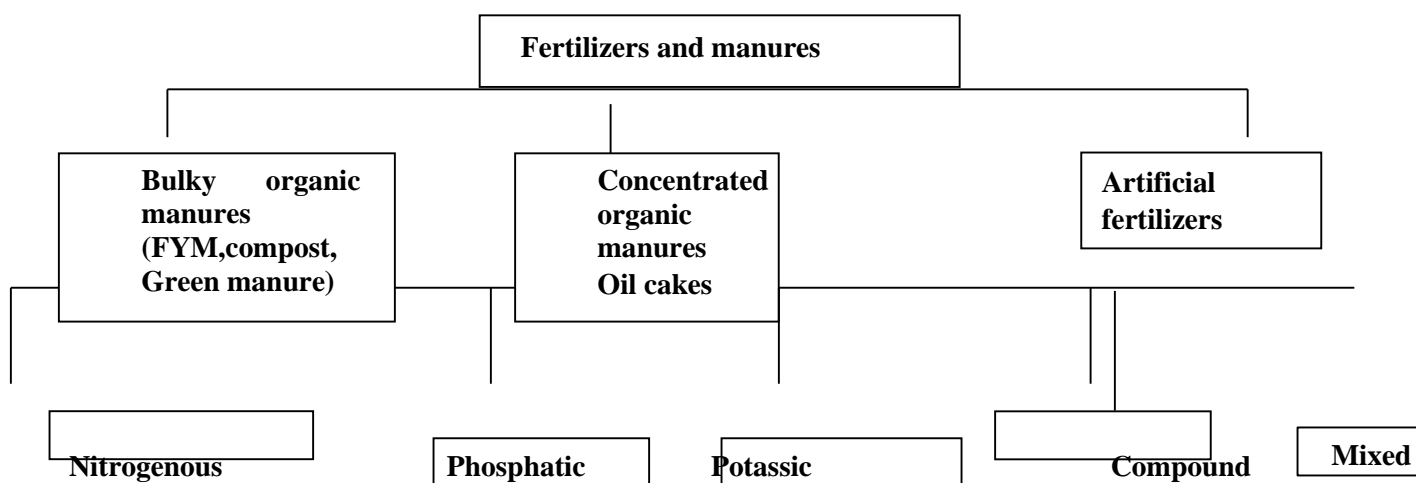




## Classification of fertilizers – N, P and K fertilizers

### Classification of fertilizers

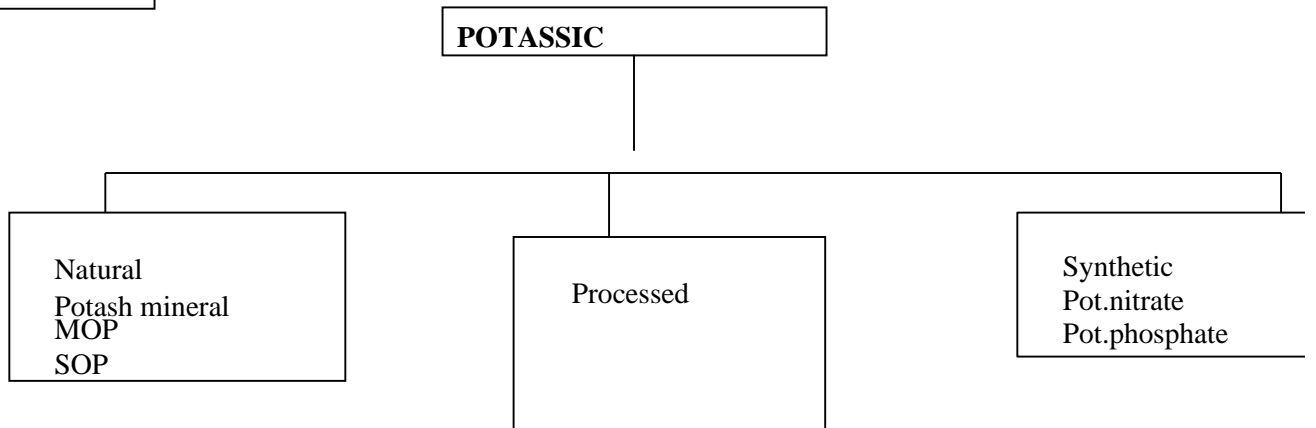
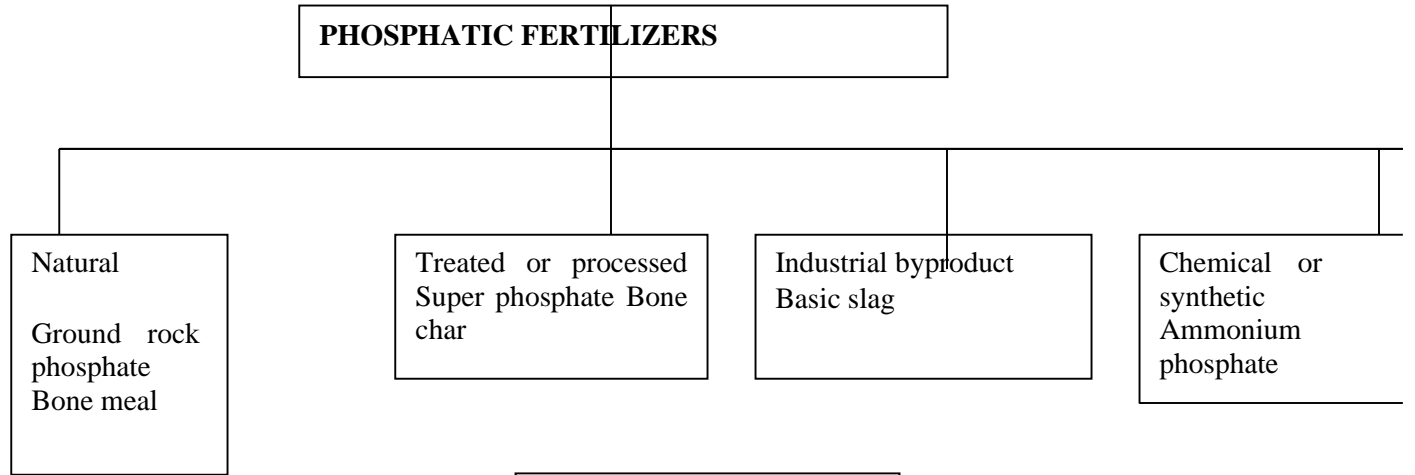
Commercial N, both organic and inorganic is desired from a wide variety of materials which are found to differ very widely in their sources, properties, method of preparation and their reactions in the soil. Classification based on chemical form seems to be more satisfactory as indicated below.



S.No.	Chemical Form of Nitrogen	Fertilizer	Chemical formula	N Content (%)
1	Ammonium [NH <sub>4</sub> <sup>+</sup> ]	a) Gaseous ammonia	NH <sub>3</sub>	82
		b) Ammonia water	NH <sub>3</sub> , NH <sub>4</sub> OH	24
		c) Ammonium sulphate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	21
2	Nitrate [NO <sub>3</sub> <sup>-</sup> ]	a) Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub>	16
		b) Sodium nitrate	NaNO <sub>3</sub>	16
		c) Ammonium sulphate nitrate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> +NH <sub>4</sub> NO <sub>3</sub>	26
3	Ammonium +Nitrate [NH <sub>4</sub> <sup>+</sup> ]+[NO <sub>3</sub> <sup>-</sup> ]	a) Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	35
		b) Calcium ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub> +CaCO <sub>3</sub>	25
4	Amide [-NH <sub>2</sub> ]	a) Urea	CO(NH <sub>2</sub> ) <sub>2</sub>	46
		b) Calcium cyanamide	CaCN <sub>2</sub>	22

The nitrogen content of different nitrogenous fertilizers is given below

Sl.No	Name of the fertilizer	N content (%)	Form of N
1	Sodium nitrate (NaNO <sub>3</sub> )	16.0	Nitrate (NO <sub>3</sub> )
2	Potassium nitrate (KNO <sub>3</sub> )	12.5-13.5	Nitrate
3.	Ammonium sulphate (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	20.6	NH <sub>4</sub> (Ammonia)
4.	Ammonium chloride (NH <sub>4</sub> Cl)	26.0	NH <sub>4</sub>
5.	Ammophos - A	11.0	NH <sub>4</sub>
6.	Ammophos - B	16.0	NH <sub>4</sub>
7.	Ammonium Nitrate (NH <sub>4</sub> )	33.0	NH <sub>4</sub> - 16.5 NO <sub>3</sub> - 16.5
8.	Ammonium sulphate nitrate	25.6	NH <sub>4</sub> - 19.5 NO <sub>3</sub> - 6.6
9.	Urea (CO (NH <sub>2</sub> ) <sub>2</sub> )	46.0	Amide
10.	Calcium cyan amide (CaCN <sub>2</sub> )	20.6	Amide
11.	Dried blood	3-14	Protein(organic)
12.	Groundnut cake	8.0	Protein(organic)
13.	Meat meal	09.0-11.	Protein (organic)
14.	Guano	10.0	Protein (organic)



## 05. Nitrogenous fertilizers – sources – fundamental processes involved in manufacturing procedures for ammonia, sulphuric acid, nitric acid and phosphoric acid

### NITROGENOUS FERTILIZERS

Elemental Nitrogen, recognized by Rutherford in 1772 as a colorless, odorless and inert gas, is the main constituent of air (approximately 79 percent by volume). Hence one might naturally expect that plants may not have any deficiency for this nutrient element and that there may be large deposits of mineral compounds of N on the surface of the earth. But actually this is not so. Though in the air over an acre of land there is a N supply of over 35,000 tons (an abundant supply) the plants, except the legumes, are incapable of utilizing this elemental N for their growth. Most of the important mineral deposits are the Chile saltpeter ( $\text{NaNO}_3$ ), or Chilean niter and Niter ( $\text{KNO}_3$ ) or Bengal saltpeter.

#### Sources of N

1. Mineral deposits: Chile saltpeter ( $\text{NaNO}_3$ ) in Northern Chile, Peru, Bolivia, California and Nevada.

Niter ( $\text{KNO}_3$ ) or Bengal saltpeter: present in Spain, Egypt, Persia, India and U.S.A. and ammonium sulphate in various “volcanic regions of the world”.

2. Addition through rain-water

A small amount of about 10 to 12 kg of N per year per acre is added to the soil during thunderstorms in these process discharges of atmospheric electricity produce nitrous oxide and rain carries this to the soil as  $\text{HNO}_3$  where it is quickly converted into nitrates.

3. Soil organic matter

This is the main source of N in the soil and the N content of any soil will depend upon the quality and quantity of organic matter of that soil.

4. N fixing organisms

The free living, Non-symbiotic E.g. Azotobacter and clostridium and symbiotic E.g.: *Rhizobium* sp. Bacteria are found to fix considerable amounts of the elemental N in a combined form. For example the non-symbiotic bacteria are found to fix 50 – 55 kg of N per year per acre while the symbiotic organisms fix about 300-350 kg of N per year per acre.

## 5. Industrial source

N is obtained from the industries in a combined form by the following processes. a.

Arc process

b. Cyanamid process and

c. Direct synthetic ammonia process.

### **Classification of Nitrogenous fertilizers and manners**

Commercial N, both organic and inorganic is desired from a wide variety of materials which are found to differ very widely in their sources, properties, method of preparation and their reactions in the soil. Classification based on chemical form seems to be more satisfactory as indicated below.

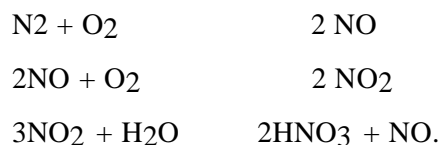
### **Industrial or synthetic fixation of nitrogen**

For the commercial manufacture of the various nitrogenous fertilizers, the elemental N has to be converted into a combined form either as  $\text{NH}_3$  or  $\text{HNO}_3$  which may serve as the basic material for the synthesis of other materials. There are three main processes of synthetic fixation of N,

1. Direct oxidation process (Arc process): The final product is dilute  $\text{HNO}_3$ .
2. Calcium cyan amide process: Final product is  $\text{CaCN}_2$ .
3. Synthetic ammonia or Haber –Bosch process: Final product is anhydrous or aqueous  $\text{NH}_3$ .

#### **I. Direct oxidation process**

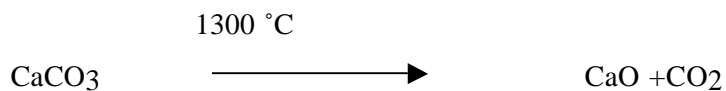
This method was demonstrated by Cavendish in 1766 on a laboratory scale. This is the most simple process of synthetic N fixation and it was first to be commercially utilized. The basic reaction of this process involved the union of N and O by means of an electric arc, the process being similar to that which is known to take place between N and O in the atmosphere in the presence of electricity produced during thunderstorms and lightning. In this commercial process, the reaction is secured by blowing air through a flaming electric arc which has a temperature of about  $3500^\circ\text{C}$ . Only about 2 percent of the air is heated and combined. The nitric oxide produced is converted to nitric acid ( $\text{HNO}_3$ ) by the action of water and atmospheric oxygen.



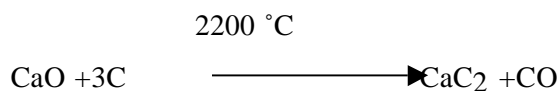
But this process requires high amount of electric power and high capital cost. It requires about five times as much electricity to fix a ton of N as is required by the cyanamide process. But this method is found to be suitable for countries like Scandinavia and Norway where the electricity is very cheap.

## II. Cyanamide process

This process was developed in Germany and is said to have been invented by two Chemists Frank and Caro in 1898. At present, this process is probably the only commercial method used for synthetic fixation of N other than the ammonia synthesis process. Calcium cyanamide was first tried as a fertilizer in 1901. The first step or stage involving burning of limestone in a vertical furnace or kiln at about 1300°C where the limestone decomposes to CaO.



The CaO obtained is reacted with coke in a continuous type electric furnace at 2200°C to form fused calcium carbide (CaC<sub>2</sub>) which is withdrawn and solidified.



In the third stage the air is liquefied by compressing and cooling from which the CO<sub>2</sub> and moisture are removed. The N is purified by fractional distillation. In the final stage, the purified N is caused to permeate a mass of finely ground CaC<sub>2</sub> in ovens under slight pressure at 1100°C.



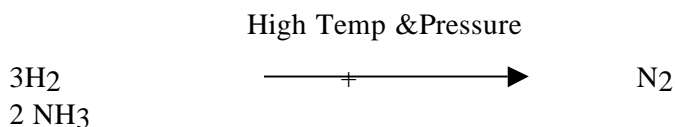
Ninety per cent of the CaC<sub>2</sub> is found to be reacted completely. The crude cyanamide is ground and treated with water to destroy residual CaC<sub>2</sub> and is brought into convenient physical condition. This method is not suitable where the coal supply is limited.

## III. Direct or synthetic ammonia process

This was developed between 1900 and 1910 by a team of German scientists, Haber, Nernst, Bosch and others. The main principle of this method is when 3 moles of

H and one mole of N are brought into contact with a suitable catalytic surface at elevated temperature and pressure, ammonia is formed. High pressure and temperature are necessary, because at high temperature and pressure alone the reaction is irreversible.

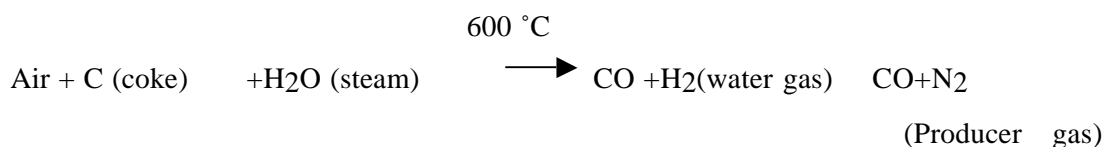
High temperature



This process consists of the following three main steps.

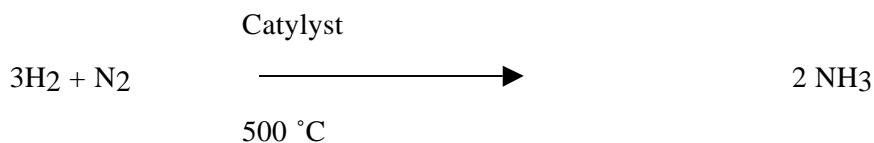
1. Preparation of H and N.
2. Purification and compression of three gases.
3. Catalytic conversion to ammonia.

To prepare H and N, the most famous water gas and producer gas procedures are followed. The method consists of passing air and steam over red-hot coke to produce a mixture of water gas (CO+H<sub>2</sub>) and producer gas (CO + N<sub>2</sub>). The coke is blasted with air at 600°C and superheated steam is passed through the coke.



After the formation of the CO<sub>2</sub>, pressure is raised to 50 atm for dissolving the CO<sub>2</sub> in water, which is removed and solidified for use in the later stages. The gas mixture is now adjusted to one volume of N to three volumes of H and compressed to 250 atm and the last traces of CO and CO<sub>2</sub> are removed by an ammoniacal solution of cuprous formate.

In the final stage, the temperature is raised to 500°C and the gas mixture is passed through special steel tower, capable of with standing high temperature and in the presence of catalyst, either platinized asbestos or iron, the N and H will react to form ammonia.



The prepared ammonia can be used as anhydrous or aqueous or it can be converted to HNO<sub>3</sub> and used.



## **Ammonia**

Pure  $\text{NH}_3$  is made up of 82.25 % N and 17.75% H. It is the most concentrated form and the lowest priced N fertilizer so far used either in the production of mixed fertilizer or for direct application. As described earlier,  $\text{NH}_3$  can be obtained, either as a by product during the destructive distillation of coal in coke oven, or from other coal industries, or by synthetic process. For fertilizer use these are two forms available.

1. Anhydrous  $\text{NH}_3$  and 2. Aqua or aqueous  $\text{NH}_3$ . Both the forms are extensively used in ammoniation of superphosphate, in the preparation of mixed fertilizers and for direct application.

Anhydrous ammonia is produced by compressing dry  $\text{NH}_3$  gas to form a liquid. The fertilizer grade of anhydrous  $\text{NH}_3$  contains 99.5%  $\text{NH}_3$  equivalent to 82.0 per cent N. It is an acid forming fertilizer and has a potential acidity equivalent to 148 lb of  $\text{CaCO}_3$  per 100 lb of ammonia. Aqueous ammonia is formed by dissolving  $\text{NH}_3$  gas in water. Commercial grades are found to have 30%  $\text{NH}_3$  which is widely used for ammoniation of superphosphate and mixed fertilizers and produce the same activity. Application of liquid  $\text{NH}_3$  through irrigation water is called 'Nitrogation' and application of gaseous  $\text{NH}_3$  directly to the field by using special devices is called 'Nitrojection'.

## **NITRIC ACID MANUFACTURE**

About 75% of the  $\text{HNO}_3$  produced is consumed in the fertilizer manufacture, while about 15% of the production goes into the manufacture of explosives. The remainder is used in a wide variety of outlets, the more important ones being synthetic fibers, dyes and plastics.

### **Production capacity**

$\text{HNO}_3$  is produced in about 50 factories in India. Out of these, 18 factories are producing above 100 t p a.

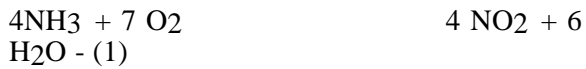
**Raw materials:**  $\text{NH}_3$  and air are required for the manufacture of  $\text{HNO}_3$

### **Manufacture**

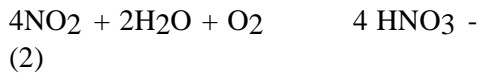
Nitric acid is produced by  $\text{NH}_3$  oxidation process. The liquid  $\text{NH}_3$  is evaporated, superheated and sent with compressed air to the converter, containing platinum –rhodium catalyst. In the converter,  $\text{NH}_3$  is converted to nitric oxide, which is

then converted to nitrogen dioxide in oxidation vessel with the help of secondary air. In the process, water absorbs nitrogen dioxide to form  $\text{HNO}_3$  while running in counter flow to the raising nitrogen dioxide in absorption column.

The various processes used can be classified as medium pressure, high pressure and combination of medium and high pressure, i.e, dual process. For fertilizer industry  $\text{HNO}_3$  of concentration from 58 to 60% is used.



Nitrogen dioxide



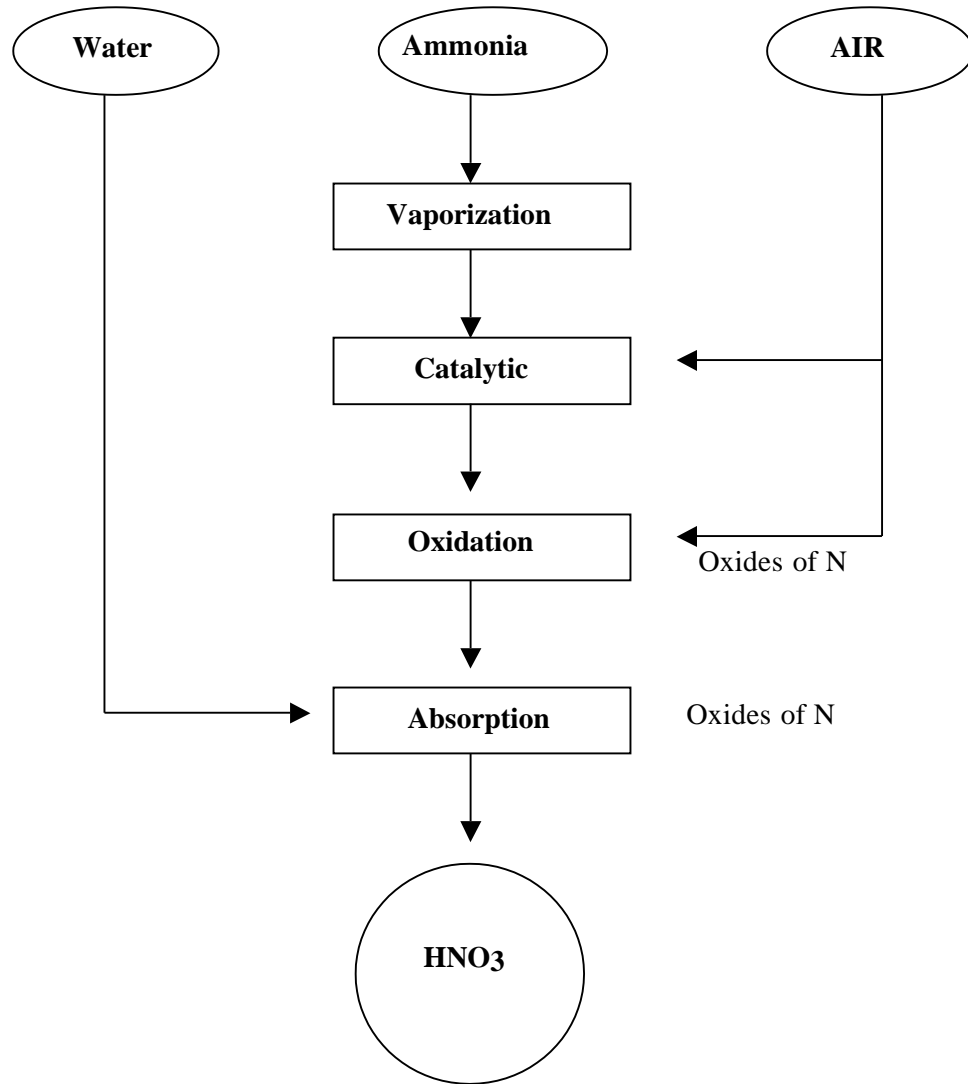
### **Concentrated nitric acid**

Nitric acid / water form a constant boiling mixture at around 68% and cannot therefore be separated by conventional distillation. The  $\text{HNO}_3$  can be further concentrated by extractive distillation with concentrated  $\text{H}_2\text{SO}_4$  or  $\text{Mg}(\text{NO}_3)_2$ . The method involves high temperature reconcentration equipment operated under highly corrosive conditions.

### **Handling, storage and packing**

$\text{HNO}_3$  is stored in stainless steel vessels. It is transported (large quantity) in stainless steel tankers or (small quantity) in stoneware bottles and glass carboys. Bottles and carboys shall be placed in an upright position on one layer of sand or ash free from cinders and the empty surrounding space shall also be filled with the same material to prevent movement.

**Flow chart for manufacture of HNO<sub>3</sub>**



## **SULPHURIC ACID**

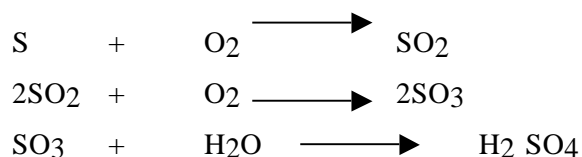
H<sub>2</sub>SO<sub>4</sub> is one of the most important heavy chemicals produced in India. It has a wider variety of industrial uses than any other chemical. Per capita consumption of H<sub>2</sub>SO<sub>4</sub> often has been used as an index of the industrial development of a country. The fertilizer industries, by far, the greatest consumer of H<sub>2</sub>SO<sub>4</sub> for acidulation of RP and for the manufacture of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>. other important fields of its use are steel works, rayon and staple fiber, alum and other inorganic chemicals and petroleum refining etc.

### **Raw materials/ sources**

H<sub>2</sub>SO<sub>4</sub> may be produced from elemental sulphur, pyrites (Sulphides of iron, copper, zinc and lead), hydrogen sulphide as contained in sour gas and petroleum, waste gases from the burning of fuel and smelting operations and sulphate salts such as anhydrite, gypsum and iron sulphates. Elemental S, pyrites and sulphates are the true basic raw materials. H<sub>2</sub>SO<sub>4</sub> produced by burning of fuel and smelting operation is called by products H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>SO<sub>4</sub> production from metallic sulphates is not economical. Thus for H<sub>2</sub>SO<sub>4</sub> production elemental S and pyrites are the only two important raw materials. In India, all the factories are based on elemental S except for Hindustan copper Ltd., Khetri and Hindustan Zinc Ltd., Udaipur which are based on flue gases from copper and Zinc smelters respectively. Also, one plant at Sindri is producing acid based on iron pyrite and a similar plant of larger capacity is under construction by the Sindri unit of FCI.

### **Methods of manufacture**

S is burnt to sulphur dioxide and pyrites are roasted to oxidize the sulphide content to SO<sub>2</sub>. SO<sub>2</sub> after catalytic conversion to Sulphur trioxide is absorbed in water to give H<sub>2</sub>SO<sub>4</sub>. the differences in H<sub>2</sub>SO<sub>4</sub> processes are in the manner in which SO<sub>2</sub> is converted to SO<sub>3</sub> and absorbed in H<sub>2</sub>O to produce H<sub>2</sub>SO<sub>4</sub>.



#### **(i) Chamber/tower process**

The oldest process is the chamber process, so called because the reactions which produce SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> take place within a lead chamber. The conversion to

SO<sub>3</sub> and then to H<sub>2</sub>SO<sub>4</sub> in the chamber is made possible by the use of nitrogen oxides as oxygen carrying catalysts. The need to attain greater output of acid resulted in the development of the so-called tower process in which packed towers are substituted for the lead chamber.

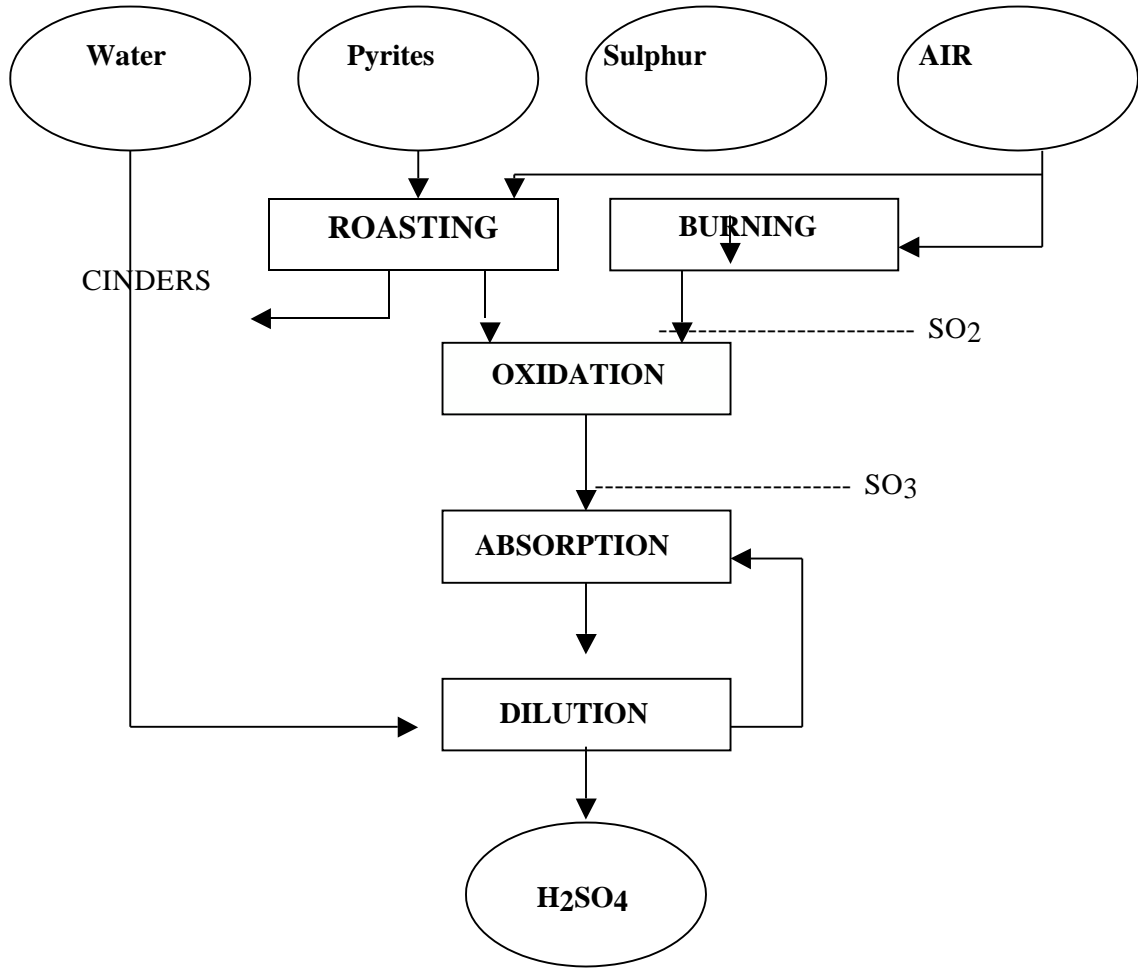
**(ii) Contact process**

In this process, SO<sub>2</sub> is converted to SO<sub>3</sub> by the use of a metal or metal oxide catalyst. The more common catalysts are platinum, iron oxide and vanadium pent oxide, although never plants use the latter almost exclusively. SO<sub>3</sub> is passed to a tower where it is absorbed in recycling con.H<sub>2</sub>SO<sub>4</sub>.

**Properties**

- i) Chemical formula - H<sub>2</sub>SO<sub>4</sub>
- ii) Molecular weight - 98.08
- iii) Appearance - Colorless, viscous liquid
- iv) Specific gravity (18°C/4°C) - 1.834
- v) Boiling point - Decomposes at 340°C
- vi) Solubility in water - Miscible in all proportions.

**Flowchart for H<sub>2</sub>SO<sub>4</sub> manufacture**



## 06. Manufacturing of ammonium sulphate, ammonium nitrate and ammonium chloride

### Ammonium sulphate

(NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> is one of the important fertilizers produced in India. It contains about 21% N and 24% S and has been traditionally been very popular in various parts of the country. It is a white crystalline salt having good keeping quality in dry conditions. **Production capacity**

The total installed capacity in the country is about one million tones of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>

### **Raw materials / sources**

The raw materials required to produce (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are

- H<sub>2</sub>SO<sub>4</sub> for its recovery from coke oven plants.
- NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> for neutralization process.
- Gypsum (natural or by product from H<sub>3</sub>PO<sub>4</sub> plants) and NH<sub>3</sub> for process using gypsum route.

### **Method of manufacture**

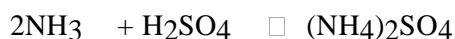
The following methods are used for producing (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>.

#### **(i) Recovery from coke-ovens**

The coke-oven gas (obtained when coal is heated to make coke) contains about 1% NH<sub>3</sub> by volume. The gas is cooled and passed into saturators containing weak H<sub>2</sub>SO<sub>4</sub> so as to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> crystals which is then recovered, centrifuged, washed and dried. This process is used in the steel plants where large coke- oven batteries are in operation.

#### **(ii) Direct neutralization**

Gaseous ammonia is directly neutralized with H<sub>2</sub>SO<sub>4</sub> to produce (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.



The neutralizer reactor and the crystallizer are interconnected so that the heat released during neutralization is used to evaporate water in the slurry. The crystallizer is designed to produce uniformly sized crystals.

Amorphous (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> is prepared by reacting gaseous NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in spray towers. The heat of reaction removes all the water present and the dry, fine product is continuously removed from the base of the tower. This product is suitable for making dry-mixed and granular fertilizers, FCI (Sindri), FACT (Alwaye) use the direct neutralization process.

In the manufacture of some granular NPK fertilizers, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is formed directly with other ammonium salts. E.g. in the 16 – 20 – 0 grade product made by FACT, a

mixture of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> is neutralized with NH<sub>3</sub> to form a slurry of (NH<sub>4</sub>) PO<sub>4</sub> and

(NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>, which is then granulated.

### (iii) Gypsum process

NH<sub>3</sub> gas is absorbed in water and then converted to (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> by absorbing CO<sub>2</sub>. The (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> is reacted with gypsum (CaSO<sub>4</sub>. 6 H<sub>2</sub>O) to produce (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and CaCO<sub>3</sub>.



CaCO<sub>3</sub> is removed by filtration (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution is evaporated, crystallized, centrifuged and dried.

Naturally occurring gypsum, or by product gypsum from H<sub>3</sub>PO<sub>4</sub> plants can be used for this process. CaCO<sub>3</sub> produced can be used for cement manufacture FCI (Sindri), FACT (Alwaye), EID-parry (Ennore), and GSFC (Baroda), produce (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> from Ca SO<sub>4</sub>.

### (iv) Byproduct

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> from caprolactum plants (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution is formed during the manufacture of caprolactum (the starting material for Nylon- 6). The solution is concentrated and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is recovered by crystallization, centrifuging and drying. GSFC (Baroda) has commissioned a 20,000 t p a caprolactum plant which will produce about 80,000 tonnes of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> per year.

### Specification as per FCO

- Moisture % by weight. Max	1.0
- NH <sub>4</sub> – N % by weight Min	20.6
- Free acidity as H <sub>2</sub> SO <sub>4</sub> % by weight max	0.025
- Arsenic (As As <sub>2</sub> O <sub>3</sub> ) % by weight max	0.01

### Handling storage and packing

Crystalline (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> is free flowing and does not normally pose any problem in handling and storage. However, it generally contains some powdered material which causes caking especially under high humidity.

Due to its susceptibility to caking and slight acidity (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is normally bagged in polyethylene lined gunny bags or high density polyethylene (HDPE) woven sacks.

### Properties

- It is a white crystalline salt and to some extent hygroscopic
- It has good storage quality
- It is very soluble in water and so called as quick acting fertiliser
- It should not be used along with alkaline materials



- It is physiologically acidic in nature

Ammonia gas is evolved when ammonium sulphate reacts with alkaline materials

When lime and ammonium sulphate is used together in the soil, ammonia gas is produced

### **Ammonium chloride (NH<sub>4</sub> Cl) 26%N**

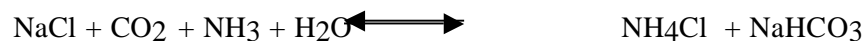
This is sometimes called nitrate of ammonia. It is commercially prepared by combining ammonia with HCl and the resultant product, NH<sub>4</sub>Cl is found to have very good physical condition. Though this fertilizer has not been used extensively as straight fertilizer, it is preferred in preparing many fertilizer mixtures because of its good physical properties. This fertilizer is also obtained as a by product of the Solvay process of making (Na)<sub>2</sub> CO<sub>3</sub>.

The commercial sample is a white, crystalline salt containing 26% N in the NH<sub>4</sub> form.

The fertilizer is suitable for many crops except for those, which are sensitive to high chlorine content. This is physiologically acidic fertilizer.

### **Manufacture**

Sodium chloride is treated with ammonia and carbon dioxide to form ammonium chloride and sodium bicarbonate. The resulting ammonium chloride is then separated



Ammonium chloride is also obtained as a byproduct of soda ash (Na<sub>2</sub>CO<sub>3</sub>) and manufactured as Solvay's process. It is prepared by reacting calcium chloride with ammonium carbonate. Ammonium chloride is obtained by double decomposition between ammonium sulphate and sodium chloride at 1300<sup>0</sup> C

### **Ammonium nitrate (NH<sub>4</sub> NO<sub>3</sub>) – 33% N**

This is mainly manufactured by passing NH<sub>3</sub> gas into HNO<sub>3</sub> and then isolating the product in a solid form suitable for use as fertilizer. The equipment should be stainless steel or other special alloys.



NH<sub>4</sub> NO<sub>3</sub> is continuously produced with the aid of a neutralization tower. NH<sub>3</sub> gas is introduced near the bottom of the tower, while air is added at a higher point to cool the solution and carry off the water vapor. The solution containing about 80% of NH<sub>4</sub> NO<sub>3</sub> is withdrawn and converted to crystals or pellets as the case may be.

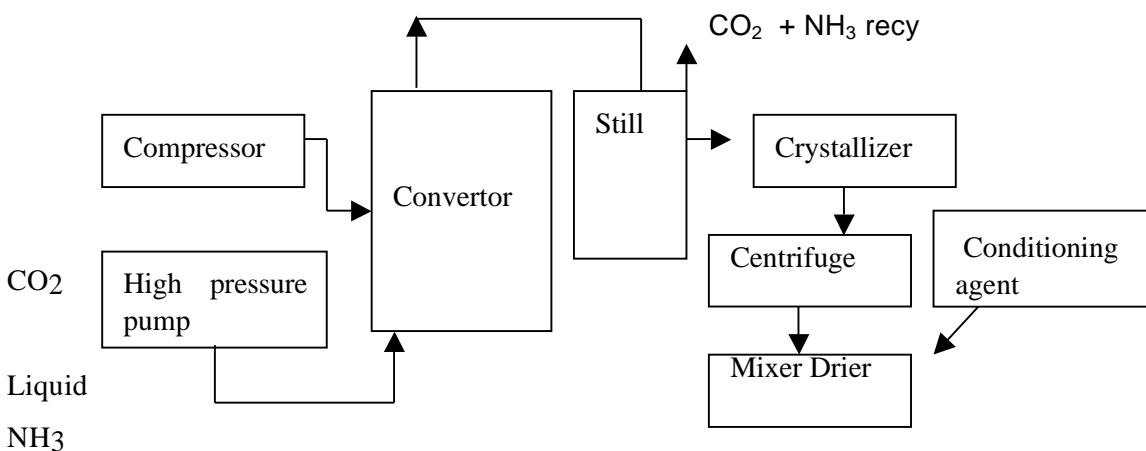
Pure  $\text{NH}_4 \text{NO}_3$  is a white crystalline salt having 33% of N, one half of which is in the  $\text{NH}_4$  form and the other half in the  $\text{NO}_3$  form. It is readily soluble in water and completely utilized by crops and hence no residues are left in the soil. It is highly hygroscopic and cakes up very soon. But, when the crystal is coated with about 5% of a conditioning agent like clay etc, it is found to have good physical properties. It is an excellent fertilizer both for direct application to the soil and for use in mixtures. It is an economical source of fertilizer N, suited to a wide range of crops, soils and climatic conditions. Its  $\text{NO}_3$  content contributes to rapid crop response while the  $\text{NH}_4$ - N makes it more resistant to leaching losses than other materials carrying their entire N in the  $\text{NO}_3$  form.

## 07.Manufacturing of urea

**Urea:**  $\text{CO}(\text{NH}_2)_2$  (42 to 46% N)

The main principle involved in the process of manufacture is combining pure ammonia with pure  $\text{CO}_2$  and removing one molecule of  $\text{H}_2\text{O}$  from the resulting  $\text{NH}_4\text{CO}_3$  to form Urea. The  $\text{CO}_2$  and  $\text{NH}_3$  are allowed to react in the liquid phase under greatly elevated pressure and temperature and this process requires highly specialized equipment. The  $\text{CO}_2$  and  $\text{NH}_3$  are compressed and heated as they enter the converter where urea is formed. A large excess of  $\text{NH}_3$  is used in order to increase the conversion rate. The un reacted  $\text{NH}_3$  and  $\text{CO}_2$  are removed by means of an evaporator still and are then recycled. The urea solution is pumped to the crystallizer where cooling and crystallization take place. The urea crystals are centrifuged and dried. The urea crystals are centrifuged and dried.

### FLOW CHART FOR UREA MANUFACTURE



**Slow release N fertilizers – coated fertilizers – types of coating – lac coated- neem cake blended and coal tar coated urea- chemically modified forms-urea formaldehyde, IBDU, CDU**

Slow-release fertilizers are excellent alternatives to soluble fertilizers. Because nutrients are released at a slower rate throughout the season, plants are able to take up most of the nutrients without waste by leaching. A slow-release fertilizer is more convenient, since less frequent application is required. Fertilizer burn is not a problem with slow-release fertilizers even at high rates of application; however, it is still important to follow application recommendations. Slow-release fertilizers may be more expensive than soluble types, but their benefits outweigh their disadvantages.

Slow-release fertilizers are generally categorized into one of several groups based on the process by which the nutrients are released. Application rates vary with the different types and brands, with recommendations listed on the fertilizer label.

**Pelletized:**

One type of slow-release fertilizer consists of relatively insoluble nutrients in pelletized form. As the pellet size is increased, the time it takes for the fertilizer to breakdown by microbial action is also increased. An example of this type is MagAmp, a 7-40-0 fertilizer that is available in a coarse grade lasting two years and a medium grade lasting one year. MagAmp is used commercially for container plants, but is appropriate for use on turf, tree seedlings, ornamentals, vegetables, and flower borders.

**Chemically Altered:**

A fertilizer may be chemically altered to render a portion of it water insoluble. For instance, urea is chemically modified to make Ureaform (ureaformaldehyde) -- a fertilizer that is 38 percent nitrogen, 70 percent of which is water-insoluble. This percentage is often listed on fertilizer labels as the Percent W.I.N., or the percent of water-insoluble nitrogen. This form of nitrogen is released gradually by microbial activity in the soil. Because microbial activity is greatly affected by soil temperature, pH, aeration, and texture, these variables can affect the release of nitrogen from Ureaform. For example, there will be less fertilizer breakdown in acid soils with poor aeration -- an environment unfavorable to soil microorganisms. Ureaform is used for turfgrass; landscaping; ornamental, horticulture, and greenhouse crops.

IBDU (isobutylidene diurea) is similar to Ureaform, but contains 32 percent nitrogen, 90 percent of which is insoluble. However, IBDU is less dependent on microbial activity than Ureaform. Nitrogen is released when soil moisture is adequate. Breakdown is increased in acid soils. IBDU is used most widely as a lawn fertilizer.

### **Coated fertilisers**

Controlled- or slow-release fertilizers are broadly divided into uncoated and coated products. Uncoated products rely on inherent physical characteristics, such as low solubility, for their slow release. Coated products mostly consist of quick-release N sources surrounded by a barrier that prevents the N from releasing rapidly into the environment. Different mechanisms, but similar (though not identical) end results.

The terms “controlled-release” and “slow-release” can mean different things to different people, but for purposes of this discussion, the two terms are synonymous. Except for a few slow-release K sources, almost all slow-release fertilizers are N sources. They represent a relatively small segment of the total fertilizer industry (3 to 4 percent), but their use is growing faster than soluble (quick-release) materials. This is primarily because they reduce the overall environmental impact of N fertilizers, as now mandated in BMPs.

### **Coated:**

Water-soluble fertilizers may be coated or encapsulated in membranes to slow the release of nutrients. For example, **Osmocote**, a controlled-release fertilizer is composed of a semipermeable membrane surrounding water-soluble nitrogen and other nutrients. Water passes through the membrane, eventually causing enough internal pressure to disrupt the membrane and release the enclosed nutrients. Because the thickness of the coating varies from one pellet, or prill, to another, nutrients are released at different times from separate prills. Release rate of these fertilizers is dependent on temperature, moisture, and thickness of the coating. Osmocote is recommended for turf, floriculture, nursery stock, and high-value row crops.

Another type of coated fertilizer is **sulfur-coated urea** (SCU), which is manufactured by coating hot urea with molten sulfur and sealing with a polyethylene oil or a microcrystalline wax. Nitrogen is released when the sealant is broken or by diffusion through pores in the coating. Thus, the rate of release is dependent on the thickness of the coating or the sealant weight. SCU is broken down by microorganisms, and chemical

and mechanical action. The nitrogen in SCU is released more readily in warm temperatures and dry soils. SCU appears to be more effective when applied to the soil surface, rather than mixed into the soil. Any method of application that crushes the granules will increase the release rate to some extent.

SCU is best used where multiple fertilizer applications are normally necessary, such as on sandy soils or in areas of high rainfall or irrigation. SCU is used on grass forages, turf, ornamentals, and strawberries.

**Nutricote** is characterized by coating nitrate compound fertilizers with a special resin. The duration of nutrient release is controlled by the porosity of the resin coating. A more porous coating results in quicker release. This technology ensures consistency and precision of nutrient release from Nutricote controlled release fertilizers.

When Nutricote is applied to the soil, the water in the soil enters the granule through micropores which dissolves the nutrient elements. The nutrient elements will then be released steadily through the same pores. Most Nutricote granules are 3 to 4 mm in diameter and the nutrient content are NPK: 14-14-14 and NPK: 20-7-10.

Nutricote's release rate is influenced by soil temperature, the higher the soil temperature, the greater the release rate. Absorption of nutrients and water by plants is generally increased with increasing temperature and plant growth will become more vigorous as a result. Nutrient supply through Nutricote nicely matches the physiology of plant response to temperature.

The release rate of Nutricote is not significantly influenced by soil moisture levels nor by soil type or pH. Nutricote does not depend upon microbiological decomposition for its action.

## **2.Polymer-coated fertilizers**

Polymer-coated fertilizers (PCF) represent the most technically advanced state of the art in terms of controlling product longevity and nutrient efficiency. Most PCFs release nutrients by diffusion through a semipermeable polymer membrane, and the release rate can be controlled by varying the composition and thickness of the coating. The type of fertilizer substrate also may influence the rate of N release.

**Meister products :** Meister products are produced by using thermoplastic resins as coating materials. The coatings are applied to a variety of substrates including urea, diammonium phosphate, potassium sulfate, potassium chloride and ammonium nitrate. Release-controlling agents such as ethylene-vinyl acetate and surfactants are added to the coating to obtain the desired diffusion characteristics, while coating thicknesses remain similar for most products. Release rates can also be altered by blending talc resin into the coating.

**Reactive Layer Coating:** A relatively new coating technology known as reactive layer coating (RLC) combines two reactive monomers as they are simultaneously applied to the fertilizer substrate. These reactions create an ultra-thin membrane coating, which controls nutrient release by osmotic diffusion. RLC products include coated basic fertilizer materials such as urea, potassium nitrate, potassium sulfate, potassium chloride, ammonium sulfate, ammonium phosphate and iron sulfate, in various particle sizes. Coating weights on urea vary from 1.5 to 15 percent, depending on the release duration desired.

**Multicote products:** In the production of multicote products, fertilizer granules are heated in a rotating pan and treated with materials that create multiple layers of a fatty acid salt. This is followed by the application of a paraffin topcoat. Coating weights are relatively large compared to other technologies, but this is offset by the comparatively low cost of the coating materials. Substrates include potassium nitrate, urea and triple superphosphate. The various coated components are blended together into different grades.





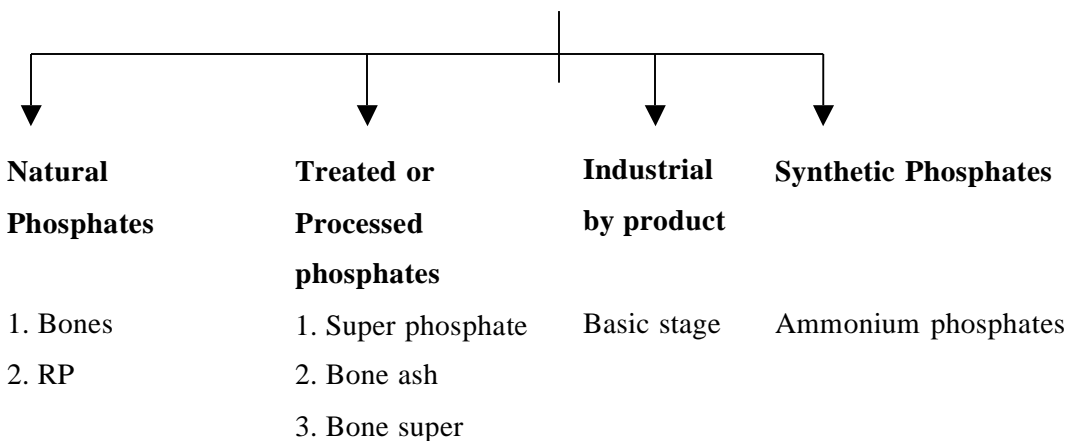


“Apatite” or “Phosphorite” or “Phosphate rock” having the general formula  $(Ca_3 (PO_4)_2)_x$ .

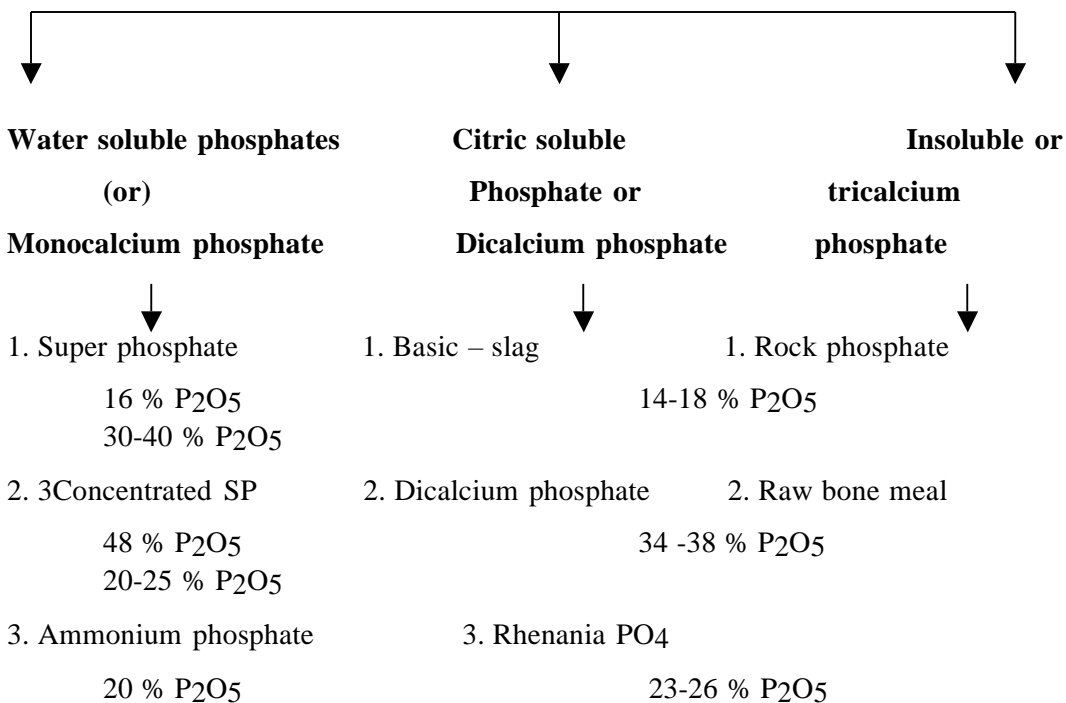
Ca X. These natural deposits serve as the basic material for the synthesis of all other phosphoric fertilizers.

### Classification of phosphatic fertilizers

#### 1. Based on nature of source or manufacture Phosphatic materials



#### 2. Based on the solubility of the phosphate



As in the case of N, the P is incapable of being utilized in the elemental form, but only in the combined form as acid ions (anions). All plants absorb P either in the monovalent (H<sub>2</sub>PO<sub>4</sub>) or divalent (HPO<sub>4</sub>) ions.

## 2.Citric –soluble phosphates

The materials, having water – insoluble phosphates, but soluble in one percent citric acid, are included in this group. The availability of P is not as quick as in the case of water – soluble P, but adequate quantities are found to be released in the available form as divalent phosphates ( $\text{HPO}_4$ ) for plant utilization. This group is found to be useful for acid soils, as under low pH of the soil the citrate soluble phosphates does not easily get converted into monocalcium phosphates or water soluble phosphates, and there are less chances of phosphate getting fixed up as iron and aluminum phosphates. Moreover, due to their basic reaction and high Ca content, they act particularly well on acidic soils and as such, this group is well suited for **lateritic** and acidic soils.

## 3.Insoluble phosphates

This group includes those materials having water and citric acid insoluble phosphates. The phosphates are being present mainly as tricalcium phosphate. The availability is very low and the phosphates will be converted to available form very slowly through various chemical reactions. Though the solubility of phosphates is low, the phosphates will be available for prolonged period of time.

These fertilizers are well suited for strongly acidic soils or organic soils which require large quantities of phosphatic materials to raise the soil P status.

The following table illustrated the phosphate ( $\text{P}_2\text{O}_5$ ) content and the form of phosphate.

Sl. No.	Fertilizers	Total $\text{P}_2\text{O}_5$ (%)	Form of $\text{PO}_4$	Avail. $\text{P}_2\text{O}_5$
1.	Ordinary super phosphate	16	Water soluble	16.5 - 17.0
2.	Concentrate super phosphate	46 – 48	-do-	
3.	Monoammonium phosphate	48 (11 N)	-do-	
4.	Diammonium phosphate	53 (21 N)	-do-	46 (18N)
5.	Ammophos – A	48 (11 N)	-do-	
6.	Ammophos – B	20 (20 N)	-do-	
7.	Basic slag	14 – 18	Citric soluble	

8.	Dicalcium phosphate	34 – 38	-do-	34.0
9.	Fused tricalcium phosphate	28	-do-	
10.	Rhenania phosphate	23 – 26	-do-	
11.	Raw bone meal	20 – 25	Insoluble	NA
12.	Steamed bone meal	22 – 25	-do-	NA
13.	Rock phosphate	30 – 40	-do-	NA

### 1. Rock phosphate

The phosphate mineral in soil is found to occur as tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  in combination with either  $\text{CaCO}_3$ ,  $\text{CaF}_2$ ,  $\text{Ca}(\text{OH})_2$  or  $\text{CaCl}_2$ . The primary mineral is called 'apatite' and its massive form is sometimes called as 'Phosphorite'. The apatite is of igneous origin found as a constituent of granites, gneisses and basalt. The apatite is usually found as crystals having a clear and transparent colour. There are five important forms of apatite that are found to occur and they are called according to the other components contained in the molecules.

**Apatite**            General formula  $(\text{Ca}_3(\text{PO}_4)_2)_3 \text{Ca}_x$  or  $\text{Ca}_{10}(\text{PO}_4)_5 \text{Ca}_x$

where  $x = \text{CO}_3, \text{Cl}_2, \text{F}_2, \text{SO}_4$  or  $(\text{OH})_2$ .

1. Carbonato apatite             $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCO}_3$
2. Fluor apatite                 $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaF}_2$
3. Chlor apatite                 $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCl}_2$
4. Hydroxy apatite             $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{Ca}(\text{OH})_2$
5. Sulphate apatite             $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaSO}_4$

All the above five apatite are primary minerals, of which the fluor apatite is the most commonly occurring one. In some acid soils the phosphate may be found in combination with titanium and iron in varying quantities and there when present in the soil are classified as secondary mineral. The apatite as such is found to occur in the amorphous form and it may be in the compact, concretionary or earthy form and these forms are commonly referred as rock or boulder phosphate, pebble phosphate and soft phosphate respectively. The apatite deposits are classified into residual deposit, replacement deposit and sedimentary deposit.

Deposits of apatite of economic importance have been found in every continent and in many island of the world. In India, the phosphoric deposits are found in Trichy district of Tamil Nadu, Udaipur of Rajasthan and Singhbhum of Bihar. The deposits in Trichy are found in the form of nodules in a bed of clay and hence are called Trichy phosphatic nodules. The exact locality is Uttalur about 30km from Trichy and the deposit

is found to spread over an area of 11 to 12 square miles. The Trichy phosphatic nodule analyses as follows

P <sub>2</sub> O <sub>5</sub>	-	24 -
27% CaCO <sub>3</sub>	-	42 - 47 %
F	-	2 - 3 %
Fe <sub>2</sub> O <sub>3</sub> & Al <sub>2</sub> O <sub>3</sub> -		4 - 9
%		

As compared to the phosphatic deposits found in other countries, this phosphate deposit contains a high content of F (2-3%), high content of sesquioxides (4-9%) and low content of phosphate. The high contents of F and R<sub>2</sub>O<sub>3</sub> made the RP unsuitable for the manufacture of other phosphatic fertilizers at a lower cost. Larger quantities of acids are required to eliminate the F and R<sub>2</sub>O<sub>3</sub> which will thus increase the cost of production. Moreover, the Trichy deposit is not suitable for direct use as fertilizer because of high F and R<sub>2</sub>O<sub>3</sub> contents. The deposit is mainly in the form of carbonate apatite and fluor apatite. The fertilizing value is nil unless the F and R<sub>2</sub>O<sub>3</sub> are removed. The ground RP is marketed, which passes through 200 mesh sieve.

### **Basic slag**

It is a by-product from the steel industry. During the steel manufacture, the P in the iron ore is removed to get a high quality steel as the steel containing more than 2% of P is brittle. The basic slag is obtained by the various processes of steel manufacture.

#### **1. Thomas and Gilchrist method**

The method was introduced as a modification to the old Bessemer process in 1877. In this, molten pig iron containing the various impurities like Ca, SiO<sub>2</sub>S and P is introduced into a limed converter with air blast arrangements. At a particular temperature, lime melts and combines with the acid forming impurities and the resulting product, which are lighter, rise to the surface of the molten mass. The floating solids are poured off as slag, cooled, powdered and marketed. This is containing 17 or 20% P<sub>2</sub>O<sub>5</sub>.

#### **2. Open Hearth method (Modern Method)**

Here the impurities are oxidized by means of the iron ore (Iron oxide) itself. Iron ore and lime are heated in an open heater and molten pig iron is then added. This carries not more than 15% P<sub>2</sub>O<sub>5</sub> and not less than 8% P<sub>2</sub>O<sub>5</sub>.

### **Properties**

The name 'basic slag' is derived from metallurgy. Any flux that is added to

remove the impurities is recovered mixed with the impurities as a slag. The flux that is added to remove basic impurities produces acid slag and the one that is added to remove acid impurities forms basic slag. The basic slag is a heavy dark powder and is alkaline to litmus. The availability of P is found to increase with the fineness of the product as well as with silica content and decrease as the F content increase.

slag should not be used as an ingredient in manure mixtures. The phosphate is found to be present in a double silicate form with lime  $[(CaO)_5 P_2O_5 SiO_2]$  but some consider it as tetra calcium phosphate  $(Ca_4 P_2O_5)$  and still others consider it is a basic silicon oxy apatite. It is only a slow acting fertilizer. This more useful for acid soils and in addition to the phosphate it is valued for the magnesium and Mn content. Following is the average composition of basic slag.

Phosphate (P <sub>2</sub> O <sub>5</sub> )	-	12 - 20 %	Lime (CaO)	-	40
- 50 % Silica (SiO <sub>2</sub> )	-	5 - 16 %	Sesquioxides (R <sub>2</sub> O <sub>3</sub> )	-	12 - 16 %
Manganese oxide (MnO)	-	5 - 10 %	Magnesium Oxide (MgO)	-	2 - 3 %

#### **Artificial Basic slag**

When PR is fused with Mg containing minerals like serpentine and olivine, the resultant product is called as artificial basic slag. The fertilizing value of basic slag is influenced by the fineness of the fertilizer and material passing through a 100 mesh sieve is found to be better. It is more suitable for acid soils because of high lime content. The presence of Mg and Mn corrects the deficiency of these elements in the soil.



## **10. Single and triple super phosphates – thermophosphates – method of manufacturing Super phosphate**

The term super phosphate is generally applied to phosphates which are present in a readily available form to plants. After the resolution passed in the meeting of the first world International congress on chemical fertilizers, 1938, the term super phosphate is restricted to refer those phosphates having less than 25% of  $P_2O_5$  and the term concentrated SSP for all those phosphates containing more than 25%  $P_2O_5$ .

The super phosphates are generally manufactured from phosphate rock, but bones and phosphatic guanoes are also extensively used for the manufacture. The super phosphates prepared from organic sources (bones & guano) are said to be having good physical condition, but with a lower  $P_2O_5$  content. In recent times only the phosphate rock is being utilized for the manufacture of various super phosphate.

Phosphate rock containing less than 50% of tricalcium phosphate are not suitable for manufacture of phosphatic fertilizers and are not used in the industry. Phosphate rocks containing  $> 4\%$  total  $R_2O_3$  are considered unsuitable and the phosphate rock should not contain  $> 2\%$  iron oxide.

The following method are commonly followed to convert the insoluble phosphate found in RP into more soluble forms.

1. Acid treatment method.
2. Phosphorus volatilization method
3. Decomposition with an alkali or silicate, and
4. Method followed in steel industry.

### **a. Ordinary super phosphate**

This is also called as Den super phosphate. Often the term ‘super’ is used to refer only to this product. This is the most extensively used fertilizers among the farmers.

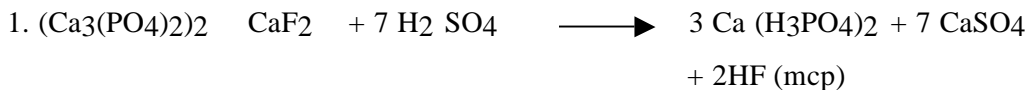
#### **Manufacture**

The principle involved in the process is the treatment of RP with acids, mainly  $H_2SO_4$  to convert the insoluble and unavailable tricalcium phosphate to available dicalcium and monocalcium phosphates. Concentrated  $HNO_3$ ,  $HCl$ ,  $H_3PO_4$  and  $H_2SO_4$  can be used, but sulphuric acid is found to be more suitable because of the fact that when it reacts with the RP,  $CaSO_4$  is formed, which is a dehydrating agent and improves the physical condition of the final product to a better condition.

The method consisted of mixing equal quantities of RP with  $H_2SO_4$  in open tanks and then powdering the resultant product after the reactions are over. The calculated



quantity of H<sub>2</sub>SO<sub>4</sub> and ground phosphate rock (material passing through a four-mesh sieve only has to be used) are introduced and mixed very thoroughly and then dropped in a pit or den. The process is also called Den method. Sufficient time of 24 to 36 hrs is allowed for the completion of the reaction. Temperature rises to 100°C and there is a loss of volume by 10% due to evaporation of water, CO<sub>2</sub> and F. The CaSO<sub>4</sub> act as a dehydrating agent and artificial drying is also done wherever necessary. Then the product is ground to a very fine powder and stored for sufficient time for the curing of the material.



### Precautions

1. An excess quantity of H<sub>2</sub>SO<sub>4</sub> should not be used.
2. The quality of the RP must be pre decided.

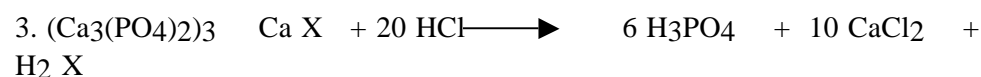
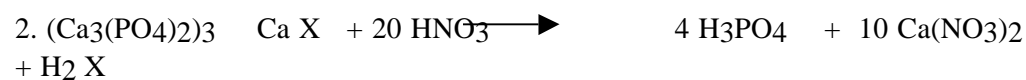
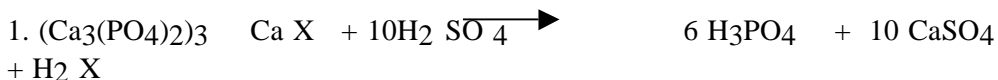
### Properties

The commercial super phosphate is grey in colour and it is only partly soluble in water. It has an acid odour and acid reactions due to the presence of some free acids and the acid salt monocalcium phosphate. In addition to the presence of phosphate, it contains gypsum, silica and aluminum sulphate, CaF etc. It contains about 20% Ca and 12% Sulphur which are the secondary nutrient elements required for the plants.

### b. Concentrated super phosphate

The main principle involved in the preparation is to first manufacture, phosphoric acid (H<sub>3</sub> PO<sub>4</sub>) by treating the RP with excess quantity of HCl or HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> and secondly the H<sub>3</sub>PO<sub>4</sub> so obtained is used for the treatment of another quantity of phosphate rock to get this fertilizer. Hence, there are two acid treatments involved and so the product is called double super phosphate (double insulation). Following are the main steps in the manufacturer of concentrated super phosphate.

1. Preparation of H<sub>3</sub>PO<sub>4</sub> using RP and one of the mineral acids.
2. Preparation of the concentrated super phosphate by treating fresh quantity of RP with the prepared H<sub>3</sub>PO<sub>4</sub>.





PR is ground and allowed to pass through a constant weight feeder to which a measured flow of  $\text{H}_3\text{PO}_4$  under pressure enters. All the mixing is done in the funnel like mixer and the mixture is allowed to stand for sufficient time for the reaction to take place. The slurry is conveyed to a troughed belt conveyor where the product sets in a few seconds to plastic mass. To get a dried material, sufficient retention time is allowed and at the end of the belt-conveyor, a rotary disintegrator reduces the lumps to less than 2" size. The disintegrated super phosphate is stored for curing at least for a period of 15 weeks.

### **Properties**

This fertilizer resembles in all respects the ordinary super phosphate. It is grey in color, a major portion being soluble in water. It contains 45 to 48% water soluble  $\text{P}_2\text{O}_5$ . It contains lesser quantity of other ingredients.

### **Thermophosphates**

These are manufactured by heating phosphate rock in varying temperatures. The

main drawbacks in thermal phosphates are

They are generally more expensive than acid derived phosphates. It contains no water soluble P. They do not have any value in the manufacture of NPK fertilizers

### **Polyphosphates**

Differ slightly from the more common orthophosphate fertilizers. Nearly all of the liquid fertilizers containing P are of the polyphosphate type. Polyphosphates are composed of a series of orthophosphate molecules connected by the process of dehydration (removal of water). Commercial ammonium polyphosphates are usually a mixture of ortho- and polyphosphate. With prolonged storage, polyphosphates will hydrolyze to orthophosphates. Solutions of ammonium polyphosphate most commonly made are 10-34-0 and 11-37-0. The most common dry polyphosphate is 13-52-0.

## 11. Potassic fertilizers – manufacturing of KCl, K<sub>2</sub>SO<sub>4</sub> and Schoenite

Potassium found to occur very commonly in the combined form as naturally occurring minerals. Common soil forming rocks like granite and gneiss are found to have about 3% K. For many years, K has been considered as important plant nutrient element. The Chinese were the pioneers among the various farmers who used K for agricultural purposes. The mineral deposits were not discovered and used as fertilizers until eighteenth century. The first product to be used as K manure was the wood ash and the practice of using wood ash existed for centuries.

In olden days, the wood ash was primarily used to get the potassium salts. The wood was burnt and the resultant ash was leached in mud pots to get the salt mixture containing chlorides, SO<sub>4</sub> and CO<sub>3</sub> of K, Ca and Mg. (Pot + ash = Potash). It would be advantageous and more correct to use P and K to refer to P and K, instead of P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O in the fertilizer technology i.e.,

$$\% K = \% K_2O \times 0.83 \text{ and } \% \text{ of } K_2O = \% K \times 1.2$$

### Source of potassium

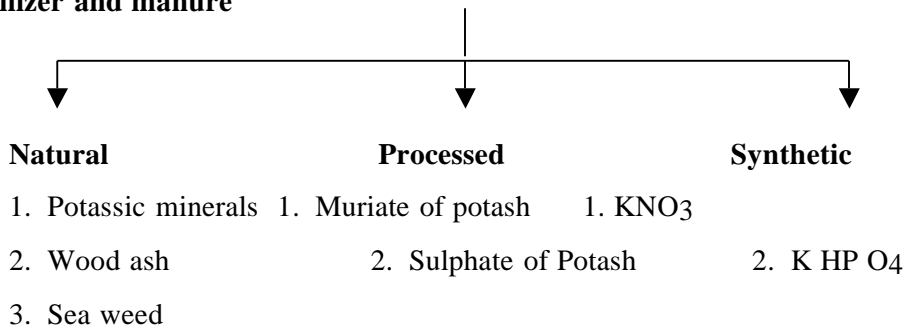
The following are the main sources of K.

1. Mineral deposits
2. Industrial by products
- and 3. Synthetic K salts

### Classification of potassic fertilizers

Potassic fertilizer are classified broadly into chlorides and non- chlorides. The following are the most important K containing materials. Wood ash, tobacco stems, wool waste, flue dust, by products from sugar and alcohol industry. Sea weed, sea water, K minerals, processed fertilizer like muriate and SO<sub>4</sub> of potash and synthetic fertilizers.

### K Fertilizer and manure



### A. Organic K fertilizer Sources

#### 1. Wood ash

Use of wood ash as K fertilizer has been there for centuries. Wood twigs and branches are burnt to get the ash. Sawdust is also used. The burnt material will contain

varying amounts at  $K_2O$  from 5 to 25%. Since wood ash is highly alkaline it should not be applied to germinating crops.

## **2. Tobacco stem**

In the manufacture of cigarette, cigar and chewing tobacco, there results considerable wastes consisting of mainly the stems and midribs of the leaves. This waste material is collected, ground and sold as manure. It Tobacco stem contains 4 to 10%  $K_2O$  and 2 to 3% N. It is found to be a valuable conditioner and adds bulk to the fertilizer mixtures.

## **3. Wool waste**

Before the raw wool could be used for spinning, it must be treated for the removal of 'suint' which is the dried sweat of sheep. This 'suint' consists largely of K salts and contains 1.5 to 5.0 %  $K_2O$ .

## **4. Flue dust**

It is a by product from the steel and cement industry. For melting the iron a mixture of iron ore, coal, coke and limestone are introduced into a blast furnace. When ignited, due to tremendous heat, the K contained in the iron ore volatilizes and when the gases containing volatilized K are burnt, the K dust will settle in the flue through which the gases pass and from time to time the dust accumulated will be collected and used. This will have 3 to 18%  $K_2O$  as  $Cl$ ,  $SO_4$  and  $CO_3$  of K.

In the same way in cement manufacture also the raw materials used are found to have appreciable amount of K and this volatilized during the cement manufacture. The flue dust obtained from this is found to have 3 to 13%  $K_2O$ . The dust can be used as a straight fertilizer.

## **5. Sea weeds**

This is referred to as the poor mans manure. It contains a high amount of  $K_2O$  varying with species of weeds. Out of many varieties 'kelp' is found to occur extensively throughout the world. The Sea weeds ash is found to have more than 25%  $K_2O$ .

## **6. Sea water**

It contains an inexhaustible amount of K. It contains 0.04 % K, 0.14% Mg, 0.05 % Ca and 1.14 % Na.

## **B. Potassic minerals**

There are as many as 50 minerals that are found to contain K but all of them are not economically important. The K containing minerals are roughly classified into

1. Minerals highly soluble in water occurring in brines or salt deposit

Sylvinite	-	KCl (Sylvite)
Carnallite	-	KCl. MgCl <sub>2</sub> . 6 H <sub>2</sub> O
Langbeinite	-	K <sub>2</sub> SO <sub>4</sub> . MgSO <sub>4</sub>
Kainite	-	KCl. MgSO <sub>4</sub> . 3 H <sub>2</sub> O

2. Minerals less soluble in water.

Polyhalite	-	K <sub>2</sub> SO <sub>4</sub> . Mg SO <sub>4</sub> . 2 CaSO <sub>4</sub> . 2 H <sub>2</sub> O
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3. Minerals insoluble in water

Glauconite	-	KFeSi <sub>2</sub> O <sub>6</sub> . 2 H <sub>2</sub> O
Feldspars	-	orthoclase - KAlSi <sub>3</sub> O <sub>8</sub>
Micas	-	Muscovite and biotite.

The following are commercially used for the manufacture of potassic fertilizers.

1. Sylvinite - KCl - contains 63.1 % K<sub>2</sub>O
2. Carnallite - KCl. MgCl<sub>2</sub>. 6 H<sub>2</sub>O - contains 17% K<sub>2</sub>O
3. Kainite - KCl. MgSO<sub>4</sub>. 3H<sub>2</sub>O - contains 18.9% K<sub>2</sub>O
4. Langbeinite - K<sub>2</sub>SO<sub>4</sub>. 2MgSO<sub>4</sub> – contains 26.6% K<sub>2</sub>O
5. Polyhalite - K<sub>2</sub>SO<sub>4</sub>. MgSO<sub>4</sub>. 2CaSO<sub>4</sub>. 2H<sub>2</sub>O – contains 15% K<sub>2</sub>O

The deposits are found to occur at a depth of 650 to 2,500 feet below the earth's surface.

### **Processed K Fertilizers**

#### **1. Muriate of potash (KCl)**

KCl is commercially manufactured using any one of the minerals; 1. Sylvinite or sylvite and 2. Carnallite . There are two main steps involved in the manufacture of this fertilizer.

1. Mining of the K mineral
2. Separation of the main ingredient and purifying.

#### **Mining**

The deposits are found to occur usually from 650 to 2,500 feet below the earth's surface. Many methods of mining are employed out of which the room and pillar method of mining is found to be familiar. After a mine shaft is sunk to a point slightly below the level of the ore body a large tunnel is driven on both sides of the shaft. At right angles to this tunnel the ore is mined in larger rooms about 25 to 50 feet wide and 300 feet long. The ore is brought over to the surface by electrically operating elevators and machineries.

## **Purification**

This involves the following process: 1. Grinding 2. Lixiviation or converting the ore into solution form 3. Crystallization 4. Separation, drying etc.

### **Grinding**

The potassic ore, after mining and bringing over to the factory site, is ground to fine size and screened to get only the ore of required size.

### **Solutioning**

The ore is dissolved in hot water and to that is added the NaCl solution (brine) for obtaining a mixture of KCl + NaCl. The temperature of the mixture is increased by which more and more of sylvinite will dissolve and the solubility of NaCl will stop after a stage. This is continued till a saturated solution of KCl is obtained.

### **Crystallization**

The saturated solution containing both KCl and NaCl is suddenly cooled in a vacuum and the KCl separates out as crystals while NaCl remains in the solution. **Separation**

Crystallized KCl can be separated out by mechanical means and it is dried, powdered and used. The above process is called the crystallization method and the principle involved is the differential solubility of KCl and NaCl in cold and hot solution. When KCl is mixed with NaCl it is much more soluble in hot water than in cold water, whereas NaCl is somewhat more soluble in cold water than in hot water. By increasing the temperature, therefore, the solubility of KCl increases while that of NaCl remains virtually constant.

### **Floatation method**

Floatation is a metallurgical process in which small quantities of special reagents are added to the pulp to coat or film some of the minerals selectively with respect to other minerals present. When the reagent added pulp is agitated in a mechanical cell in such a manner that air is drawn into the pulp to create a frothing action or condition, the finely divided air bubbles attach themselves to the reagent filmed particles and float them to the surface of the cell, where the froth rich with the selected mineral may be skimmed off. Some are found to be very effective to NaCl that is present in sylvinite.

First, after grinding and passing through the screen, the desired sized sylvinite mineral is dissolved in water to get a pulp and the reagent is added to the pulp. The reagent will form a coating or film round the NaCl molecules and this reagent added pulp is allowed to pass through a series of floatation cells in which air is introduced at the

bottom in such a manner as to form a small bubble froth that attaches to NaCl. The commonly used reagents are (1) Sulphonated aliphatic alcohols of KCl and (2) 20% of mono-n-octadecyl- amines neutralized with acetic acid and a 0.5% solution of this is used for NaCl.

It is found that at least 90% of the potassic fertilizers consumed is in the form of muriate of potash. It contains 48 to 62% K<sub>2</sub>O and 35 to 47% Cl. The commercial product is either granular or powdery having white or red colour.

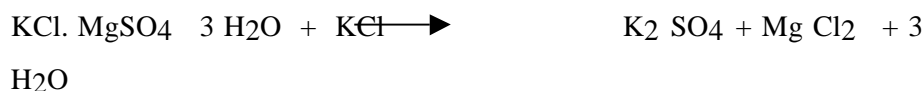
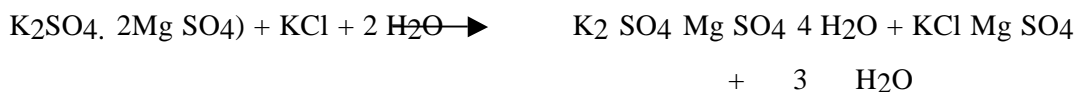
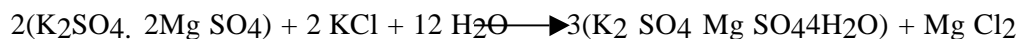
## 2.Potassium sulphate – K<sub>2</sub>SO<sub>4</sub>

This is manufactured from kainite ( KCl. Mg SO<sub>4</sub>, 3H<sub>2</sub>O) or langbeinite (K<sub>2</sub> SO<sub>4</sub>, Mg SO<sub>4</sub>), the latter being commonly used. The raw materials required are the mineral langbeinite and KCl



The MgCl<sub>2</sub> is rejected. The KCl is used in the form of a mother liquor obtained from KCl manufacturing process.

The method is found to be efficient only in the presence of a proper ratio between K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> of the raw material and to maintain a proper ratio, KCl or Kainite is added. The reactions are found to take place in different ways

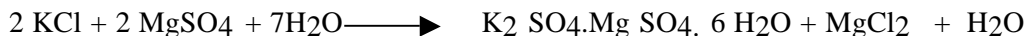


Langbeinite, ground to pass through a 200 mesh sieve and the mother liquor from the KCl process is mixed and then the salts are recycled with water and fresh quantity of langbeinite. The reactions are allowed to take place in interconnected tanks and the crystallized K<sub>2</sub>SO<sub>4</sub> is separated out by means of centrifuge. The used K<sub>2</sub>SO<sub>4</sub> is separated out by means of centrifuge. The wet K<sub>2</sub>SO<sub>4</sub> is dried and conveyed to storage place. It contains 48% K<sub>2</sub>O. Only limited quantities of K<sub>2</sub>SO<sub>4</sub> are manufactured, as the cost of manufacture is more, but is preferred for those crops where quality is desired or where chlorine toxicity will result when K Cl is used.

## 3.Potassium Magnesium sulphate

In U.S.A. it is manufactured by mere washing of langbeinite (K<sub>2</sub>SO<sub>4</sub> . Mg SO<sub>4</sub>) to remove the impurities and is sold under the name sulphate of potassium and magnesium. It contains 18.5% MgO and 22.6% K<sub>2</sub>O. Since, the langbeinite is soluble in

water; the washing is done very easily. In Germany, it is prepared by dissolving  $MgSO_4$  and adding  $KCl$  to it.



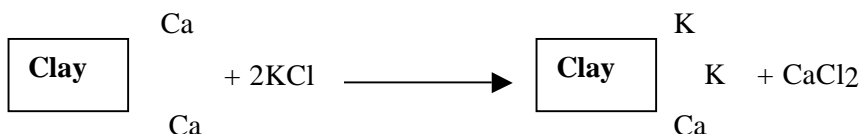
### Manure salts

The ground and partially processed potassium mineral is sold under the name manure salt or mine run potassium salt. Various grades are available in different counties; Carnalite of 9-12 %  $K_2O$  and other salts of 12-15 %  $K_2O$ , 18-22%  $K_2O$ , 28-32 %  $K_2O$ , 38-42 %  $K_2O$  are also marketed and used on a limited scale.

The muck, peat, sandy, lateritic and laterite soils are deficient in  $K$  and response will be more in these soils for  $K$  fertilizers. Clayey soils are found to give poor response for  $K$  fertilizers. Potassic fertilizers can be added to these soils in which heavy feeders of  $K$  are grown such as tuber crops, coconut, arecanut, banana etc. The vegetables are found to respond well to  $K$  application.

### Reactions of potassic fertilizers in the soil

Application of any potassic fertilizer does not change the pH of the soil. When a potassium salt is applied to a soil it is immediately dissolved and undergoes ionization. A portion of  $K^+$  ions remains in the soil solution, another portion gets adsorbed to clay complex by CEC reactions and a third portion is converted into unavailable form.



Hence, in the soil the  $K$  will be in the solution, exchangeable and fixed forms. The solution form is readily available and the exchangeable form is slowly and steadily available to plants. The fixed  $K$  is unavailable but always in any soil there is a constant equilibrium among these three forms and hence mostly exists no deficiency of  $K$ . A small quantity of  $K$  is fixed by clays like illite, and this fixation of  $K$  depends upon the type of clay, temperature, wetting and drying and soil pH. In this case the fixation is beneficial as it reduces leaching loss and the availability of  $K$  will be there for a long time.

### Factor affecting $K$ fixation in soils

#### 1. Nature of Colloids

The ability of various soil colloids to fix  $K$  varies widely. Kaolinite fixes little, while montmorillonite and illite fix more.

#### 2. Wetting and Drying

When soils containing exchangeable  $K$  are alternatively wetted and dried, a large portion of exchangeable  $K$  is converted to the less available form.



This has been explained by assuming an entrapment of K ions between contracting structural units when the soil dries some release of the ions thus held occurs upon rewetting but the liberation is slow.

### **3. Influence of lime**

Soils with high degree of base saturation lose less of their exchangeable K by leaching than the soils with a low degree of base saturation. Liming is the common means by which the base saturation of soils is increased and so liming decreased the loss of exchangeable K. The K ions are more readily replaced by calcium.

### **Application**

The K fertilizers are usually applied before the crop is planted or sown, that is the basal dressing. Since the applied K is not lost from the soil either by leaching or by fixation, K fertilizers can be applied well in advance but it is preferable to apply only just before planting. Top dressing with K fertilizers can also be done for vegetables and other crop.

