

## 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 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 sources 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**

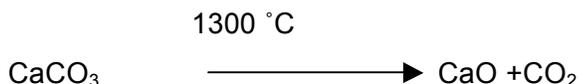
This method was demonstrated by Cavendish in 1766 on a laboratory scale. This is the most simple process of synthetic N fixation and it was first to be commercially utilized. The basic reaction of this process involved the union of N and O by means of an electric arc, the process being similar to that 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.



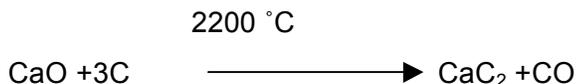
But this process requires high amount of electric power and high capital cost. It requires about five times as much electricity to fix a ton of N as is required by the cyanamide process. But this method is found to be suitable for countries like Scandinavia and Norway where the electricity is very cheap.

## II. Cyanamide process

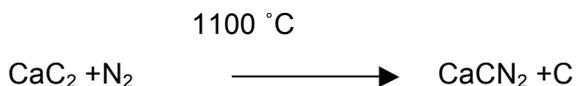
This process was developed in Germany and is said to have been invented by two Chemists Frank and Caro in 1898. At present, this process is probably the only commercial method used for synthetic fixation of N other than the ammonia synthesis process. Calcium cyanamide was first tried as a fertilizer 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.



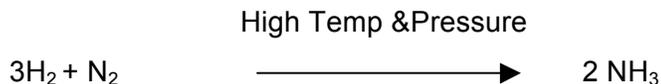
Ninety per cent of the CaC<sub>2</sub> is found to be reacted completely. The crude cyanamide is ground and treated with water to destroy residual CaC<sub>2</sub> and is brought into convenient physical condition. This method is not suitable where the coal supply is limited.

## 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.

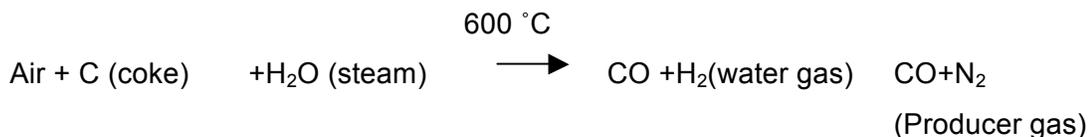
High temperature



This process consists of the following three main steps.

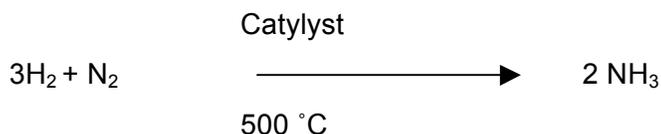
1. Preparation of H and N.
2. Purification and compression of three gases.
3. Catalytic conversion to ammonia.

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 are 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**

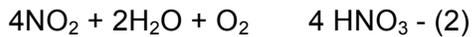
Nitric acid is produced by  $\text{NH}_3$  oxidation process. The liquid  $\text{NH}_3$  is evaporated, superheated and sent with compressed air to the converter, containing platinum –rhodium catalyst. In the converter,  $\text{NH}_3$  is converted to nitric oxide, which is

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 rising 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



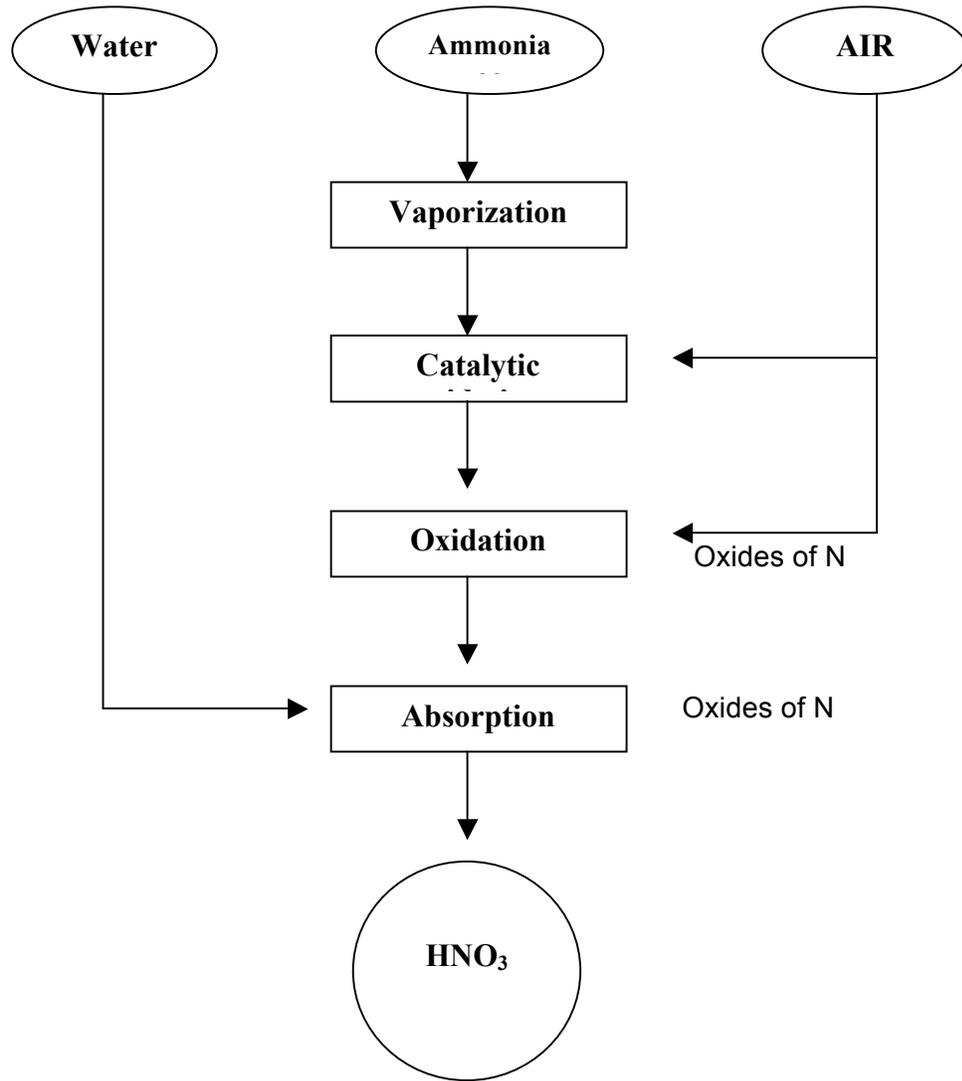
### **Concentrated nitric acid**

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**

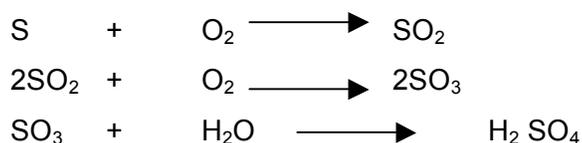
$H_2SO_4$  is one of the most important heavy chemicals produced in India. It has a wider variety of industrial uses than any other chemical. Per capita consumption of  $H_2SO_4$  often has been used as an index of the industrial development of a country. The fertilizer industries, by far, the greatest consumer of  $H_2SO_4$  for acidulation of RP and for the manufacture of  $(NH_4)_2 SO_4$ . 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**

$H_2SO_4$  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.  $H_2SO_4$  produced by burning of fuel and smelting operation is called by products  $H_2SO_4$ .  $H_2SO_4$  production from metallic sulphates is not economical. Thus for  $H_2SO_4$  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  $SO_2$ .  $SO_2$  after catalytic conversion to Sulphur trioxide is absorbed in water to give  $H_2SO_4$ . the differences in  $H_2SO_4$  processes are in the manner in which  $SO_2$  is converted to  $SO_3$  and absorbed in  $H_2O$  to produce  $H_2SO_4$ .



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

The oldest process is the chamber process, so called because the reactions which produce  $SO_3$  and  $H_2SO_4$  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**

