Chapter 3
Fertilizer Raw Materials

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Availability and Sources of Raw Materials

- **The primary raw materials for nitrogen fertilizers are:**
  - ✓ **Natural gas**
  - ✓ **Naphtha**
  - ✓ **Fuel oil**
  - ✓ **Coal**
- **The manufacture of phosphate fertilizer most often requires:**
  - ✓ **Sulfur and phosphate rock.**
- **Naturally occurring potassium salts form the basis of the production of most potash fertilizers**

- **Natural gas, naphtha, fuel oil, and sulfur are substances or mixtures to which clearly definable specifications can be applied.**
- **Compositions may vary little regardless of where they are obtained or produced.**
- **Potash ores vary greatly in composition from locality to locality.**
- **The end products of mining, beneficiation, and processing generally have relatively constant compositions.**

- **Phosphate rock and coal are products that can vary significantly in composition and other characteristics.**
- **These variations can have significant effects on the processes used to upgrade the as mined ores or on the processes in which they are used to manufacture fertilizers from beneficiated products.**

- **A fertilizer plant or power plant may be designed to use a particular phosphate rock or coal.**
- **Changes in the sources of raw materials may adversely affect processing and lead to lower efficiency, the loss of output, and/or serious operational difficulties.**
- **Coal and phosphate rock supplies are generally secured with medium-to-long term contracts.**
- **Plant designs should allow for variations in the quality of both phosphate rock and coal.**

Nitrogen Feedstocks

- **Ammonia is a basic building block for most nitrogen fertilizers.**
- **In ammonia manufacture, nitrogen is actually fixed from the earth’s atmosphere.**
- **At about 78%, nitrogen is the most common gas in the earth’s atmosphere.**
- **Hydrocarbon and coal feedstocks for ammonia manufacture perform a dual role as sources of both hydrogen and energy.**
- **Water also contributes a portion of the hydrogen needed for ammonia manufacture.**

- **It is widely accepted that plankton living in ocean's water were the sources of nearly all petroleum.**
- **Fine grained muds rich in planktonic remains are deposited offshore.**
- **Slow decomposition by anaerobic bacteria turns the planktonic remains into an amorphous material called sapropel.**
- **As the muds are buried and form shales and mudstones, the sapropel is converted to petroleum compounds by biologic, chemical, and physical processes.**

- **Young petroleum tends to have compounds of higher molecular weight and produces heavy crudes.**
- **When deeper burial, increased temperature and pressure break down the organic structures into lighter and simpler hydrocarbon compounds.**
- **At great depth, methane may be the only remaining hydrocarbon.**
- **Crude oils are separated into components such as gasoline, naphtha, and fuel oils by distillation.**

- **Natural gas will be the dominant feedstock for the production process of ammonia.**
- **Coal use will decline because of environmental aspects and high plant costs.**
- **Oil and naphtha will continue to be used as feedstocks primarily in those regions or areas that do not have natural gas reserves and are unable to receive natural gas by pipeline.**

Phosphate Rock

- There are two main types of phosphate rock deposits:
    1. Sedimentary
    2. Igneous
- Sedimentary phosphate deposits are exploited to produce more than 80% of the total world production of phosphate rock.
- Igneous phosphate deposits are often associated with carbonatites and/or alkalic (silica deficient) intrusions.

- **Sedimentary rock** is a type of rock that is formed by sedimentation of material at the Earth's surface and within bodies of water.
- Sedimentation is the collective name for processes that cause mineral particles to settle and accumulate or precipitate from a solution.

- **Igneous** derived from the Latin word *igneus* meaning of fire, from *ignis* meaning fire.
- Igneous rock is formed through the cooling and solidification of magma or lava.
- Igneous rock may form with or without crystallization, either below the surface or on the surface as rocks.

- **Sedimentary phosphate rocks occur throughout the geological time scale.**
- **They exhibit a wide range of chemical compositions and great variations in physical form.**
- **Insular deposits are a type of sedimentary deposit associated with oceanic islands.**
- **Insular deposits have been an important source of phosphate rock for more than 100 years.**
- **However, intensive exploitation has caused several deposits to be totally depleted.**

- Depending on their origin, phosphate rock have widely different mineralogic, textural, and chemical characteristics.
- Under conditions near the surface of the earth, a wide spectrum of secondary minerals can form that may be common to both igneous and sedimentary phosphate rocks.
- These minerals include iron, aluminum phosphates, clays, and iron oxides.

Potash

- **Potassium salts produced and used as fertilizers are generally referred to as potash.**
- **A term that originated from the burning of wood in pots or retorts to obtain potassium salts as pot-ash.**
- **Large, deeply buried potash deposits are mainly associated with marine evaporite sequences and less commonly with non-marine evaporites throughout the world.**

- **The most abundant potash mineral in commercial potash deposits is sylvite (KCL).**

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Buried Potash Deposits

- **The potash deposits of the world vary widely in their size, grade, and factors that impact economics, such as their location and the cost of mining and processing.**
- **Mining costs depend upon capacity, depth to the ore, thickness and uniformity of the potash bed, dip of the beds, strength and integrity, danger of water flooding, amount of impurities present.**

Brine Potash Deposits

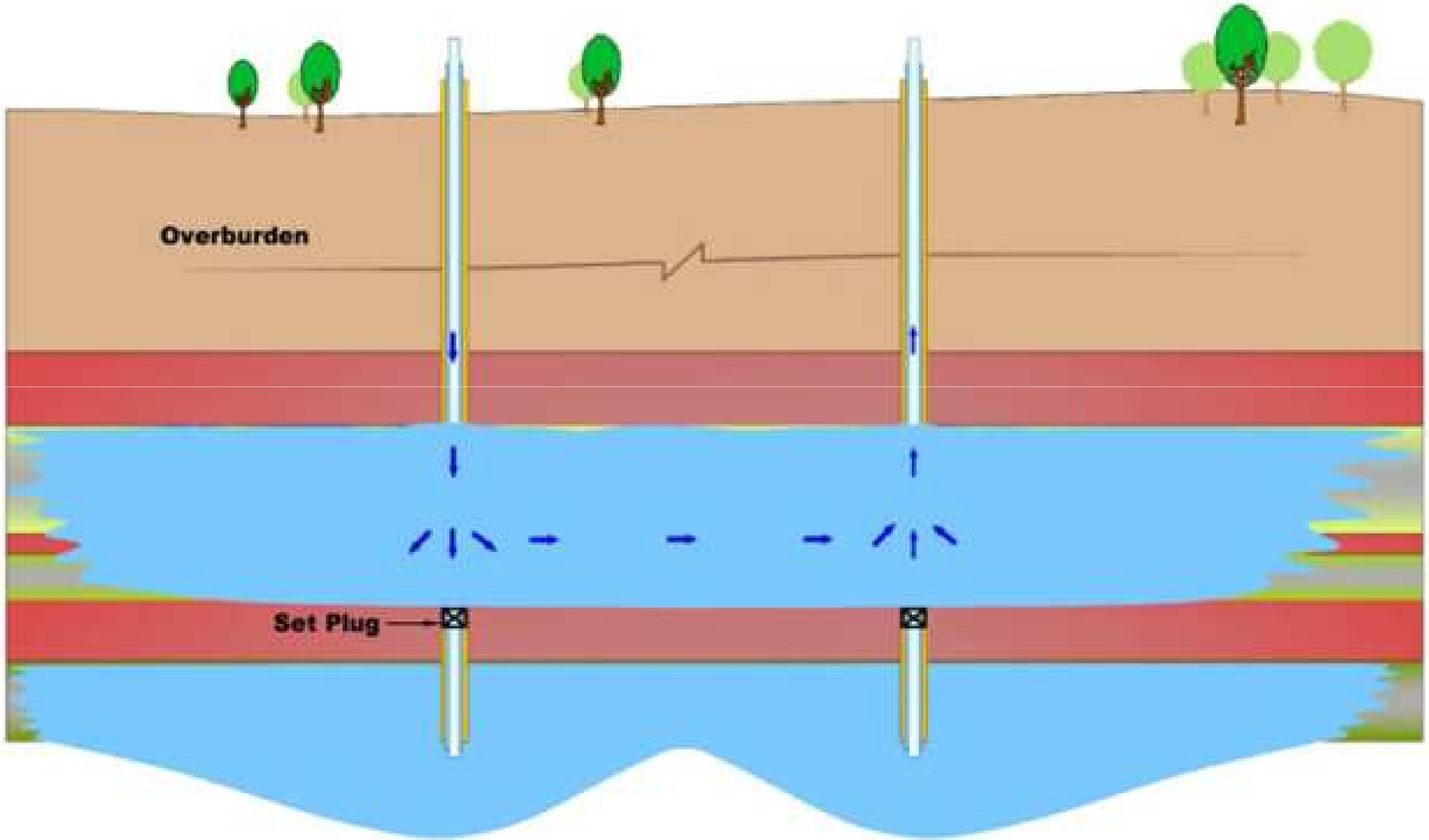
- **In addition to the buried potash deposits, there are brine or surface potash deposits in North America, South America, and Asia/Middle East.**
- **The Dead sea is 76 km long and 16 km wide; it has an area of 930 km^2 and a mean depth of 329 m.**
- **It contains an estimated 47 x 10^9 tones of salts, of which perhaps 1 x 10^9 tones is KCl.**
- **The brine in the Dead Sea has a high $MgCl_2$ and $CaCl_2$ content, and this composition is quite unusual.**

Potash Mining

- **There are two basic types of potash mining:**
- **Conventional mining, which encompasses several standards methods, modified as necessary for specific situation.**
- **Solution mining where pipes inject water to withdraw brine from the bottom. This method take advantage of a major thickening mines of about 1650m depth. Brine from the well field is evaporated in triple effect evaporators to crystallize dissolved halite, and the brine is then cooled to crystallize the potash salts.**

Conventional mining

Solution mining



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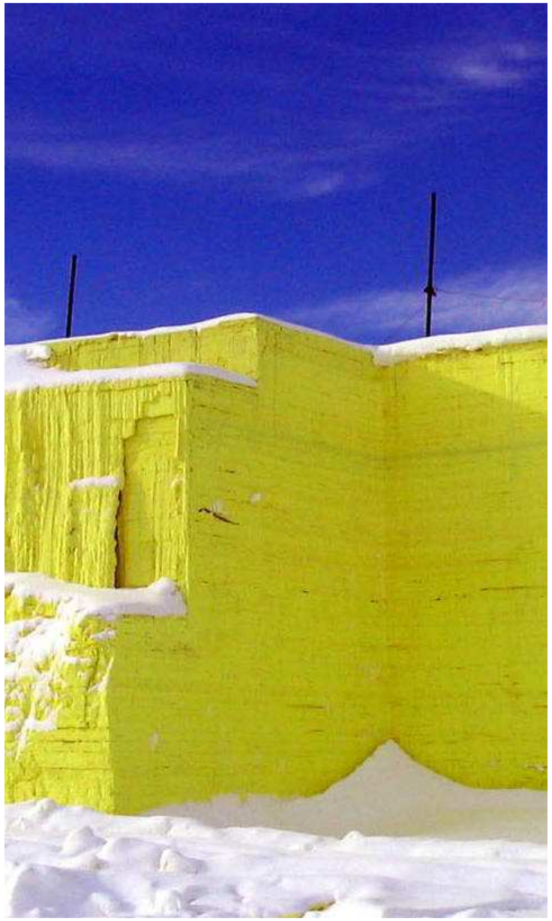
Sulfur

- **Sulfur is one of the more common constituents of the earth's crust and can be ranked as the 16th or 17th most abundant element.**
- **Sulfur naturally occurs as elemental sulfur, metal sulfides in coal and mineral ores, sulfates, hydrogen sulfide in natural gas, and complex organic sulfur compounds in crude oil and coal.**
- **All of these various forms of sulfur are used as sulfur sources, but the most important sources are elemental sulfur, hydrogen sulfide in natural gas, and iron pyrites.**



Iron Pyrite

Elemental Sulfur

Hydrogen Sulfide

Sulfur

- **Approximately 80-85% of the sulfur that is produced is used to manufacture sulfuric acid.**
- **Approximately half of this is used in fertilizer production, mainly to convert phosphates to water soluble forms.**

Sulfur Sources

- **Native sulfur or brimstone, sulfur naturally occurring in the elemental form, is found in several geologic environments.**
- **During volcanic activity, sulfur may be sublimated directly around volcanic vents.**
- **Sulfur production from volcanic deposits is generally limited.**
- **Native sulfur may be formed from gypsum and anhydrite in evaporative deposits through the movement of saline waters and hydrocarbons and the influence of anaerobic bacteria.**

Sulfur Production

1. **Production from native sulfur deposits.**
2. **Sulfur recovery from gases.**
3. **Sulfur production from sulfide ores and sulfates.**

- **It is difficult to make a significant estimate of the total world reserves of sulfur because of the wide variety of forms in which it occurs.**
- **Total resources are probably about 5 to 7.5 x 10^{11} tones, of which more than 99% is present in coal, oil shales, and gypsum.**

	Reserves[a,b]	Reserve Base[a,c]
	(tonnes x 10^3)	
United States	140,000	230,000
Canada	158,000	330,000
China	100,000	250,000
France	10,000	20,000
Iraq	130,000	500,000
Italy	10,000	15,000
Japan	5,000	15,000
Mexico	75,000	120,000
Poland	130,000	300,000
Russia	NA	NA
Saudi Arabia	100,000	130,000
Spain	50,000	300,000
Ukraine	NA	NA
Other Countries	470,000	1,300,000
World Total	**1,400,000**	**3,500,000**

	1992		1993		1994	
	All Forms	Elemental	All Forms	Elemental	All Forms	Elemental
	(thousand tonnes S-equivalent)					
Belgium/Lux	330	150	335	156	341	160
Finland	617	46	612	32	636	40
France	1,232	988	1,326	1,073	1,369	1,084
Germany	2,140	1,350	2,206	1,451	2,131	1,400
Greece	140	130	100	100	80	80
Italy	630	310	639	350	590	345
Netherlands	401	273	441	318	440	323
Norway	229	13	144	16	105	15
Spain	889	159	822	180	798	160
Sweden	183	54	157	55	146	50
United Kingdom	232	165	248	183	219	154
West Europe[a]	**7,114**	**3,715**	**7,119**	**3,991**	**6,946**	**3,889**
South Africa	575	167	618	171	572	190
Africa[a]	**802**	**170**	**801**	**174**	**765**	**193**
Canada	7,406	6,521	8,474	7,567	8,993	8,048
United States	11,604	9,368	11,779	9,568	12,252	10,101
North America	**19,010**	**15,889**	**20,253**	**17,135**	**21,245**	**18,149**
Brazil	301	77	270	77	287	85
Chile	353	24	372	1	489	-
Mexico	1,893	1,593	1,252	912	1,212	860
Latin America[a]	**2,917**	**1,969**	**2,358**	**1,340**	**2,485**	**1,328**
Iran	763	763	881	881	935	935
Iraq	375	375	375	375	375	375
Kuwait	-	-	246	246	490	490
Saudi Arabia	1,650	1,650	1,650	1,650	1,680	1,680
Turkey	177	78	178	71	220	65
Middle East[a]	**3,200**	**3,101**	**3,689**	**3,582**	**4,262**	**4,107**

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