

Fertilizer Feedstocks and Raw Materials

For production of various fertilizers, certain feedstocks and raw materials are required which are either available locally or they are transported from other places within the country or imported from global suppliers.

Raw Materials for Nitrogen Fertilizers

The most important raw material required for production of nitrogen fertilizers is ammonia which provides nitrogen to all the nitrogen fertilizers and nitrogen based compound fertilizers. Requirement of other materials depends on the choice of nitrogen fertilizer to be produced. For instance, urea production requires carbon dioxide and ammonia, whereas manufacture of ammonium sulphate requires sulphuric acid which is produced from sulphur.

Feedstocks for Ammonia

Ammonia is the key input required for manufacture of nitrogen fertilizers and nitric acid. It is produced by synthesis of nitrogen and hydrogen gases under high pressure and temperature. Nitrogen gas is available in abundance (78%) in the atmosphere. All the nitrogen required in ammonia synthesis is derived from air. The hydrogen gas is obtained from various raw materials such as natural gas, naphtha, oil or coal. These raw materials are called as “feedstock”. The feedstocks for ammonia plants may broadly be grouped into three categories, viz. gaseous, liquid and solid.

Gaseous feedstocks: This category includes natural gas, refinery gas and coke oven gas. These feedstocks have lower calorific value but are the most suitable raw materials due to their high H_2/C ratio (2 for natural gas) and higher conversion efficiency.

Natural gas occurs either in association with crude petroleum or as non-associated gas. Accordingly, it is known as associated gas or free gas. The recoverable reserves of natural gas in India have been estimated as over 700 billion m^3 . New locations of the gas reserves are also being discovered.

Table 2.2 Typical analysis of fuel oil and low sulphur heavy stock (LSHS) from Indian refineries

<i>Property</i>	<i>Fuel oil</i>	<i>LSHS</i>
Specific gravity	0.896-0.928	0.92
Sulphur (%)	1.57-2.07	0.91
Ash (%)	0.018-0.03	–
Carbon (%)	84.67-86.64	87-88
C/H ratio	6.33	7.72
Calorific value (kcal/kg)	9421-9932	10,360

Liquefied petroleum gas is mainly propane and butane separated by liquefaction from natural gas or refinery gas. Its impurities are olefins, COS and other sulphur compounds.

Use of water as a source of H₂ gas requires availability of abundant cheap electricity for its electrolysis. The fertilizer plant at Nangal, Punjab (National Fertilizers Ltd.) was initially planned to obtain H₂ from electrolysis of water but shortage of power in Bhakra grid compelled to switch over to liquid feedstock.

Solid feedstocks: This category includes coal, coke, lignite, etc. The solid raw materials have the lowest calorific value and the lowest H₂/C ratio. The thermal efficiency of conversion of these materials into synthesis gas (3H₂ + N₂) is poor and they require large and elaborate processing and purification systems to handle the oxides of carbon. The disposal of the ash is another problem.

India has a large coal reserve estimated at 211.6 billion tonnes (Table 2.3), of which 77% is located in three states of Orissa, Jharkhand and Chhattisgarh. The proven minable reserves are estimated at 72.7 billion tonnes. The coal mined from most of the Indian coalfields has relatively high ash content (38-44%). Typical analysis of non-coking coal is shown in Table 2.4. Also the process of gasification of coal or coke is not very flexible. For these reasons ammonia synthesis plants based on solid feedstocks are restricted to places where their cost is very low in comparison with liquid or gaseous raw materials.

In India, three large size coal based fertilizer plants have been established at Ramagundam (Andhra Pradesh), Talcher (Orissa) and Korba (Chhattisgarh).

Table 2.3 Coal reserves in India

<i>State</i>	<i>Reserve (million tonnes)</i>
Andhra Pradesh	13.5
Jharkhand	69.1
Madhya Pradesh and Chhattisgarh	43.4
Maharashtra	7.1
Orissa	50.4
Uttar Pradesh	1.1
West Bengal	25.9
Others	1.1
Total	211.6

Table 2.4 Analysis of non-coking coal

<i>Constituent</i>	<i>Value (%)</i>
Moisture	85–1.76
Ash	38.8–43.7
Sulphur	–
Volatile matter	16–19
Fixed carbon	35.8–43.3
Calorific value (kcal/kg)	3994–4395

Raw Material for Phosphate Fertilizers

The essential raw material for phosphate fertilizer is rock phosphate which provides phosphorus or P_2O_5 . Sulphuric acid, nitric acid or electric energy are other essential materials or inputs required for manufacture of phosphate fertilizers from rock phosphate. Sulphuric acid is produced from sulphur whereas nitric acid is obtained from the oxidation of ammonia.

ROCK PHOSPHATE

Natural Phosphate Deposits

The original source of phosphorus in the manufacture of phosphate fertilizers in early days was bones, but the supply was soon exhausted. Today, rock phosphate is the only important raw material for phosphate fertilizers.

The earth is richly endowed with phosphate. There are two types of phosphate deposits: igneous and sedimentary. Both have essentially the same phosphate mineral—calcium phosphate of apatite group. Igneous deposits occur in veins and replacement bodies commonly associated with magnetite. Such deposits are not much extensive in size and number and not so easily mined and processed as sedimentary deposits. Major igneous deposits are located in Russia, South Africa, Brazil, Uganda, Botswana and Sri Lanka. About 15% of the world phosphate production is from igneous deposits.

Important phosphate deposits of the world are of sedimentary origin. These deposits are also referred to as *phosphorite*. About 95% of the world phosphate reserve and 82% of the commercial deposits are sedimentary. Major sedimentary deposits are located in USA, Australia, Togo, Morocco, Algeria, Jordan and Asian countries.

Guano is also sedimentary deposit which originated chiefly through accumulation of excrements of sea fowl and such deposits are largely confined to islands in southern latitudes. Some guano deposits are found in Chile, Peru, Seychelles and Philippines but much of the material has been exploited.

World Reserve of Rock Phosphate

In spite of the universal distribution of phosphate in nature, 99% of the world production of phosphate is contributed by 17 major countries and only three countries: China, USA and Morocco

produce more than 60%. Estimates of worldwide reserves are placed at 50 billion tonnes (Table 2.5) and annual mine production of rock phosphate in 2006 was 145 million tonnes.

With increasing demand for phosphate fertilizers, the production of rock phosphate will have to be stepped up. Since phosphate is non-renewable natural resource, the exploitation of the deposits should be done in keeping with the future requirements.

Table 2.5 World reserve and production of rock phosphate (million metric tonnes)

<i>Country</i>	<i>Reserves</i>	<i>Reserve base</i>	<i>Production (2006)</i>	<i>% of world mine production</i>
China	6600	13,000	32	22.1
USA	1200	3400	30.7	21.2
Morocco	5700	21000	25.3	17.4
Russia	200	1000	11	7.6
Tunisia	800	600	8.4	5.8
Jordan	900	1700	6.4	4.4
Brazil	260	370	5.5	3.8
Syria	100	800	3.6	2.5
Israel	180	800	3.0	2.1
Egypt	100	760	2.74	1.9
South Africa	1500	2500	2.6	1.8
Australia	77	1200	2.05	1.4
Senegal	50	160	1.5	1.0
Togo	30	60	1.2	0.8
Canada	25	200	1.0	0.7
Other countries	800	2200	6.7	4.6
World total	18000	50,000	145	100

Phosphate Deposits in India

Considering the increasing need of phosphate fertilizers in India, the reserves of rock phosphates known to date are very meagre. The total reserve of phosphates of all categories in the country is estimated at 145 million tonnes. The major deposit of 79 million tonnes is found at Jhamarkotra near Udaipur in Rajasthan. Other deposits are located at Jhabua and Hirapur in Madhya Pradesh, Mussoorie in Uttarakhand and Purulia in West Bengal. Of these, only the deposits at Jhamarkotra (Udaipur), Jhabua and Hirapur are of high quality (30% P₂O₅), whereas all other deposits have poor quality ore with low phosphorus content (15-20% P₂O₅). Small quantities of rock phosphate deposits have also been discovered at Kashipatnam (Andhra Pradesh), Singhbhum (Jharkhand), Tiruchirapalli (Tamil Nadu) and Lalitpur (Uttar Pradesh).

At present, mining is being done at Udaipur, Jhabua and Purulia with total production of about 1.5 million tonnes annually.

Mining of Rock Phosphate

Depending on the thickness of overburden and depth of the phosphate matrix either strip mining or underground mining is followed.

Strip mining: This is a surface mining method which is also called as open cut method. In this method overburden is first removed by mobile dragline excavators or power shovels or caterpillar powered scrapers. The phosphate matrix is dug by separate dragline scraper and deposited in sumps where it is broken up.

Underground mining: When phosphate matrix lies beneath a very deep or hard rock overburden tunnels are made into the hillside. The phosphate matrix is either drilled or blasted and taken out by conveyors. Underground mining is quite expensive, hence less popular.

Beneficiation of Rock Phosphate

Fertilizer industry requires a high grade rock phosphate in order to produce fertilizers of desired quality. For instance, superphosphate industry would not use a rock phosphate containing less than 30% P_2O_5 (13.1% P). Generally, rock phosphate with +31% P_2O_5 , Fe_2O_3 and Al_2O_3 below 2%, silica below 5%, fluorine 3.5%, MgO 0.5% and chlorine below 100 parts per million (ppm) is considered as good raw material for production of phosphate fertilizers. If the rock phosphate obtained from the mine is of high grade, it is shipped as such to the fertilizer industry. It is however often poor in quality containing 15-20% P_2O_5 and a number of impurities. Such ores are upgraded by beneficiation process. Beneficiation is a process of ore dressing in order to remove impurities and thereby to improve the grade of the ore. The impurities are collectively referred to as *gangue*. Main impurities are iron and aluminium oxides, calcium carbonate, silica, clay, etc. These impurities not only lower the grade of the ore but also consume substantial quantity of acid or energy while converting the rock phosphate into finished products. For example, iron and aluminium oxides would cause formation of undesirable phosphate compounds in the product. If silica content is too high, the requirement of power for grinding would be more. Presence of free carbonates (usually $CaCO_3$) would increase the acid consumption. For these reasons, the impurities must be reduced to the acceptable limits by the beneficiation process. Beneficiation would also ensure consistency of the product grade. There are three main processes of beneficiation of rock phosphate: washing, flotation and calcination.

Washing: Crushing or grinding is the first step which reduces the size of pebbles and nodules, and releases impurities. This is followed by water washing to remove soluble impurities such as sodium chloride, free lime and fine materials like clays, silica and other debris. A sizing operation may follow the washing step. Wet sizing as well as dry sizing is practised.

Flotation: Generally, two stages of flotation are used to obtain high grade rock phosphate. In the first stage, deslimed feed (after removal of clay) is subjected to fatty acid or amine flotation for phosphate enrichment. This is followed by amine or cationic flotation of the residual silica. The flotation agent selectively films the desired particles leaving others in the suspension. In the flotation cell, air is drawn by agitation and air bubbles attach to the filmed particles which then float to the surface. The froth is mechanically skimmed off.

SULPHUR

Sulphur is the essential raw material for sulphuric acid. About 80 to 85% of the world's sulphur production is used to manufacture sulphuric acid. It is also used for direct application as soil amendment to alkali (sodic) lands and source of nutrient to sulphur deficient soils.

Sources of Sulphur

There are two principal sources of elemental sulphur:

- the natural deposits of sulphur; and
- sulphur recovered from sour gas, petroleum refining or metallurgical operations.

Sulphur Deposits in the World

Natural deposits of elemental sulphur are found in two forms. Either they occur in dome-like formations in association with gypsum deep below the earth surface or they are deposited on the earth surface by volcanic activity. Dome sulphur deposits occur along the coast of the Gulf of Mexico in USA and Mexico. Elemental sulphur is found near hot springs and volcanic regions in many parts of the world. Such volcanic deposits are currently mined in Indonesia, Chile and Japan. Sicily is also famous for its sulphur mines. Significant deposits of elemental sulphur also exist in evaporates in Eastern Europe and western Asia.

The largest world reserves of sulphur are in Iraq, Canada, Spain, China, Poland and the United States. It is estimated that the world resources in terms of sulphur associated to oil, natural gas, metallic sulphides, evaporates and deposits of volcanic origin may amount to 5 billion tonnes.

Method of Extraction

The world production of sulphur in 2006 was approximately 66.5 million tonnes. The major producers are the United States (14%), followed by Canada (13.5%), Russia (10.5%) and Japan (5%).

There are two principal methods of producing elemental sulphur:

- mining of the natural deposits; and
- recovery from sour gas, petroleum refining or metallurgical operations.

Sulphur Mining

Sulphur is extracted from the natural deposits mainly by two processes: the Sicilian process and the Frasch process. The Sicilian process, which was first used in Sicily, was used in ancient times to get sulphur from rocks present in volcanic regions. In this process, the sulphur deposits are piled and stacked in brick kilns built on sloping hillsides, and with airspaces between them. Then powdered sulphur is put on top of the sulphur deposit and ignited. As the sulphur burns, the heat melts the sulphur deposits, causing the molten sulphur to flow down the sloping hillside. The molten sulphur then can be collected in wooden buckets.

The second process used to obtain sulphur from underground deposits is the Frasch process. In this process, three concentric pipes are used: the outermost pipe contains superheated water, which

POTASH

Raw Materials for Potash Fertilizers

The natural salt deposits of potash and brines in the salt lakes provide the raw material for processing into potash fertilizers. About 95% of the global potash supply is used for fertilizer industry.

Potash Resources and Reserves

Potassium occurs abundantly in nature. It is the 7th most common element in the earth's crust which contains 2.4% potassium. Certain clay minerals associated with heavy soils are rich sources of potassium, containing as much as 17% potassium. Sea water typically contains 390 mg K/L representing a huge total amount of the element globally.

Large potash bearing rock deposits occur in many regions of the world deriving from the minerals in ancient seas which dried up millions of years ago. Potassium deposits occur as beds of solid salts at varying depths below earth's surface and also as brines in drying lakes and sea. At present underground potassium salt deposits are the major raw materials for fertilizer production and account for over 90% of the world potassium reserve. Potash for fertilizer is mainly derived from this potash rock, requiring only separation from the salt and other minerals and physical grading into a form suitable for fertilizer manufacture or farm spreading.

Principal potash deposits and annual production in the world are listed in Table 2.7. Total potash deposits reserves are estimated as 8265 billion tonnes with a reserve base of 16545 billion tonnes. The largest reserve of potash salts is found in Canada. Nearly half of the world potash reserve occurs in Canada alone. Russia has also a large deposit of potash and ranks second in the world. So far, there are no known deposits of potassium in India, though it is fourth largest consumer of potassium fertilizers in the world.

Table 2.7 World mine production, reserves and reserve base potash

<i>Country</i>	<i>Mine production in 2006 (million tonnes)</i>	<i>Reserve (million tonnes)</i>	<i>Reserve base (million tonnes)</i>
United States	1,200	90,000	300,000
Belarus	4,000	750,000	1,000,000
Brazil	405	300,000	600,000
Canada	10,200	4,400,000	9,700,000
Chile	350	10,000	50,000
China	700	8,000	450,000
Germany	3,660	710,000	850,000
Israel	2,100	40,000	580,000
Jordan	1,200	40,000	580,000
Russia	5,300	1,800,000	2,200,000
Spain	500	20,000	35,000
Ukraine	65	25,000	30,000
United Kingdom	600	22,000	30,000
Other countries	—	50,000	140,000
World total	30,280	8,265,000	16,545,000

Brine Sources of Potash

Relatively high concentration of potassium salts is present in brines of some salt lakes, Dead Sea and underground wells. Commercially important salt lakes for potassium extraction are Searle's Lake, California; the Great Salt Lake, Idaho; and the Dead Sea. Brines contain mainly potassium chloride with several impurities such as sodium chloride, sodium sulphate, calcium chloride, magnesium chloride, etc. Great Salt Lake of Utah and Searle's Lake of California are two important salt lakes providing brines for extraction of potassium chloride. Typical brine composition of Searle's Lake, California (USA) is given in Table 2.9.

Table 2.9 Typical brine composition of Searle's Lake, California

<i>Component</i>	<i>Formula</i>	<i>Upper structure</i>	<i>Lower structure</i>
Potassium chloride	KCl	5.02	2.94
Sodium chloride	NaCl	16.06	15.51
Sodium sulphate	Na ₂ SO ₄	6.75	6.56
Sodium carbonate	Na ₂ CO ₃	4.8	6.78
Sodium tetraborate	Na ₂ B ₄ O ₇	1.63	1.96
Potassium bromide	KBr	0.12	0.08
Sodium sulphide	Na ₂ S	0.08	0.04
Phosphates (as P ₂ O ₅)		0.07	0.04
Lithium (Li ₂ O)		0.15	0.006

Dead Sea is also a salt lake which lies in the Jordan Rift Valley between Israel and the West Bank in the west, and Jordan in the east. It is 422 metres below sea level and is 378 m deep, the deepest hypersaline lake in the world. It is also one of the world's saltiest bodies of water, with 33.7 per cent salinity, which is 8.6 times saltier than the ocean. The Dead Sea is 67 kilometres long and 18 kilometres wide. Typical brine composition of Dead Sea is given in Table 2.10.

Table 2.10 Typical brine composition of Dead Sea

<i>Component</i>	<i>Concentration (g/kg)</i>
Chloride	181.4
Bromide	4.2
Sulphate	0.4
Calcium	14.1
Sodium	32.5
Potassium	6.2
Magnesium	35.2

Selected References

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