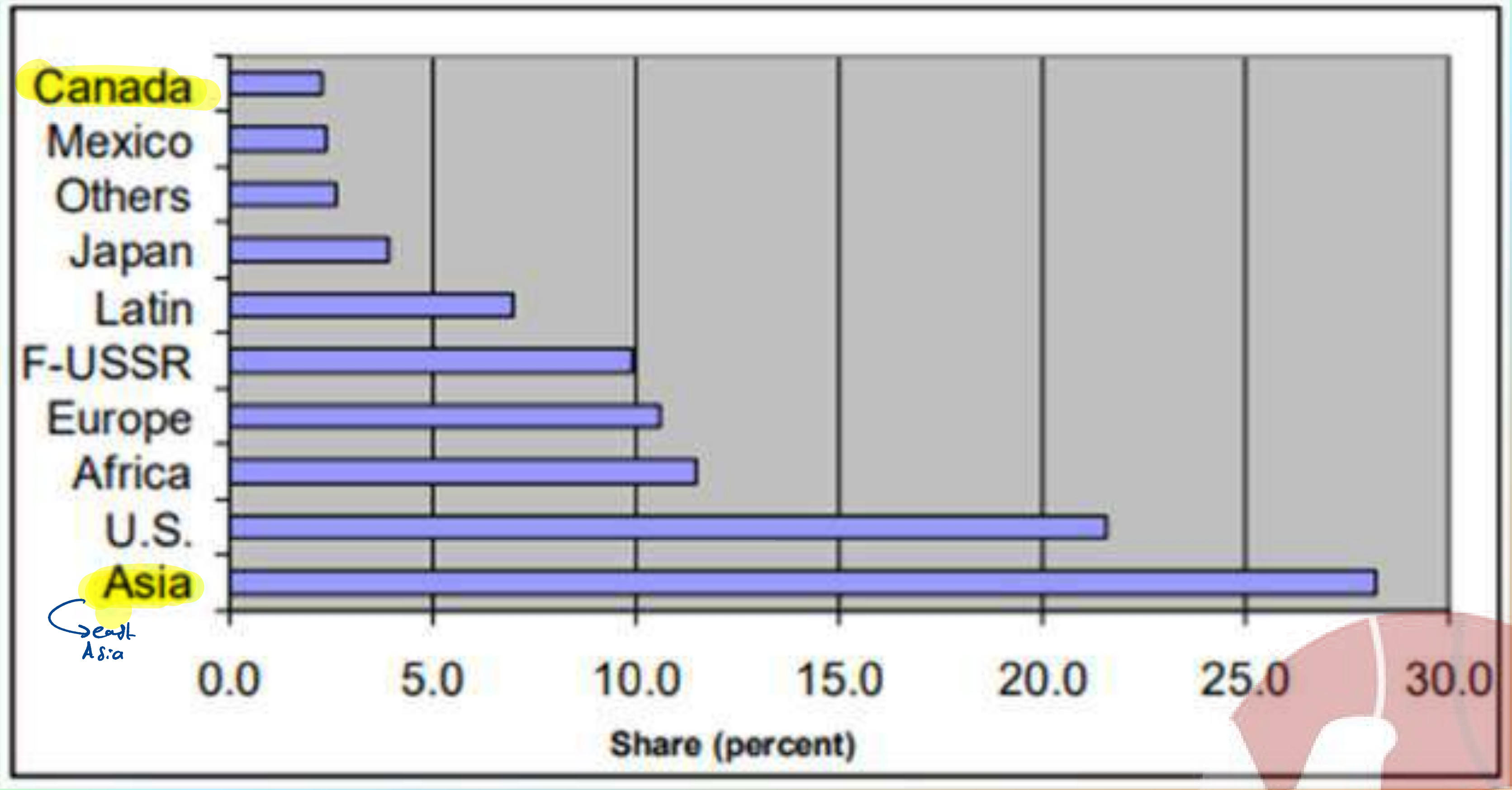
SULFURIC ACID WORLD PRODUCTION

→ Always there is Demand.

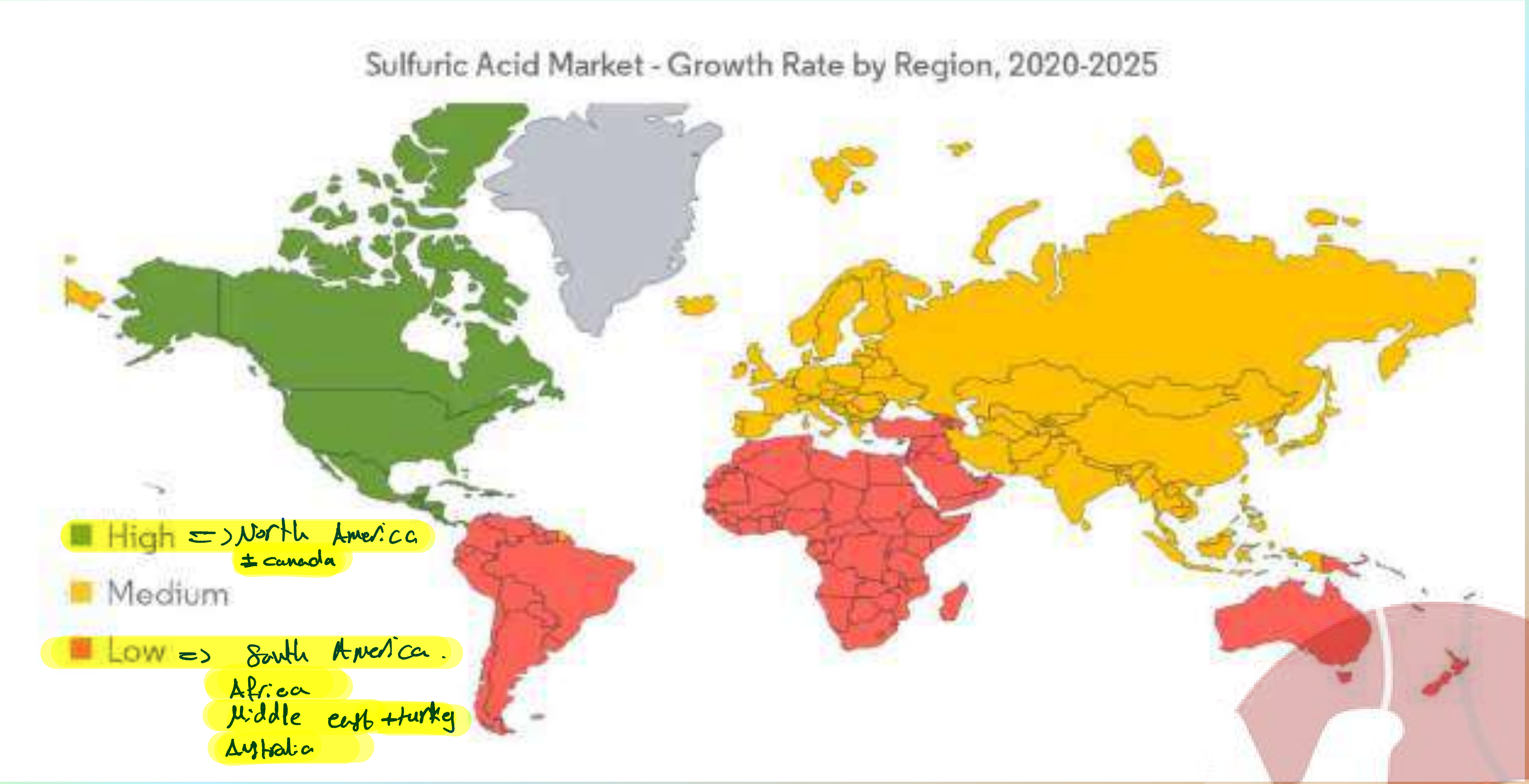
لأنه كتير بيتم استخدامه بمجالات مختلفة

30 million ton increase by 2026*

SULFURIC ACID PRODUCTION BY COUNTRY



SULFURIC ACID MARKET


Sulfuric Acid Market - Growth Rate by Region, 2020-2025

High => North America + canada

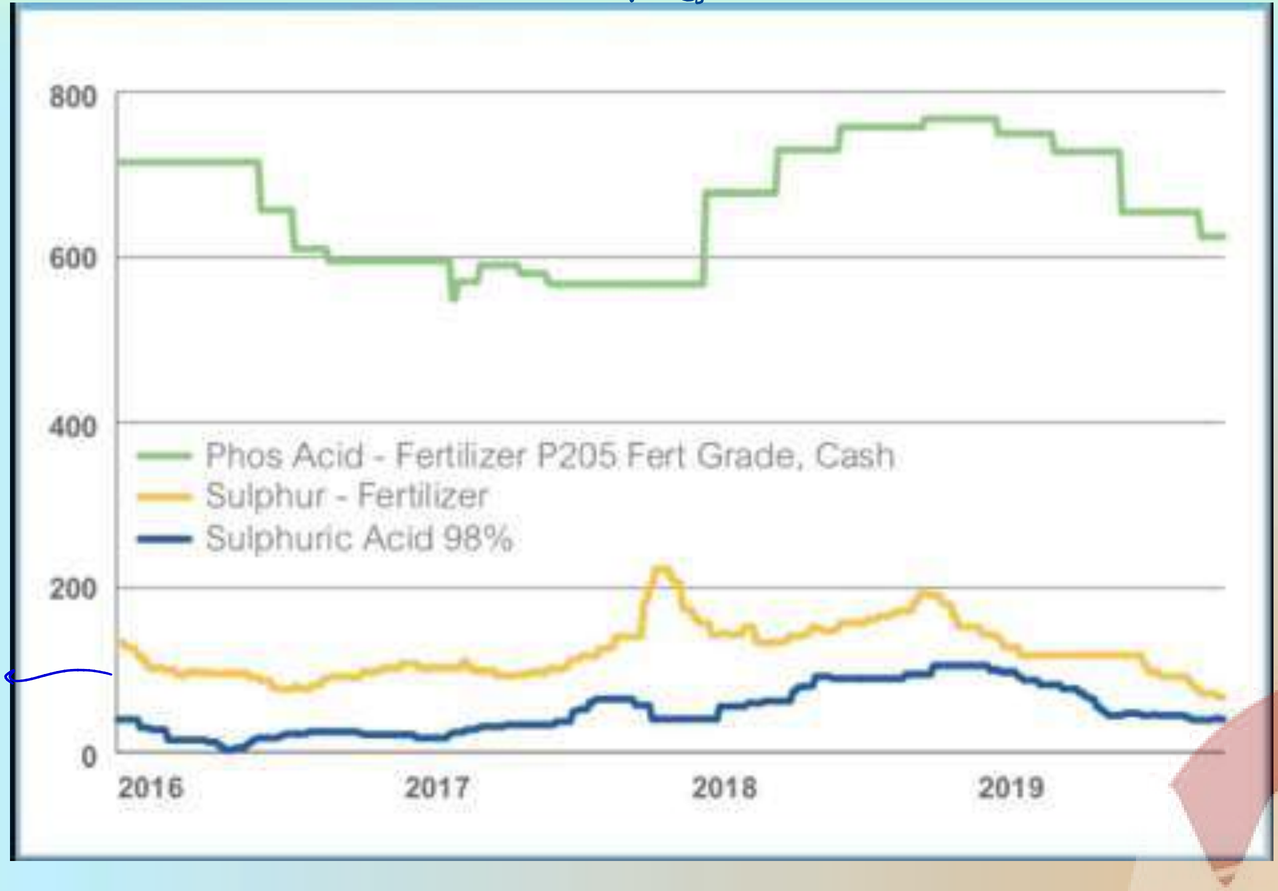
Low => South America.
Africa
Middle east + turkey
Australia

why does the price of phosphoric Acid >> Sulfuric Acid?

because the product of H_2SO_4 is concentrated but the phosphoric Acid is dilluted → to make it concentrated it should be done in heat exchangers thus, it will need energy energy ↑ cost ↑

SULFURIC ACID PRICES

fluctuation in prices



على الرغم من قلة سعره إلا إنه مهم
ورا كمية الطاقة الهائلة إلّي بقدر
أخذها منه .

metals
plastic
petrochemical industries → not constant source for Sulfric Acid Manufacturing. → SO_2 from these sources may be full of impurities → So, the treatment process is a must here → instead of increasing the cost we shall use elemental sulfur.

but the constant source → elemental Sulfur.

if it's not clean the catalyst will poisend. or damage
and it should be dry → why?
to prevent to produce H_2SO_4 in the bed (it will cause corrosion)

Main raw material
→ Dry SO_2

(*) بحطوا الكبريت بحجرة و بيجروا عليها steam خطوط
ب coil فانذوب الكبريت بشكل غير مباشر + by conduction

SULFURIC ACID PRODUCTION PROCESS

- The starting material for sulfuric acid manufacture is clean, dry SO_2 gas.
- This can be obtained by burning molten sulfur, from metallurgical off-gases or by decomposing spent sulfuric acid.

→ how do we convert solid sulfur to molten sulfur?
→ by heating it until the temperature exceeds it's m.p (≈100 °C)
by steam (indirect) by conduction

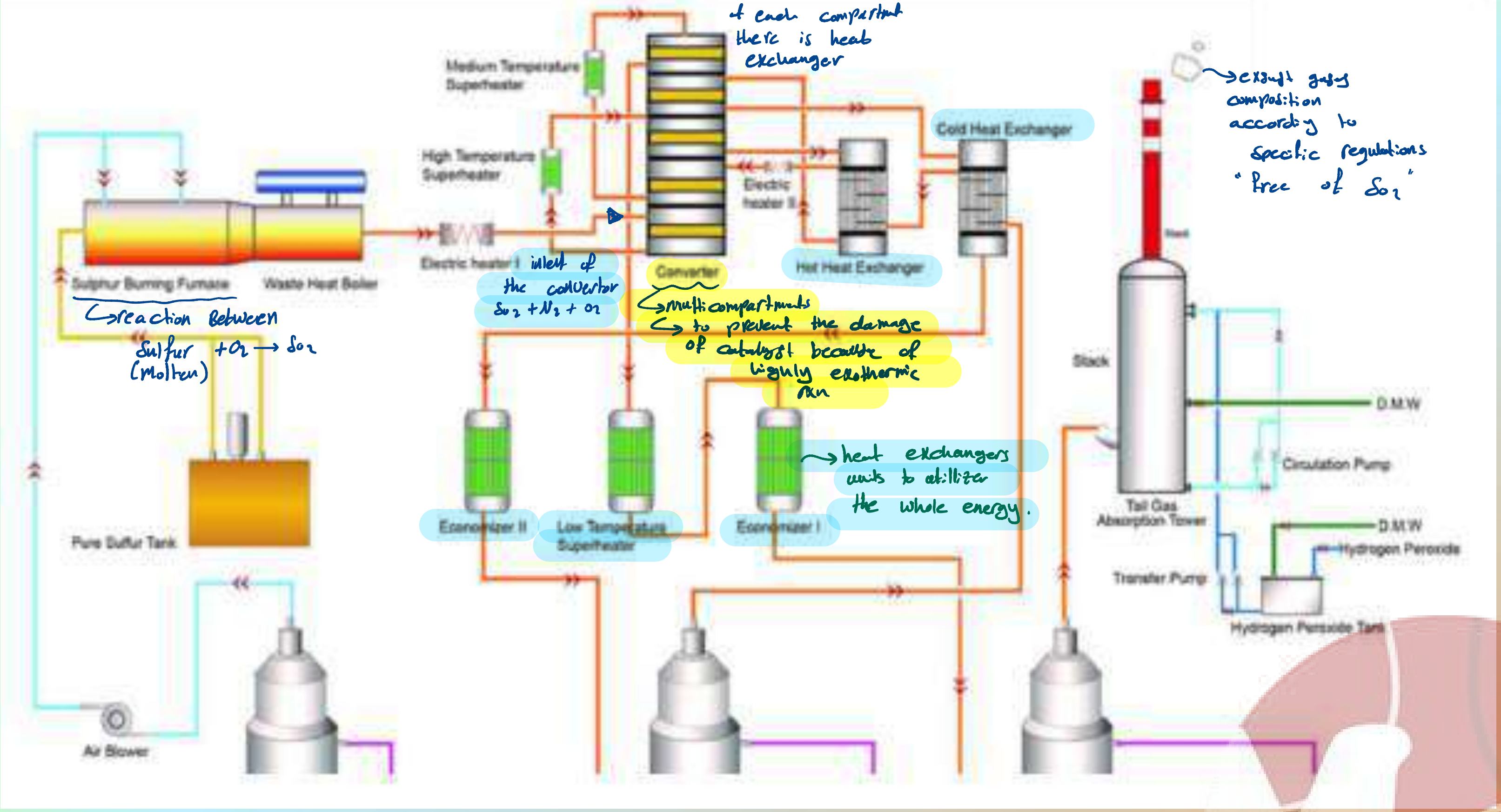
- Over the last decades the contact process has been used to produce sulfuric acid, replacing the traditional «Lead Chamber» process dating back to the 18th Century.

→ high conversion
→ depends on V_2O_5

- In the contact process SO_2 is oxidized to sulfur trioxide (SO_3) at high temperature (about 450 ° C) in the presence of a vanadium catalyst.
- SO_3 then is dissolved in concentrated sulfuric acid forming fuming sulfuric acid (oleum). This can then be reacted safely with water to produce concentrated sulfuric acid.

SULFURIC ACID PRODUCTION PROCESS

(*) مشكلة ال sulfur إنه لما أوصله لل m.p الكثافة رح تتغير



→ at each compartment there is heat exchanger

→ exhaust gases composition according to specific regulations "free of SO_2"

→ reaction between sulfur (molten) $+ O_2 \rightarrow SO_2$

inlet of the converter $SO_2 + N_2 + O_2$

→ multicompartments → to prevent the damage of catalyst because of highly exothermic rxn

→ heat exchangers units to utilize the whole energy.

RAW MATERIALS

- The main raw material for sulfuric acid production is SO_2 gas.
- It is obtained by:
  - (a) Burning elemental sulfur with air
  - (b) Smelting and roasting metal sulfide minerals (Cu_2S, ZnS).
  - (c) Decomposing contaminated (spent) sulfuric acid catalyst.
- Elemental sulfur is far and away the largest source.

Ⓐ extraction of sulfur
↳ we can obtain high concentration of SO_2

→ contains of concentrated unreacted SO_2

CONVERTERS FEED COMPOSITION

- Compositions of acid plant feed gases entering SO_2 oxidation “converters” may also contain small amounts of CO_2 or SO_3.

	Sulfur burning furnace	Smelters and roasters	Decomposition furnace
Gas	Volume %		
SO_2	11	10	9
O_2	10	11	11
N_2	79	79	76

Close to each other

⇒ هو أعلى من هيك
O_2 لأنه في معه
N_2 +
وهو أقل من هيك
عشان تضل البروسيس
مربحة.

MAIN REACTIONS

Three Step Process:

- In the first stage of the contact process, sulfur is burned in air to make sulfur dioxide:

$$S_{(s)} + O_{2\,(g)} \xrightarrow{1150\,^oC} SO_{2\,(g)} \qquad \Delta H_R = -296{,}810\ Kj/kmol$$

excess + catalyst

- In the second stage, sulfur dioxide reacts with more oxygen to make sulfur trioxide:

← عشان يضل بال forward direction لازم يضل جهاز الريتج

$$SO_{2\,(g)} + 0.5\ O_{2\,(g)} \overset{400-630\,^oC}{\Longleftrightarrow} SO_{3\,(g)} \qquad \Delta H_R = -96{,}323\ Kj/kmol$$

بكل حجرة لازم أسحب الغاز
وأبرده بعدين أرجعه كمان مرة
لأنه T رح يحرق الكاتليست
لازم ما يتعدى بكل حجرة 630°C
⊕ عشان أخلي التفاعل forward
Don't increase % Backward rxn

- In the final stage, sulfur trioxide reacts with water to make sulfuric acid:

$$SO_{3\,(g)} + H_2O_l \xrightarrow{80-110\,^oC} H_2SO_{4\,(l)} \qquad \Delta H_R = -132{,}000\ Kj/kmol$$

Sollium

⊛ حكينا ليش لازم أضل على حرارة 630 وما أتعداها

١) عشان أضمن إنه ما يصير في Damage for catalyst

٢) عشان ما نزيد ال % Backward

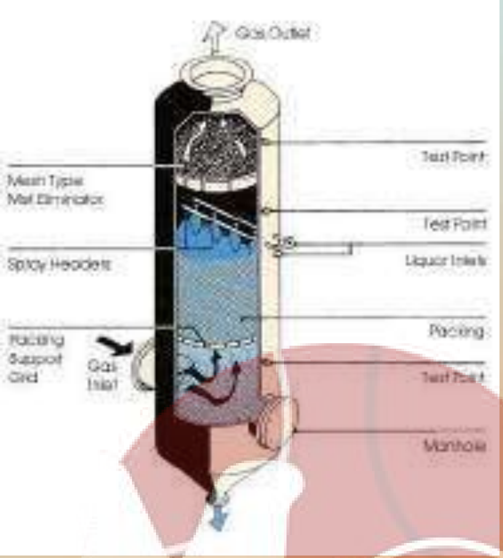
MAIN STEPS

- Sulfuric acid is made from SO_2 and O_2 gases by:
  - (a) Catalytically reacting SO_2 and O_2 to form SO_{3} (g) using catalytic converter.
  - (b) Reacting product $SO_{3(g)}$ with the $H_2O_{(l)}$ in 98.5 mass% H_2SO_4 , 1.5 mass% H_2O sulfuric acid.

ما بتتفاعل بشكل مباشر
مع المي لهيك لا أخففها
بال H_2SO_4 مركز

- Industrially, both processes are carried out rapidly and continuously.

↳ because residance time
in the main 3 units
must be low.



MAIN EQUIPMENT

melting of sulfur

1. Sulfur melting pit
2. Molten sulfur filter → to get rid from sulfur's impurities.
3. Sulfuric large molten sulfur storage tank. ⇒ must contain jacket ⇒ to keep it moltem

production of SO_2

4. The combustion air filter and air dehydration tower. → must be free of moisture content. + filtration of air to get rid of the impurities
5. The sulfur burning furnace
6. Catalytic converter.
7. Twin H_2SO_4 absorption towers.

Catalytic converters are typically 12 m diameter.

SULFUR MELTING

- Sulfur is non-metallic, a yellow solid at normal temperature, it dissolves in carbon disulphide at normal temperature.

→ other mediums requires higher Ⓣ

- Liquid sulfur at the melting point is yellow, as the temperature of the liquid is raised up it darkens and becoming deep orange.

→ rapture the ring and convert to long chain

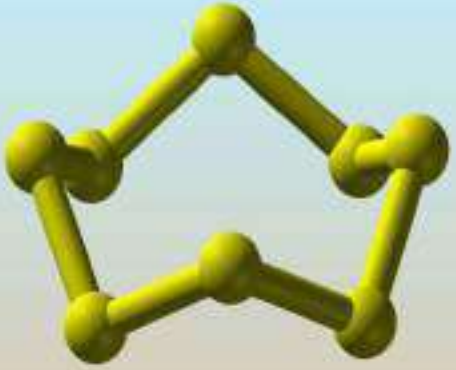
- The viscosity of the molten sulfur drops with rising temperature; above 158ºC the viscosity increases drastically with rising temperature up to 188ºC. Above 188ºC its viscosity falls somewhat as the temperature continues to rise.

(*) industrially the melting of sulfur is at 140 ~ 145°C

industrially → 155 ~ 188 must be avoided because it will become highly viscouse fluid

Commercially ⇒ below 155 °C → عشان أوفر طاقة

SULFUR MELTING



- Sulfur boils at atmospheric pressure at 445°C, the increase in viscosity as the temperature rises from 158°C to 188°C is assumed to result from rupturing of the puckered rings of S_8 to form chains of varying lengths.
- Sulfur has a melting point of about 116°C to 118°C, viscosity of sulfur affects the flow through pipelines and having high viscosity flows very slowly while liquids having low viscosity can flow easily.
- Solid sulfur is melted by steam coils in the melting pit, these steam coils are made of carbon steel.

made from concreet underground + lining with materials that can keep up with high temperature

± not indirect

± concrate not metal → to prevent corrosion

SULFUR MELTING

- The molten sulfur is maintained on between 135ºC and 145ºC for best performance of the pumps.

→ Best performance to decrease energy required by the pumps.

- The pits are lined with acid proof bricks and mortar; it is recommended to use:
  - ✓ 7 bar steam for sulfur melting pits.
  - ✓ 4 bar steam to maintain the temperature of the sulfur in other pits.

→ عشانه تذوب ال S

→ عشانه أحافظ على سيولته باستخدام عزل وبعزز فيه Steam 4 Bar ← كل الأنابيب والكل عشانه يضل سائل وأحافظ على درجة حرارته

⊛ even valves + tanks it should be jackted by 4 bar steam to keep sulfur molten.

- The impurities in the liquid sulfur are moisture and weak sulfuric acid formation in the solid sulfur.

Source of impurities
1) weak acid formation
SO_2, slow rxn with
$O_2 \longrightarrow SO_2 + H_2O \longrightarrow H_2SO_4$
2) moisture contact
4) impurities with elemental sulfur itself.

⊛not in direct contacts

لتحمل الأحماض

→ mortar cement.

SULFUR MELTING

- Sulfur when exposed to atmosphere in open space it gets oxidized to SO_2, and further this SO_2 is oxidized to SO_3 . ⇒ in open pit
- And when in contact with moisture it form H_2SO_4
- The H_2SO_4 present in sulfur is highly corrosive to the steam coils and metallic equipment and pumps.
- To reduce the acidity of sulfur, hydrated lime or ammonia gas should be used to act as filter media up to a certain extent.

④ Adding lime to reduce acidity of the sulfur by absorbing the moisture content

→ or ammonia to neutrilize with H_2SO_4 formed.

Sulfur FILTRATION

organic from amorphous silica + micro crystalline material.

- For filtration of sulfur diatomaceous earth is added.
- Diatomaceous earth consists of tiny skeleton of microorganism called as diatom and is composed of amorphous silica containing a small amount of micro crystalline material.
- The advantages of diatomaceous earth over other filter aid material are that it is:

1. Basically, very economical.
2. Withstand high temperature.
3. Inert to all chemicals except hydrofluoric acid, strong sulfuric acid, and strong alkalis.

Already not exsist in molten sulfur

SULFUR FILTRATION

- For filtration it is required initially to precoat the filter leaves with this filter aid, the filtration can be done when the coat formation is uniform over all the leaves of the sulfur filter.

بحطوه من البداية عشانه أمنع من أي other imp إنه تمرقه → capture All the impurities (mainly Ash)

- The addition of diatomaceous earth also depends upon the ash content in the sulfur according to the laboratory report.

main pit.

- The molten sulfur is neutralized with limestone addition on the solid sulfur belt conveyor feeding the smelter.
- The two filters will be operated in parallel each one 20 hours per day. 4 hours foreseen for one filter cleaning.

ممكن الح يكونوا شغال وممكن واحد

لسه مستعمل والعملية يضل continuous.

plate filters.

SULFUR FILTRATION

- Each filter is fed from the filtration pit located at the outlet of a sulfur smelter by a vertical pump.
- The filters are located few meters above ground level to allow easy discharge and removal of the cake, when leaving the filters.

  → because of the replacement every 20 hr. ± cleaning.
- Clean sulfur is sent either to a pit at ground level or to a storage tank.

  → free of ash
  → dry
  → free of traces of H_2SO_4
- Sulfur temperature in each filter is 140ºC and kept by injecting steam at for T=150ºC, P=4.3 bar in a jacket.
- Pipelines carrying molten sulfur should be heated in order to maintain the liquid above its freezing point and below 160ºC, insulation helps to control the temperature.

مشكلة هاد ال furnace
بال shut down

SULFUR FILTRATION

- Pipelines made from mild steel, galvanized iron.
- Valves are generally steam-jacketed, lubricated, plug valves.
- Pumps are centrifugal, rotary, and reciprocating piston. + steam heated.
- The sulfur stream starts with pumping molten filtered cleaned sulfur to the combustion chamber where it is received in finely divided droplets (→ by guns) (spray) by injection through sulfur guns to mix with air where self ignition of the sulfur in the already heated furnace takes places.

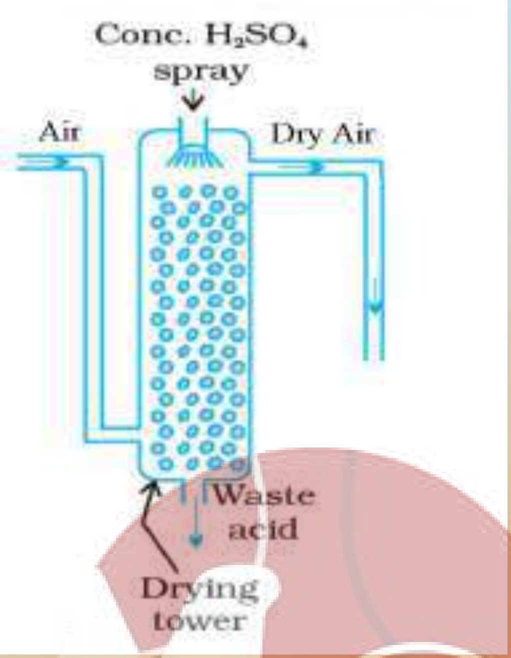
why spray ?
1) increasing the
Surface area → high conversion

* رفعت حرارة الفرن لـ 900
لتجنب طفي ال Burners ليش؟
لأنه أصلاً التفاعل highly exothermic

→ to remove moisture content.

FEED GAS DRYINGS

- It starts by pumping air from atmosphere using a blower which is driven electrically or by steam turbine.
- The air leaving the blower (→ to remove solid contents) sent to sulfur combustion chamber passing firstly through a drying tower where the atmospheric humidity is absorbed by concentrated sulfuric acid 98.5 %.
- The received air at 60ºC mixes in the combustion chamber with the sprayed sulfur, the combustion gases constitute of sulfur dioxide, oxygen, and nitrogen and just traces of sulfur trioxide.



هون جزء ال Drying ال air عن طريق
Spraying H_2SO_4 on it
(H_2SO_4 will react with the H_2O in the air)

SULFUR BURNING

- About 70% of sulfuric acid is made from elemental sulfur while all the sulfur obtained as a byproduct from refining natural gas and petroleum contribute to less than 30%.
- The sulfur is made into SO2 acid plant feed by:
  1. Melting the sulfur
  2. Spraying it into a hot furnace
  3. Burning the droplets with dried air.
- The reaction is:

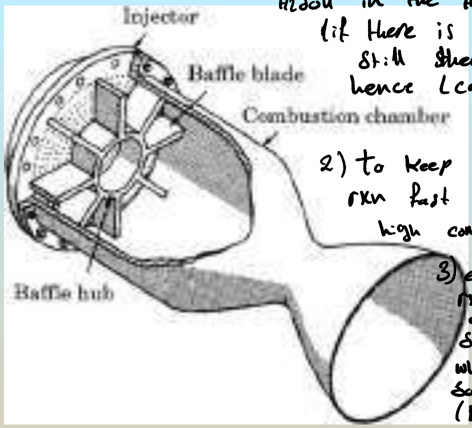
$$S_{(l)} + O_{2\,(g)} \xrightarrow[\substack{\Delta \\ \text{initiation}}]{1420\ K} SO_{2\,(g)} \qquad \Delta H_R = -297\ \overset{\text{mega}}{\text{MJ}}/kmol$$

I have to utilize it by absorb these hot gases and convert it into a hot steam

SULFUR BURNING

if there is an excess O_2 it may convert to ↓

- Very little SO_3 (g) forms at the 1420 K flame temperature of this reaction. → why? not more?
  1) we don't want to produce H_2SO_4 in the furnance. (if there is humidity still there → hence (corrosion))
  2) to keep the forward rxn fast (maintain high conversion)
  3) essential:- rxn rate of S and SO_2 → high @ high T while SO_2 → SO_3 (low at high T)
  4) SO_2 requires accelarator (catalyst) to convert to SO_3
  وصونه أصلا ال catalyst بخرب عل P عالي الحرارة
- This explains the need for two-step oxidation, i.e.:
  - (a) Burning of sulfur to SO_2 then:
  - (b) Catalytic oxidation of SO_2 to SO_3 , 700 K.
- The product of sulfur burning is hot, dry SO_2 , O_2 , N_2 gas.
  ↳ may contain Arsenic or other poisoning material → لازم نوخدها قبل. بدخرب الـ catalyst
- After cooling to 700 K, it is ready for catalytic SO_2 oxidation and subsequent H_2SO_4 making.
- The gases at 800 – 1000 °C flow through the baffled chamber to leave at this temperature and pass in a fire tube boiler where the steam is generated. (Not indirect)
  ↑ heat exchange



SULFUR BURNING

- Gases enter the convertor at a controlled temperature of 410 – 422 ºC where SO_2 converted to SO_3 on the surface of the vanadium catalyst.
- Feed gas is always dry. This dryness avoids:

(a) Accidental formation of H_2SO_4 by reaction of $H_2O_{(g)}$ with the $SO_{3\ (g)}$ product of catalytic SO_2 oxidation.

(b) Condensation of the H_2SO_4 in cool flues and heat exchangers.

(c) Corrosion.

- The $H_2O_{(g)}$ is removed by cooling/condensation and by dehydration with $H_2SO_{4\ (g)}$.

CATALYST

- At its operating temperature, 375 – 480 °C, SO_2 oxidation catalyst consists of a molten film of V, K, Na, (Cs) pyrosulfate salt on a solid porous SiO_2 substrate.

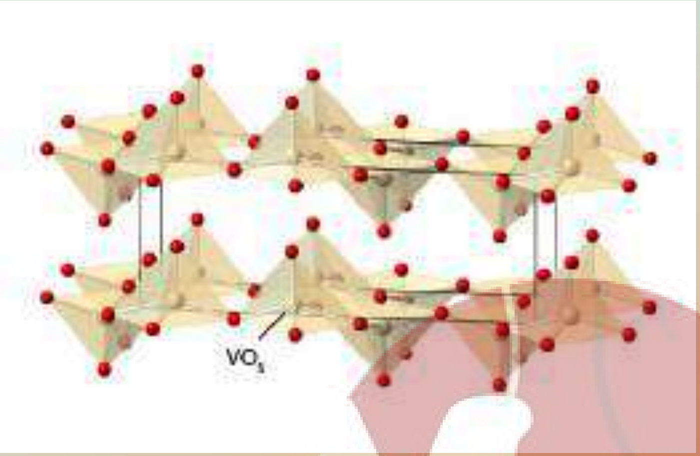
هاي المادة الحاملة المادة الفعالة لهاد ال Catalyst

→ at any location on it's surface can convert $SO_2 \rightarrow SO_3$

- The molten film rapidly absorbs $SO_{2\,(g)}$ and $O_{2\,(g)}$ - and rapidly produces and desorbs $SO_{3\,(g)}$.

→ the rxn is fast

← برضو بذوب على السطح بسبب الحرارة العالية



(*) why? because there is a little amount of SO_3 is produced (low saturation) So the rxn is very fast in the forward direction so we don't need that much amount of the catalyst

TYPICAL CATALYST DISTRIBUTION

each compartment is separated from the rest and has its own inlet + outlet + contain specific quantity of the catalyst

Catalyst Bed	% Catalyst	Conversion %
1	(*) 19.4	63
2	25	83
3	26.7	93
4	28.9	99.5

19.4 → least amount

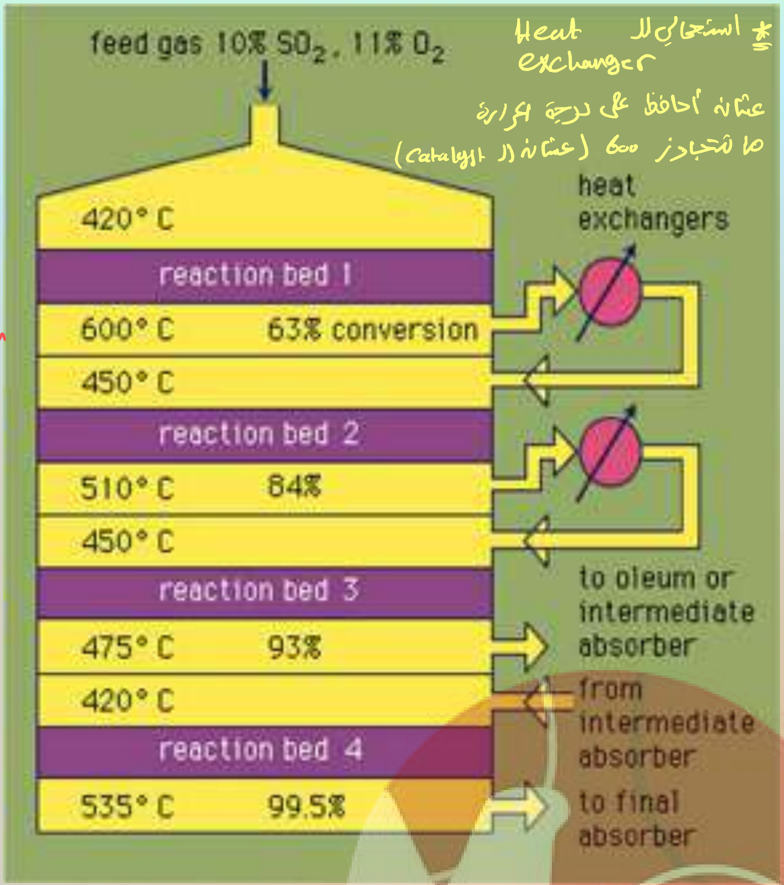
63 → أعلى X يعني أقل كمية catalyst driving force ↑

83 → here driving force is ↓ so → we need more catalyst to keep the rxn in the forward direction

99.5 → Also there is unreacted SO_2

* catalyst height ~ 0.5 – 1 m in the bed

(*) زمانه كانوا ياخذوه من غرفة ٣ ويولدوه ال ٤ بشكل مباشر ← كانت تؤدي لرفع كمية ال SO_2 الطالع للجو 3000 ppm وهسه ال regulations كانت تمنعها اليوم و التكنولوجيا الحالية صارت تستعمل ال double absorpers وهو إنه يسحبوا ال SO_3 من غرفة ٣ و ٤ ويعملولها absorption فصار الكمية يلي بتطلع للجو بدل ٣ آلاف ← صارت 500 ppm SO_2



* استعمالي للـ Heat exchanger عشانه أحافظ على درجة الحرارة ما تتجاوز 600 (عشانه ال Catalyst)

Converters are 15 m high and 12 m in diameter.

They typically contain four, 0.5 - 1.0 m thick catalyst beds.

FACTORS AFFECTING CATALYST

* Source of impurities
1) gas stream inlet to the furnance
2) molten S
3) gas stream out

1. **Arsenic (As)** (10 ppm in gas): It cause poisoning which is partially reversible, and the arsenic maybe removed from the catalyst by contacting it with gas containing hydrogen chloride.
2. **Selenium (Se)**: Partially harmful to the catalyst surface.
3. **Ammonia (NH_3)**: Harmful to the catalyst surface and when exists it will be oxidized to nitrogen oxides.
4. **Chlorides (1 ppm in gas)**: Chlorides causes vanadium loss and a reduction in catalyst activity.

   not more than 1
5. **Fluorides (0.3 ppm in gas)** : Attacks the catalyst carrier.
6. **Iron oxide** will plug the catalyst bed causing an increase in pressure drop.

Some of iron types may melt or solidification such as magnetite

VANADIUM LOSS

1. Formation of oxychloride or oxyfluorides of vanadium which are volatile compounds.
   → causes decrease in wt% of the catalyst
2. Ash and dust accumulated on the surface of the catalyst; this decreases the surface area available for catalysis.
   → from the inactive material ± impurities.

CATALYST REGENERATION

- The regeneration of the catalyst is carried out by screening.

→ remove any by-product, dust, ash, broken catalyst (inactive) that accumulated on the external surface

why?

لأنه الـ carrier صار مكشوف
لح يجي الغاز SO2 على سطحه
ورح يصير تفاعل !!

- Factors affecting screening loss:

  1. Condition of catalyst:
     - ✓ Pellet hardness → depends on the strength of the barrier.
     - ✓ Pellet size (compremisation between particle size and strength of the this particles)
     - ✓ Pellet environment

types on the impurities exsist

  2. Screen size — Size mesh ↑ losses ↑ "top"
  3. Screening rate/technique.

→ by → ↑↓ effeciency ↑
→ ↑↓ effeciency ↓ → without the circular motion it will cause some dead zones inside the shacker.

* important :-
assume that the total weight of the catalyst = 10 ton, then after screening it becomes 7 ton → here I have to redistribute these 7 ton in the same percentage in the compartments (see the percentage in slide 31) to keep the conversion as is

* if its one bed → we'll still work not above 600 °C
conversion → 80 ~ 90%

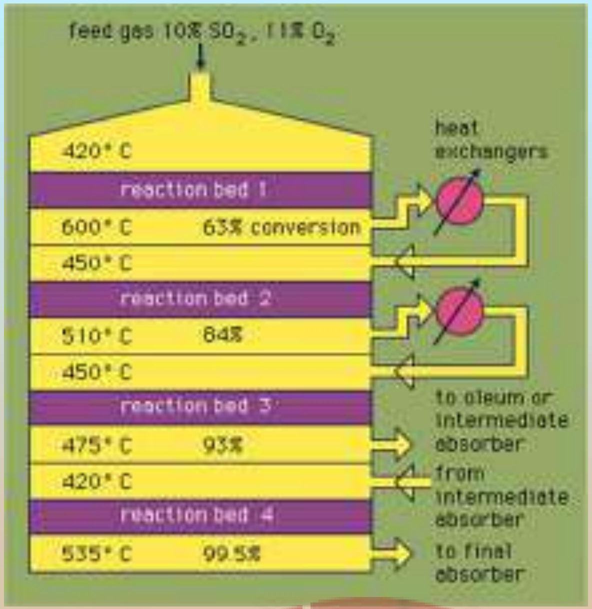
CONVERTOR

→ operating in temperature window because

- The conversion of SO_2 to SO_3 is exothermic reversible reaction producing heat.
- In order to achieve the maximum conversion, the convertor is split into number of beds with provision of removing heat of reaction after each stage. → to utilize heat.
- This will tend to increase the forward reaction. → when we exchange heat
- At each time the gas leaves any of the catalyst beds has to enter another equipment (super heater or heat exchanger) where the heat in excess is eliminated with another medium.

CONVERTOR

- The gas leaving the heat exchanger enters the other bed at controlled predetermined lower temperature of 420-440°C
- The sulfurous gases enters 1st catalyst bed at 420°C and leaves at 600°C.
- Gas enters a super heater at 600°C and leaves at 450°C where it superheats the steam generated in the boiler.
- Gas enters the 2nd catalyst bed at 450°C and leaves at 510°C.
- Gas enters a hot gas-gas heat exchanger at 510°C and leaves at 450°C.

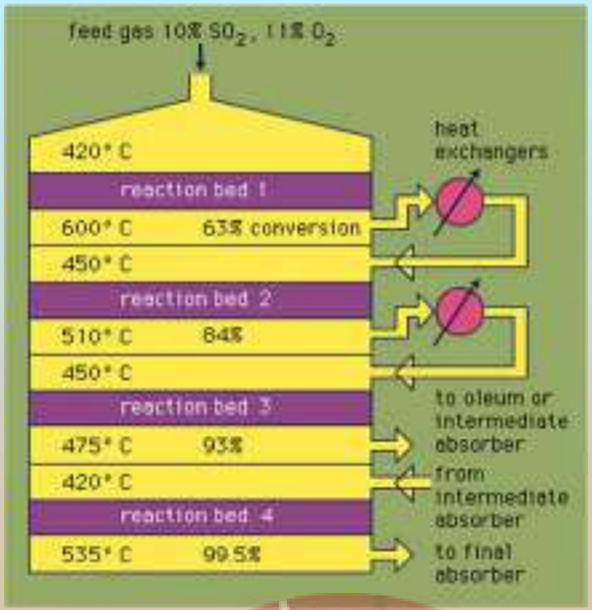


ليش ما بفاعل ال SO_3 بشكل مباشر مع الميّ ليش مع ال H_2SO_4؟
وليش أبرده على 200؟

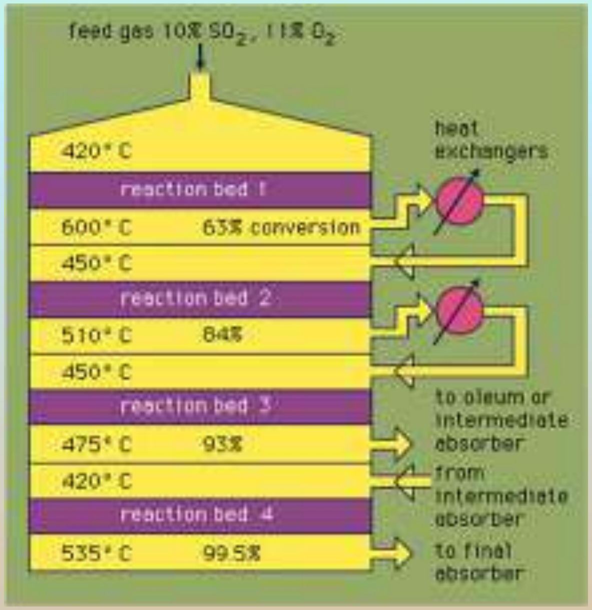
الجواب لازم يكون التفاعل بشكل غير مباشر مع الميّ خارو أدخل H_2SO_4 98.5% هاي ال 1.5% إلي ضلت
رح تتفاعل مع SO_3 لأنه التفاعل Highly exo رح يطلع كل ال H_2SO_4 لو تفاعلناه مع ميّ gas + little fraction liquid

رح أضطر أعمل condensation رح يعمل corrosion لأنه بالإضافة بنستعمل Steel
التبريد ← حتى نمنع من رفع درجة حرارة H_2SO_4 produced
± رح ندخل كميات ضخمة من H_2SO_4 عشانه يكمل التفاعل.

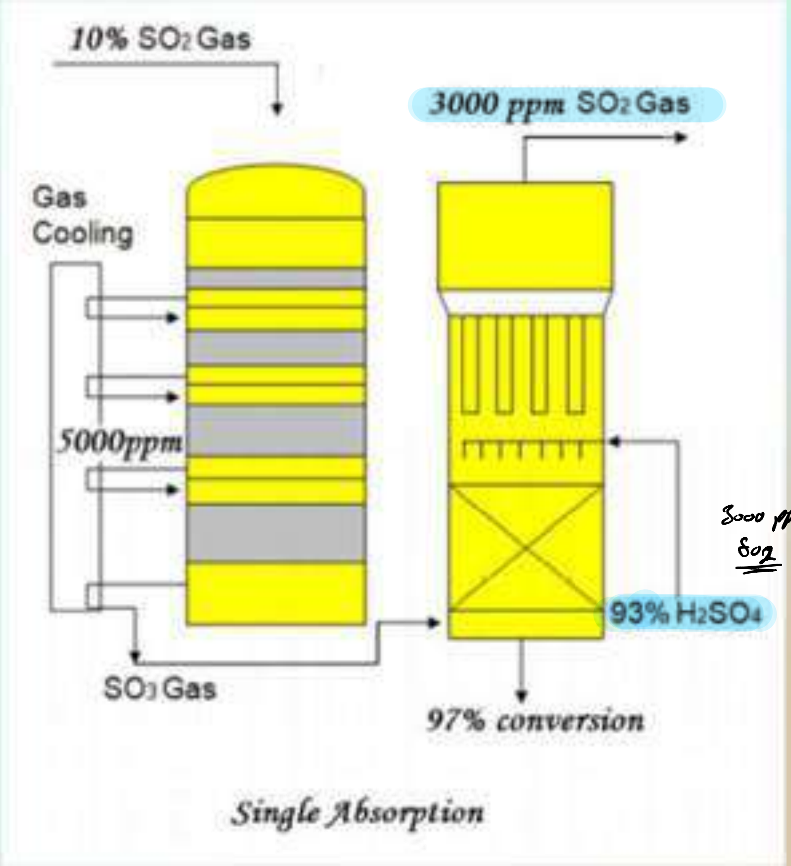
- Gas enters the 3rd catalyst bed at 450°C and leaves at 475°C.
- Gas passes through two gas heat exchanger and water economizer successively where it is cooled down from 475 to 200°C. ⇒
- After water economizer the gas enters inter- pass absorbing tower where SO3 is absorbed by the downward flowing concentrated sulfuric acid 98.5%.
- Gas leaving the tower passes through the gas- gas heat exchanger where it gains heat and temperature elevated from 75 up to 420°C.



- Gas enters the 4th catalyst bed at 420°C and leaves at ~~550~~°C. 535°c
- Gas enters a final water economizer and leaves to a final absorbing tower where the SO_3 is absorbed also with the downward flowing concentrated sulfuric acid 98.5%. Also must be cooled to 150~200°C
- The gas leaves the absorbing tower to atmosphere at 80°C.



SINGLE ABSORPTION



Single Absorption

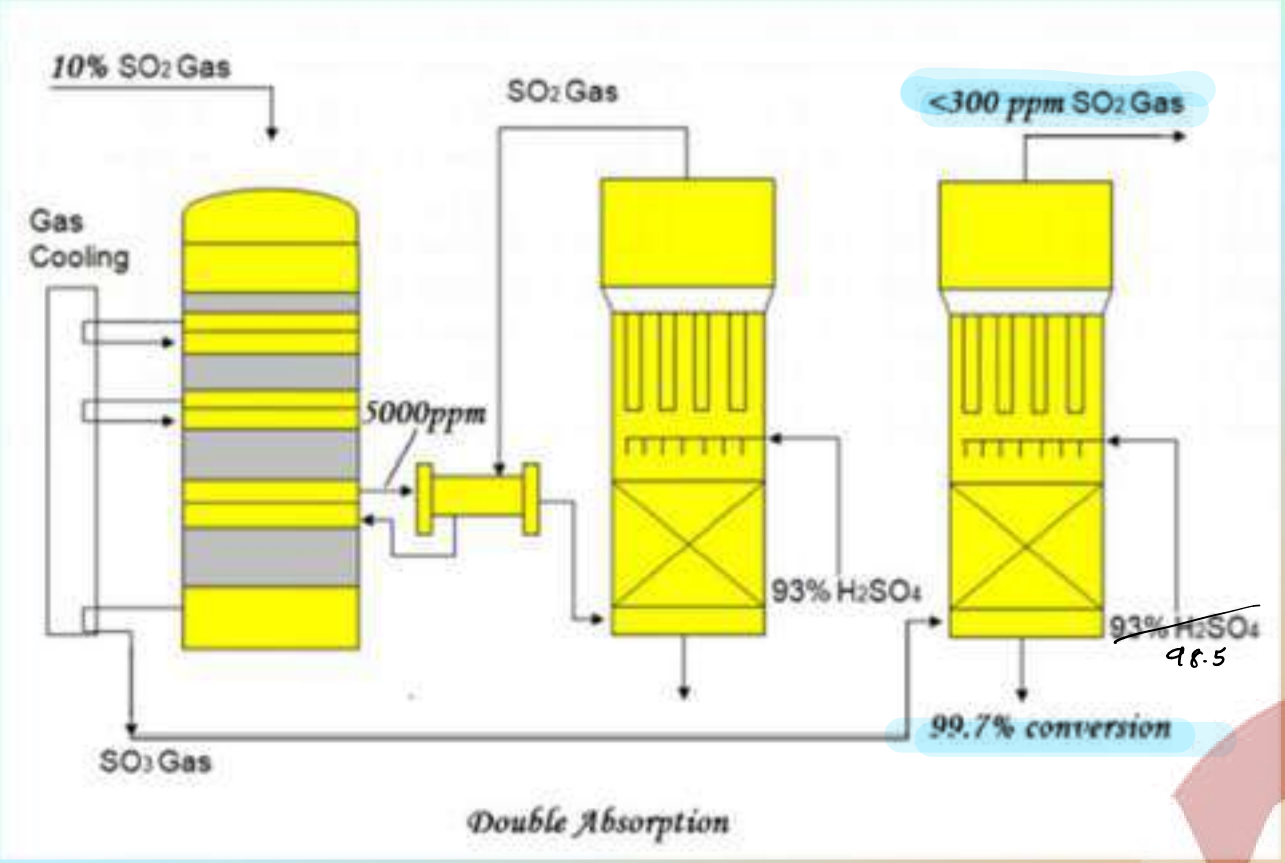
<u>old technology</u>

كان يستعمل single absorber

بالغالب كان يدخلوا 93% عشان H_2SO_4

اخر تركيز الغازات بس بالغالب كان يطلع 3000 ppm SO_2

DOUBLE ABSORPTION



Double Absorption

H_2SO_4 PRODUCTIONS

- Catalytic oxidation's SO_3 (g) product is made into H_2SO_4 by contacting catalytic oxidation's exit gas with strong sulfuric acid (98.5% Acid and 1.5% H_2O).
- The reaction is:

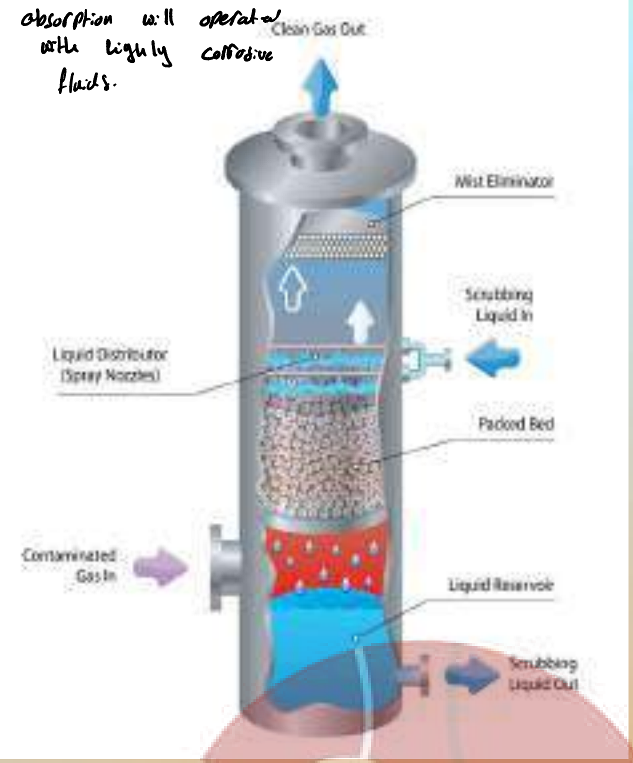
$$SO_{3\,(g)} + H2O_{(l)} \xrightarrow{350\text{-}380\ K} H_2SO_{4\,(l)}$$

- This reaction produces strengthened sulfuric acid because it consumes $H_2O_{(l)}$ and makes $H_2SO_{4\,(l)}$.
- It is strongly exothermic (ΔH = -132 MJ per kg- mole of SO_3).

عن حالي الحرارة كفيلة تشوي خليانه ← ليش ما بيغليش ؟

لأنه كمية ال flow of acid اللي داخلة كبيرة كثير وفيها شوية مي (1.5%)

فالحرارة عالي ح تسخن كل ال bed مو بس المي. فال exit stream مع هيك بتزيد 25° بس !!



must be lined if the absorption will operated with highly corrosive fluids.

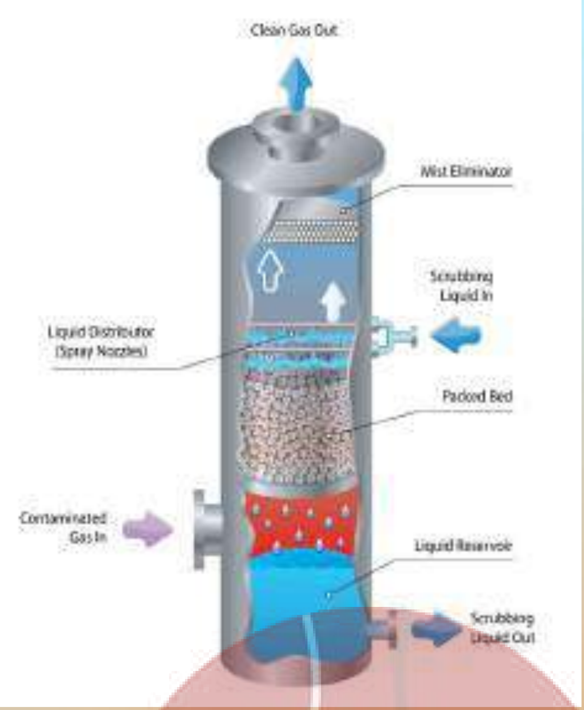
★ Best solution to avoid to convert the H2SO4 from (l) → (g) is to increase the flow amount to make sure I can utilize this amount of heat produced

H_2SO_4 PRODUCTIONS

- Catalytic H_2SO_4 (l) is not made by reacting SO_3 (g) with water.
- This is because the reaction of SO_3 (g) with water (l) is so exothermic that the product of the $SO_3\text{ (g)} + H_2O\text{ (l)} \rightarrow H_2SO_4$ reaction would be hot H_2SO_4 vapor- which is difficult and expensive to condense.
- The small amount of H_2O (l) and the massive amount of H_2SO_4 (l) in the reaction's input acid avoids this problem.
- The small amount of H_2O (l) limits the extent of the reaction.
- The large amount of H_2SO_4 (l) warms only 25 K while it absorbs the reaction's evolved heat.

ABSORPTION TOWER

- The most common type of absorption tower is packed columns which used in order to bring intimate contact between the two fluids.
- A gas and liquid of counter current flow is normally employed with the gas entering at the bottom and the liquid at the top.
- The shell of the tower maybe constructed of metal ceramic material, or it maybe steel a corrosion-resistance lining.
- The packing is supported on a rigid or screen which must be of an open pattern so as not to offer a high resistance to flow.



ABSORPTION TOWER

- The liquid is introduced at the top and must be evenly distributed over the whole cross section.
- The smaller the packing the larger is the interfacial area for a given volume of column and in general the greater the transfer per unit height, but the higher the ΔP so the backing should be of uniform size so as to produce a bed of high voidage, and low pressure drop.

→ will cause flooding.

* عشانه أبعد عن زيادة ΔP صح رح توصلني للـ flooding stage

رح أختار حجم مناسب دبحسب الـ ΔP يلي رح يسببه هاد الشي

- Towers used are constructed of shell lined by anti acid resistant plastic lining of polyisobutylene sheets and anti acid stone, the backing is anti-acid ceramic saddles or rings.
- The liquid distributer is made of cast iron.

ABSORPTION TOWER

- The tower is packed with ceramic saddles. → must be packed randomly
  ↳ to keep channeling + ↑ voidage + avoid increase ΔP
- 98.5 mass% H_2SO_4 , 1.5 mass% H_2O sulfuric acid is distributed uniformly across this packed bed.
- The acid flows through slots in the downcomers down across the bed.
- It descends around the saddles while SO_3 -rich gas ascends, giving excellent gas-liquid contact.
- The result is efficient H_2SO_4 production.
  → increase surface area and decrease the height at enough residance time.
- A tower is 7 m diameter; its packed bed is 4 m deep.
  ↳ why? to decrease ΔP
- About 25 m^3 of acid descends per minute.

ABSORPTION TOWER

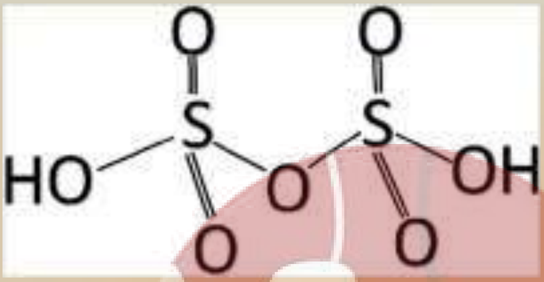
- The absorption of SO_3 in H_2SO_4 is believed to be taking place in the following manner:

$$SO_{3\,(g)} + H_2SO_{4\,(l)} \longrightarrow H_2S_2O_{7\,(l)}$$

$$H_2S_2O_{7\,(l)} + H_2O_{\,(l)} \longrightarrow 2H_2SO_{4\,(l)}$$

$$H_2SO_{4\,(l)} + xH_2O_{\,(l)} \longrightarrow 98.5\%\ H_2SO_{4\,(l)}$$

- The formula $H_2S_2O_7$ is called oleum.
- Oleum is a term referring to solutions of various compositions of sulfur trioxide in sulfuric acid.



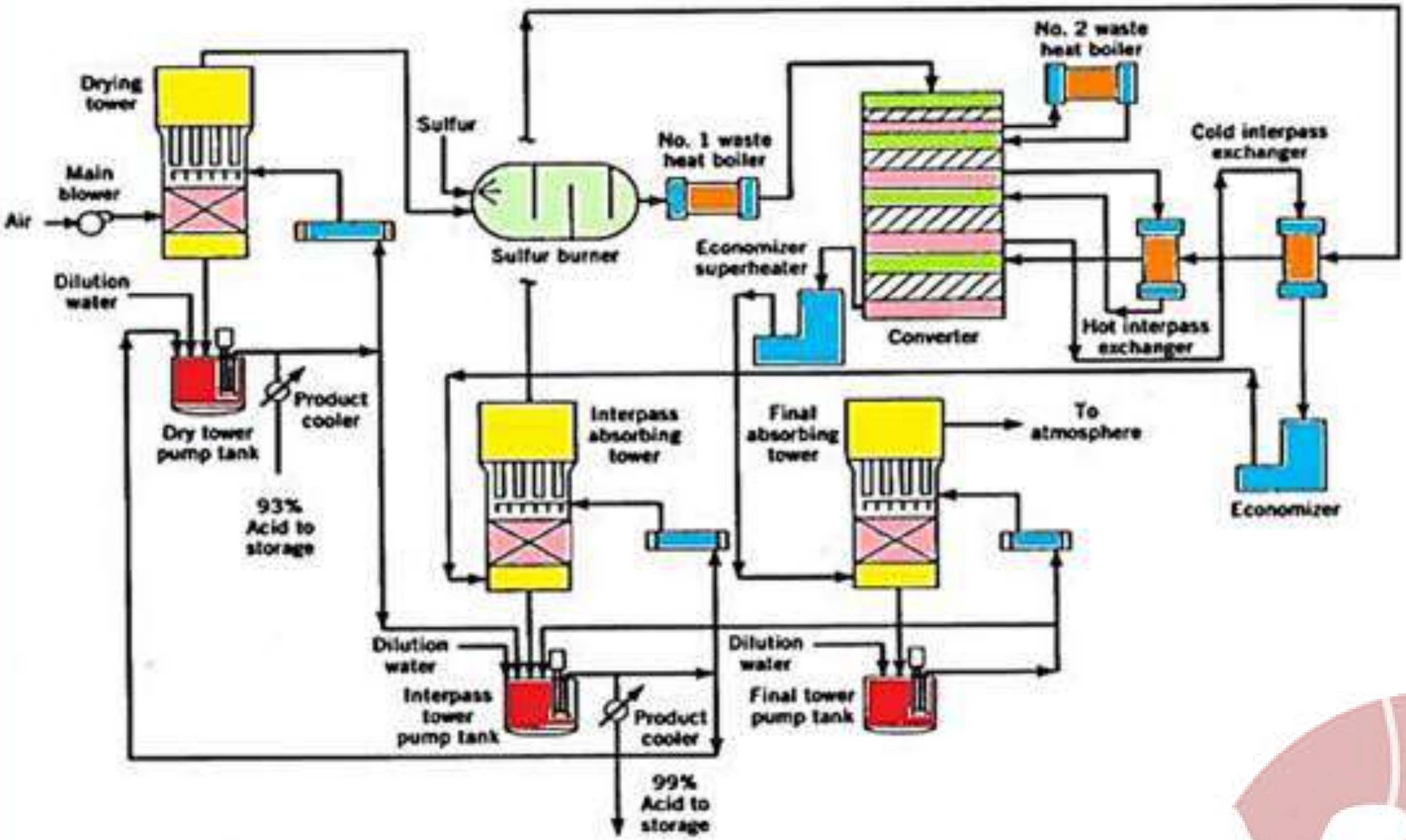
* Cooling by shell al tube
where the sea water in
the shell al the Acid
in the tube ⇒ why ?

Sea water in the shell ⇝ to make it easier with cleaning
(it cause scalling)

al the acid it will cause in all scenarios
the corrosion (because of the nature of the
acid, concentrated & hot)
so ⇒ by design number of tube
will be higher than
the need. by (10~30%)
increase.

COOLERS

- To cool down the hot H_2SO_4 acid sea water is used as a cooling medium.
- Anodic protection is applied to decrease the corrosion of the cooler.
- Usually, the number of tubes in the cooler is greater than the required number because whenever a tube is corroded it will be closed from both sides “in and out”.
- H_2SO_4 produce from the absorber is 99.5% concentration then in the dilute tank water is added to get 98.5%.


Drying tower
Main blower
Air
Dilution water
Dry tower pump tank
Product cooler
93% Acid to storage
Sulfur
Sulfur burner
No. 1 waste heat boiler
No. 2 waste heat boiler
Converter
Economizer superheater
Cold interpass exchanger
Hot interpass exchanger
Economizer
Interpass absorbing tower
Final absorbing tower
To atmosphere
Dilution water
Interpass tower pump tank
Product cooler
99% Acid to storage
Dilution water
Final tower pump tank

FERTILIZERS TECHNOLOGY

CHEM 0905554

First Semester 21/22

* H_2SO_4 + Phosphate acid → H_3PO_4

CHAPTER 1

PHOSPHORIC ACID PRODUCTION

→ wet acid process

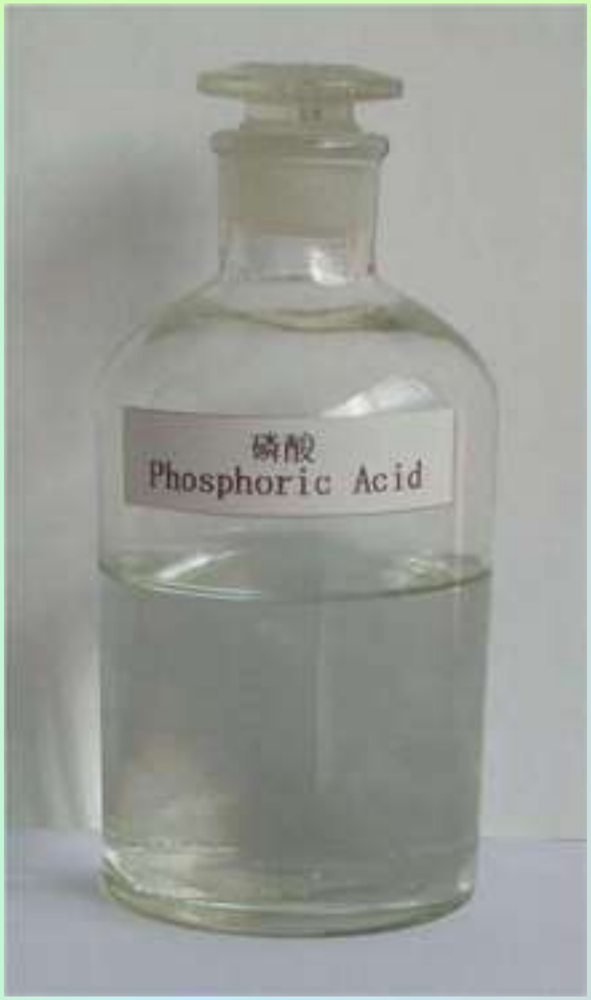
↓

reaction in liquid media (H_2SO_4)

→ it's the Base of phospharic fertilizers (main raw material)

* in this process => wet process acid.
↳ why the H_3PO_4 have green color
the green color from the phosphate rocks (sedimentary)
⇓
organic material (gives that color)

Furnance grade H_3PO_4



P_2O_5

95 ~ 97% H_3PO_4

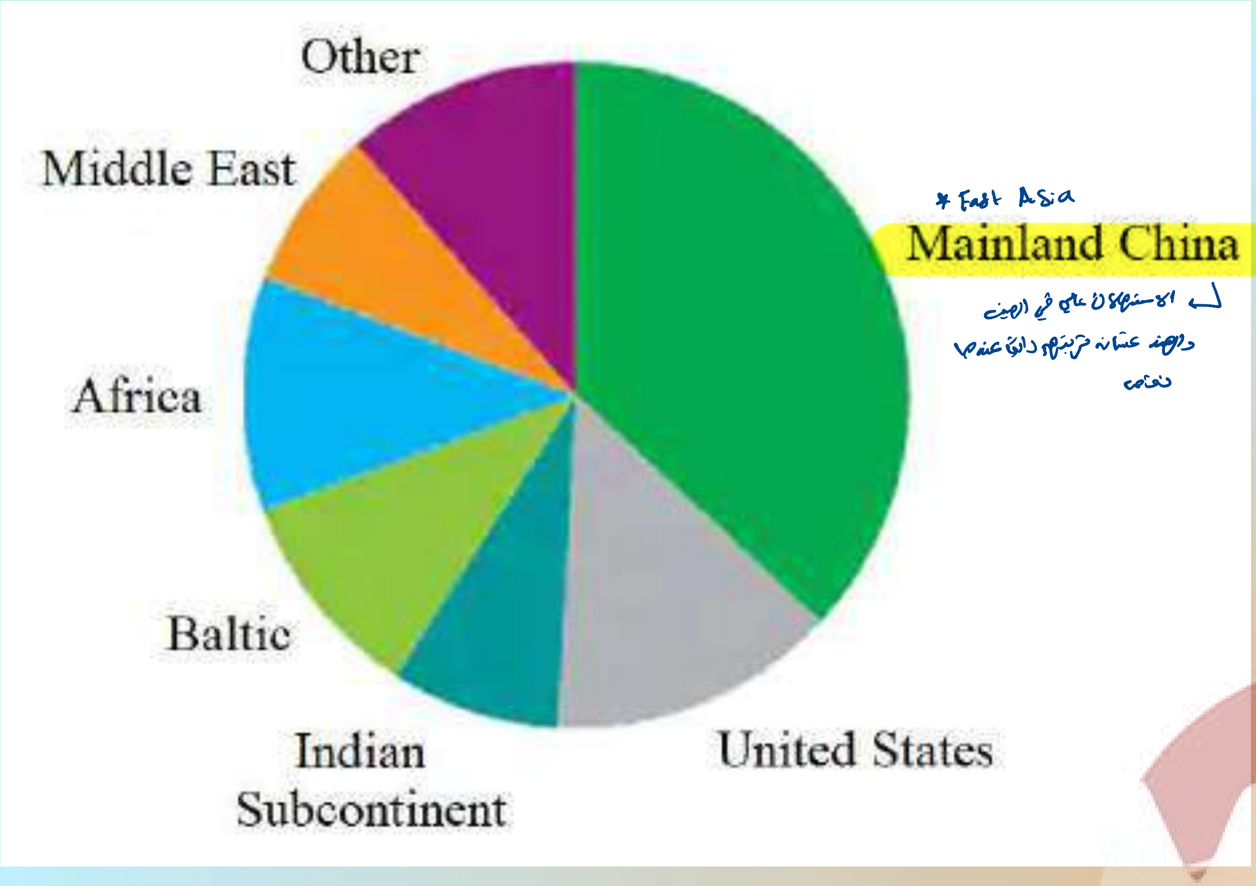
↳ this produced from elemental phosphure but it's not used nowadays.
Because:-
1) it's not exsist in large quantity
2) the main reason because requires energy (in huge quantity)

* one of the problems of this process
↳ main raw material is phosphate rock (variation in composition)
↳ it should adaptate this variation

* Some impurities in the phosphate rock can be separated (Beneficiated)

* أكثر مستورد لل phosphate rock في الأردن ← الهند.

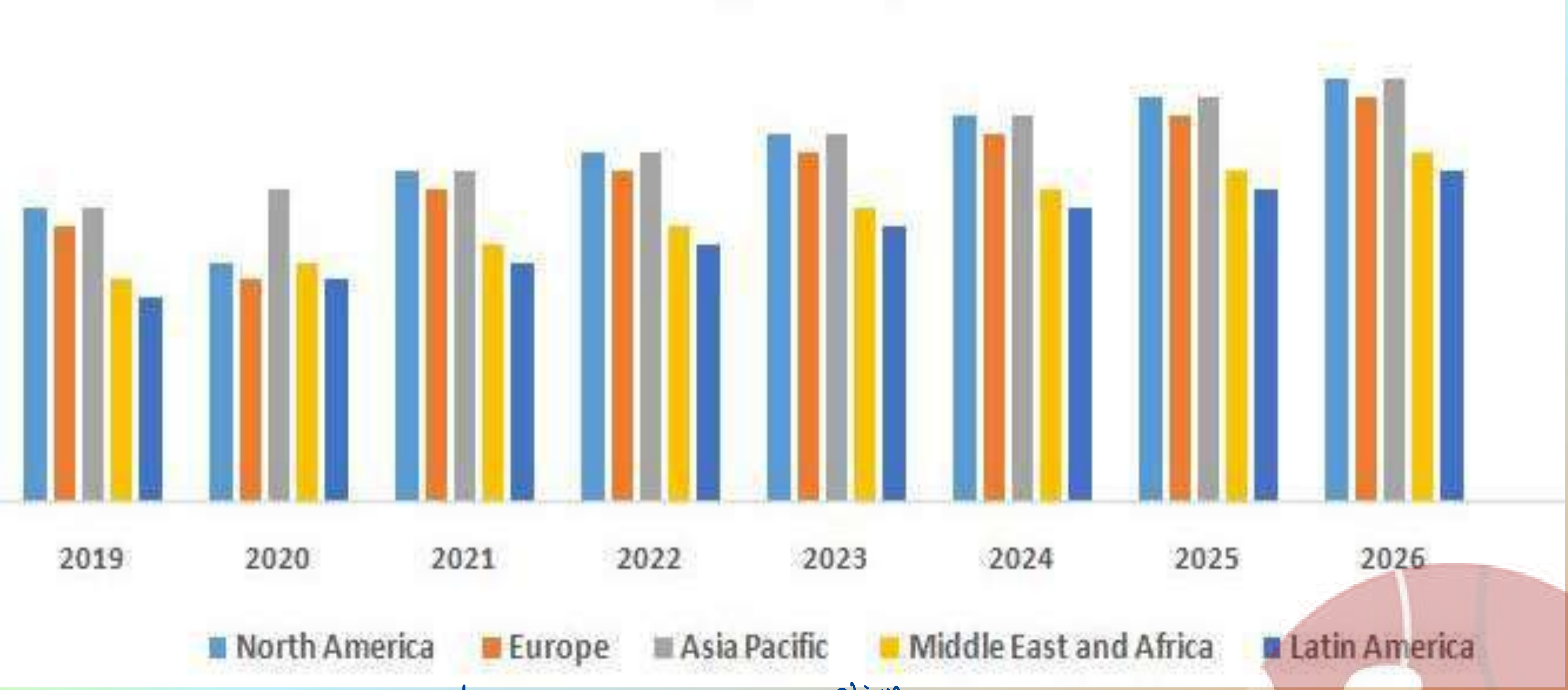
WORLD CONSUMPTION OF PHOSPHORIC ACID



* East Asia

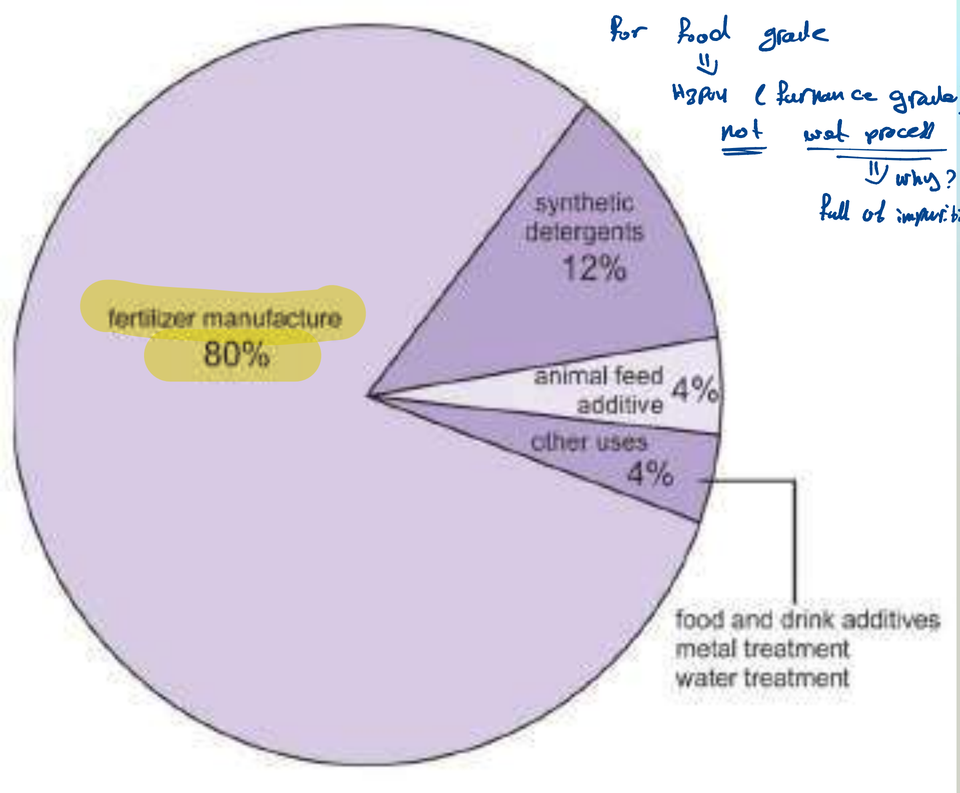
↳ الاستهلاك عالي في الصين والهند عشان تربتهم دايمًا عندها نقص

GLOBAL PHOSPHORIC ACID MARKET – BY REGION

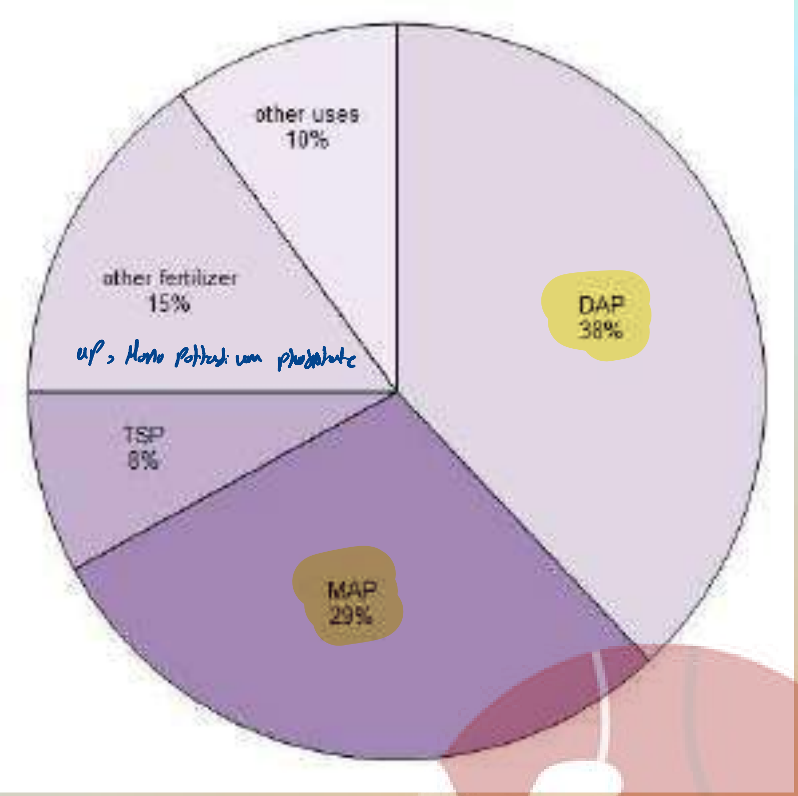


↳ increasing the consumption

GLOBAL PHOSPHORIC ACID MARKET SHARE

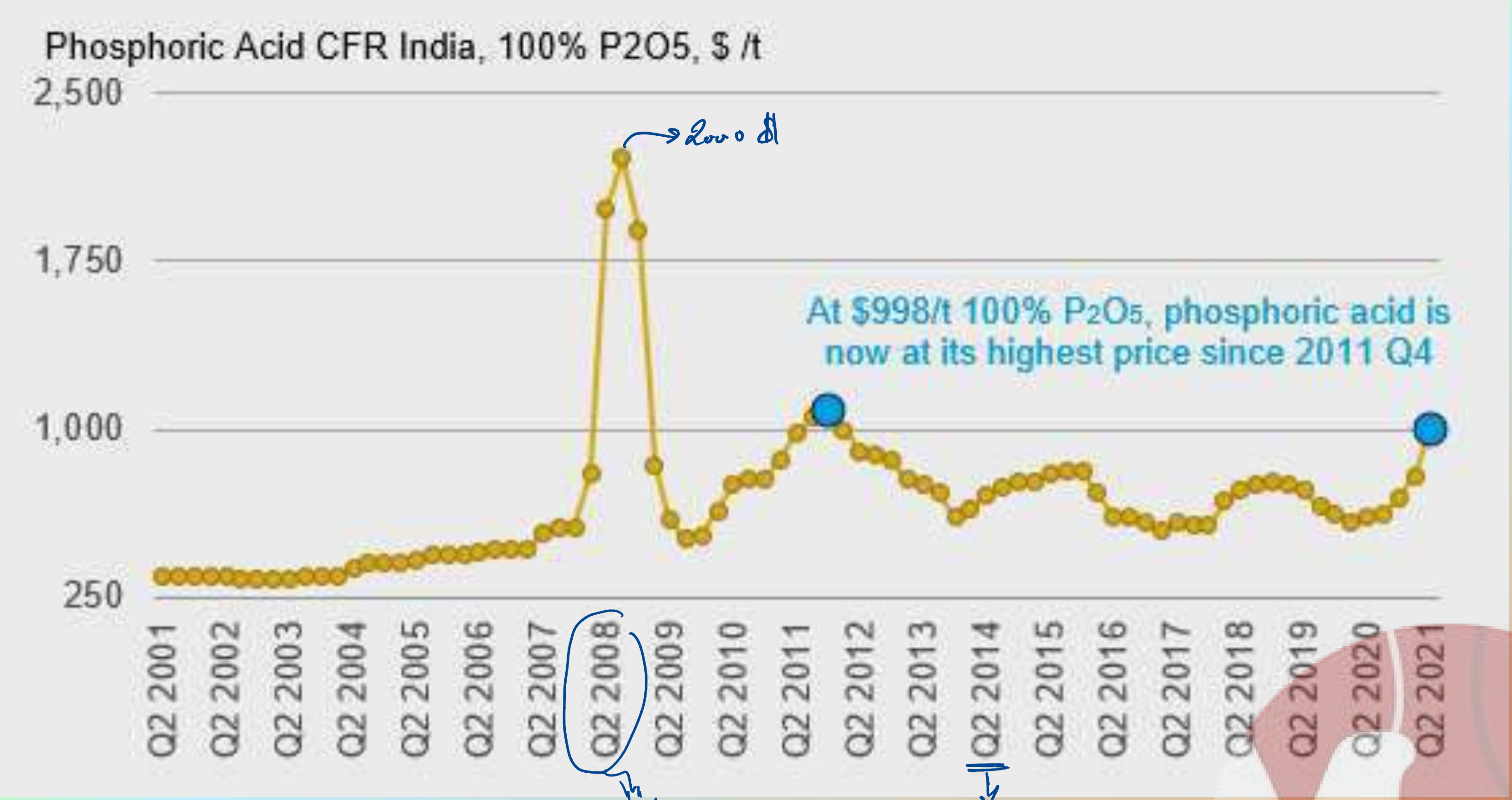


for food grade
⇓
H_3PO_4 (furnance grade)
not wet process
⇓ why?
full of impurities.



MP, Mono Pottasium phosphate

PHOSPHORIC ACID PRICES



الأزمة المالية.

أعلى قفزة

INTRODUCTION

⇒ raw materials to produce H_3PO_4

→ elemental phosphorus ⇒ used 1) food grade
2) any application requires high concentration of H_3PO_4 "P_2O_5" (clear)

→ Sedimentary phosphate rock "dominant" ⇒ fertilizers or any application requiring commercial P_2O_5

⊕ → requiring less energy

- Processes with different raw materials are used in the manufacture of phosphoric acid.
- The process is known as "thermal" when the raw material is elemental phosphorus.
- This process has been abandoned because of the amount of energy which is needed.
- The processes that use phosphate minerals which are decomposed with an acid, are known as "wet processes" and they are the only economic alternative way to produce phosphoric acid.

INTRODUCTION

- Three possible subgroups of wet processes depending on the acid that is used for the acidulation.
- This may be nitric, hydrochloric or sulfuric acid.
- The sulfuric acid route is the process normally used in the production of fertilizers.
- There are three types of sulfuric acid process, according to the condition of the calcium sulfate produced, since it can be obtained in the form of:

1. Anhydrite ($CaSO_4$) ⇒ largest particle size (easy to seperate) but requires high T → So, very corrosive!!
2. Hemihydrate ($CaSO_4.0.5H_2O$)
   its better but requires more T
3. Dihydrate ($CaSO_4.2H_2O$) ⇒ least particle size.

⇒ producing based on the operating conditions

the most preferable to produce ⇒ why ?

energy wise, least corrosion attack @ ~80 °C

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- Bones used to be the principal natural source of phosphorus, but phosphoric acid today is produced from phosphatic ores mined in various parts of the world.
- Phosphate ores are of two major geological origins:

1. Igneous as found in South Africa, Brazil, etc. ⇒ it's stronger
2. Sedimentary as found in Morocco, Algeria, Jordan, U.S.A., etc.

معادن الفوسفات في كلا النوعين من الركازات هي من مجموعة
الأباتيت ، والتي من أكثر المتغيرات التي نواجهها شيوعًا هي:

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are:

1. Fluorapatite $Ca_5(PO_4)_6F$ ⇒ in ignious rock "does not contains impurities
2. Francolite $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$ → Sedimentary.

→ organic matter: "hard to remove them"

- Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks.
- The most easily mined phosphate deposits are found in the great sedimentary basins.

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- These sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds.

other impurities.

- These phosphates are interposed with sedimentary strata of the waste materials interpenetrated by gangue minerals and thus sedimentary phosphate ores have differing compositions within the same source.
- Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market.

يتم تداخل هذه الفوسفات مع الطبقات
الرسوبية لمواد النفايات التي تخترقها
معادن الشوائب ، وبالتالي فإن خامات
الفوسفات الرسوبية لها تركيبات مختلفة
داخل نفس المصدر.

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

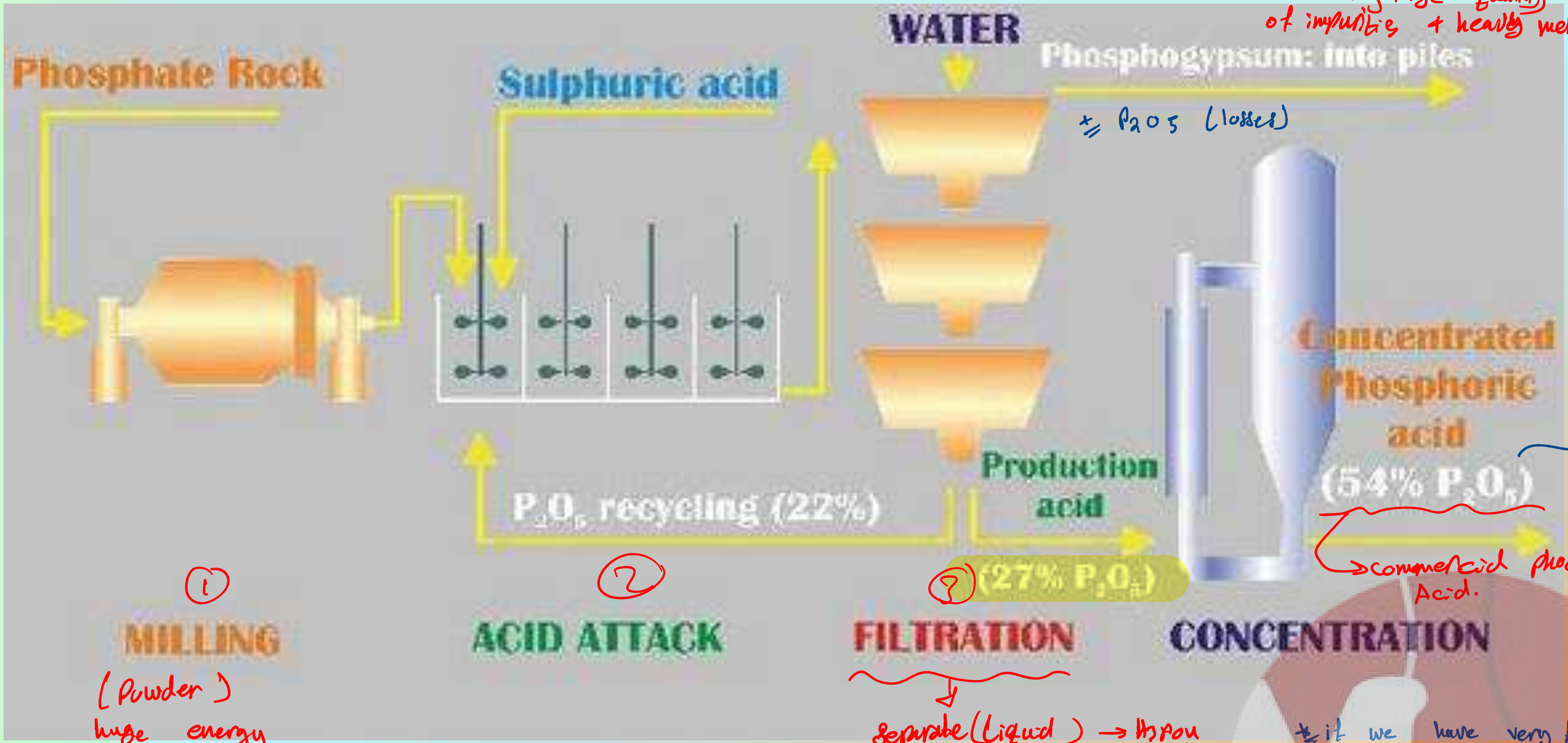
- Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities.
- This gives rise to further variations in the finished ore concentrate product.
- Phosphoric acid technology, having to rely on raw materials of great variety, has to readapt itself constantly.

يجب على تقنية حامض الفوسفوريك ، التي تعتمد على المواد الخام
ذات التنوع الكبير ، أن تعيد تكييف نفسها باستمرار

* حالة لو كانت منطقة العقبة ممطرة
بصير leaching لل gypsum وينزل للبحر
أو ground water.

PHOSPHORIC ACID PRODUCTION

gypsum causing a huge problem → 1) 1:4 every one ton from P_2O_5 produce 4 ton of gypsum
2) have very large quantity of impurities + heavy metals.



* P_2O_5 (losses)

→ to produce DAP

→ commercial phosphoric Acid.

① MILLING (Powder) huge energy consumption

② ACID ATTACK

③ FILTRATION → separate (Liquid) → H_3PO_4 from solid → gypsum

* if we have very fine particles ⇒ settling for long time (unsettled H_3PO_4)

* $CaSO_4$ → basically in Jordan we produce $CaSO_4 \cdot 2H_2O$
↳ fine particles

PRINCIPLES OF THE PROCESS

- The basic chemistry of the wet process is exceedingly simple.
- The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulfuric acid into phosphoric and the insoluble salt calcium sulfate.

$$\boxed{Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4}$$

→ digestion → attack
(not require high T)

- The insoluble calcium sulfate is then separated from the phosphoric acid, most usually by filtration.

↳ rotating disks

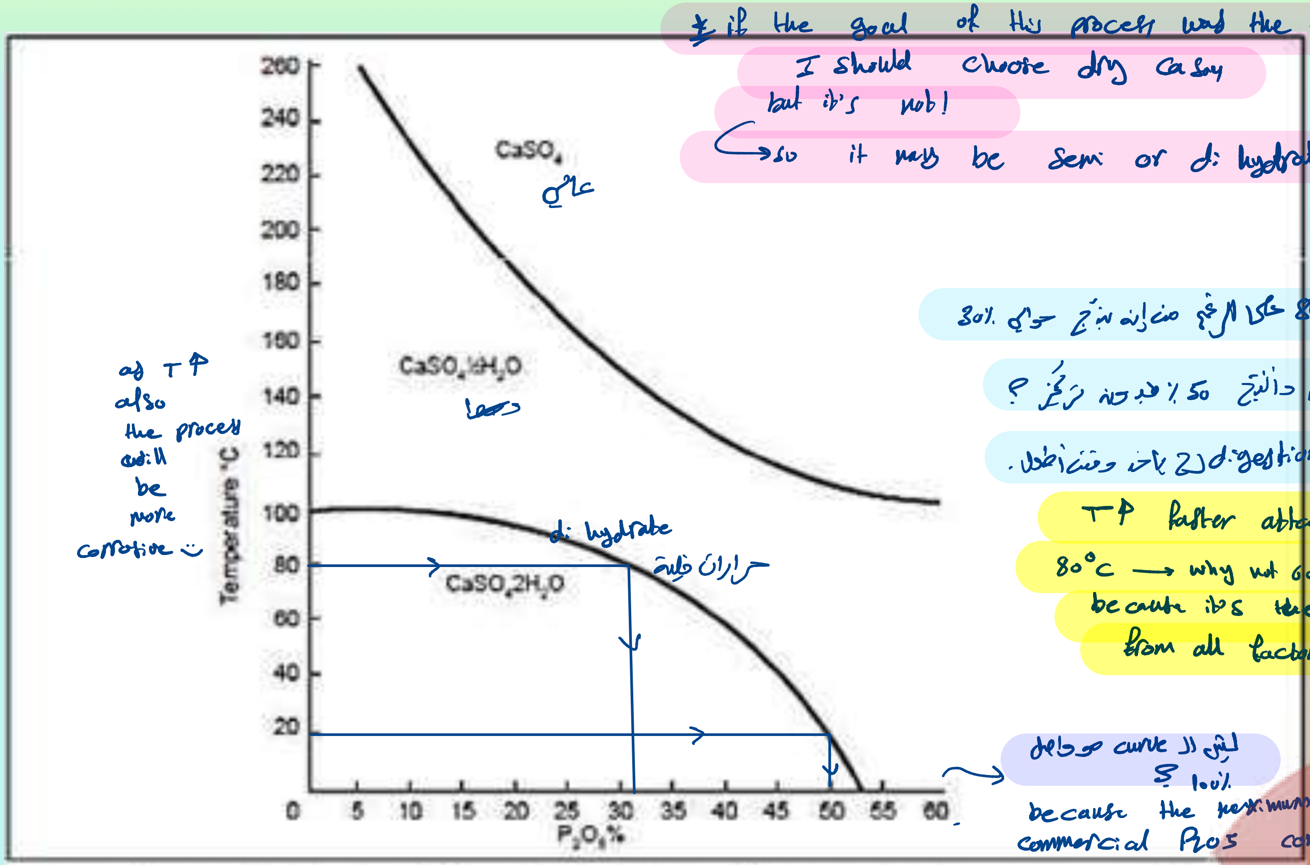
* Basic principle of this process
(attack of H_3PO_4)

- Calcium sulfate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulfate content.

الظروف السائدة لدرجة الحرارة

PRINCIPLES OF THE PROCESS

* if the goal of this process was the gypsum
I should choose dry CaSO4
but it's not!
→ so it may be semi or di hydrated



Dependance of Calcium Sulphate Hydrate Crystallisation on Temperature and P_2O_5.

as T ↑
also
the process
will
be
more
corrosive ☺

بالمصنع بنشتغل على حرارة 80% على الرغم من إنه بنتج حوالي 30%.

بس ليش ما اشتغل على حرارة ﻫ والناتج 50 % فبحسنه تركيز ؟

عشانه لو اشتغلت على ﻫ الـ 2) digestion باخد وقت أطول.

T ↑ faster attack ↑

80°C → why not 60° ? why not 100°C
because it's the temperature optimized
from all factors → 1) cost (energy)
2) attack time
3) prevent corrosion of the
material of construction

ليش الـ curve موجودة
؟ 100%

because the maximum
commercial P_2O_5 concentration in H_3PO_4
is 54 or may exceed
60% @ High T.

↳ to prevent corrosion in
concentration unit
1) evaporation @ vacuum
2) the unit is lined from carbon blocks.

- The operating conditions are generally selected so that the calcium sulfate will be precipitated in:
  1. The dihydrate.
  2. Or the hemihydrate form.
- 26 - 32% P_2O_5 at 70 - 80 °C for dihydrate precipitation.
- 40 - 52% P_2O_5 at 90 - 110 °C for hemihydrate precipitation.

IMPURITIES

- There are many impurities in phosphate rock, the amounts and proportions of which are very variable. → variation from bed to bed and from height to height @ the same bed
- Fluorine is present in most phosphate rocks to the extent of 2 - 4% by weight.
- This element is liberated (release) during acidulation, initially as hydrogen fluoride but in the presence of silica this readily reacts to form fluosilicic acid, H_2SiF_6. ⇒ Hf will be in all units.
- Other components such as magnesium and aluminum can also react with HF to form compounds ($MgSiF_6$ and H_3AlF_6).

IMPURITIES

- Emphasis must also be placed on another group of impurities such as arsenic, cadmium, copper, lead, nickel, zinc and mercury, which are present in most phosphate rocks, and which may pass into the acid during acidulation.
- Impurities such as iron, aluminum, sodium, potassium, chlorine, etc have some influence during the production of phosphoric acid and on the quality of the acid produced.

HEMI-HYDRATE WET PROCESS ACID PRODUCTION

- The Hemi-hydrate phosphoric acid production is the new invented technology at which it is being applied in many phosphoric acid production plants.
- In this process phosphoric acid can be produced directly with a concentration of 40 - 52% with consequent valuable saving in energy consumption and that is what make this process the leading process in wet phosphoric acid production

DI-HYDRATE WET PROCESS ACID PRODUCTION

- The Dihydrate processes for phosphoric acid production are still the most popular one until now.
- Many plants for phosphoric acid production nowadays still operate using this process due to its ease and simplicity, the major advantage of this process is its flexibility and reliability.
- It has high adaptability to phosphorus ore, and it accepts any kind of phosphorus ore.
- More moisture is allowed and permissible in the phosphate feed, and there is more acceptance to the use of weak sulfuric acid since the overall water balance in the dihydrate system is not so critical

DI-HYDRATE WET PROCESS ACID PRODUCTION

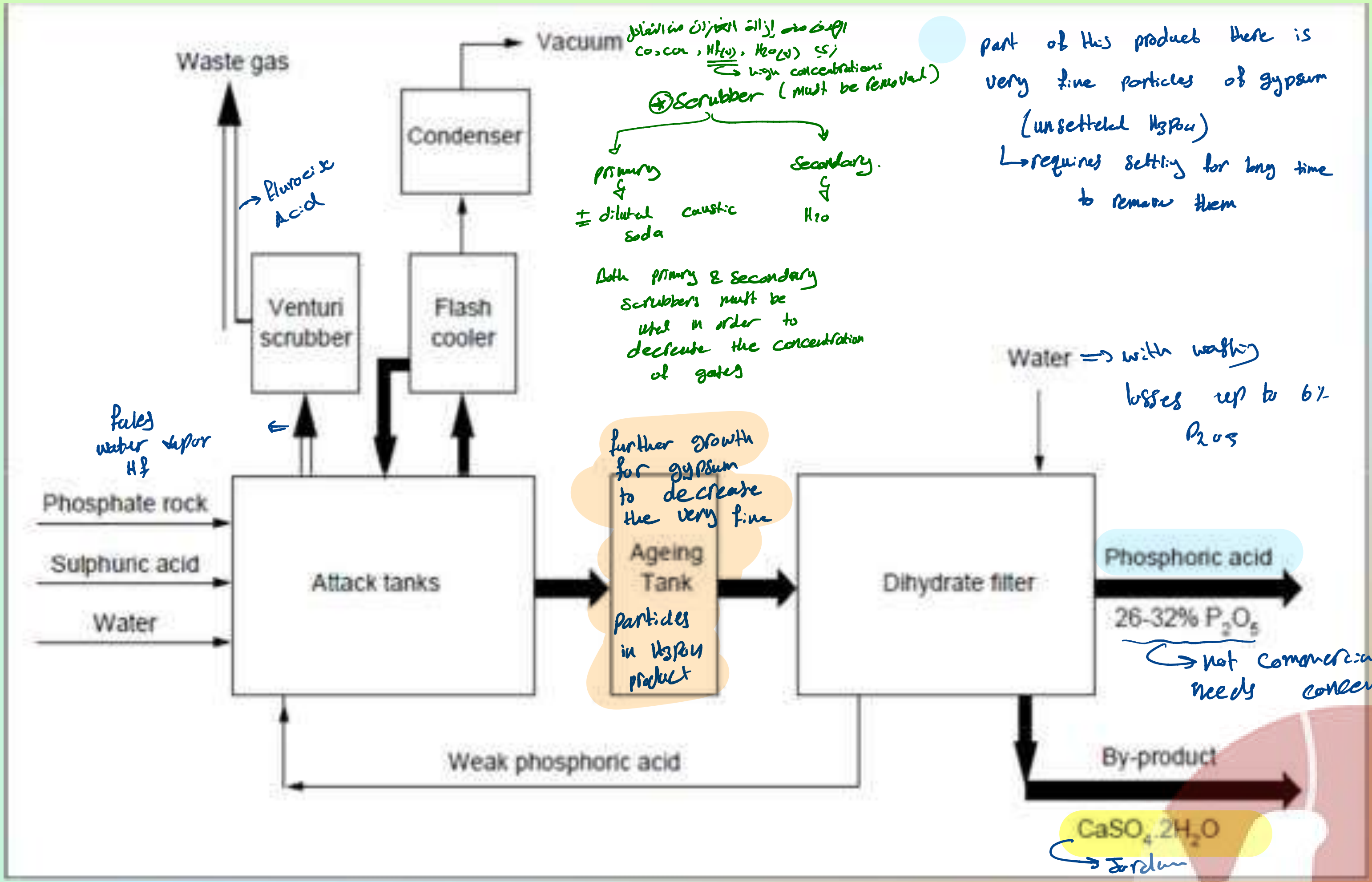
- Drawbacks of the di-hydrate process include:
  - ✓ Relatively low acid concentration produced which is about (28 – 30% P_2O_5) and
  - ✓ Higher energy consumption than other processes, → water + HF] → vapors
  - ✓ 4 - 6% P_2O_5 losses, most of them co-crystallized with the calcium sulfate
- Despite these drawbacks, the process is considered:
  - ✓ Simple startup and shutdown operation, and
  - ✓ Easy scalability

and these make the di-hydrate process the most widely used technique for phosphoric acid production

ADVANTAGES OF THE DIHYDRATE PROCESS

This is the most diffused process and the advantages of dihydrate systems are:

1. There is no phosphate rock quality limitation
2. Operating temperatures are low
3. Start-up and shut-down are easy
4. Wet rock can be used (saving drying costs)



→ Fluroic Acid

fumes
water vapor
Hf

الهدف منه إزالة الغازات من الشعال
co, co2, $Hf_{(v)}$, $H_2O_{(v)}$ زي
→ high concentrations
⊛ Scrubber (must be removed)

primary → ± diluted caustic soda

secondary → H_2O

Both primary & secondary
scrubbers must be
used in order to
decreate the concentration
of gases

part of this product there is
very fine particles of gypsum
(unsettled H_3PO_4)
↳ requires settling for long time
to remove them

further growth
for gypsum
to decrease
the very fine
particles
in H_3PO_4
product

Water ⟹ with washing
losses up to 6%
P_2O_5

↪ not commercially
needs concentration

↪ Jordan

PHOSPHORIC ACID PRODUCTION IN JORDAN

PHOSPHORIC ACID PRODUCTION IN JORDAN

- The Phosphoric Acid plant in the Industrial Complex (Aqaba) was designed to produce 1250 Ton/day of 54% P_2O_5 concentration.

1) Penetbes unit
→ to produce stream + electricity + ion
2) H_2SO_4 plant (2)
3) H_3PO_4
4) DAP (2)
5) Alumminum fluride

- The main row materials for phosphoric acid plants are:

1. Phosphate rock. ⇒ الشيدية ، الأبيض ، الحسا ـ النقل عبر Trucks or railway.
2. Sulfuric acid of 98.5% by weight H_2SO_4.
3. Caustic soda 3% NaOH.
4. Pond and industrial water. ⇒ cooling for water by aeration
5. Steam used at the start up and used for warming up the process water.

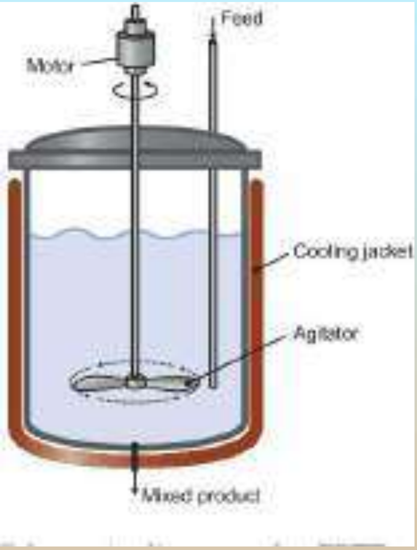
عشان بدهم حرارة 80 عشان يوصلوها ؟

PHOSPHORIC ACID PRODUCTION IN JORDAN

The process of producing phosphoric acid consists of the following sections:

→ increasing surface Area
conversion ↑ accelerate rxn ↑

1. Grinding of the phosphate rock.
2. Attack and filtration.
3. Concentration.



GRINDING OF THE PHOSPHATE ROCK

* if the raw material
contain more than 3%
moisture content => drying
must be required => why?
because during milling
this raw material will
agglomerate + clogging "slurry"

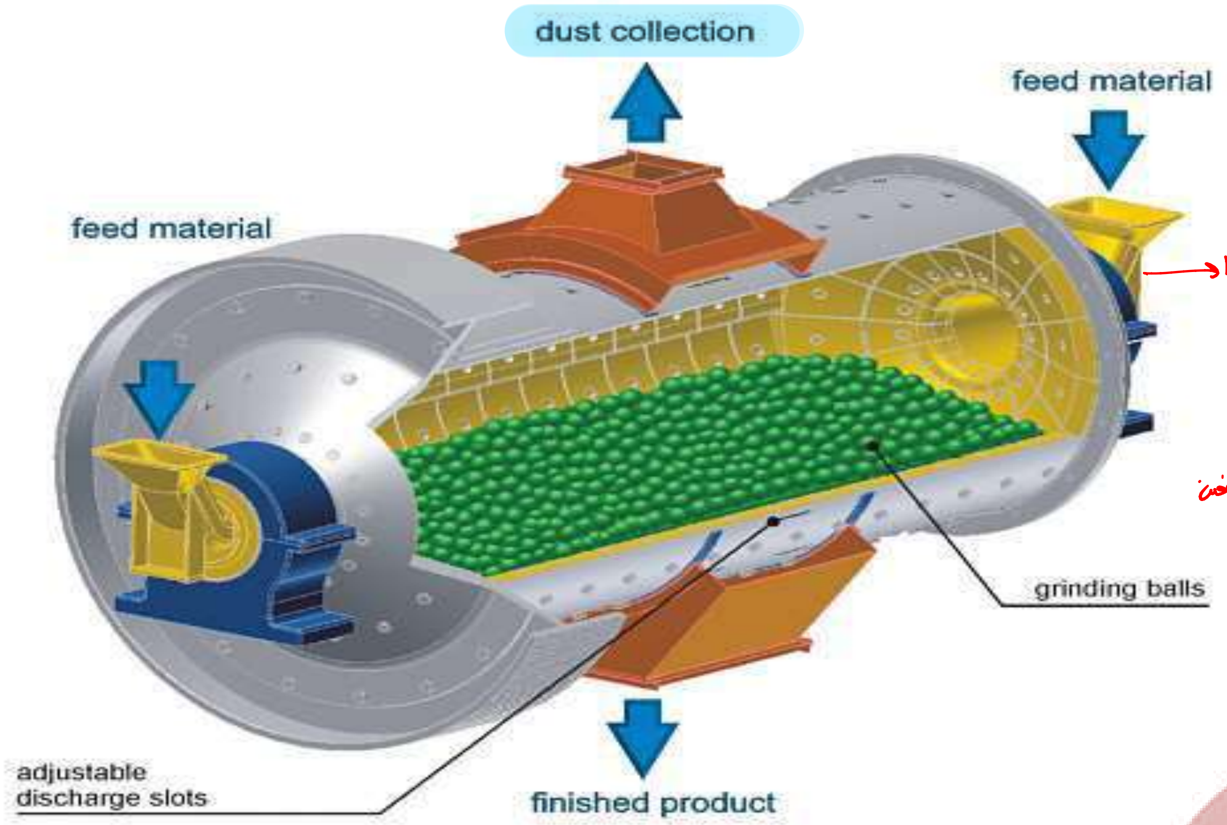
- The raw phosphate has the following analysis.

H_2O by weight	1.5 – 3 % max
Sizing	0 – 6 mm
Density	1.2 – 1.4 Ton/m^3
Temperature	Ambient

- In the H_3PO_4 plant the phosphate rock needs to be ground because the bigger the specific surface is the more product surface is submitted to acid attack and the best the plant efficiency will be.

GRINDING OF THE PHOSPHATE ROCK

- Phosphate rock is transported from storage area to the grinding system using a grinding mill with a capacity of 175 ton/h.
- Phosphate rock enter a hopper above the mill then to chain feeder.
- From the chain feeder the rock is poured into the feed duct from which it falls into the mill.
- The mill is a big cylindrical shell coated with steel sheets from the inner.
- Inside the mill there is 240 Ton of the balls have been placed.



→ milling by free falling of the ball (grinding by gravity)

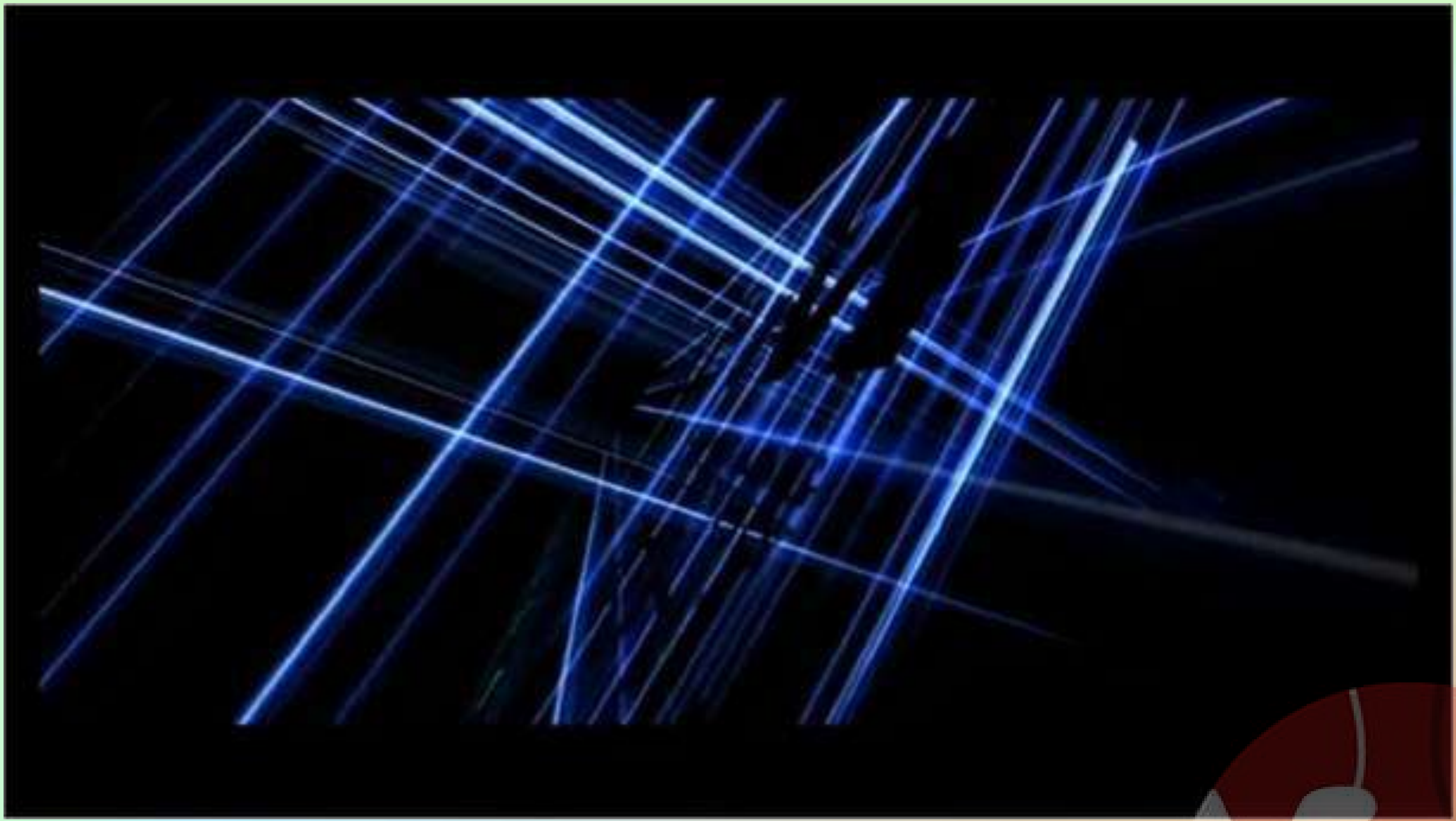
* حلوة في ميزته بجهاز ال mill عشانه أصغر

residance time كافية وبالنهاية ع mesh لتوسيع

ال particles بالعبور بالحجم يلي بدي إياه

وال coarse حيضل جوّا ويكمل طحنه.

~~Stop~~



GRINDING OF THE PHOSPHATE ROCK

- Ground phosphate drops out of the mill by overflow while a screen keeps the balls inside the mill.

Numerically

- At the mill outlet the product is taken away by an air flow which brings to the classifier in order to get fine particles.

centrifuge ال coarse رح تنزل للتحت.

أوقات بطلع ال product أحجام أكبر من إلي بدي إياها هون رح أستعمل ↑ عن طريقة

تقلل السرعة عشان يبطل الهوا قادر على حمل ال coarse وينزل رح ينفصلوا

- A classifier with wide diameter is used to decrease the speed of air which carry the coarser particles which will fall down to the classifier bottom and then to the mill to re-crush.

→ Based on the reduction + expansion (↑ or ↓ diameter) to controll air speed.

- In the classifier there is a turning plates equipped with blades; their adjustable rotation speed will create a centrifugal force that will throw the coarser particles against the walls. ⇒ not very efficient

GRINDING OF THE PHOSPHATE ROCK

- The higher the rotation speed of plates the smaller the particles to the cyclones and the fineness is increased and fineness increases by the increase of ball load and decrease of mill sweep.
- In order to collect the fine particles, the flow from the classifier is conveyed by the air flow to the cyclone where they deposit under centrifugal effects and fall into the silo.
- The air from cyclone still contain some dust and the phosphate particles contained in the air collected by the filter bags and the air leaves the filter clean from dust.
- To clean the bags a compressed air injects to the filter and the dust is then sent to the silo.

GRINDING OF THE PHOSPHATE ROCK

- If the phosphate contains a percent of moisture, we should use hot gases coming from furnace to make the phosphate dry and prevent clogging of the mill.
- The final grinded phosphate has the following analysis:

H_2O (by weight)	<= 1%
Finesses	98 % < 315 μm
Temperature	65/80 °C

→ grinding + friction + rotation
↳ produced energy enough to evaporate this water.

⇒ by experience

* I have to compramize the particle size + rxn
1) handling
2) energy input

GRINDING PARAMETERS

The grinding unit operation parameters are:

1. The phosphate rock flow controlled mainly by the feeder speed. نقل الكميات بناءً على ال moisture content
2. The product fineness controlled mainly by the classifier efficiency ⇒
3. The grinding efficiency controlled mainly by the grinding medium quantity. ⇒ Not full capacity (@ constant volume holdup ⇒ 33% – 40% the rest for create atmosphere to grind.
4. The air process and flows in the circuit controlled by the various valves.

- The circuit pressure caused by fans in the system can be controlled with various valves and depend on classifier speed mill throughput.
- Fans used to produce a vacuum system in order to transfer the product from equipment to another because we handle with solid which is difficult to be pumped by pumps.

ATTACK AND FILTRATION

- The 30 % P_2O_5 acid unit includes two main parts:

→ to maintain it 80 °C otherwise → T will ↑ → will produce hemihydrate ⇓ filter ال [illegible] 2

1. An attack section contains agitated reactor and reactor cooling system, a gas scrubbing system with possibly a sulfuric acid dilution and cooling stage, grinded phosphate handling.
2. A filtration section including a pumping system, a vacuum unit and gypsum handling facilities.

- Phosphoric acid and gypsum are obtained as a result of the attack of a raw phosphate and H_2SO_4 as follows.

$$Ca_3(PO_4)_2+6H_2O+3H_2SO_4 \longrightarrow \underbrace{3(CaSO_4.2H_2O)}_{} + 2H_3PO_4$$

→ to dillute H_2SO_4 to 80%.

- Five tones of gypsum are generated for every tone (P_2O_5) of product acid produced.

REACTION OPERATING PARAMETERS

The main operating parameters which must be kept constant are:

1. Concentration of strong acid.

The acid has to be concentrated with a good attack of the phosphate and good filtration; the chosen concentration may have a range of (27 - 30) % P_2O_5 .

2. Sulfuric acid content of slurry.

Below (20 g/l) filtration becomes bad and above (30 g/l) sulfuric acid consumption becomes undue.

REACTION OPERATING PARAMETERS

3. Solid content of slurry.

The best solid content is (30-40) % because increasing the solid ratio leads to:

- ✓ Slurry is more difficult to filtrate.
- ✓ Attack – ratio falls.
- ✓ Slurry is more difficult to pump.

4. Temperature of slurry.

The higher the temperature is more complete the attack and the better the filtration will be (75-90 ^{o}C).

(*) ليش بلزم سرعة ال agitator
ذكرنا سريعة لتخلي ال solid particles
تضل معلقة بال reactor
غير هيك رح تترسب .

REACTION OPERATING PARAMETERS

- The sulfuric acid must be diluted with industrial water before entering the reactor from 98.5% to 80%.
- Since the dilution process is exothermic then sulfuric acid cooled in a carbon block heat exchanger to 50 °C.
- Then sulfuric acid introduced to the reactor by surface agitator and phosphate introduced to the bottom of the reactor in order to give the reaction a good residence time to complete the reaction before the overflow sent to the filter.
- The time needed for this reaction is approximately 15 minutes.

رح ادخله من تحت
عشان اعطيه residance time كافي

* particles in the reactor must be suspended

* how to gruntee that we have enough residance time?
1) speed of the screw of the pipe
2) volume of the reactor
3) height of the liquid inside

* the reactor is not open to atmosphere ⇒ why?
because we are produce Acid ⇒ volatile

* exit stream → to the scrubbing system (gases)

REACTION OPERATING PARAMETERS

- Because the attack reaction of the phosphate by sulfuric acid is exothermic, the heat quantity is removed by forced circulation of air.
- This air carries off the emitted gases due to the reactions and mainly formed of water-steam, carbonic gas, and fluorine compounds.
- Fluorine polluting substance and removed from the gases by water absorption system and the overflow is collected to be used in filtration washing process, and a cleaned gases leave the column to the atmosphere.
- The absorption system consists of a primary washing tower using water for absorption and a secondary washing tower using water with caustic soda (NaOH).

REACTION OPERATING PARAMETERS

عشانه تقدر تسحب ال slurry

→ to create pressure drop

- The overflow slurry from the reactor is pumped to a vacuum filter cloth to separate the gypsum from the acid, the filter consists of six parts. → least amount of cake is in compartment six

- The first part is fed continuously with the slurry and the liquid of the first part flow to the vacuum box and then to a separate tank and mixed with the medium acid return to the reactor. filtrates from this stage may ate → either back to the reactor → or washing the cake on the filter → products

- From the second part the acid (30% P_2O_5) is filtered and collected in the multi (six) compartment separator, then pumped to the desaturation acid tank.

2800 ton/day → production of gypsum

أقل كمية من ال cake بجي العملية بتكون مرحلة 6 لأنه لبعد كل مرحلة ال packing ↑

cake in compartment (6)
must be removed
other wise, it will cause
overpressure on the filter
hence, damage this unit
the cake from (6) → cake for disposal

doing washing → scrubbing
→ then to the Belt conveyor → disposal
→ why? cake is wet } → will not cause pollution.
± packing (✓)

- In the fourth part a weak acid is filtered and collected in a multi-stage separator then pumped to the sixth section where after removing the gypsum by the screw a small thickness of the cake is washed counter-currently by high pressure water mixed with the weak acid from the fourth part and the filter from this stage is pumped to the fifth part where a very weak acid is filtered and pumped to the fourth section.
- The makeup of the water cycle comes from the overflow water of the absorption tower for gas washing because this water contains some acid.
- The vacuum in the filter is caused by a big fan.
- The acid coming from the attack-filtration section is warm and loaded with gypsum and fluosilicate.

REACTION OPERATING PARAMETERS

- These solids cause quick sealing of the concentration circuit especially the heat exchanger, to avoid this phenomenon the diluted acid from the attack and filtration section is kept in a stirred aging tank not more than (24 h).
- The acid thus desupersaturated is then decanted before being stored for use in the concentration section and the sludge formed in this tank is removed by a screw and pumped to the reactor.
- The 30% P_2O_5 slide from the decanted tank to the settled acid storage tank.
- All gases from the storage tank of 30% P_2O_5 are passes through a water absorption tower to remove these gases and the air leaves the tower cleaned.

to increase the concentration
of P2O5 from 30% → 54 %
by evaporation ☺ (in order to remove
water)

CONCENTRATION UNITS

- P_2O_5 concentration section consist of three identical lines having similar operating conditions.

- Every line designed for the concentration of 450 Ton/day of P_2O_5 from 30% to 54% and the purpose of the concentration section is to evaporate the water in excess.

- In the concentration section in order to get the evaporation at lower boiling temperature the evaporation takes place under vacuum and the pressure is approximately (70mm Hg).

why? prevention of corrosion

→ the unit material of construction
carbon Block

The unit for concentration
is (carbon black heat
exchanger)

T.B.P 40°C

- At this pressure 54% P_2O_5 acid boils at about 80ºC and the heat load is obtained by low pressure steam 3.5 bar.

جاي من
تسخين الماي على حرارة 80 °
عن طريق تمرير steam

CONCENTRATION UNITS

- Saturation takes place in a carbon block heat exchanger in which the acid to be concentrated passes by means of forced circulation in order to prevent scaling and to increase the heat transfer, since water under 70 mm Hg boils at 42ºC then superheated steam and fluorine are observed in the gases let out form the evaporator and chlorine with some P_2O_5 carried off as fine droplets in the gaseous flow so it is necessary to forecast a demister.

* By products from this process are → fluride → they utilize it (H_2SiF_6) → Then use it as a raw material in Aliminium fluride production

→ gypsum → no

HF → reaction
→ filtration (least one)
→ concentration
→ convent to (H_2SiF_6)

CONCENTRATION UNITS

- In order to concentrate the phosphoric acid from 30% to 54%, a carbon block heat exchanger is used.
- To raise the temperature of the phosphoric acid from 80°C to 88.5°C to introduce it in a vacuum boiler evaporator with a temperature of 87°C.
- So, 30% P_2O_5 acid with a temperature of 38-40°C is mixed with the acid leaving the heat exchanger with 88.5°C and the two streams gives a temperature of 87°C which enters the vacuum evaporator.
- The heating medium in the carbon block heat exchanger is low pressure steam used counter currently with circulated phosphoric acid enters from the bottom and leaves from the top comes from the basket filter.

CONCENTRATION UNITS

- In the vacuum evaporator the other compounds such as $H_2O.H_2SiF_6$ and traces of H_3PO_4 leaves as gases and the 54% H_3PO_4 remains in the bottom of the boiler and the product is drain from the boiler at a height of 90 cm from the bottom of the boiler, at this stage the acid sent to the acid production pump to storage tanks.
- Below this height the flow is taken to the basket filter then to the circulation pump which send it to the carbon block heat exchanger.
- The droplets of the acid with steam of gases passes through the demister in order to remove the H_3PO_4 traces and drain to the acid production pump which pumped it to storage tanks as 54% H_3PO_4.

FLUORIDE

- During the reaction of phosphate ore and sulfuric acid, silicon tetrafluoride (SiF_4) and HF are formed as byproducts.

todd with HF

- These gases are usually scrubbed with water, forming fluorosilicic acid, H_2SiF_6 (FSA) as a waste stream.
- The process used is the absorption under vacuum of the fluorine by water addition.
- Gases flows to the demister to remove any traces of H_3PO_4, and the gases leaves the demister at 80°C and enters a primary vacuum fluorine absorber using industrial circulating water as absorbent.
- Then gases leaves to the secondary fluorine absorber with temperature of 47°C.

FLUORIDE

- After these two processes the water gases leaves with temperature of 43ºC from the secondary absorber and enters a vacuum condenser.
- The Flosilicic acid is produced from the primary absorber with 20% H_2SiF_6 and sent to storage tanks.
- These are the equations takes place in the vacuum absorber

$$4HF+SiO_2 \overset{\text{Heat}}{\rightleftharpoons} SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \rightleftharpoons H_2SiF_6$$

GYPSUM DISPOSAL

- Around 5 tones of gypsum are generated per tone of P_2O_5 produced as phosphoric acid.

2ton acid → 5 ton gypsum

- This represents a serious disposal problem.
- Two methods can be used to dispose of gypsum:

  1. Disposal to land
  2. Disposal into water

- By-product gypsum contains four types of impurity that are considered to be potentially harmful:

washing (of gypsum) by → dillute acid
→ water.

  1. Residual acidity (P_2O_5)

ليش الفلتر ما بشيل كل كمية P2O5 يلي بال acid ؟

because of it's viscosity (P)

GYPSUM DISPOSAL

2. Fluorine compounds → من أسباب منع الإزالة
من التخلص من ال gypsum بالبحر.

These are only harmful if disposal is into fresh water because disposal into sea water results in the formation of insoluble calcium fluoride.

3. Undesirable trace elements

4. Radioactivity → uranium

- Disposal on land, under proper conditions, is the best environmental option although it is not possible everywhere because it requires space and certain soil qualities where the gypsum stack is situated.

GYPSUM DISPOSAL

Main reason to use dihydrate process to produce H_3PO_4

→ low Ⓣ

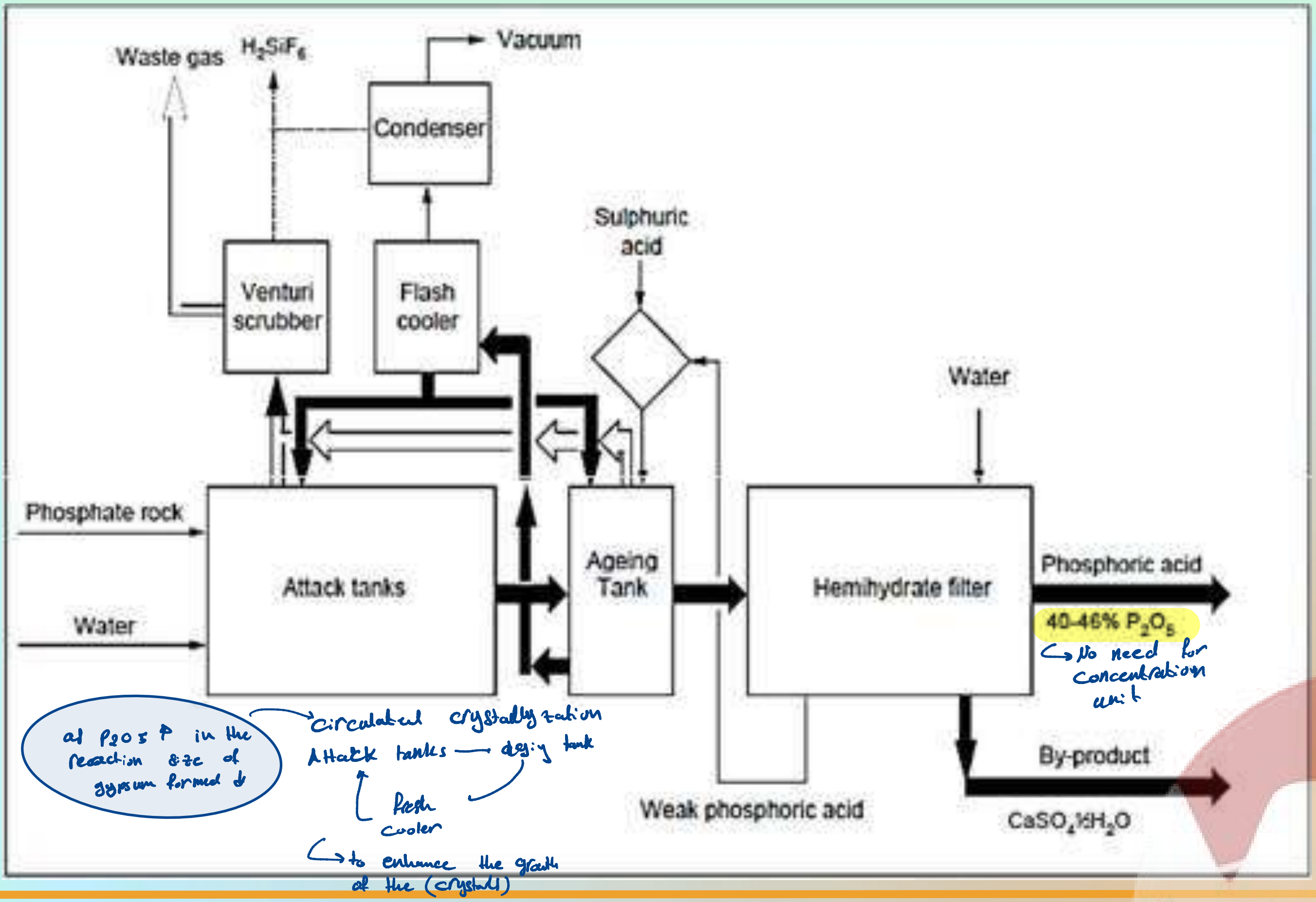
HEMIHYDRATE (HH) PROCESS

→ reaction

→ filtration.

- Operating conditions are selected in this process so that the calcium sulfate is precipitated in the hemihydrate form.
- It is possible to produce 40-52% P_2O_5 acid directly, with consequent valuable savings in energy requirements.
- The figure shows a simplified flow diagram of a HH process.
- The stages are similar to those of the dihydrate process, but grinding may be unnecessary.

HEMIHYDRATE (HH) PROCESS



↳ No need for concentration unit

al P_2O_5 ↑ in the reaction size of gypsum formed ↓

circulated crystallization

Attack tanks → aging tank

flash cooler

↳ to enhance the growth of the (crystals)

ADVANTAGES OF THE HH PROCESS

- The main advantages of this process, apart from the reduction or elimination of evaporation heat requirement, are:

1. Capital savings.

why? → size of gypsum ↑

2. Purer acid: acid from the HH process tends to contain substantially less free sulfate and suspended solids and lower levels of aluminum and fluorine than evaporated dihydrate process acid of the same strength.

3. Lower rock grinding requirements: a satisfactory rate of reaction can be achieved from much coarser rock than in the dihydrate process, because of the more severe reaction conditions in the HH process. (600 – 500) μm

DISADVANTAGES OF THE HH PROCESS

1. Lower Filtration rate.

- Hemihydrate crystals tend to be small and less well formed than dihydrate crystals and thus, hemihydrate slurries tend to be more difficult to filter than dihydrate slurries unless

الهدف هون ← بدي أقلل عدد الأنوية يلي بدي تتكوّن
عشان تكبر حبة الكريستال ← كيف ؟
عن طريق إضافة (supress nucleation agent) → enhance growth & number of nuclers ↓

- Crystal habit modifiers are used to suppress excessive nucleation.

nucleation → number of nucleation ↑ crystal size ↓
crystallyzation

- With a good HH process however, there is no need to use crystal habit modifiers. There are examples of phosphate rocks that produce hemihydrate crystals achieving higher filtration rates than obtained with dihydrate crystals.

DISADVANTAGES OF THE HH PROCESS

2. Phosphate losses.

- Water balance considerations restrict the amount of wash water that can be used.
- At the same time, the amounts of both soluble and insoluble P_2O_5 remaining in the filter cake are greater because of the higher P_2O_5 concentration of the slurry being filtered.
- Nevertheless, the simplicity of the HH plant and the absence of silicofluoride scaling in the HH filter, may compensate for the higher insoluble P_2O_5 loss via HH cake.

★ الطحنة بنركز أحياناً عشان
يوصل التفاعل ال core تبع
phosphate rock ما رح يطلع
unreacted P2O5

DISADVANTAGES OF THE HH PROCESS

Stability → dihydrate > hemi > annhydrus

3. Scaling.

for high scale ← تغيّر ال operating condition
2) يتفكك ال gypsum

- Hemihydrate is not a stable form of calcium sulfate and there is a tendency for it to revert to gypsum even before the acid has been filtered off.
- The conditions are even more in favor of rehydration during washing.
- In a good HH plant there is no conversion in the reactor.
- A small quantity of anti-scale agent may be required in a single-stage HH plant filter to avoid scaling.

DISADVANTAGES OF THE HH PROCESS

4. Filter cake impurity.

- The cake is more acidic than gypsum filter cake because of the extra P_2O_5 losses and it also contains more fluorine and cadmium.(particle size ↑)

5. Corrosion.

- The demands on susceptible items of equipment, particularly agitators and slurry pumps, are increased because of the higher temperature (100°C) and acid concentration (40 - 50% P_2O_5) compared to a dihydrate plant.

FERTILIZERS TECHNOLOGY

CHEM 0905554

First Semester 21/22

CHAPTER 7

DIAMMONIUM PHOSPHATE PRODUCTION

→ DAP 18, 46 → DAP is more preferable world wide

→ MAP 11, 61

same process but different in How they will utilize the Acid

كم نتج أشكال من الأمونيا عشانه مشاكله بال handling.

عشان أميز لو كانت ال crystals ولا granules

crystals ⇐ لما أذوب بعزم يطلع clear water

بينما ال granules ← turbid water

* طيب ليش هيك؟ ليش ال granules فيها impurities؟
هسا بال crystals عشان أعمل crystallization الأيونية يلي رح
تتكون رح تجذب المادة من نفس النوع لحالها وما فيها
شوائب والشوائب رح تضل بالمحلول
بينما ال granules ما في losses أعلى

(*) H_3PO_4 → in web process
only used in this process

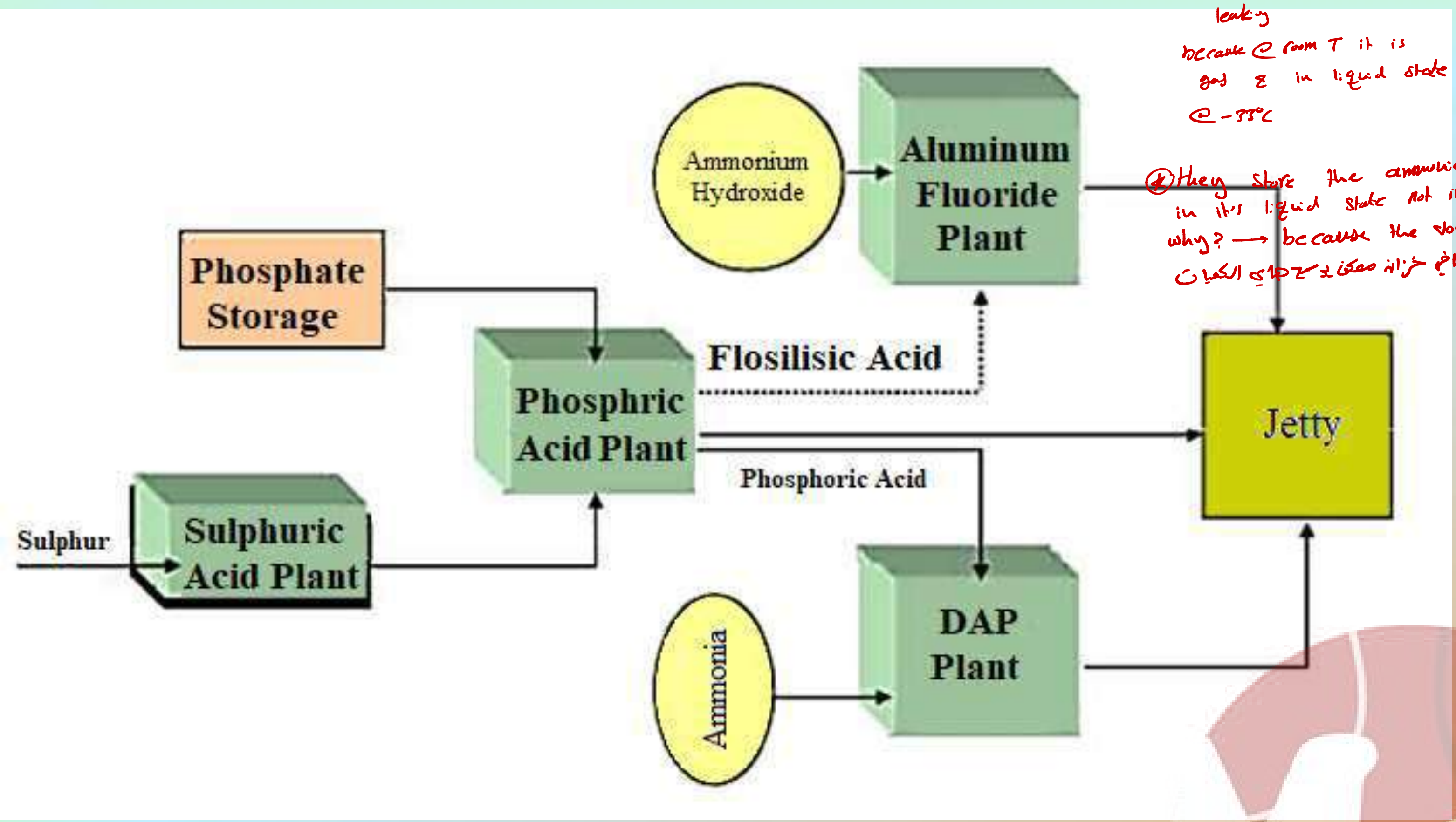
* DAP raw materials $\rightarrow NH_3$ / $\rightarrow H_3PO_4$

شركة مناجم الفوسفات الأردنية + اليابانية ← NH3 is available ت

JORDAN PHOSPHATE MINES INDUSTRIAL COMPLEX

* the problem of this process is How I will keep NH_3 in the storage tank without leaking
because @ room T it is gas & in liquid state @ -33°C

⊛ They store the ammonia in it's liquid state not in gas state
why? → because the volume ↑
وما في خزانة ممكن تحوي الكميات



QUANTITIES PRODUCED at the INDUSTRIAL COMPLEX IN AQABA

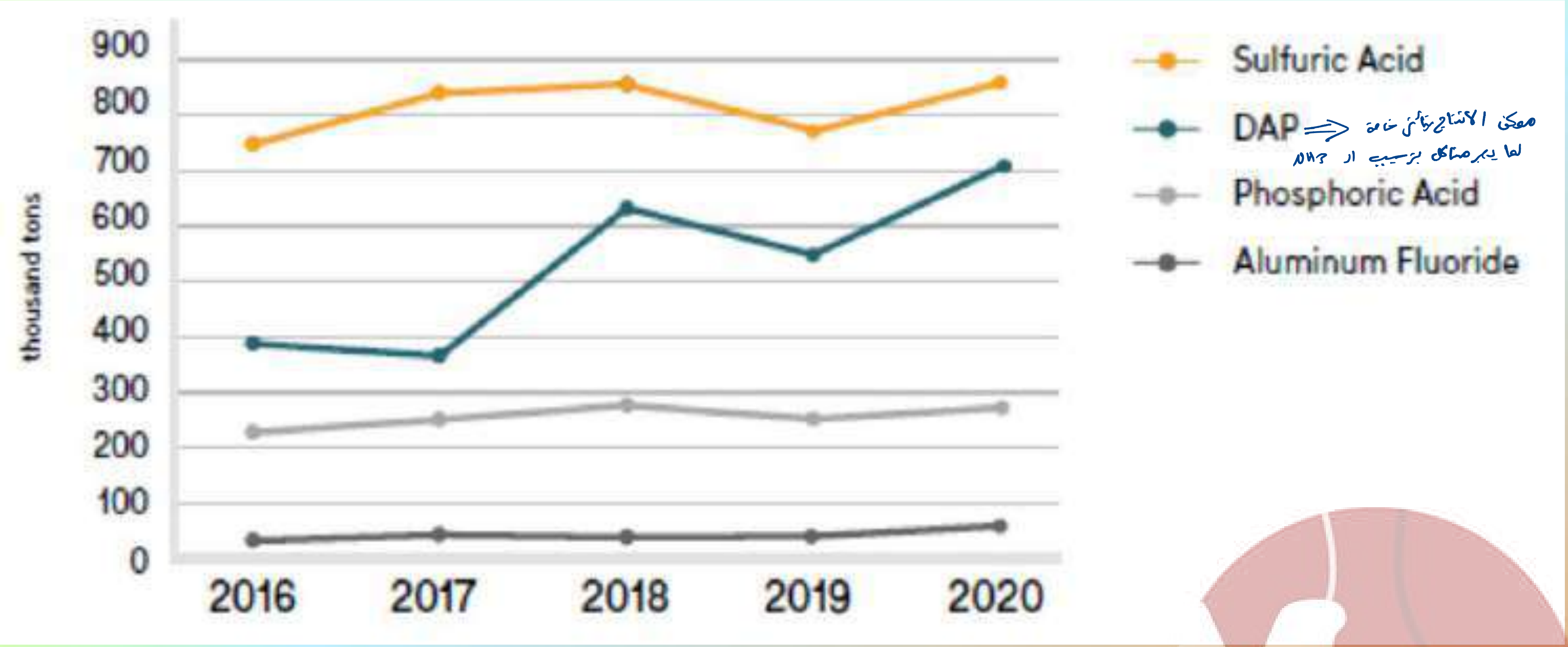
Product	2020	2019	2018	2017	2016
DAP	707	550	632	379	396
Phosphoric Acid	282	252	281	264	228
Sulfuric Acid	863	780	856	839	738
Aluminum Fluoride	10	6	6	6	4

الزيادة ثابتة

* electricity

* in the industrial complex
where there they produce H_3PO_4
as H_3PO_4 P → fulosilisic acid P

QUANTITIES PRODUCED at the INDUSTRIAL COMPLEX IN AQABA



ممكن الانتاج يتأثر خاصة
لما يصير مشاكل بترسيب ال NH_3

★DAP → crystals / granules → same amounts of N_2 & P_2O_5

★DAP exported to East Asia
but locally → the consumption is low

★عنا بالأردن عنا ضعف بال N لهيك بستخدموا يوريا
لانه فيها N أكثر.

INTRODUCTION

- Di-Ammonium Phosphate (DAP), as a fertilizer is produced by Jordan Phosphate Mines Company at a capacity reaching to 3000 metric tons daily.
- It contains 18% Nitrogen, and 46% Phosphorus pentoxide, which is soluble granular, and leads to easy absorption by the plants and vegetation.

  → high nutrients

- It can be used by farms machinery, for all crops and trees, and for either rain-fed or irrigated lands.

  1) direct in the soil (granules)
  2) drip irrigation (crystals + granules (Based in the filler))
  وكانه حول ممنوع بس لو كان DAP أو لا عادي.

- The material of composition are ammonia, wet-process phosphoric acid, sulfuric acid.

  → from wet process I can obtain granules only
  & to obtain crystals (DAP) → you must use furnace grade H_3PO_4

- Raw Materials:

  1. Wet process phosphoric Acid.
  2. Ammonia.

PROPERTIES OF DAP

- Molecular formula: $(NH_4)2HPO_4$
- Appearance: Brown to black granules → Based on the impurities exsists in H_3PO_4
- Molecular weight: 132.07
- Specific gravity (H_2O = 1): 1.619 (heavier than water)
- Melting point: Decomposes at 155°C (311°F)
- Solubility in water: 588 g/L at 20°C (68°F)
- Odor: Odorless or slight ammonia odor
- Physical state: Solid
- pH: Approximately 8 (1% aqueous solution)
  → Because of NH_3

THE PROCESS

- The process is initiated by charging the reactor with phosphoric acid and gaseous ammonia.

(*) to make sure in the reactor get the enough residance time → introduce it in the Bottom → exit gases ($NH_3 + H_2O$) → recycle again

- In the reactor the phosphoric acid is partially neutralized by the ammonia.

ما بنتج DAP بالراكتر → mixture Between DAP & MAP ← &

ما بدخلوا كمية من excess NH_3 ← ليش؟ عشان رح يطلع high viscouse slurry

- Anti foam is added to the reactor to control the potential foaming hazard, such as olives oil.

* in the granulator :- رح أمرر بالك على الـ slurry وجو
بتحتجب عشانه يكمل التفاعل

(*) ما بقدر أحوله كله DAP ليش بكونه أغلبه DAP وشوية MAP.

عشانه أكمل التفاعل بدي أطلع DAP لازم أضيف بعده
كمية إضافية من NH_3 → in the granulator ←

- The reaction generates heat which is utilized to evaporate water from the slurry.
- Control is maintained over the heat of reaction by adding process water from the tail gas scrubber.

→ عشانه أتحكم بالحرارة
+ flowability
وبزيادة عشانه conversion ما يتأثر

- This water dilutes the slurry and maintains it in a readily flowable state.

عشان أنتج MAP or DAP
رح أتحكم بمرحلة التفاعل ب
$H_3PO_4 + NH_3$
ratio

THE PROCESS

- The slurry moisture content must be high enough for pumping (16-20) and low enough for high production rates.
- From the reactor, the slurry is pumped to the granulator where it is distributed over a rolling bed of recycle material.

Seeds → Sand
Seeds → DAP (very fine particles)

very fine → use as seeds
required
oversize → griding → fine → seed
oversize → griding → required

- The recycle consists of cyclone dust, undersize granules, crushed oversize and some product size granules.
- Simultaneously, liquid ammonia is sparged in the granulator to complete the acid neutralization.
- The ammoniated granules are then discharged to the dryer.

Reaction → granulator → drying → screens

THE PROCESS

- The granulator vent air is drawn into a duct where it combines with vent out from the reactor.
- The flow enters the reactor–granulator scrubber, where any un-reacted ammonia is reclaimed.
- The scrubber also serves to control fluorine emission to atmosphere.
- In the dryer, hot air flowing co-current with the granules reduced the granule moisture to approximately 1%.

THE PROCESS

- The stream out of the dryer are elevated to the screen feed conveyer the material then flows to the screens where oversize (+6 mesh) and undersize granules (-16 mesh) are separated.
- The oversize particles flow to chain mills where they are partly crushed and discharged directly to the recycle conveyer.
- Product size-granules flow to the product surge bin.
- The product flows from the surge bin by means of a variable speed conveyor and deliver it in the cooler.
- The cooler lowers the temperature of the product.

THE PROCESS

- From the cooler, the product flows to an elevator and then to a polishing screen where oversize granules or fine are removed and directly back to the recycle conveyor and the finishing product is sent to the storage area.
- The exhaust stream of saturated air vented to the atmosphere after cleaning of objectionably impurities by means of a primary scrubbing system and the tail gas scrubber.
- The primary scrubbers act as dust absorbers and also reclaim any un-reacted (NH_3).

THE PROCESS

- In the case of DAP, the scrubbing liquid contains phosphoric acid but when MAP is in process the scrubber liquid is water.
- The tail gas scrubber receives the exhaust from the primary system and acts as an independent gas cleaning system, it uses re-circulated water as its scrubbing medium.
- The exhaust from the tail gas scrubber is vented to the atmosphere.

PROPERTIES OF DAP

- The main chemical compounds present in the granular products are:

Pipe line (NH3)
↳ (Liquid) → عشان نضمنه سائل
بنبرده بشكل مستمر

Ammonia	NH3
DAP	(NH4)2HPO4
MAP	(NH4)2H2PO4
A.S.	(NH4)2SO4
Sulfuric Acid → H_3PO_4	H2SO4
Phosphoric Acid	H3PO4
Flousilicic Acid	H2SiF6
Gypsum	CaSO4.2H2O
Iron Phosphate	FePO4
Ammonium Fluoride	NH4F
Sodium Hydroxide	NaOH
Aluminum Phosphate	AlPO4

(*) Storage tanks
material of construction
↳ carbon Steel
± thickness → 2cm
but there is insulation
thickness → 1m

How to guarantee to let
the NH_3 in (L)
liquefaction ⤶
system

REACTION

$$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4 + \text{heat}$$

→ reactor

- After MAP is formed and if ammonia is in excess

$$NH_3 + NH_4H_2PO_4 \longrightarrow (NH_4)_2HPO_4 + \text{heat}$$

→ reactor
+ granulator

- Excess ammonia in the outgoing gases is recovered by reaction with phosphoric acid in the primary scrubbers.
- The reactor is operated to form specific mixture of MAP and DAP, this is because the mixture of the two is much more soluble than either one alone and easier to pump at lower moisture contents.

REACTION

- The ammonia to phosphoric acid mole ratio in the reactor is 0.6 (MAP) or 1.4 (DAP).
- Specific gravity of slurry 1.53 and temperature range (110ºC) DAP to (115ºC) MAP.

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)SO_4 + \text{Heat.}$$

2%

- All of the fertilizer products to some extent have ammonium sulfate since phosphoric acid normally contains (3-4%) sulfuric acid.
- The physical action that takes place in the granular is the coating and sticking together of dry recycle particles with the liquid slurry.
- These coated and agglomerated particles are then rounded by the rolling action of the acid.

REACTION

- Granulated product leaves the granulator at about 85 to 100°C and it is fed to a rotary dryer where the granules are hardened by removal of moisture.
- Anhydrous ammonia comes in two forms liquid and vaporized.
- The liquid form is more dangerous from the safety standpoint, because it has a high coefficient of expansion.
- When it is confined in a pipeline or in a full tank and warms up it will exert huge enormous pressure that will tend to either open a safety valve or break the line at the weakest point.
- If it is allowed to be released into air, it lowers its temperature at once to -35°C and therefore it will freeze anything containing moisture that it touches.

REACTION

- The phosphoric acid can cause sever burns when it is hot, if the acid is both hot and concentrated then the danger will be more severe due to the dehydrating and effect.
- The sulfuric acid is a colorless to cloudy liquid which must be properly handled.

hurtful

- Concentrated solutions are rapidly destructive to body tissue with which they come in contact producing severe burns.
- Contact with eyes will case severe damage and it may result in total loss of sight.
- Always we must wear required protective equipment.

MAIN EQUIPMENT

REACTOR

- The reactor functions as a pre-neutralizer, Ammonia vapor, recycled acid, and phosphoric acid are metered to the reactor and phosphoric acid is partially neutralized by the ammonia.

MAIN EQUIPMENT

GRANULATOR

- Three process streams are charged to the granulator they are:

  1- The slurry from the reactor. 2- Recycle granules. 3- Liquid ammonia.

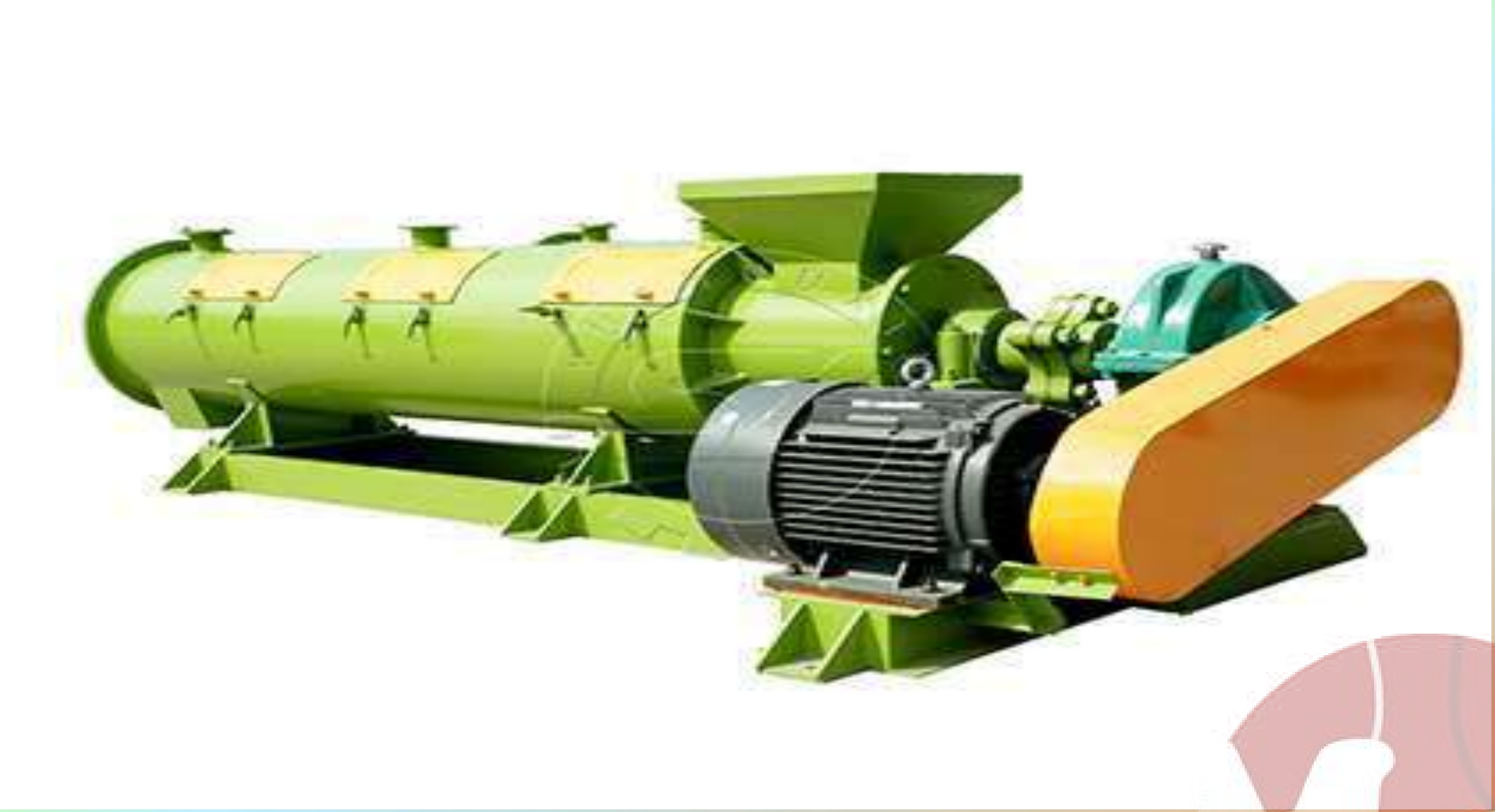
- Two major events occur simultaneously within the granulator:

  1- The ammonia reacts with the slurry to form either DAP or MAP.

  2- The coating of the recycles granules with the reactor slurry coupled with the rotating action of the granulator generates uniform spherical particles.

- Vapors and dust are discharged to the reactor-granulator scrubber.

GRANULATOR



MAIN EQUIPMENT

DRYER

→ moisture < 1%

- The discharged from the granulator and combustion gases from the oil-fired combustion chamber, these two streams flow co-currently through the dryer.

→ مابدي إياها ترتفع حرارته عشانه مايخرب

- The temperature of air varies from app. 205 to 324°C, the dryer is oriented at an angle to the horizontal and this downward slope with the aid of an inducted draft gives the granules their forward motion.

يتم توجيه المجفف بزاوية على المستوى الأفقي وهذا المنحدر الهابط بمساعدة تيار محرض يعطي الحبيبات حركتها إلى الأمام.

- The function of the dryer is to remove moisture from the product.

DAP is not sensitive

→ but why co-current?

عشانه هدفي بالتجفيف نشيل كل المي فابدي driving force عالية بالبداية.

DRYER


FEED
Process Gas Inlet (Heating or Cooling)
Process Gas Outlet
FINAL PRODUCT

MAIN EQUIPMENT

COOLER

→ هو نفس rotary dryer

بس للتبريد ← ليش ؟

1) ↓ losses NH_3

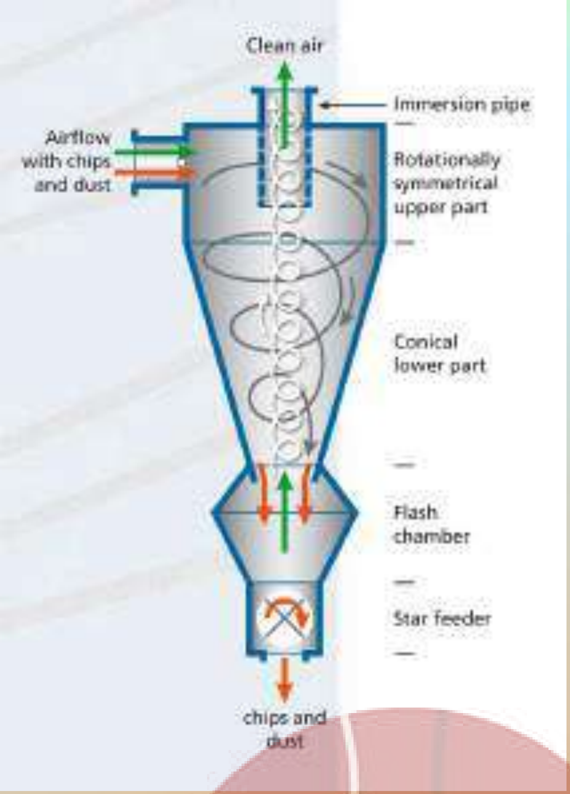
2) prevent caking.

3) T ↑ moisture ↓

- Two process streams enters the rotary cooler.
- They are the discharge from the dryer and cool air.
- The function of the cooler is to lower the temperature of the product, this reduces ammonia loss and the product agglomeration during storage.
- The product depending on the grade enters the cooler at 85 to 100°C and exit at approximately 54°C, the cool air which flows counter current to product steam enters at about 30°C or less.

CYCLONES

- Dryer cyclone, Dust-vent cyclone, Cooler cyclone.
- The vent air enters the cyclone tangentially and is subjected to a centrifugal spinning action which throws the larger dust particles against the cyclone wall.
- These large particles flow by gravity down the cyclone walls to the double-flap discharge valve from where they are discharged to the recycle conveyor.
- Exhaust gases from the cyclones are discharged to the primary scrubbers.



MAIN EQUIPMENT

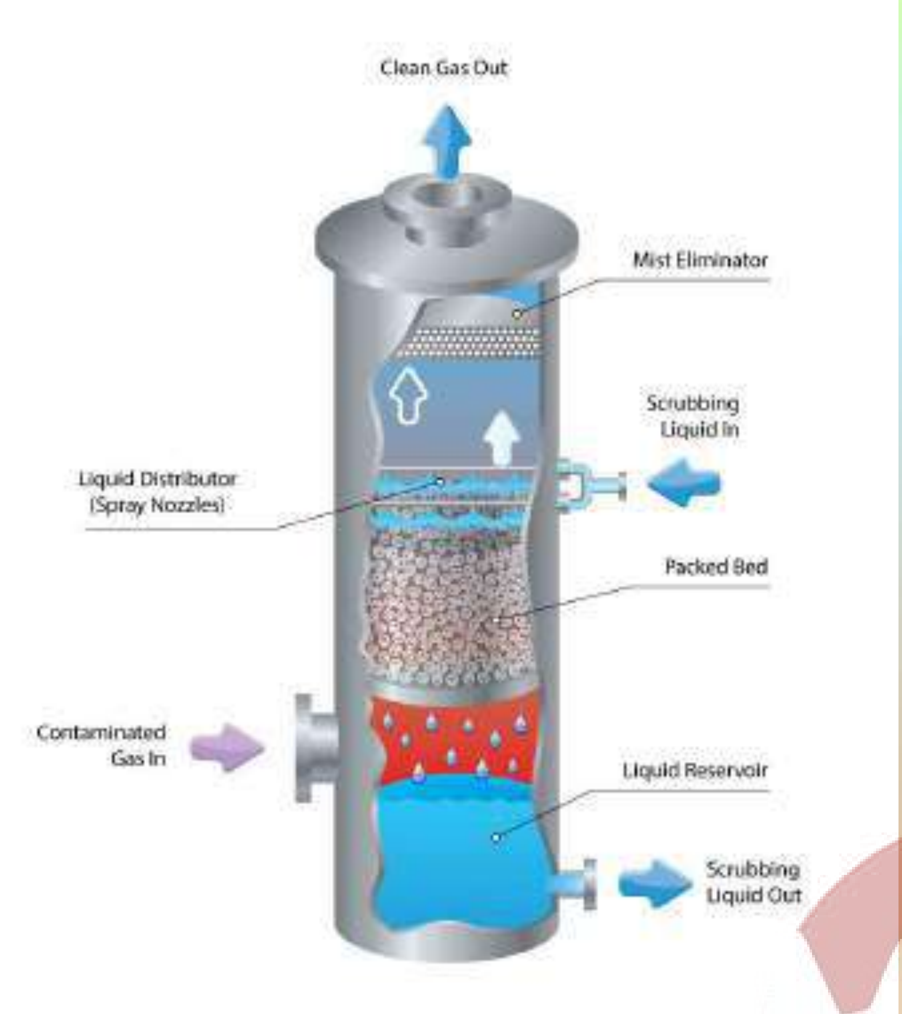
SCRUBBER

- Primary scrubbers

  1. One scrubber receives the vent gases from the reactor and granulator.
  2. One scrubber receives the vent air from the dryer.
  3. One scrubber receives other vent air as well as the vent air from the cooler.

- These scrubbers' function to remove any un- reacted ammonia and dust from the air streams.
- The air stream and low-pressure scrubber acid enter the venture portion of the scrubber.

SCRUBBER


Clean Gas Out
Mist Eliminator
Scrubbing Liquid In
Liquid Distributor (Spray Nozzles)
Packed Bed
Contaminated Gas In
Liquid Reservoir
Scrubbing Liquid Out

MAIN EQUIPMENT

- At the throat of the venture the exhaust stream has obtained a high velocity which generates an infinite mixing of gas and acid.
- The mixed stream then enter the cyclonic portion of scrubber where it is treated with a spray of high-pressure acid while being subjected to a centrifugal force which separates the acid from the gas.
- The-clean gas is then discharged to the tail-gas scrubber, while the scrubber acid is returned to the recycle tank.
- In the case of DAP production, the acid from the tank is phosphoric acid which reacts with NH_3 but in production of MAP water is used.

MAIN EQUIPMENT

- The exhaust from the primary scrubber system flows to the tail-gas scrubber where it receives further cleaning.
- The scrubbing medium is water.

MAIN EQUIPMENT

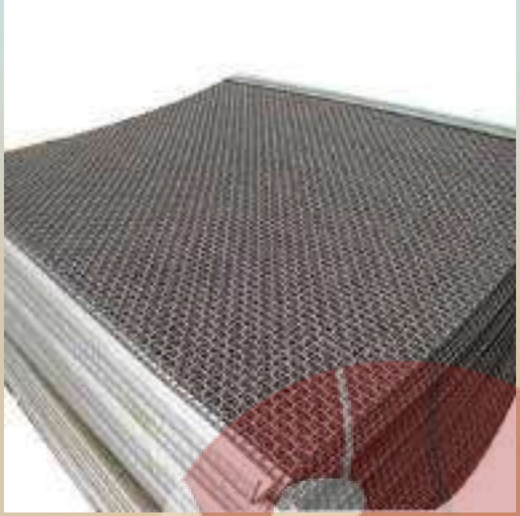
AMMONIA VAPORIZER

- The vaporizer converts liquid ammonia to vapor for use in the reactor.
- The exchanger is a horizontal shell and tube type with the steam on the tube side.

MAIN EQUIPMENT

SCREENS

1. Frame vibrating screen.
2. Mesh vibrating screen.



MAIN EQUIPMENT

AMMONIA TANK

- Ammonia is imported from several Arab and foreign countries by ships.
- It is pumped from ships through a 14 inch pipe to two storage tanks, the storage capacity of the first is (30,000) tons, and the second is (10,000) tons.
- Temperature inside the tanks is kept around (-33) °C at one atmospheric pressure, using special compressors.

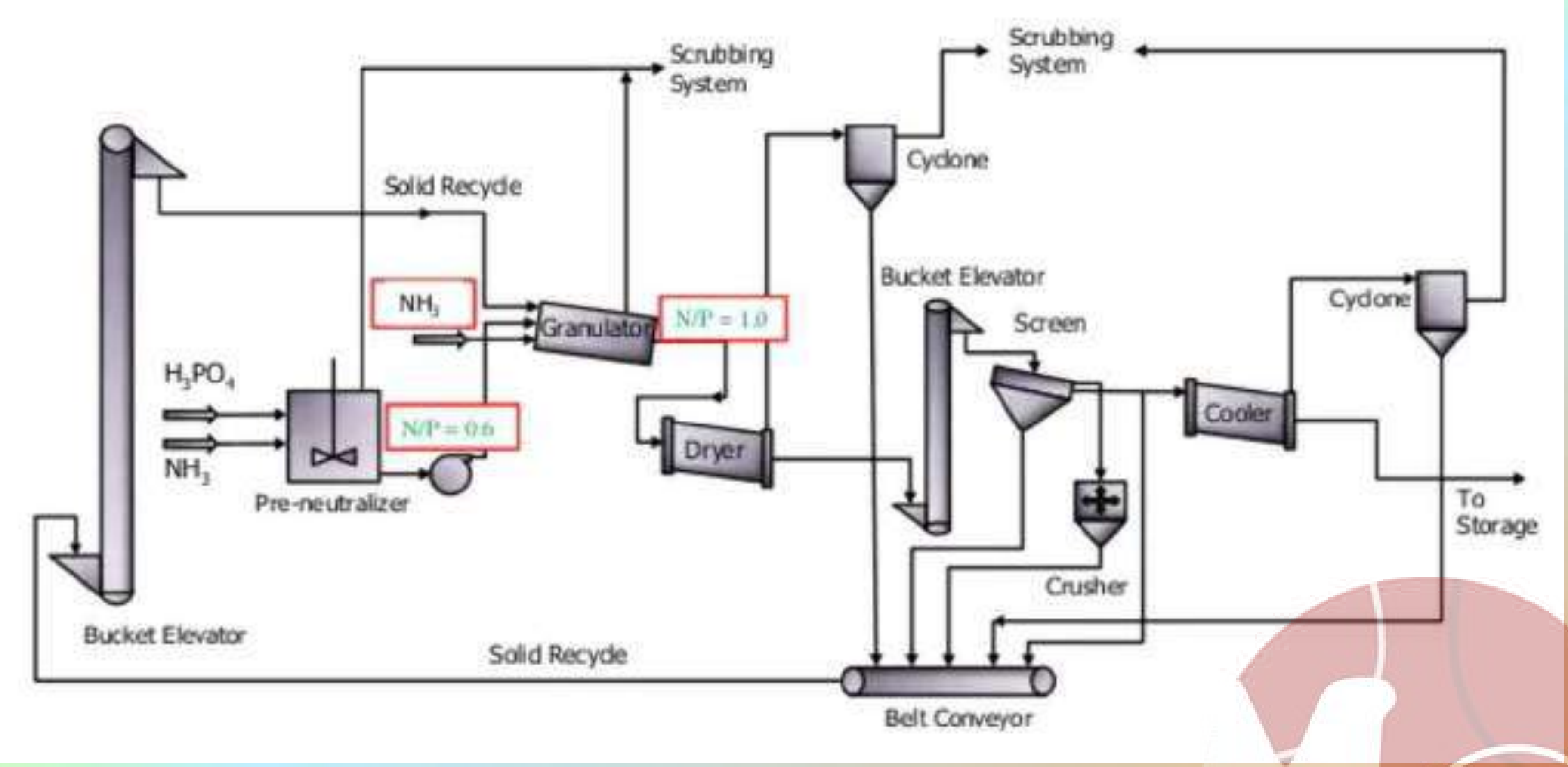
MAIN EQUIPMENT

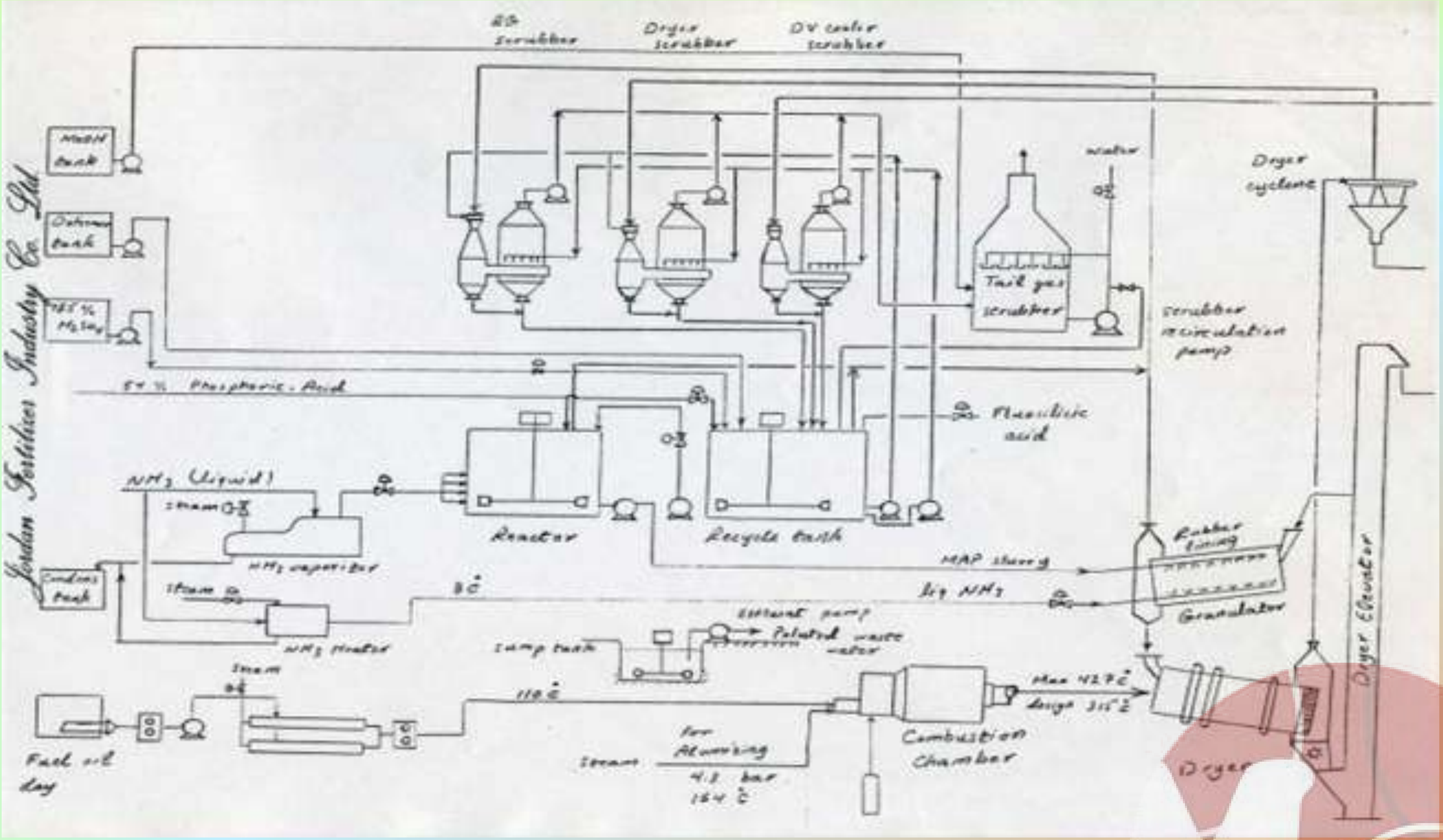
PROBLEMS:

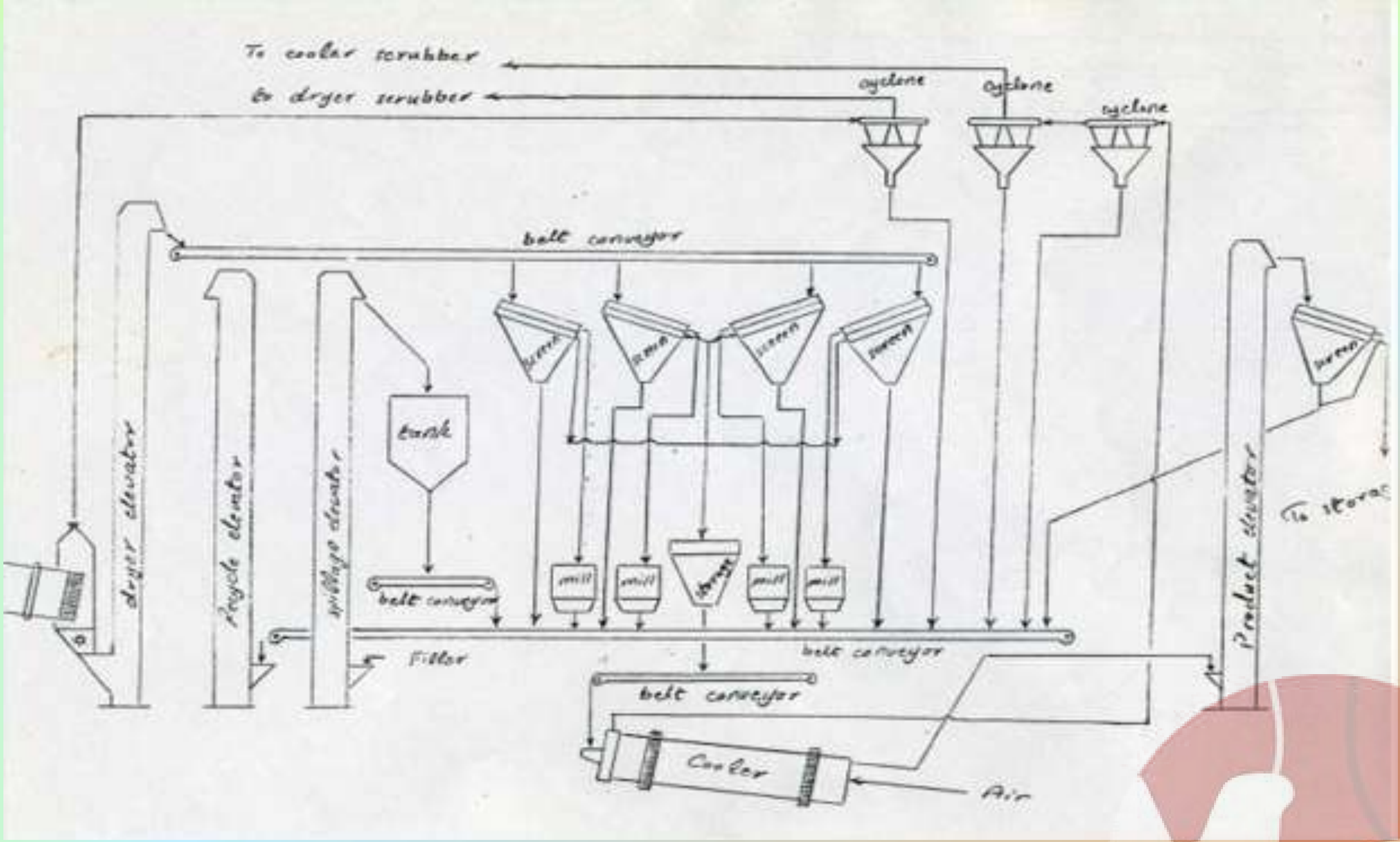
- To overcome any of the following problems:

1. High moisture: increase dryer heat.
2. Low N and low PH: increase ammonia flow (total).
3. Low P_2O_5: increase P_2O_5 (total).
4. All low analysis: decrease filler low.

DAP PRODUCTION FLOWSHEET




Jordan Fertilizer Industry Co. Ltd
RG scrubber
Dryer scrubber
DV cooler scrubber
NaOH tank
tank
98.5 % H_2SO_4
54 % Phosphoric - Acid
NH3 (liquid)
steam
NH3 vaporizer
Condens tank
Steam
NH3 Heater
8 °C
Reactor
Recycle tank
Fluosilicic acid
Tail gas scrubber
water
Dryer cyclone
scrubber recirculation pump
Rubber lining
MAP slurry
liq NH3
Granulator
Effluent pump
Polluted waste water
sump tank
Steam
110 °C
Fuel oil day
Steam
for Atomizing
4.3 bar
164 °C
Combustion Chamber
Max 427 °C
design 315 °C
Dryer
Dryer Elevator


To cooler scrubber
to dryer scrubber
cyclone
cyclone
cyclone
belt conveyor
screen
screen
screen
screen
screen
tank
dryer elevator
Recycle elevator
spillage elevator
belt conveyor
mill
mill
mill
mill
Filler
belt conveyor
belt conveyor
Product elevator
To storage
Cooler
Air

* تم تصنيعه قبل MAP + DAP

→ still has demand because it is consider as a straight fertilizer

TRIPLE SUPERPHOSPHATE

→ single superphosphate → phosphate rock + H_2SO_4 → triple super phosphate add H_3PO_4 on single super phosphate → enhance the recovery of P_2O_5

- One of the advantages of TSP is that it is the most highly concentrated straight solid 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 of the rock and acid.

* phosphate rock → no limitation on it's quality

TSP DISADVANTAGES

- TSP has three main disadvantages:

1. The total nutrient content is lower than that of ammonium phosphate.
2. Its acidic character may cause deterioration of some types of bags. → must be anti-corrosive.
3. It is not well suited for blending with urea because of reaction that cause deterioration of physical condition.

→ physical

because the urea
is hydroscopic
(Absorp moisture)
the urea will react with
remaing H_3PO_4 in (TSP)
so it will cause clogging

⊛ التكنولوجيا الحالية.
بطحن phosphate rock لحد أقل من 100 μm
بحيث تكون (very fine) وبضيف عليه H_3PO_4
بشكل مباشر مو زي زمان على ال Single Super !

TSP PREPARATION

- TSP may be prepared in either granular or nongranular form.
- The non-granular form is preferred for use as intermediate for production of compound fertilizer by granulation process, whereas the granular form is preferred for direct application or for blending.
- The basic chemical reaction involved in production of TSP is as follows:

→ ratio (1:4) + water

$$Ca_3(PO_4)_2+4H_3PO_4+H_2O \longrightarrow 3Ca(H_2PO_4)_2.H_2O + 172.58\ kcal$$

→ heat → will cause further evaporation of water ± fluorine compounds (requires treatment)

- In most processes, a large percentage of the fluorine remains in the product, probably as fluosilicates and possibly as calcium fluoride.

TSP PREPARATION

Imp

- 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:

$$\frac{Acid\ P_2O_5 + Rock\ P_2O_5}{Rock\ CaO} = 2.41\ to\ 2.54\ (weight\ ratio)$$

→ otherwise it will produce mixture of single & TSP

- However, various impurities in the acid and rock cause variations in the optimum acid : rock ratio.

TSP BY DEN PROCESS

- The manufacture of TSP by this route involves the following 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 is required per 1 kg of rock P_2O_5.

→ 85% P_2O_5 by adding water to diluted.

→ wet process

✓ The phosphoric acid used is merchant-grade acid at 52% P_2O_5 concentration.

⊛ لا يمكن انتاج ال TSP باستخدام H_3PO_4 furnace grade

ليش ؟ لأنه إصدار يعتبر أنا بكل الأحوال رح أنزل التركيز تبعه ل 52%

⊕ أصلاً غالي.

TSP BY DEN PROCESS

2. **Denning:** further reaction
solidification ± crystallyzation + evaporation

- ✓ The fluid material from the mixer goes to a Den where it solidifies.
- ✓ Solidification results from the continued reaction and crystallization of mono-calcium phosphate. → by-product
I don't want it
→ further digstion to produce (calcium phosphate) → TSP.
- ✓ The Denning times of 10-30 minutes are suitable for TSP. → Solidification
+ crystallyzation
+ further evaporation
- ✓ The Den must be enclosed and connected to a fume exhaust system to direct fluorine containing gases to a scrubber.

TSP BY DEN PROCESS

3. Storage/Curing: (further reaction completion

± further recovery of P_2O_5 in rock ← [illegible]

- ✓ The product is removed from the Den and conveyed to storage piles for final curing which requires 3-6 weeks depending on the nature of the raw materials. → may add H_3PO_4 to enhance the reaction

  ← بحجل حبك لما أسوي تحليل سيطلع عندي نقص بالكمية فقط.

- ✓ During curing, the reaction approaches completion.

- ✓ The free acid, moisture and un-reacted rock contents decrease, and the available and water-soluble P_2O_5 content increase.

- ✓ Small amounts of fluorine compounds continue to be evolved during storage curing. (أقل بكثير)

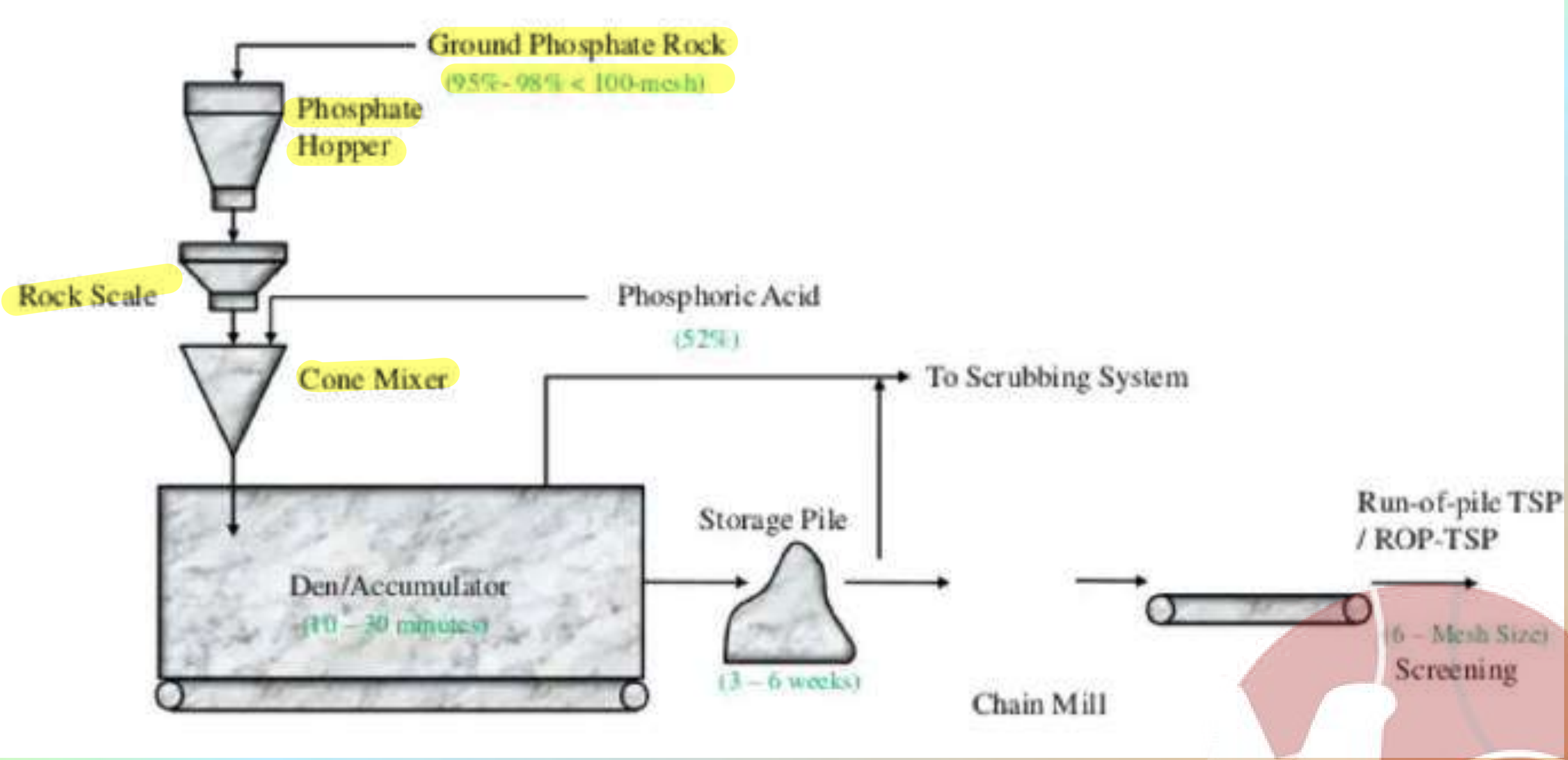
TSP BY DEN PROCESS

- A good ventilation is needed to remove the fluorine from the working area.
- Scrubbing exhaust gas may be necessary to prevent atmospheric pollution.

زي مرحلة عشانة بكره Breakers

- After storage curing, the TSP is reclaimed with a power shovel and disintegrated in a cage or chain mill to pass 6-mesh screen (3.3 mm). → final product (granulation not required)
- The disintegrated TSP may be used for making compound fertilizer by agglomeration granulation, or it may be used as is for direct application.

TSP BY DEN PROCESS



TSP BY DEN PROCESS

4. Granulation:

الهدف عشان أوحّد الحجم تبع TSP
هاي زي خطوة إضافية.

- Granulation of powder or cured TSP is granulated by the process shown on figure.
- After milling and screening, the cured powder TSP is conveyed to a rotary drum granulator.

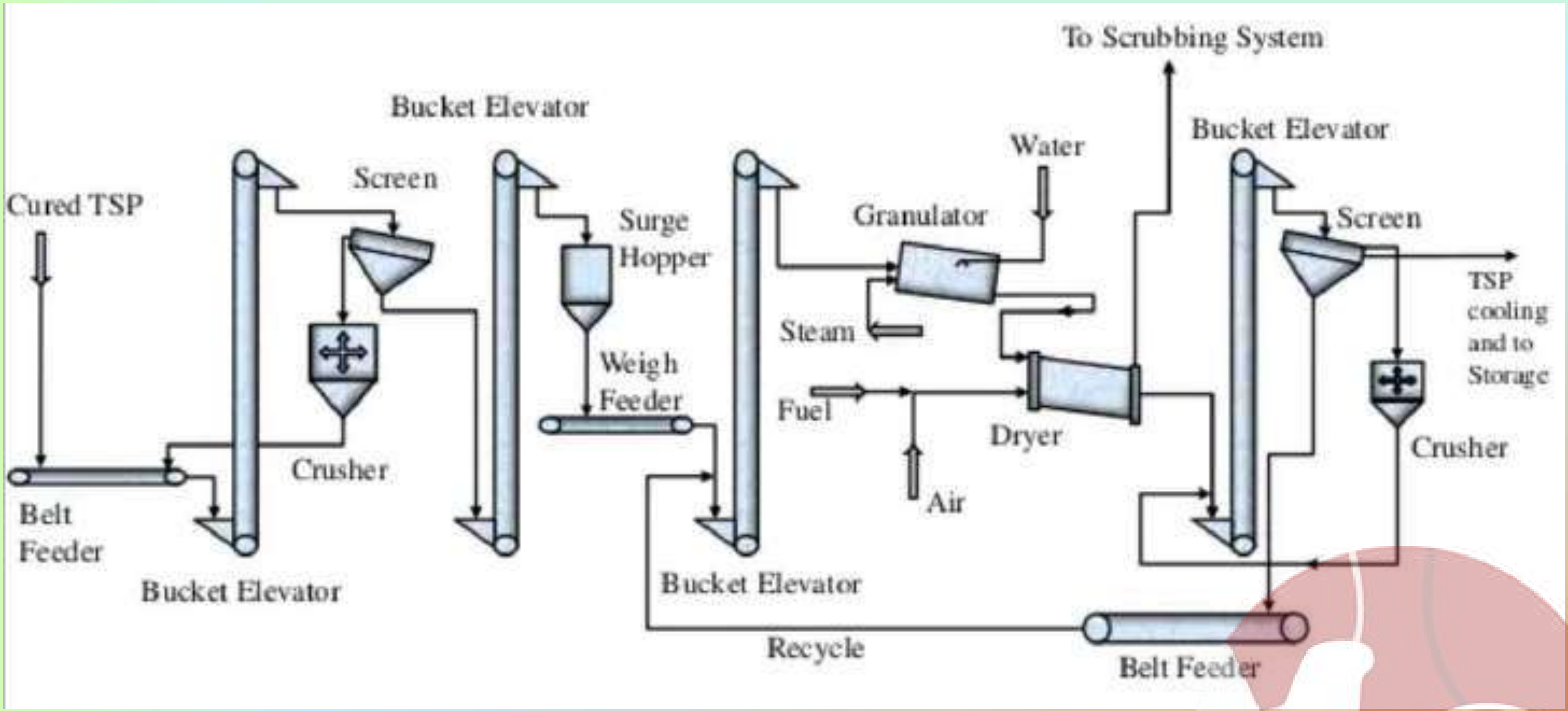
water + steam

ال water عشان تبلل (TSP)
و ال steam عشان تسبب agglomeration
مع الحركة الدورانية رح يتوحد الشكل و يتحبحب عشان يصير uniform spherical particle

- 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.

زي DAP

GRANULATION OF CURED TSP



TSP BY DEN PROCESS

- Dust and fumes from the dryer are scrubbed in a water scrubber.

Before

- Alternatively, dust may be removed by a big filter prior to the wet scrubbing.

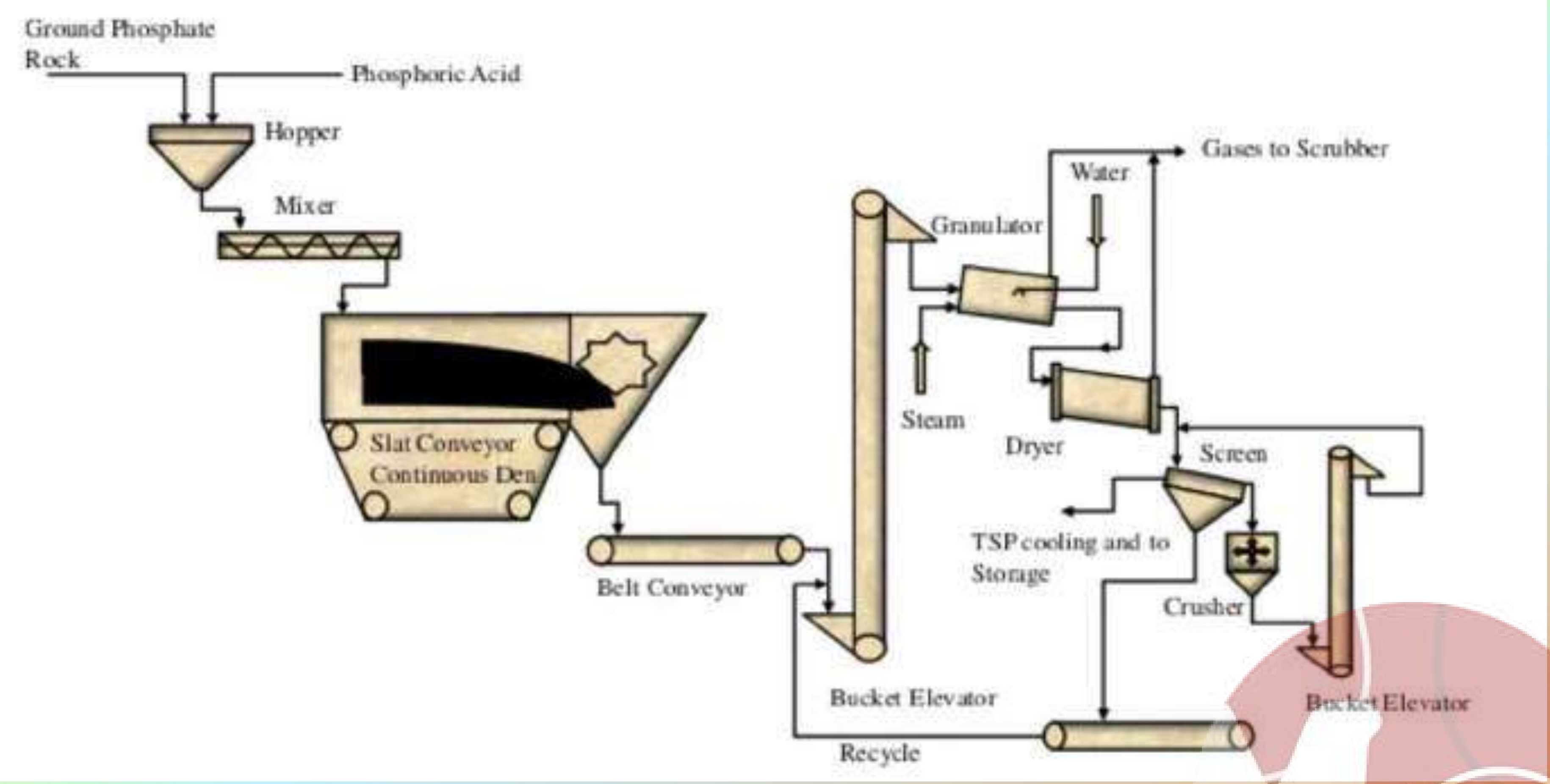
Inputs	Construction per tone product
Cured TSP, Ton	1.02
Steam, kg	75
Cooling water, kg	250
Fuel, GJ	0.67
Electric energy, kWh	29
Operating labor, work hours	0.3

for each 1 ton

EX-DEN GRANULATION → slurry after

- The acidulation and Denning steps are similar to those described for producing non-granular 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.

EX-DEN GRANULATION OF TSP



→ ex-den

DIRECT SLURRY GRANULATION

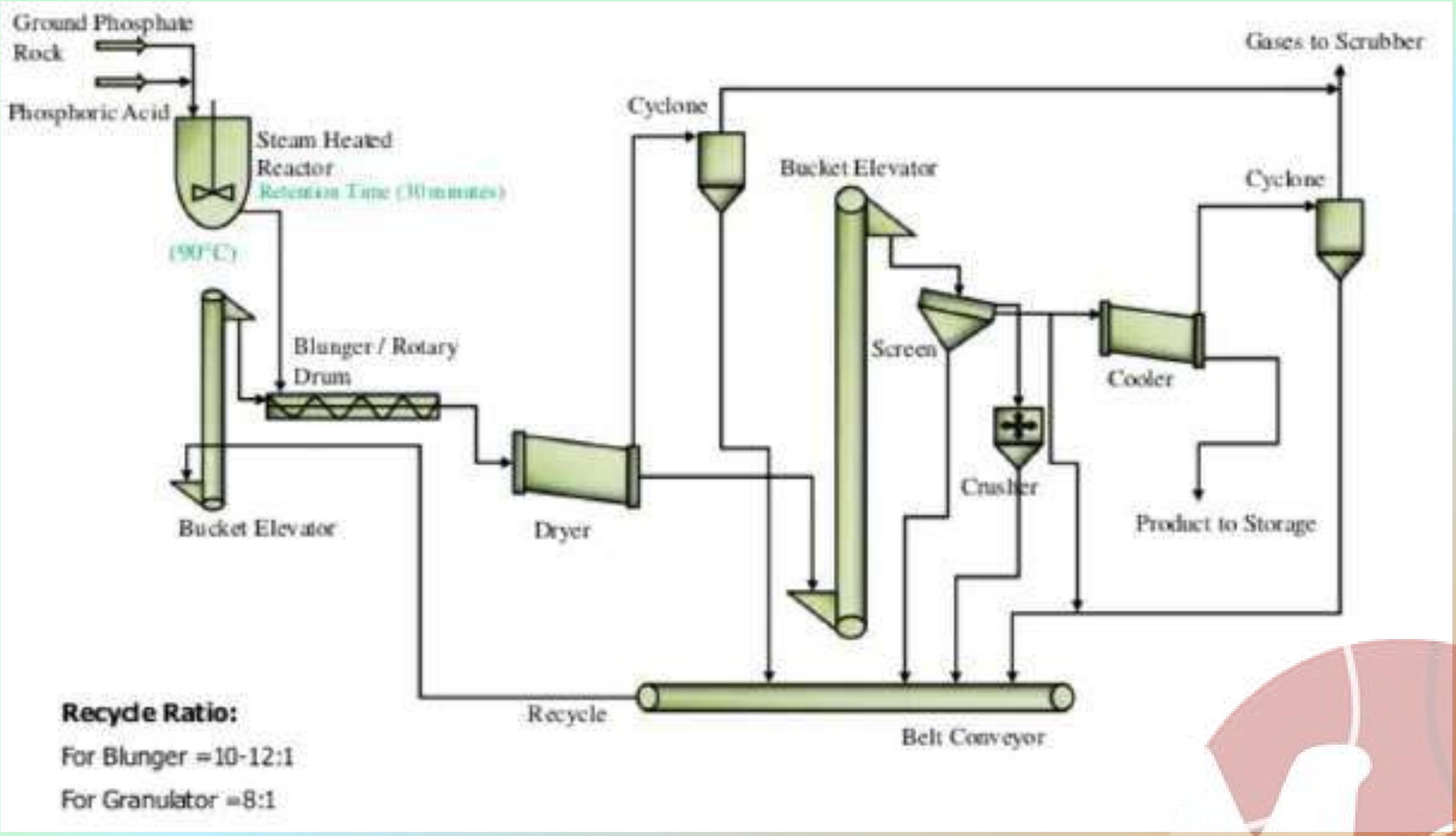
- When granules TSP is the desired end product, it is usually preferable to produce it directly rather than by granulation of powder TSP.
- Some advantages of direct granulation processes are:

1. Cost is usually lower.
2. Granules are denser and stronger.
3. Granulation equipment can be used interchangeably for producing TSP and ammonium phosphates.

بقدر أشتغل أنتج TSP
و DAP , MAP
بس نغير بدل ما أدخل أمونيا
بدخل water + steam

DIRECT SLURRY GRANULATION

- :



DIRECT SLURRY GRANULATION

There are two main disadvantages of direct granulation:

1. Owing to the limited reaction time, un-reactive rocks are poorly suited for use in the direct granulation process.
2. 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.

NON-GRANULAR MAP

→ to increase % of P_2O_5 from 56 → 61
& Nitragine is 12% of crystals → total nutrients 73

- 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 materials to be granulated with others in an agglomeration granulation of compound fertilizers.
- Many processes for making non-granular MAP have been developed.
- In general, all processes aim at a simple, low-cost method by eliminating granulation, recycling, and drying.

NON-GRANULAR MAP

- However, the product should have sufficiently good physical properties to permit storage, handling, and transportation without excessive caking or dust problems.
- MAP powder is the most concentrated P_2O_5 (52%) product and can be considered as an important component for the production of complex fertilizers.

Powder

Crystalline

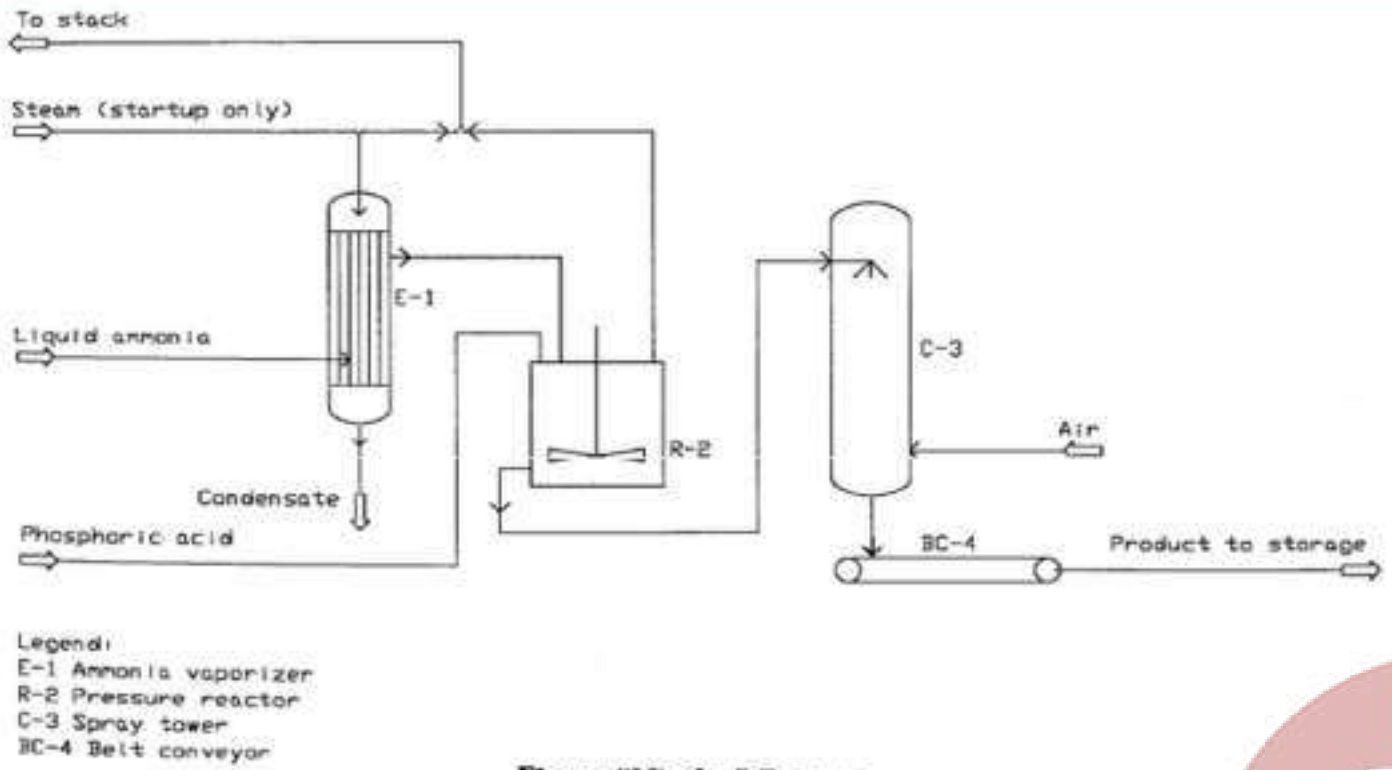
FISONS PROCESS

- In the Fisons process, 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 170ºC, and the pH is 3.5 – 4.0.
- This hot slurry is released into a spray tower through a special spray nozzle.

FISONS PROCESS

- More water is flashed off and evaporates as the droplets cool and solidify by falling through an ascending airstream.
- The product contains about 6% moisture; the grade range 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 ranging from 0.1 to 1.5 mm.

FISONS PROCESS

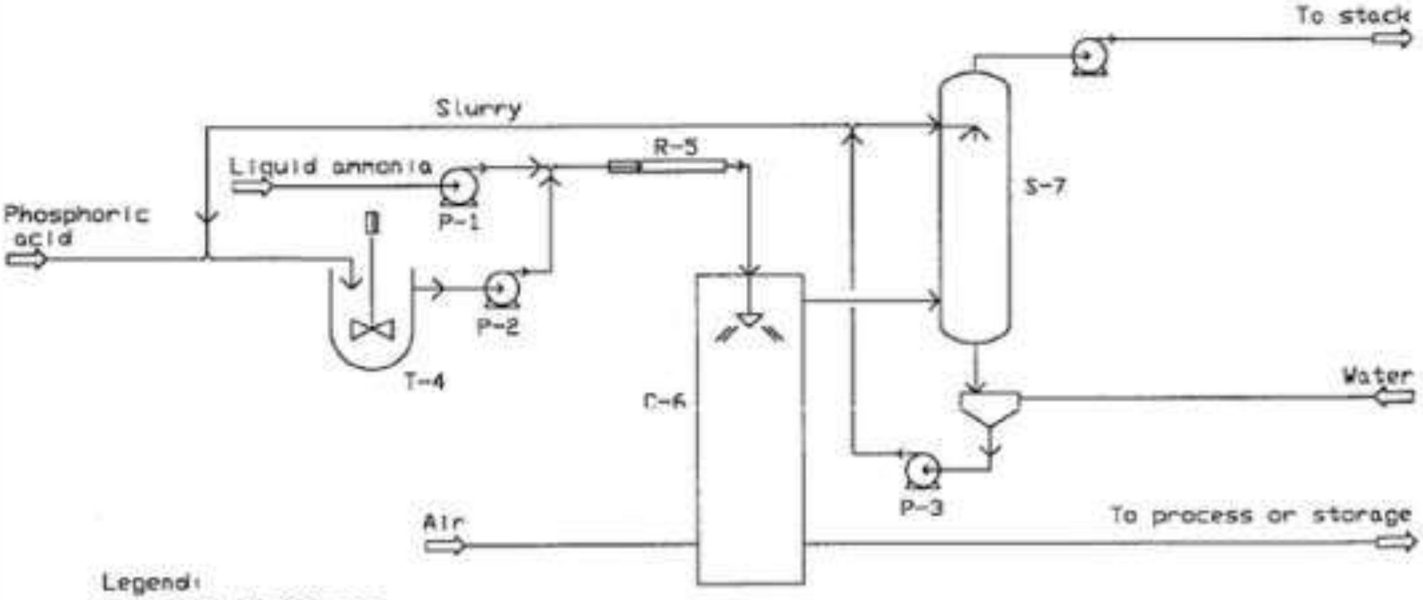


Fisons "Minifos" Process.

SWIFT PROCESS

- In the Swift process, 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%.

SWIFT PROCESS



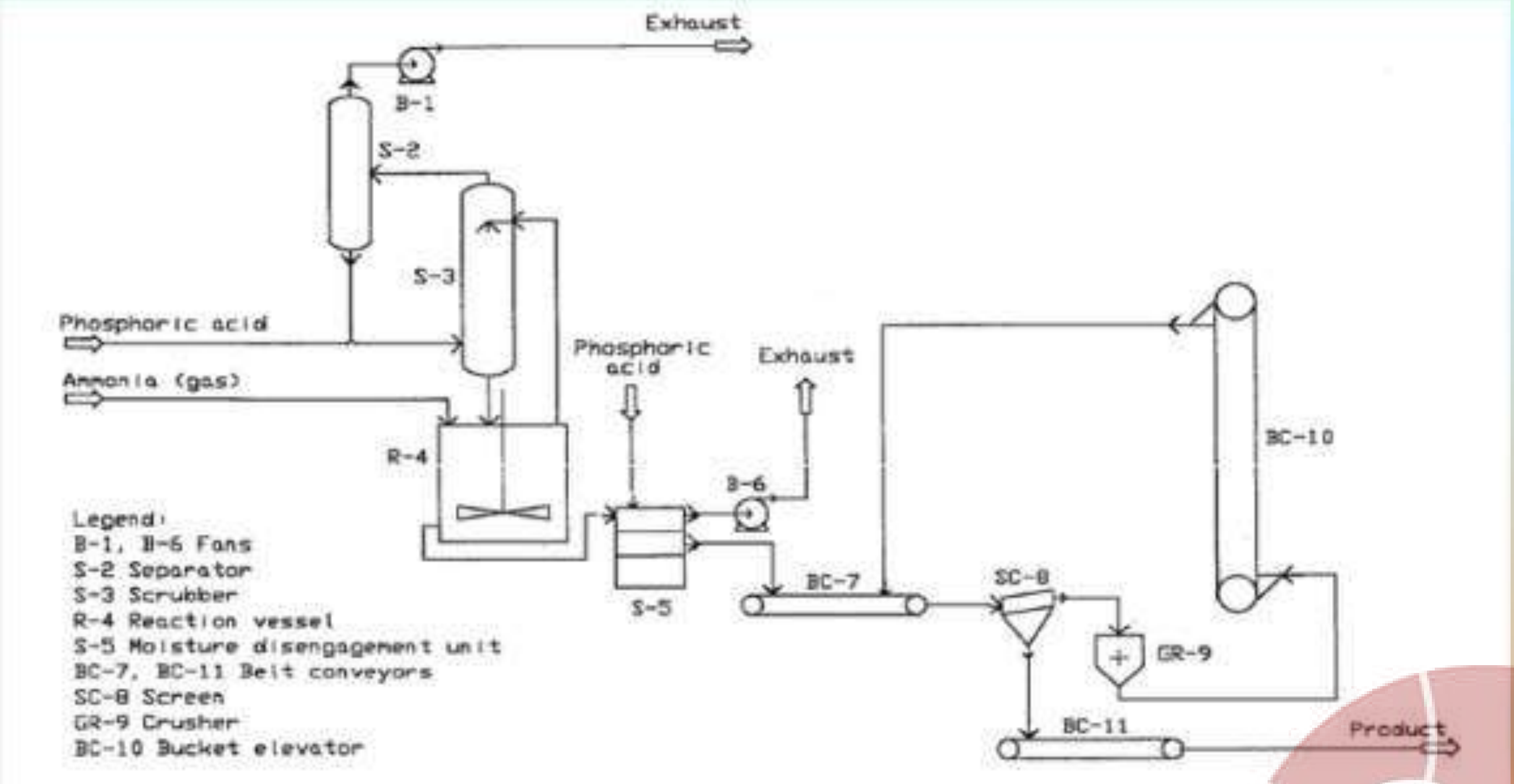
Legend:
- P-1, P-2, P-3 Pumps
- T-4 Surge tank
- R-5 Pipe reactor
- C-6 MAP tower
- S-7 Scrubber

Swift Powder MAP Process.

SCOTTISH AGRICULTURAL INDUSTRIES PROCESS

- This process 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 disintegrate the mass into small particles releasing water vapor.
- The product typically contains 6% moisture, 11% N, and 50% water-soluble P_2O_5.

SCOTTISH AGRICULTURAL INDUSTRIES PROCESS



Legend:
B-1, B-6 Fans
S-2 Separator
S-3 Scrubber
R-4 Reaction vessel
S-5 Moisture disengagement unit
BC-7, BC-11 Belt conveyors
SC-8 Screen
GR-9 Crusher
BC-10 Bucket elevator

SAI Process for Producing Nongranular MAP.

FERTILIZERS TECHNOLOGY

CHEM 0905554

First Semester 21/22

⊛ بالبداية كانوا يحلّوا الأمونيا بالمي ⇐ ٣٣٪ N

CHAPTER 1

UREA PRODUCTION

→ urea is the most used as N-fertilizers → Alternative of NH_3 (because of the handling)


O
C
H2N
NH2

urea → source of N

$\boxed{46N56\%}$ ⇒ which the highest source of (N) of Solid fertilizer.

Ready to handling
2) low caking
3) common between farmers

USES

→ for physical Blending
they ground it → powder.

- Urea is used as a fertilizer because of its high nitrogen content and its ability to readily convert to ammonia in the soil.
- It is incorporated into many mixed fertilizers. It can be applied alone to soil or sprayed onto foliage.
- Methylene-Urea fertilizers are created when urea is treated with formaldehyde. This process allows the nitrogen to release slowly, continuously and uniformly.
- Urea is used as a significant part of livestock food to meet protein requirements.

علف الحيوانات.

USES

→ Polymer. غراء

- Urea-formaldehyde resin is created when the two (2) components are heated in the presence of mild alkalis. They undergo a condensation reaction that combines them and forms a water-soluble polymer. This polymer is used to formulate adhesives and coating agents or when mixed with other substances to produce powders that can be molded into solid objects.

→ add urea to absorb NOx gases.

- Urea is also used in the Power Industry as a reducing agent. When it is appropriately mixed with combustion air, it reduces NOx emissions.

PHYSICAL DATA

لما حرارة عالية

- Odorless or slight ammonia odor
- pH: 7.2 (10 % water solution)

$\boxed{NH_3 + CO_2 \longrightarrow urea}$

- Decomposes at 270.8 °F (132.7 °C); decomposes into ammonia and carbon dioxide.

→ I can store it safely

- If burned, emits small amounts of nitrogen oxides.
- Solubility in water is 119g per 100g water at 77 °F (25 °C)

→ main advantage.

- Specific gravity: 1.34 at 68 °F (20 °C); heavier than water
- Molecular weight: $[CO(NH_2)_2]$ 60.06

– most Nitrogine fertilizers when it dissolve in water the (T) will ↓ because of (NH_3)

→ any reaction needed source of heat → to maintain the (T)

STORAGE AND HANDLING

→ Safe

- Urea is not listed as a Hazardous Material by the Department Of Transportation (DOT), Transport Canada (TC), International Maritime Organization (IMO) and the United Nations (UN).
- Urea is most commonly stored in silos or warehouses.
- A hopper or pneumatic truck is used in the transport and delivery of urea.

→ تعبئة وتوزيع

* مو سهل نعلمها

UREA PELLETS (SOLID)

- Urea is approximately up to 56% in terms of nitrogen content. Commonly 46% N

ADVANTAGES:

- Eliminates requirement for large storage systems and requires less handling for delivery and storage.

DISADVANTAGES:

- Adds to system complexity because of the need for de-mineralized water and these systems typically have higher operating and maintenance costs.

مشكلتها إنه بدها ضغط وحرارة عالية (elevated)

← هاي كانت سائل بعدين حولتها لـ Solid

UREA LIQUID → difficult to handling
بخزنها بياخد وسع
أكتر.

الأصل حول

~30% N

- Urea liquid is similar to Aqua Ammonia as it can be directly injected into system processes.

ADVANTAGES:

- It eliminates system complexity because there is no need to convert the urea to ammonia.

DISADVANTAGES:

عشانه ما يكوّن كريستال خاصة على حرارة عالية

- It increases product cost due to the dilution factor and requires containment areas in the event of liquid releases. + concentration of N

UREA ($CO(NH_2)_2$) PRODUCTION

very high → Rate of conversion → urea.

- The commercial synthesis of urea involves the combination of ammonia and carbon dioxide at high pressure to form Ammonium Carbamate.
- This is a fast, exothermic reaction that goes to completion.

→ concentration (endo thermic)

- The Ammonium Carbamate goes through dehydration by the application of heat to form urea and water.

التفاعل بدا
أمونيا + CO_2 ← رح يعطي Amm.carba-

هاد التفاعل exo + سريع هادا اللي بدي أفكك عناصره ال dehydration رح يفكك لليوريا + مي (endo) + ما بوصل لل completion بسرعة ← بحتاج ل recycle عشان أزيد ال yield

- This is a slow, endothermic reaction that does not go to completion.

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.

  200°C is recommand

  بس درجة الحرارة ممكن تأثر على

  material of construction

- The rate of reaction increases with temperature: it is slow at 150 °C and below and quite rapid at 210 °C.
- A satisfactory approach to equilibrium can be obtained in the temperature range of 180 - 200 °C.
- 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.

عدم
يكونه سائل.

- A further increase in pressure is not beneficial.

الزيادة عن
حد معين
ابجاب إله تأثير
مهم على العملية

- The critical ~~temperature~~ pressure is a complex function of the temperature and composition of the reactor's content.
- For example, at 150ºC 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.

requires
special Alloy + special thickwall

- At the preferred temperature of 180 - 210ºC, pressures of 140 - 250 atm are commonly used.

at this pressure it may be explosive

(*) Best operating conditions:

1) 180° — 210°C
2) 140 — 150 atm
3) conversion 50%

to get

MOLE RATIO OF NH_3:CO_2 → LR

$NH_3 : CO_2$ $1 : 2$ → But common $4 : 2$

زيادة

- 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 the percentage of HN_3 converted to urea is decreased.
- Because recycling of excess NH_3 is relatively simple, most processes use 50% or more excess ammonia.
- Today all processes account for a balance of both CO_2 and NH_3 conversion to reduce total recycling to a minimum plantwide.

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 minimizing corrosion.

AVAILABLE PROCESSES

1. Advanced cost and energy saving process (ACES)
2. Carbon dioxide stripping process → L.R → NH_3
3. Ammonia stripping process → L.R is CO_2
4. Isobaric double recycle (IDR) process

وحدة من مشاكل اليوريا الأساسية إنه التفاعل
يلّي ما بين الأمونيا وثاني أكسيد الكربون
هو إنه التفاعل ما بوصل للنهاية (reversable)
وفي جزء من الـ (AC) برجع بتفاعل Backward

AVAILABLE PROCESSES

- Urea is produced from ammonia and carbon dioxide in two equilibrium reactions:

exo ↓ (AC) ↓

$$2NH_3 + CO_2 \longleftrightarrow NH_2COONH_4\ (ammonium\ carbamate)$$ → reversable reaction

endo ↓

$$NH_2COONH_4 \longleftrightarrow NH_2CONH_2 (urea) + H_2O$$ ⇒ hygrolysis

- The urea manufacturing process, shown schematically in the next slide is designed to maximize these reactions while inhibiting biuret formation:

→ decomposing of urea to produce a new compound called (Beurite)

مشكلة أخرى →

$$2NH_2CONH_2 \longleftrightarrow NH_2CONHCONH_2 (biuret) + NH_3$$

- This reaction is undesirable, not only because it lowers the yield of urea, but because biuret burns the leaves of plants.

- This means that urea which contains high levels of biuret is unsuitable for use as a fertilizer.

1- ADVANCED COST AND ENERGY SAVING (ACES) PROCESS

- In this process the synthesis section operates at 175 bar with an NH_3/CO_2 molar ratio of 4 and a temperature of 185 to 190 ºC. (severe conditions)

→ stripping by CO_2 to recover more unreacted NH_3 in order to maximize the conversion

- The reactor effluent is stripped at essentially reactor pressure using CO_2 as stripping agent.
- The overhead gas mixture from the stripper is fed to two carbamate condensers in parallel where the gases are condensed and recycled under gravity to the reactor along with absorbent solutions from the HP scrubber and absorber.

→ synthesis stage

- The heat generated in the first carbamate condenser is used to generate 5 bar steam and the heat formed in the second condenser is used to heat the solution leaving the stripper bottom after pressure reduction.

ADVANCED COST AND ENERGY SAVING (ACES) PROCESS

- The inerts in the synthesis section are purged to the scrubber from the reactor top for recovery and recycle of NH_3 and CO_2.

high pressure

- The urea solution leaving the bottom of the stripper is further purified in HP and LP decomposers operating at approx. 17.5 bar and 2.5 bar respectively.

& low pressure

→ recovery from reactor + decomposing step

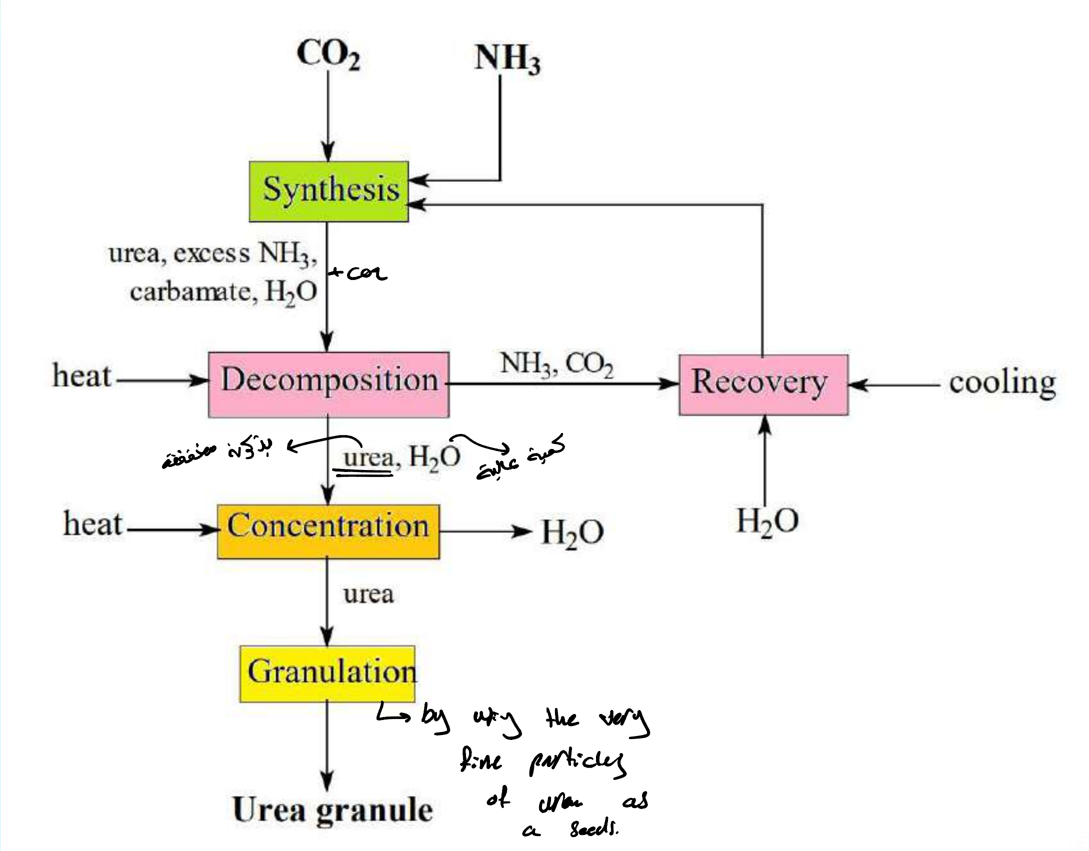
- The separated NH_3 and CO_2 are recovered to the synthesis via HP and LP absorbers.

- The aqueous urea solution is first concentrated to 88.7%wt in a vacuum concentrator and then to the required concentration for prilling or granulating.

there are two concentrator
1) pre-concentrator
2) main concentrator

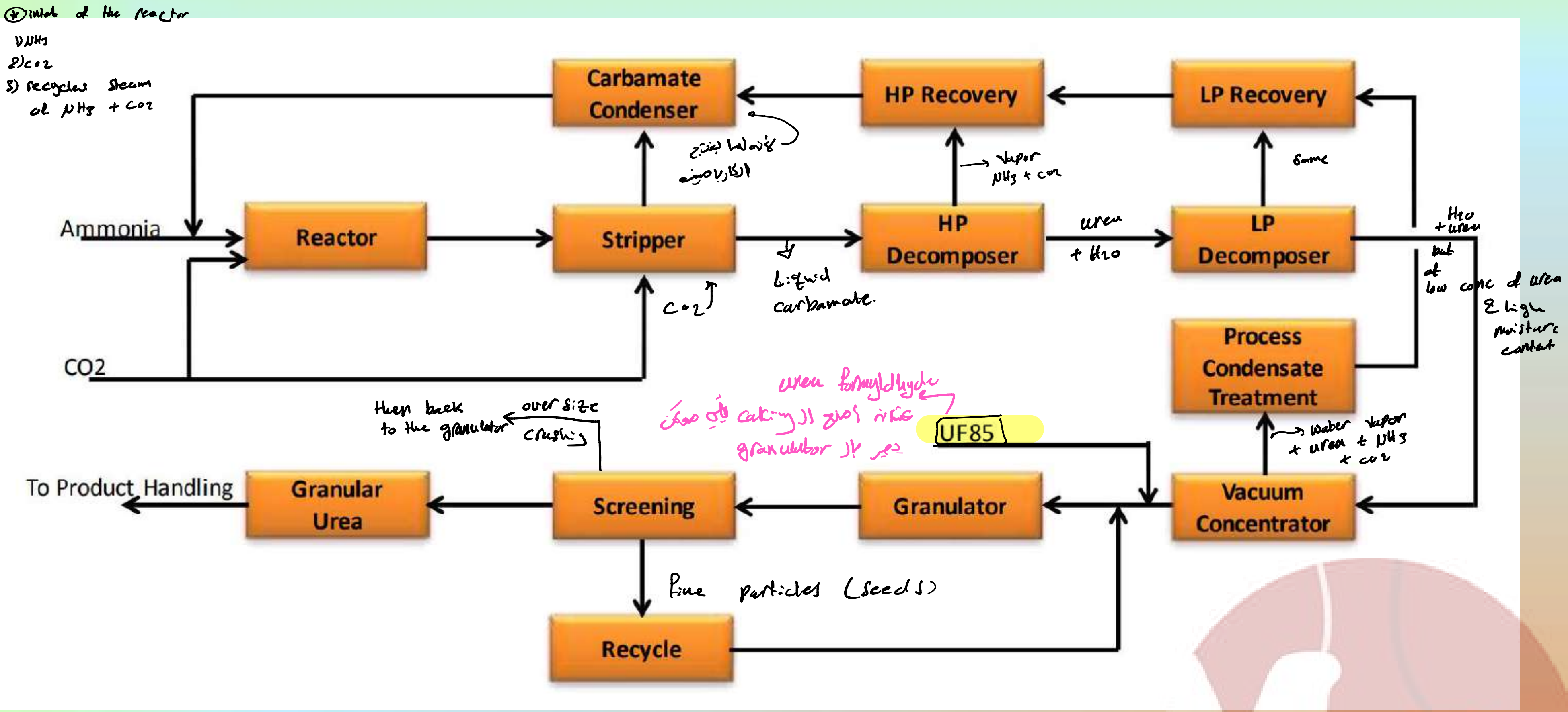
الأول بركّزه 88.7% يوريا.

SCHEMATIC REPRESENTATION OF UREA SYNTHESIS



by using the very fine particles of urea as a seeds.

SCHEMATIC REPRESENTATION OF UREA SYNTHESIS



(*) inlet of the reactor
1) NH_3
2) CO_2
3) recycled steam of $NH_3 + CO_2$

Ammonia

CO2

Reactor

Stripper

CO_2

Liquid carbamate.

Carbamate Condenser

لأنه لما ينتج الكاربامين

HP Recovery

→ vapor $NH_3 + CO_2$

HP Decomposer

urea + H_2O

LP Decomposer

same

LP Recovery

H_2O + urea but at low conc of urea & high moisture content

Process Condensate Treatment

→ water vapor + urea + NH_3 + CO_2

Vacuum Concentrator

UF85

urea formyldhyde

عشان أمنع ال caking اللي ممكن يصير بال granulator

Granulator

Screening

over size crushing

then back to the granulator

Fine particles (seeds)

Recycle

Granular Urea

To Product Handling

UREA PROCESS FLOW

Urea process is characterized by the following main process steps:

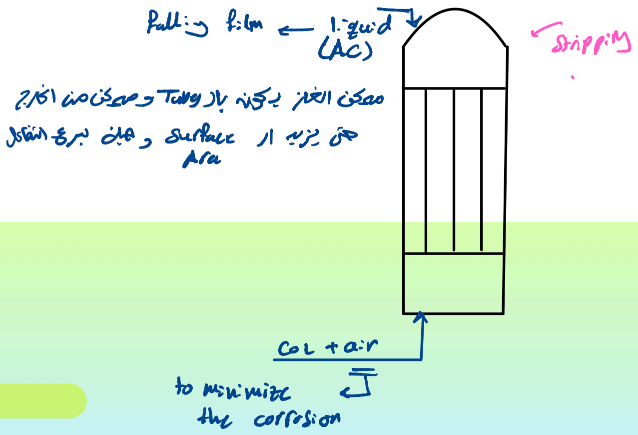
A. Urea synthesis, NH_3 & CO_2 recovery section at higher pressure

B. Urea purification along with NH_3, CO_2 recovery at two lower pressures (decomposer)

C. Urea concentration

D. Process condensate treatment ⇒ 1) to recover co_2 , NH_3
2) to utilize the heat from steam generated

E. Granulation.



UREA PRODUCTION PROCESS

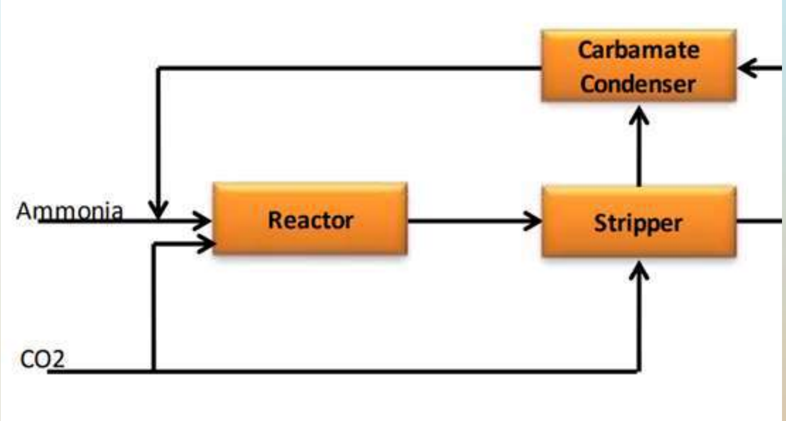
A. UREA SYNTHESIS , NH_3, CO_2 RECOVERY AT HIGH PRESSURE

- Urea is produced through the reaction of ammonia and carbon dioxide.
- The ammonia and carbon dioxide react to form ammonium carbamate, a portion of which dehydrates to urea and water.
- The fraction of ammonium carbamate that dehydrates is determined by the ratios of various reagents, the operating temperature, pressure and the residence time in the reactor.
- The reaction products leaving the reactor flow to a stripper, a vertical tube falling film decomposer in which the liquid, distributed on the heating surface as a film, flows by gravity to the bottom.

→ further conversion

UREA PRODUCTION PROCESS

- As the liquid film flows, it gets heated and decomposition of carbamate through surface evaporation takes place.
- Generated vapors (essentially ammonia and carbon dioxide) are removed by flowing to the top of the stripper.
- This gaseous stream with the recovered solution from the downstream sections is condensed and recycled to the urea reactor by means of carbamate ejector.

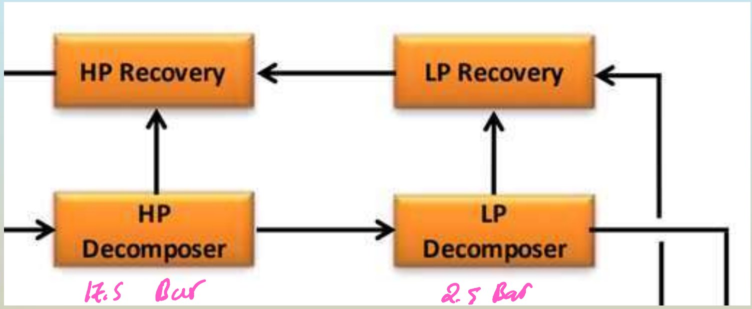


UREA PRODUCTION PROCESS

B. UREA PURIFICATION AND NH_3, CO_2 RECOVERY AT TWO LOWER PRESSURES

- Urea purification and overhead vapors recovery take place in two stages at decreasing pressures.
- The exchangers where urea purification occurs are called decomposers.
- In these equipment, the residual carbamate decomposition takes place.

further decomposition



UREA PRODUCTION PROCESS

B. UREA PURIFICATION AND NH_3, CO_2 RECOVERY AT TWO LOWER PRESSURES

- The decomposed carbamate vapors are condensed and recycled back to the synthesis loop while the inerts are washed in the washing column before being sent to the flare stack.
- The urea solution exiting this section is purified to generate Urea solution of 69-71 wt %.

UREA PRODUCTION PROCESS

C. UREA CONCENTRATION SECTION

- In order to granulate Urea, concentrated Urea solution of 97 wt% is necessary.

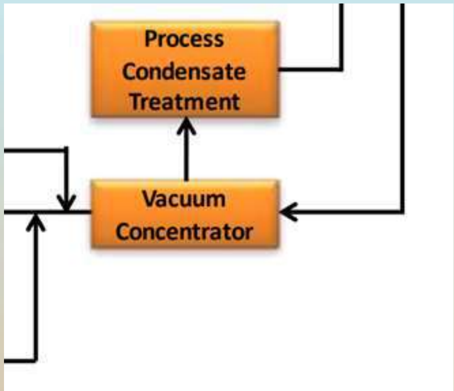
بدي أبخر ثلث الكمية عشان
أحصل على هاد الشي

- This is achieved in vacuum concentration stage.
- The Urea solution leaving the purification sections having about 70% wt Urea, along with the Urea solution recycle coming from granulation unit, is sent to the Urea concentration section.
- The concentration happens in vacuum conditions employing vacuum generation system.
- The concentrated Urea solution (~97 % by wt.), is sent to granulation unit, after mixing with UF85 additive (Urea Formaldehyde Concentrate) as anti-caking agent.

UREA PRODUCTION PROCESS

D. PROCESS CONDENSATE TREATMENT

- The process condensates containing NH_3, CO_2 and Urea coming out from vacuum system is treated in this section to ensure that the condensate is almost free-of contaminants.



- The treated process condensate is further sent to the Polishing unit.
- The NH_3 & CO_2 separated from the process condensate stripper are mixed with the Low Pressure Decomposer overhead vapors, condensed and further recycled back to the synthesis loop.

UREA PRODUCTION PROCESS

E. GRANULATION

بنرش ذاته برشاشات المحلول على الـ fine particles بالـ U

- The Urea solution is fed on the Urea seeds in the granulator bed through the multi spray nozzles to enlarge the recycle particles (seeds) through agglomeration of the solution to seeds.

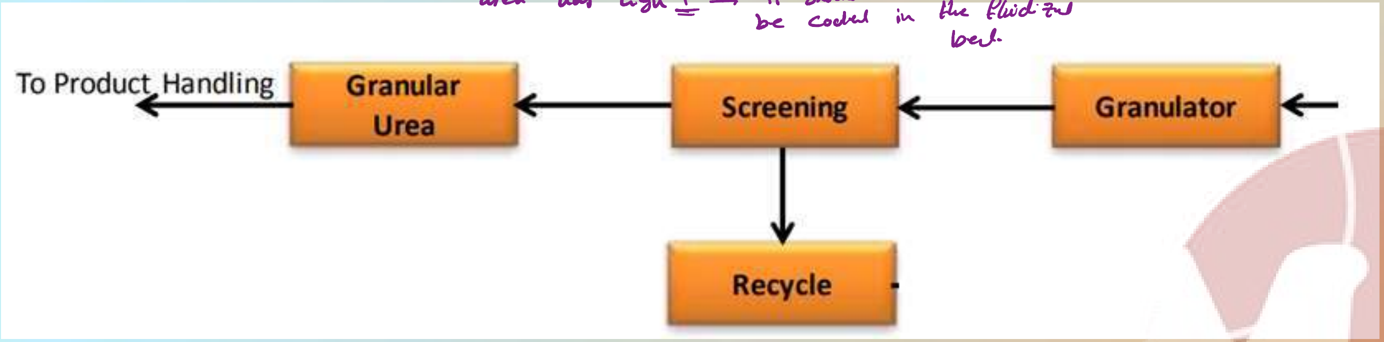
factors affects on the size of U
1) rotation speed
2) slope + inclination of the granulator
3) time for granulating

Particle size should not exceed 4mm

further.

- The water in the feed Urea solution is evaporated in the granulator.
- The enlarged granules are cooled to a suitable temperature by fluidizing air on the internal fluidized beds in the granulator.

→ at the end of the granulator, in case if the urea has high T → it should be cooled in the fluidized bed.



UREA PRODUCTION PROCESS

- Urea granules produced in the granulator are screened to separate the product size granules from over and under size granules through the double deck screen.

3 layers
1) over size
2) required size → cooling
3) under size

- Small sized granules are recycled back to the granulator as the seed and oversized granules are crushed through the double roller type crusher and recycled back to the granulator together with the under sized granules as the seeds.
- Exhaust air from the granulator and cooler is scrubbed in the wet type dust scrubber to recover the Urea dusts in the exhaust air.

why wet dust scrubber

- The water used in the dust scrubber to dissolve the urea dust is recycled back to the Urea plant to recover the Urea by evaporating the water. => then again → granulator

مشكلتها إنها مكلفة بس مكملين فيها لأنه
كمية الي يلي رح أخسرها قليلة (تجربة اقتصادياً)

عشان اليوريا عنده high
solubility
in water.

UREA GRANULE SPECIFICATIONS

Component	Concentration
Nitrogen	46 % minimum by weight
Biuret	1.0 % minimum by weight
Moisture content	0.3 % minimum by weight
Sizing	90 % 2 – 4 mm by weight

2- CARBON DIOXIDE STRIPPING PROCESS

- In all CO_2 stripping processes, ammonia and carbon dioxide are fed directly to the synthesis section.
- Optimum process conditions of approx. 140 bar and 180 °C are maintained.
- Carbon dioxide, to which a small quantity of air is added to prevent corrosion, is compressed to synthesis pressure in a multistage compressor, while the ammonia pressure is raised by a high-pressure pump.

ejector

عشان أوصل لل P المطلوب بدون رفع زائد لدرجة الحرارة.

P → Cooler → P --

- Hydrogen is removed from the fresh carbon dioxide feed stream in the H_2 removal reactor located between the compression stages.

during the multi stage compressing @ each stage H_2 must be removed.

CARBON DIOXIDE STRIPPING PROCESS

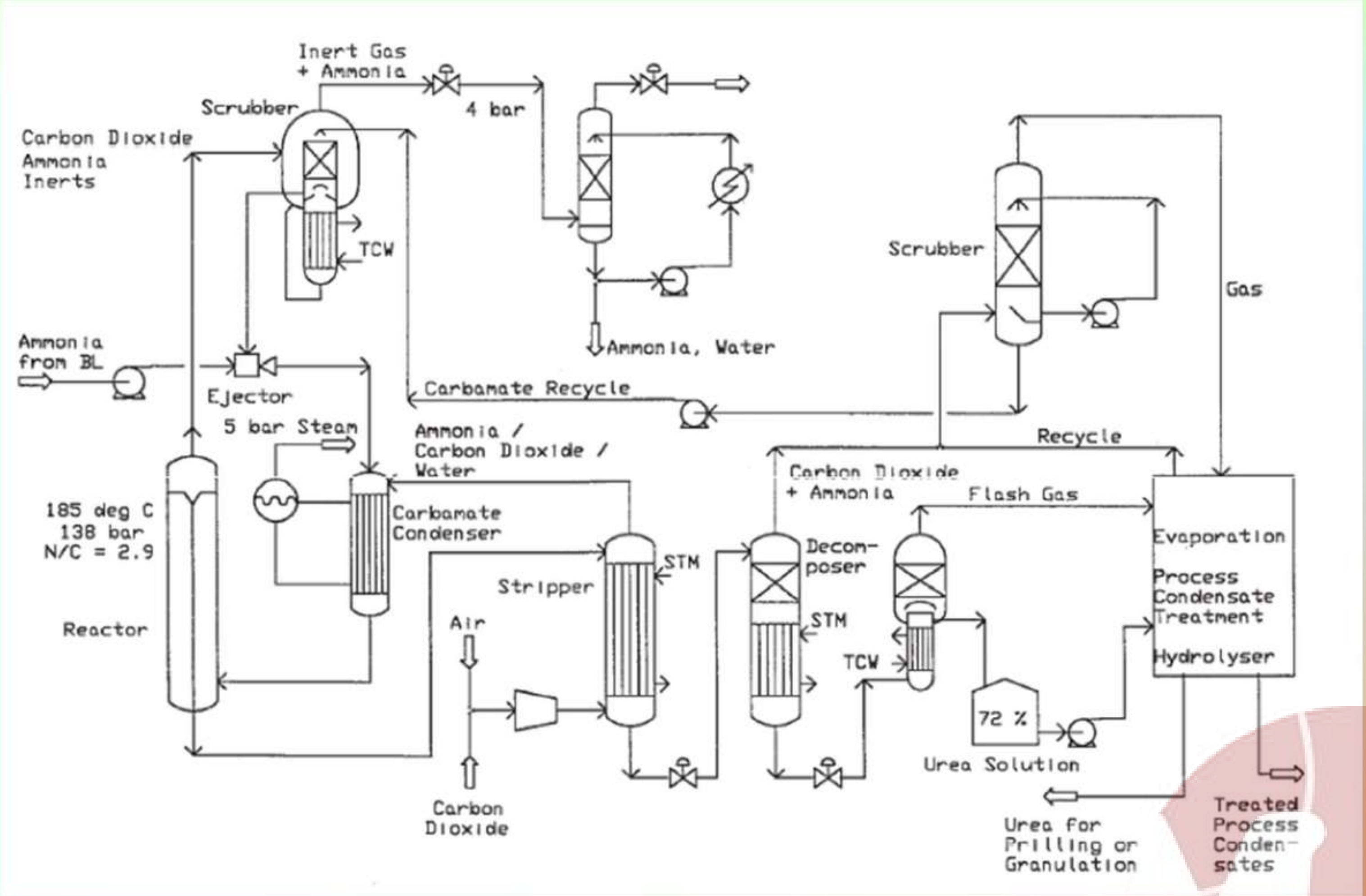
- The exothermic condensation to ammonia carbamate as well as the endothermic dehydration of the carbamate to urea and water takes place in the synthesis section.
- The reaction described results in a chemical equilibrium; part of the ammonia and carbon dioxide is not converted to urea and water.
- For this reason, the reaction mixture is subjected to a stripping process, using carbon dioxide to strip off the unreacted ammonia.
- This design feature is highly effective because of its low energy requirement and Keep retention of unconverted reactants in the synthesis section.

CARBON DIOXIDE STRIPPING PROCESS

- The stripper off gases are introduced into the high-pressure pool condenser together with the carbamate solution from the low- pressure scrubber and fresh ammonia.
- The heat released by the formation of carbamate in the high-pressure pool condenser is recovered to generate low- pressure steam.
- Subsequently, the mixture of gas and liquid flows into the urea reactor in which the main urea formation takes place.
- The liquid reaction mixture which leaves the reactor via an overflow is introduced into the stripper top. ⇒ further decomposition of AC & further conversion to urea

CARBON DIOXIDE STRIPPING PROCESS

- The exhaust gases (inert gases, NH_3, CO_2 and H_2O), which are separated from the liquid at the reactor top, are scrubbed in the high- pressure scrubber with carbamate solution from the low-pressure recirculation section.
- Thus, most of the gases are recovered and returned to the pool condenser via the high-pressure ejector.
- The non-condensables withdrawn from the high-pressure scrubber are scrubbed in a low- pressure absorber, thereby minimizing ammonia emissions.


Inert Gas
+ Ammonia
4 bar
Scrubber
Carbon Dioxide
Ammonia
Inerts
TCW
Ammonia, Water
Ammonia
from BL
Ejector
5 bar Steam
Carbamate Recycle
Scrubber
Gas
Recycle
Ammonia /
Carbon Dioxide /
Water
Carbamate
Condenser
185 deg C
138 bar
N/C = 2.9
Reactor
Stripper
STM
Air
Carbon
Dioxide
Carbon Dioxide
+ Ammonia
Decom-
poser
STM
Flash Gas
TCW
72 %
Urea Solution
Evaporation
Process
Condensate
Treatment
Hydrolyser
Urea for
Prilling or
Granulation
Treated
Process
Conden-
sates

3- AMMONIA STRIPPING PROCESS

lower pressure

- NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of 150 bar and a temperature of 180 °C.
- A molar ratio of 3.5 is used in the reactor giving a CO_2 conversion of 65%. The reactor effluent enters the stripper where a large part of the unconverted carbamate is decomposed by the stripping action of the excess NH_3.
- Residual carbamate and CO_2 are recovered downstream of the stripper in two successive stages operating at 17 and 3.5 bar respectively.

AMMONIA STRIPPING PROCESS

- NH_3 and CO_2 vapors from the stripper top are mixed with the recovered carbamate solution from the High Pressure (HP)/Low Pressure (LP) sections, condensed in the HP carbamate condenser and fed to the reactor.
- The heat of condensation is used to produce LP steam.
- The urea solution leaving the LP decomposition stage is concentrated in the evaporation section to a urea melt.

4- ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

$\Rightarrow$ Combined method
between NH_3 & CO_2 stripping
@ high $\underline{\underline{P}}$

- In this process reactor pressure is about 200 bar, the molar NH_3/CO_2 ratio is 4.5 and the reactor effluent temperature 185 to 190 °C.
- The conversion rates to urea in the reactor are 71% for CO_2 and 35% for NH_3 .
- Unconverted materials in the effluent from the reactor bottom are separated by heating and stripping in two consecutive decomposers operated at reactor pressure and heated by 25 bar steam.
- Carbamate is decomposed/stripped by NH_3 in the first stripper and the remaining NH_3 is evolved in the second stripper using CO_2 as stripping agent.

ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

- The overheads from stripper 1 are fed directly to the reactor and the overheads from stripper 2 are recycled to the reactor via the carbamate condenser. → then to the reactor.
- Heat of condensation is recovered as 6 bar steam and used downstream in the process.
- Most of the CO_2 fed to the plant goes to the second stripper and the remainder goes directly to the reactor for fine temperature control when needed.
- About 40% of the NH_3 goes to the first stripper and the remainder to the upper and lower sections of the reactor in two streams.

ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

- Unconverted carbamate, NH_3 and CO_2 leaving the stripper with the urea solution are recovered/vaporized in two successive distillers operating at 20 bar and 6 bar respectively.
- The vapors are condensed and recycled to the synthesis after condensation to carbamate solution
- The latent heat present in the 20-bar stage off gases is used as a heat source for the evaporation of water in the first stage evaporator.
- Further concentration of the urea solution leaving the LP decomposition stage is carried out in two vacuum evaporators in series, producing urea melt for prilling or granulating.