Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester V
Industrial chemistry (Vocational)
US05CICV02: Heavy and Fine Inorganic chemicals
UNIT – 1

Syllabus

Synthetic nitrogen products: Ammonia, ammonium nitrate and ammonium sulfate, nitric acid
Phosphorous chemicals: phosphorus, phosphoric acid, ammonium phosphate, super phosphate, triple superphosphate
Industrial carbon: carbon black, manufacture of graphite and carbon, lime gypsum, silicon, calcium carbide, silicon carbide

SYNTHETIC NITROGEN PRODUCTS

1.0 INTRODUCTION

Nitrogen plays extremely important role in nature and human life without which a living cell cannot exit. Chilean saltpetre ($NaNO_3$) and nitrogen from air are significant source of fixed nitrogen. Nitrogen is one of the major ingredients for production of fertilizer. Soil takes up nitrogen in the form of ammonium or nitrate ions and forms amino acids with carbon compounds through the complex chemical system of plants. The amino acids are then converted into proteins and enzyme. The main sources of nitrogen are

- ➢ Fertilizers
- ➢ Organic nitrogen compounds formed in soil by recurring natural process
- ➢ Atmosphere

1.1 AMMONIA

It is of the most important nitrogenous material. It is a base from which all the nitrogen containing compounds are derived. Mostly is produced synthetically, but during some chemical processes obtained as by product.

1.1.1 Raw material
Basis: 1 tonne of NH_3
H_2 = 210 kg   Power = 850KWH
N_2 = 960 kg   Fuel gas for compressors = 3800K.cal
Catalyst = 0.2Kg   Cooling water = 12,500kg

1.1.2 Catalyst
Commercial synthesis of ammonia requires an **efficient catalyst**. Most widely used catalyst is **iron with added promoters** e.g. oxides of aluminium, zirconium or silicon at about 3% concentration and potassium oxide at about 1%. These prevent sintering and make the catalyst more porous. Iron catalysts lose their activity rapidly, if heated above 520°C. Also, is deactivated by contact with copper, phosphorous, arsenic sulphur and   Carbon monoxide

1.1.3 Reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = - 22.0 \text{ k.cals}$$

1.1.4 Manufacture
(a) Haber and Bosch Process
The manufacture of ammonia is carried out by passing a mixture of pure **Hydrogen** and **nitrogen** in the proportion of **3:1** by volume under pressure over a catalyst heated to an optimum temperature. The method was first developed by Haber and Bosch therefore known as Haber and Bosch Process.
**Manufacturing consists essentially of six phases**
1. Manufacture of reactant gases
2. Purification
3. Compression
4. Catalytic reaction

5. Recovery of ammonia formed and
6. Recirculation

   Cost is greatly influenced by the pressure, temperature, catalyst, raw-materials purity and most importantly heat recovery and reuse. For achieving quality material at lower cost modification in Haber and Bosch Process are initiated.

(b) Modern method/ Kellogg ammonia process

The flow diagram of modern method of ammonia manufacture is shown in figure
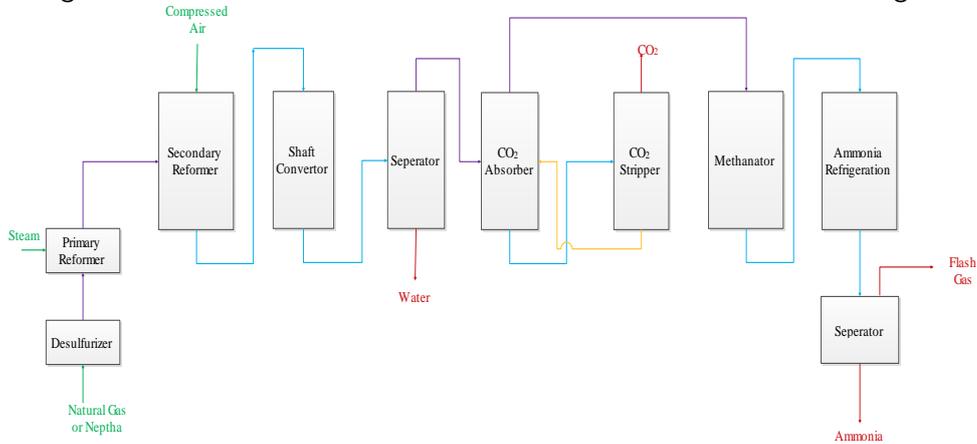
Figure: Flow diagram of manufacture of Ammonia by Kellogg process

   In the process **natural gas** is used for production of nitrogen and hydrogen. The purified nitrogen and hydrogen is thus reacted to give ammonia gas. In commercial production sulphur free natural gas is mixed with steam in the volume based ratio of **3.7:1** and compressed to **40atm**. The mixture is preheated with the recycled flue or effluent gases and fed into the furnace. At **800-850⁰C** in the presence of **iron catalyst** promoted with other metal oxides conversion of methane takes place with the formation of CO. The residual gas is mixed with air and fed into shaft converter to get complete conversion. The waste heat is utilized for the steam generation and generation of ethanolamine which are used in CO_2 and H_2S removal. The exit gas containing poison was regenerated in the methanator at 280-350⁰C which ultimately used for heating the feed water.

   Purified N_2 and H_2 mixture was compressed to **300atm at 320 to 380⁰C** in the presence of catalyst converted to NH_3. 14-20% conversion per pass was achieved. NH_3 condensed and separated from exit gas, whereas unconverted N_2 and H_2 gases were recycled along with the fresh gases.

   Ammonia synthesis is being exothermic the process requires an effective temperature control system at every stage of reaction.

(c) Latest method

   The manufacture of ammonia may be carried out by the **partial oxidation** of hydrocarbon (derived from naphtha, natural gas or coal) by oxygen enriched air in the presence of catalyst. CO is removed by passing through ammonical solution of cuprous formate. The remaining N_2 and H_2 gas are utilized for the manufacture of ammonia by Haber process.

1.1.5 Uses

 ➢ Ammonia is major raw material for fertilizer industries.

1.2 <u>AMMONIUM NITRATE</u>

   Ammonium nitrate is important nitrogenous fertilizer. Ammonium nitrate plants are found in most of the fertilizer producing countries.

1.2.1 Raw material

 ➢ Ammonia
 ➢ Nitric acid

   Both of these are usually produced at the same installation. Particularly all nitric acid is made by oxidizing ammonia and absorbing the resulting nitrogen oxides in water.

1.2.2 Manufacture

There are three important methods of producing of ammonium nitrate
➢ Crystallization
➢ Flaking
➢ Prilling

The latest and most important method is prilling. Modern ammonium nitrate prilling plant consists of the following operations.

➢ **Neutralization**

Heated ammonia vapour and 60-80% nitric acid (prepared by oxidation of ammonia) are introduced at the base of a neutraliser tower operating under a pressure of 3-5 atmosphere and through which neutralized solution is recycled. The neutralization reaction is exothermic

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \quad \Delta H = -20.60 K.cals$$

➢ **Evaporation**

Solution obtained from the neutralizer contains about 83% NH_4NO_3. This solution is allowed to pass through heater supplied with steam from the neutralizer. Means are provided to recover ammonia flashed off the neutralizer with the steam. The heated solution from the heater is then passed to a vacuum evaporator when its concentration increased to about 95%, 83% solution is drawn off at this point and used in making solution.

➢ **Prilling**

The concentrated solution is now sprayed into prilling tower. The falling solution in the tower is cooled by an ascending current of air; the prilling towers are quite high, up to 185 ft. The solution is sprayed through spray nozzles in such a manner that the liquid breaks up into drop of uniform and adequate size. The prills solidify sufficiently as they reach the bottom of tower. They must be handled carefully until they are dried.

➢ **Drying and Finishing**

It is very difficult to dry the prills of ammonium nitrate, because it is deliquescent in nature. The drying temperature must be low to avoid melting.

Various, methods of drying are available. In one method, the material is cooled to below 90°F and the remaining moisture is removed in a second dryer.

In other method known as short tower prilling, ammonium nitrate solution concentrated to about 99.5% rather than the usual 95% is prilled in the usual way in a short tower, making use of the fact that strong solution solidifies faster. The last trace of water may be removed by the process of evaporation than removing it in dryers. However, the quality of ammonium nitrate obtained by this method is not as good as it should be.

➢ **Handling**

The latest practice is to store in bulk in buildings equipped with dehumidification equipments.

➢ **Explosive nature**

A major drawback of ammonium nitrate is its explosive nature. It is very sensitive to heat and shock. The risk of explosion may therefore be avoided by mixing it with chalk. A mixture of NH_4NO_3 and $CaCO_3$ called nitro-chalk contains 16% nitrogen and does not explore. Ammonium nitrate can therefore be used safely by avoiding contact with oxidisable material keeping fire and open flames away and prompt disposal of bags.

1.2.3 Properties

The most important properties of ammonium nitrate (which are of great value in the fertilizer field) are given in the following table:

Percent of nitrogen	35%
Solubility, g/100gm water	
0^0C	118
100^0C	843
Melting point	170.4^0C
Particle size	95% - 6 mesh, 16 mesh
Hygroscopic point	59.4
Specific gravity , 20.4^0C	1.725

Crystal state	State	Temp. ^{0}C	System
	1	170 to 125	Cubic
	2	155 to 84	Tetragonal
	3	84 to 32	Rhombic
	4	32 to – 18	Rhombic
	5	Below – 18	Tetragonal

1.2.4 Uses
- ➢ Over 80% of the world wide ammonium nitrate production goes into fertilizers
- ➢ Minor amounts to other uses, mainly to industrial explosive.

1.3 AMMONIUM SULPHATE

Ammonium sulphate containing **21% nitrogen** is another important nitrogenous fertilizer. It can be obtained **as a by-product** or may be **manufactured synthetically**. Ammonium sulphate is obtained as a by-product; in the steel industry in which ammonia (another by-product)-from   coke ovens is absorbed in sulphuric acid.

Ammonium sulphate is also manufactured by reacting synthetic ammonia with sulphuric acid.

Waste streams from various chemical and metallurgical industries are other sources of ammonium sulphate e.g. ammonia leaching of ores, production of pigments and synthetic fibres, manufacture of caprolactam etc produce by product; solutions containing ammonium sulphate.

Flue gases are another source of the ammonium sulphate. The metallurgical smelters and coal burning power plants liberate large quantities of SO_2 that pollute the atmosphere. The sulphur dioxide is collected and converted into sulphuric acid, Ammonium sulphate is then produced by passing ammonia gas through 60% sulphuric acid placed in lead lines vats at about 60°C the crystals of ammonium sulphate separate out on cooling.

$$2NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2H_2O$$
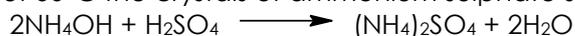
1.3.1 Manufacture
From by-product

Manufacture of by-product ammonium sulphate may be carried out by passing cleaned **coke even gases** into an **absorption column**, counter current to a re-circulating stream of saturated solution of ammonium sulphate. A **96-98% sulphuric acid** is now introduced into the stream at another point. The **neutralisation** takes place and the effluent solution containing ammonium sulphate is passed to a **crystalliser**, where crystals of ammonium sulphate separate out on cooling. The crystals are separated either by filtering or by centrifuging and then dried. The mother liquor overflowing from the crystalliser is acidified and recycled to the absorber.

In an **old saturation process** ammonium sulphate is produced by passing coke oven gas and sulphuric acid into a vat containing a saturated solution of ammonium sulphate and then setting out the crystal.

Synthetic Manufacture: Ammonium sulphate **made with manufactured ammonia** is called **synthetic** ammonium sulphate. Both **saturator's and crystallizers** are also employed in the synthetic manufacture of ammonium sulphate. The heat of reaction of anhydrous ammonia and concentrated sulphuric acid obtained by contact process is very high. Hence water evaporated from the crystallizer must be returned either by means of a condenser or by addition of water.

Sulphuric acid may also be obtained as a by-product from alcohol manufacture, nitrating process, alkylation in petroleum refining and benzene production. The acid obtained by such processes is called spent acid and contains a large number of impurities.

Ammonium sulphate is dried throughoutly to prevent caking. Free sulphuric acid is removed either by washing on a centrifuge or filter or by neutralising with weak ammonia solution.

Ammonium sulphate from gypsum or anhydrite (CaSO$_4$.2H$_2$O)

A new method which is used at Sindri in India consists of passing a concentrated **aqueous solution of ammonia** down a **tower packed with aluminium rings** against a current of CO$_2$, so as to form ammonium carbonate.

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$
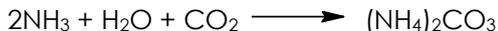
Ammonia is manufactured by Haber process and CO$_2$ is manufactured by heating limestone.

$$CaCO_3 \longrightarrow CaO + CO_2$$
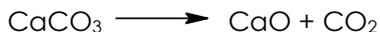
Now proper proportion of finely ground **gypsum or anhydrite** is fed into the aqueous solution of **ammonium carbonate** in large tanks, whereby calcium carbonate is precipitated gradually as a result of double decomposition.

$$(NH_4)_2CO_3 + CaSO_4 \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

CO$_2$ and NH$_3$ are passed until all the gypsum is converted into CaCO$_3$. The resulting CaCO$_3$ is separated by filtration and the ammonium sulphate solution is evaporated and crystallised in vacuum. CaCO$_3$ is used as a raw material for the manufacture of cement.

1.3.2 Action of (NH$_4$)$_2$SO$_4$ as fertilizer

It reacts with lime present in the soil to for ammonium hydroxide which is oxidised by air with the help of nitrosifying bacteria into nitrous acid. The latter is then converts into nitrites. The nitrous acid and nitrites also undergo oxidation by means of air in presence of nitrosifying bacteria and form nitric acid and nitrate.

1.3.3 Properties

Properties of fertilizer grade ammonium sulphate are given in the following table.
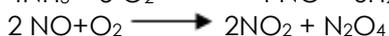
Percent of nitrogen	20-21%
Solubility, g/100gm water	
32F	70.6
912F	103.8
Melting point	513^{0}C
Specific gravity , 20.4^{0}C	1.769
Bulk density	50
Particle size	28% + 16 mesh

1.4 NITRIC ACID

1.4.1 Introduction

➢ Nitric acid is a strong acid that occurs in nature only in the form of nitrate salts.

➢ Nitric acid is the most important and useful oxyacid of nitrogen.

➢ It is of great commercial importance as it is used in manufacture of various fertilizers (ammonium nitrate, ammonium phosphate etc), explosives (TNT, nitroglycerine, cellulose polynitrate, ammonium picrate etc.) fibres, plastics and dyestuffs.

➢ A growing and potentially very important use of nitric acid is the replacement of sulphuric acid in acidulation of phosphate rock.

➢ Nitric acid was known to the ancient Egyptians because of its special ability to separate gold and silver.

1.4.2 Raw Material

Ammonia

Air

water

1.4.3 Reaction

$$4NH_3 + 5 O_2 \longrightarrow 4 NO + 6H_2O$$
$$2 NO + O_2 \longrightarrow 2NO_2 + N_2O_4$$
$$3NO_2 + H_2O \longrightarrow 2 HNO_3 + NO$$

1.4.4 Manufacture

Nitric acid is made by the oxidation of ammonia, using platinum or platinum-10% rhodium as catalyst, followed by the reaction of the resulting nitrogen oxides with water. The industrial production of nitric acid by the Ostwald process is described in this section. The process involves three chemical steps.

1. Catalytic oxidation of ammonia with atmospheric oxygen to yield nitrogen monoxide:

2. Oxidation of the nitrogen monoxide product to nitrogen dioxide or dinitrogen tetroxide
3. Absorption of the nitrogen oxides to yield nitric acid
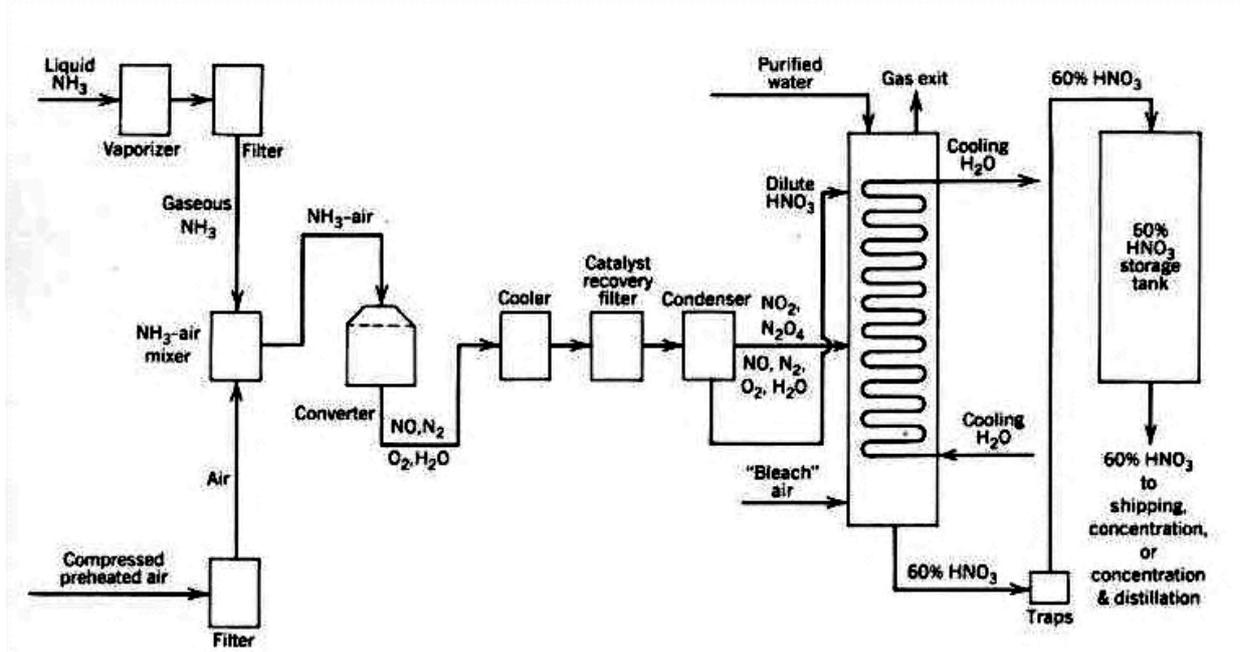
Figure: Flow chart for nitric acid manufactured by oxidation of ammonia

Compressed air is mixed with anhydrous ammonia, fed to a shell and tube convertor designed so that the preheater and steam heat recovery boiler-super heater are within the same reactor shell. The convertor section consists of 10-30 sheets of Pt-Rh alloy in the form of 60-80 mesh wire gauge packed in layers inside the tube. Gas passes downward with a velocity designed to give a contact time of about 2.5×10^{-4} sec in the catalyst zone at 800^0C.

Product gases from the reactor, containingv10-12% NO, are sent through heat recovery units, a quenching unit for rapid cooling to remove large fraction of product heat, and into the oxidizer-absorber system. Air is added to convert NO to NO_2 at the more favourable temperature (40-50^{0}C) environment of the absorption system. The equipment in the absorption train may be series of packed or sieve tray vertical towers or a series of horizontal cascade absorbers. The product from this water absorption system is 57-60% HNO_3 solution which can be sold as or concentrated as follows

1.4.4.1 Concentration by H_2SO_4

Rectification with 93% H_2SO_4 (66^{0}Be) in silicon-iron or stoneware tower produces concentrated nitric acid and 70% H_2SO_4 which can be re-evaporated to 93% H_2SO_4 or used as it is.

1.4.4.2 Concentration by $Mg(NO_3)_2$

Magnesium nitrate solution containing 70-75% $Mg(NO_3)_2$ is fed to dehydrating tray along with dilute HNO_3 from the absorption tower. The salt solution act as an extractive distillation agent, removing water at 100^{0}C or higher, thus allowing rectification within azeotropic formation. The dilute $Mg(NO_3)_2$ solution re-concentrated by evaporation

Advantages
➢ operating cost is half compare to H_2SO_4 process
➢ Acid quality and yield improved

Disadvantage
➢ Increase in 70% capital expenditure

1.4.5 Physical Properties.
➢ Molecular weight 63.013
➢ Miscible with water in all proportions.

- Pure nitric acid is colourless, fuming and pungent smelling liquid.
- The impure nitric acid is yellow due to dissolved oxides of nitrogen, mainly NO_2.
- It has a corrosive action on skin and causes painful blisters.

1.4.6 Chemical Properties
- **Acidic properties:** Nitric acid is a strong monobasic acid and ionization in aqueous solution.
- **Oxidizing properties:** It acts as a powerful oxidizing agent, due to the formation of nascent oxygen.
- **Action on metals:** Nitric acid reacts with almost all the metals, except noble metals, like Pt and Au. The metals are oxidized to their corresponding positive metal ions while HNO_3 is reduced to NO, NO_2. N_2O, NH_2OH or NH_3, depending upon the conditions such as temperature, nature of metal and concentration of the acid.

1.4.7 Uses
- As a starting material in the manufacture of nitrogen fertilizers. Large amounts are reacted with ammonia to yield ammonium nitrate.
- Weak acid (ca. 60 % HNO_3) is most suitable for this purpose. Smaller amounts of weak acid are used to digest crude phosphates.
- Nitric acid is used as a nitrating agent in the preparation of explosives and organic intermediates such as nitroalkanes and nitroaromatics.
- It is also used in the production of adipic acid.
- Other applications include use as a chemical in metallurgy and in rocket fuel production

PHOSPHOROUS CHEMICALS

1.5 INTRODUCTION

The use of artificial fertilizers, phosphoric acid and phosphate salts and its derivatives has increased greatly because of aggressive and intelligent consumption. However before full consumption of these products could be achieved, more efficient and less expensive methods had to be developed. During recent decades, various phosphorous industries have made rapid strides in cutting the cost of both production and distribution. Thus, phosphorus, phosphoric acid and its salt to be employed in wider fields and newer derivatives to be introduced.

1.6 YELLOW PHOSPHORUS

1.6.1 Raw materials
Phosphorus is now manufacture from calcium phosphate obtained from bone phosphate' or phosphate rock, $Ca_3(PO_4)_2$

1.6.2 Manufacture
A mixture of crushed **rock phosphate, sand** (or crushed quartz) and crushed **coke** in requisite proportion is fed through the **hopper** H provided at the top of a **closed electric furnace** made of brick work. The base is fitted with thick carbon blocks provided with short wall made of carbon. The furnace is also provided with an outlet B near the top for the escape of carbon monoxide and phosphorus vapour. These outlet is also joined to the cooling system and then to the cooler. There is an out let A at the bottom for tapping out molten slag. Two stout carbon rods are fixed at the bottom of the furnace, through which a current of electricity is passed; so as to form an arc.
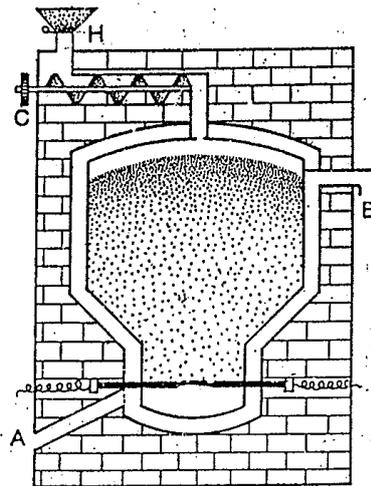
Figure: Extraction of phosphorous

Silica reacts with calcium phosphate at about **1150°C** to form P_2O_5.

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow P_2O_5 + 3CaSiO_3$$

When the temperature is   further increased to about **1500⁰C** P_2O_5 is also reduced by carbon to phosphorus vapour.

$$P_2O_5 + 5C \longrightarrow 2P + 5CO$$

The residual **calcium silicate** forms a molten slag at about**1400°C** and settles down at the bottom. It is trapped out periodically, through the outlet A provided at the bottom of the furnace. The mixture of **phosphorus** vapour and CO escapes through exit B form where it is led in to cold water, when phosphorus solidifies and carbon monoxide liberates off. The cooled phosphorus is purified by melting it with a mixture of potassium dichromate and concentrated sulfuric acid (chromic acid), so that the impurities such as carbon, silicon etc, are oxidized and phosphorus collects at the bottom. The pale yellow phosphorus thus obtained is washed with hot water and then filtered through bags of canvas. It is then cast into sticks. Crude products can also be purified by re-distillation. India has abundant supply of calcium phosphate, salt and coke, but the manufacture of phosphorus largely depends upon the production of cheap electric power.

1.7 RED PHOSPHORUS

1.7.1 Manufacture

The manufacture of red phosphorus is carried out by making use of apparatus shown in figure
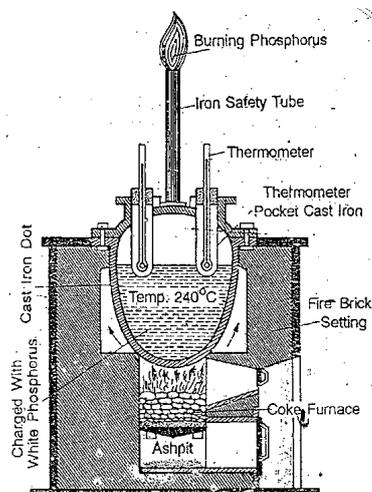

Fig. 6. Manufacture of phosphorus.

Yellow phosphorus made by above method is taken in a massive **pot** made of iron and provided with a pipe shown as iron safety tube. The iron pot is also provided with two jackets for thermometers which recorded the temperature of bath. The **conversion** of yellow or white phosphorus to red phosphorus is an **exothermic** reaction; the temperature of the pot is maintained at **240-250°C**. An increase in temperature **beyond 260°C** may cause whole of the phosphorus to various suddenly and cause the **pot to burst**. Hence a **safety valve** is provided with the pot. The pot is heated in a coke furnace made of brick. The resulting red phosphorus containing some unconverted yellow phosphorus is powdered and boiled with sodium hydroxide solution to remove yellow phosphorus is again washed with hot water and dried.

1.7.2 Modern method

The latest method of manufacturing red phosphorus is known as **continuous process**. In this process liquid **white phosphorus** is maintained at its boiling point in a reaction vessel for a period of **5 to 6 hours** as a result of which **35 – 50 %** of white phosphorus is converted into solid red phosphorus. The resulting slurry is allowed to flow continuously into a heated **screw conveyer** in which it is carried counter to a current of hot inert gas. The white phosphorus is now vaporized and condensed to a solid mass and then recrystallized. The red phosphorus of high purity neither requires treatment with caustic soda nor grinding.

1.7.3 Uses

Phosphorus is used to prepare red phosphorus used in match industries. It is also used in the manufacture of PCl_3, PCl_5, P_2O_5 and phosphorus bronze etc.
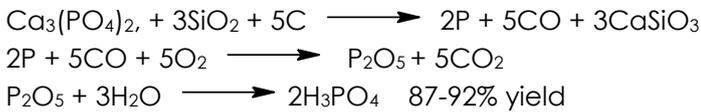
1.8 PHOSPHORIC ACID FROM PHOSPHATE ROCK BY ELECTRIC FURNACE

1.8.1 Raw materials

Basis: 1 ton phosphoric acid (100%) plus 4600 lb slag

Phosphate rock(70BPL)	4900lb	Caron electrode consumption	17 lb
Sand(silica)	1495lb	Air(minimum)	100000 cu ft.
Coke breeze	880lb	Electricity	4070 kw/hr

1.8.2 Reactions

$$Ca_3(PO_4)_2, + 3SiO_2 + 5C \longrightarrow 2P + 5CO + 3CaSiO_3$$
$$2P + 5CO + 5O_2 \longrightarrow P_2O_5 + 5CO_2$$
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad \text{87-92\% yield}$$

1.8.3 Manufacture

In the **electric-arc-furnace** process, **phosphate rock** is **reduced** to elemental **phosphorus** by the action of **coke and heat** in the presence of **sand**. Subsequent **oxidation** by **air** gives phosphorus pentoxide followed by **hydration** yields **phosphoric acid**.
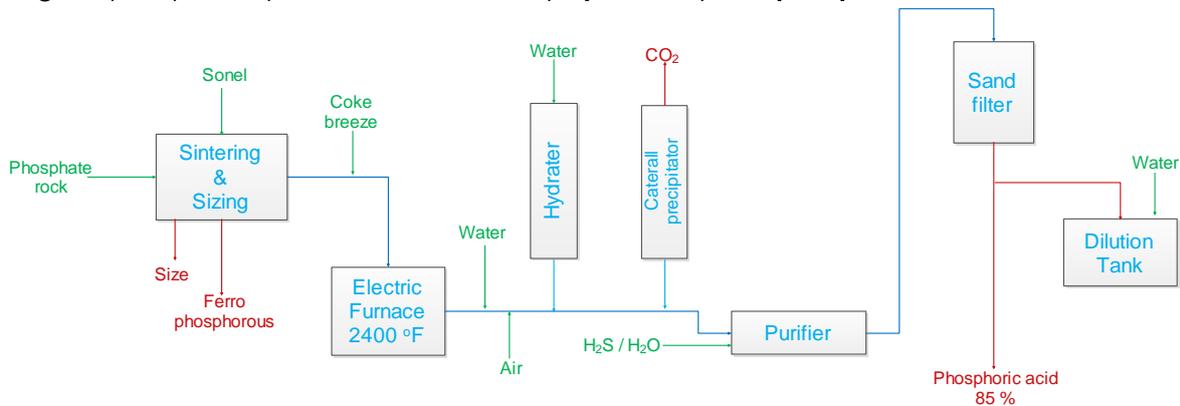

Figure: H_3PO_4 from phosphate rock by electric furnace

Phosphate rock is charged into a **sintering oven**, where it is nodulized to facilitate escape of **phosphorus vapors** in the **electric furnace** and to prevent the entrainment of dust or fines (in the vapors). The raw material is sized, and the fines are returned to the sintering oven. **Coke** (generally in the form of breeze) and **sand** are added in carefully controlled

ratios, determined by rock analysis, to the sintered rock, and the mixture is charged into the **shaft of** an electric furnace. In the shaft hang three **carbon electrodes**, which are connected to a three-phase alternating current. The charge on reaching the level of the arc, is fused at approximately **2400⁰F**, resulting in the reduction of the phosphate rock with liberation of elemental phosphorus vapors. Since phosphate rock usually contains fluorides as impurities, calcium fluoride and fluosilicates are also formed. The slag (mostly calcium silicate) is use as aggregate for road construction. Ferrophosphorus (resulting from the iron impurities) runs out with the slag. The amount of this material produced may be increased by adding iron slugs to the furnace charge. The ferrophosphorus is separated from the slag and marketed.

The gases from the furnace, phosphorus and carbon monoxide, are with-drawn from the furnace by means of a fan. In the **one-step system**, a current of air is drawn down through the charge by the suction induced by the fan. The **two-step method** produces phosphorus, which is stored for subsequent processing. The two currents (reaction gases and air) mix in the flue at a temperature sufficient to burn the phosphorus to phosphorus pentoxide (P_2O_5) and the carbon monoxide to the dioxide. The gases pass into a tall **packed tower**, where they are sprayed with water (forming a mist of phosphoric acid), and thence through a **Cottrell electrostatic precipitator** made of graphite (to resist the action of hydrofluoric acid) to remove any remaining phosphoric acid.

The **crude phosphoric acid** (85 per cent) is generally purified with respect to arsenic by the action of hydrogen sulfide. Depending on conditions, the acid may be purified further by adding sulfuric acid to remove calcium salts. Sufficient **sulfuric acid** is used to precipitate calcium sulfate and also to leave a slight excess to inhibit the corrosive action of the phosphoric acid. This slight excess of sulfuric acid permits the use of lead-lined equipment. Residual hydrofluoric acid may be removed by the addition of finely powdered **silica**. These purification steps usually take place before arsenic removal. The excess silica, calcium sulfate, arsenic trisulfide, and any suspended material are removed by passage of the acid through a **sand filter**. The clarified phosphoric acid (85percent) may be diluted with water to yield 75% and 50% acid. An overall **yield** of about **90%** is realized on the calcium phosphate content of the rock raw material.
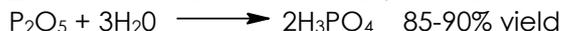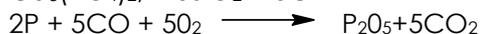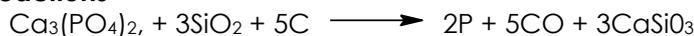
1.9 PHOSPHORIC ACID FROM PHOSPHATE ROCK BY BLAST FURNACE

1.9.1 Raw materials
Basis: 1 ton phosphoric acid (100% H_2PO_4)
(Equivalent to 72% P_2O_5)

Phosphate rock (27% P_2O_5)	5050lb	Coke	7000 lb
Sand (Silica)	15000lb	Briquette binder	500 lb
		Air	450000 cu ft

1.9.2 Reactions
$$Ca_3(PO_4)_2, + 3SiO_2 + 5C \longrightarrow 2P + 5CO + 3CaSiO_3$$
$$2P + 5CO + 5O_2 \longrightarrow P_2O_5 + 5CO_2$$
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad 85\text{-}90\% \text{ yield}$$

1.9.3 Manufacture
The raw materials and reactions in the blast furnace process are essentially the same as those of the electric furnace process. The shaft furnace used is similar in appearance to the blast furnaces as used by the steel industry.

Phosphate rock is pulverized and mixed with ground **coke**, which serves **as** the **reducing agent**, **binder** is added, and the mixture is **compressed** at about **5000 psi** into **briquettes**, which are **dried** to a moisture content of less than 1% in a **continuous dryer**. The briquettes, sand (as flux), and additional coke are charged into the top of the shaft of the blast furnace. **Preheated air** (from the hot blast stoves) is blown in at the bosh (the lower part of the furnace). The blast develops a temperature of **2400 to 2500°F**, which furnishes the necessary reaction heat. **Slag** (consisting chiefly of calcium silicate) is tapped from the furnace hearth once an hour, and the heavier ferrophosphorus (formed from the iron impurities in the rock and coke) is tapped every 12 hr.
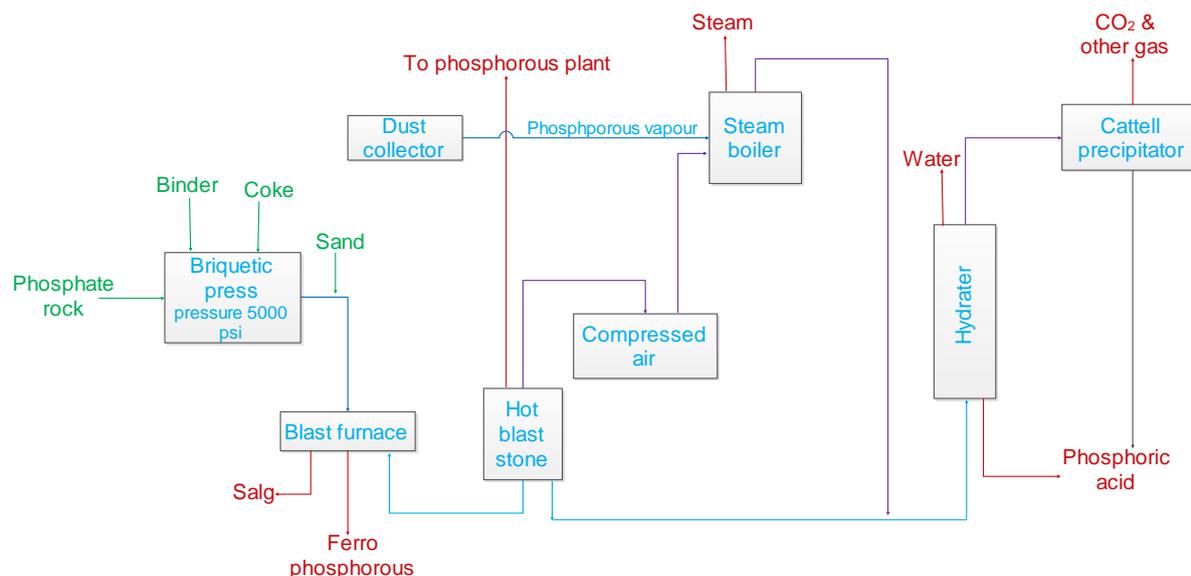
Figure: Phosphoric acid from phosphate Rock by Blast Furnace

The gas containing **phosphorus, carbon monoxide** and **nitrogen** pass from the top of the shaft through **cyclone** dust collectors and special fume collectors. The clean gas may be split into two or three portions. **One portion** may be passed through phosphorus condensers to produce the elemental product and anhydrous phosphorus pentoxide. A **second portion** may be passed into special boilers for steam generation. The phosphorus pentoxide formed in the steam boiler is added to the main gas stream. The **third portion** (generally the largest) is passed into hot blast regenerative stoves, where it is oxidized to phosphorus pentoxide. The **stoves** furnish the prevented air for the furnace blast. The **gaseous products** from the stoves and steam boilers are led into **hydrating towers** for hydration and cooling and hence through **Cottrell precipitators** for entrained phosphoric acid removal. The condensed acid (85 to 95 percent H_3PO_4) may be purified (arsenic removed) by treatment with hydrogen sulfide and subsequent filtration. About 95% of the phosphorus in the rock raw material is volatilized, giving a **yield** of about **90%** based on the P_2O_5 content of the raw material and product.

1.10 PHOSPHORIC ACID FROM PHOSPHOROUS OXIDATION AND HYDRATION

1.10.1 Raw materials

      Basis: 1 ton phosphoric acid (100% H_3PO_4)

Phosphorus	655 lb
Air	46000 cu ft (STP)
Steam and water	Variable

1.10.2 Reactions

$$2P + 2\tfrac{1}{2}O_2 \longrightarrow P_2O_5$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \ (94 – 97\% \ \text{yield})$$
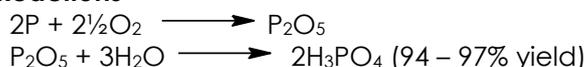
1.10.3 Manufacture

Elemental **phosphoru**s is often converted to phosphoric acid at locations other than the original point of production. The conversion involves **oxidation** of molten phosphorus to phosphorus pentoxide and subsequent **hydration** of the oxide to phosphoric acid.

Molten **phosphorus** is sprayed into a **combustion chamber** along with **air** and **steam**. Flame temperature approached **3600°F**. Chamber design varies from one plant to another, but construction materials are usually limited to acid-proof brick, structural carbon, and stainless steel, both vertical and horizontal chambers are used, in either case some glassy meta-phosphoric acid is formed and drops to the bottom of the chamber.
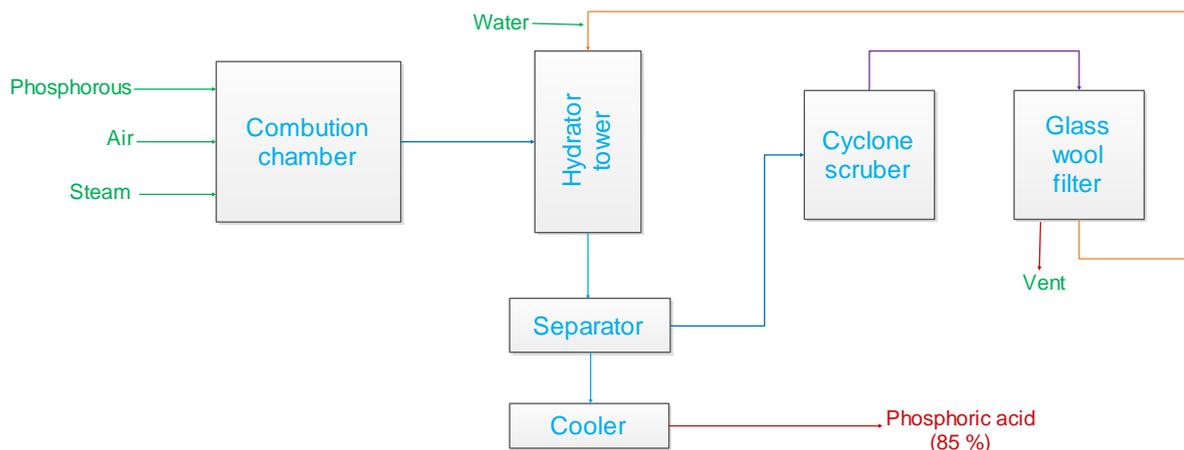
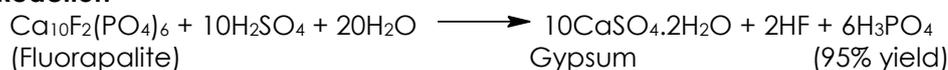Figure: Phosphoric acid from phosphorous by oxidation and hydration

The **effluent gases** leaving the chamber (P_2O_5, steam nitrogen, and some oxygen) are mixed with a **spray** of dilute phosphoric acid in the **hydration tower**. If the tower is externally cooled, it too may be built of stainless steel. By proper adjustment of reacting streams, various strengths of phosphoric acid (as high as 116%-equivalent to 84 % P_2O_5) may be produced. The usual product is in the range of 75 to 85 % H_3PO_4. Some acid mist leaves the hydrator and must be recovered by appropriate means, such as a **packed tower** or **electrostatic precipitator**. In the process shown in the flow diagram a combination cyclone scrubber and glass-wool filter is used.

1.11 PHOPHORIC ACID FROM PHOSPHATE ROCK AND SULFURIC ACID(WET PROCESS)

1.11.1 Raw materials
Basis:1 ton phosphoric acid (54% P_2O_5)
Phosphate rock(70BPL)   3600 lb
Sulfuric acid (94%)   3000 lb

1.11.2 Reaction
$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \longrightarrow 10CaSO_4.2H_2O + 2HF + 6H_3PO_4$$
(Fluorapalite)   Gypsum   (95% yield)

1.11.3 Manufacture
The sulfuric acid or **wet process** produces phosphoric acid by the action of **sulfuric acid on phosphate rock** accompanied by the **precipitation** of **calcium sulfate**; the resulting phosphoric acid solution is separated from the precipitated gypsum by **filtration** and then concentrated by **evaporation**. **Phosphate rock** is charged into a special **ball mill**, where it is ground in a **dilute** solution of **phosphoric acid** obtained **as** a **filtrate** from an ensuing operation. The **slurry** is passed into single or multiple tanks, where it is allowed to react with **sulfuric acid** diluted with sufficient phosphoric acid to yield a 55 per cent sulfuric acid solution, In **multiple tank** operations, acid is recycled to maintain uniform temperatures in the several reactors. In both single tank and multiple tank operations vigorous agitation is maintained by propellers or turbines; Heat of reaction is removed by blowing air through the reaction mass or by flash evaporation under vacuum. In both cases water vapor and gaseous impurities are carried to an absorber, where fluosilicic acid (H_2SiF_6)is recovered by spraying the gases with water.

Usually **acid digestion** of slurry **4 to 8 hr at 165 to 175°F** The purpose of the **violent agitation** (for uniform reaction time) and **close temperature control** is the production of uniform easily-filtered and easily washed calcium sulfate (gypsum) crystals. If temperature were too high, anhydrite would form, hydrate later and plug pipes.

The slurry from the digester passes to a horizontal rotating tilting-pan-type **vacuum filler**, where phosphoric acid (30 to 35 per cent P_2O_5) is removed from the cake. Most plant use tilting-pan fillers because liquors from the various washing stages can be kept separate, thus increasing recovery and minimizing dilution. Polypropylene cloth makes an excellent

filter medium. The washed gypsum cake is slurried with waste water to a setting pond from which water is ordinarily pumped back to the plant.
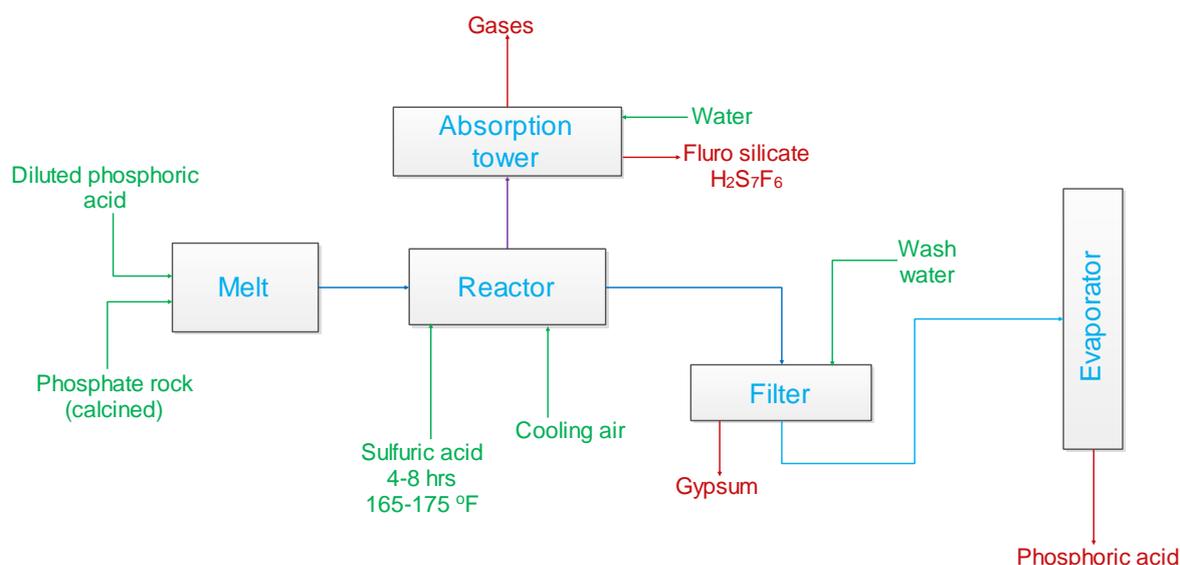

Figure: Flow diagram of wet process

The **acid filtrate** is then **evaporated** to the **desired concentration**, usually *54* per cent P_2O_5. Forced circulation evaporators with outside heat exchangers are most commonly used. Fluorine-containing compounds may be recovered from the flash chamber condensate. Submerged-combustion evaporators are also used, but high-efficiency scrubbers are required to recover P_2O_5 fumes.

Throughout the plant, **corrosion resistant materials** of construction must be used. The most common ones are structural carbon or nickel alloy for evaporator heat exchangers; rubber or carbon-brick for reactor linings; polyester-fiber glass in pipes, ducts, and small vessels. **Yield** of phosphoric acid based on phosphorus content of raw material is **95%**

Various modification of the process described are in use. Each process strives to produce a rapidly filterable crystal, to minimize P_2O_5 losses, and to produce acid of high concentration.

1.12 AMMONIUM PHOSPHATES

1.12.1 Raw Materials

A completely integrated fertilizer complex produces NH_3 and H_3PO_4 Potash (KCl) has to be imported as India has only small reserves in terms of sea bitterns which have not yet been developed.
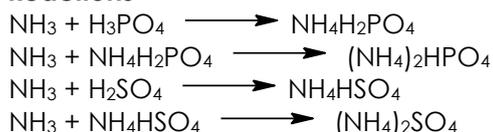
Quantitative Requirements

Depends on grade of material, compute stoichiometric ratios and allow 99% yield and 3% NH_3 handling loss.

1.12.2 Chemical Fertilizer

A mixture of ammonium phosphate and sulfate plus potash (KCl)

1.12.3 Reactions

$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4$
$NH_3 + NH_4H_2PO_4 \longrightarrow (NH_4)_2HPO_4$
$NH_3 + H_2SO_4 \longrightarrow NH_4HSO_4$
$NH_3 + NH_4HSO_4 \longrightarrow (NH_4)_2SO_4$

1.12.4 Manufacture

The two principal steps are **neutralization** and **granulation**. For neutralization, **phosphoric and sulfuric acids** are added to the first of **three** continuous mixed reactors, Anhydrous liquid **ammonia** is added beneath the slurry level in the first neutralizer in an amount equivalent to 80% neutralization. Further ammonia is added in the 2nd and 3rd tanks to obtain conversion to the diammonium salt if a higher N fertilizer is needed.

The **exothermic** reaction heats the slurry nearly to the boiling point (130°C). Unreacted and excess NH_3 vapor is collected from the top of each tank and recharged below the liquid level. This cuts NH_3 losses to less than 3%.

Slurry from the third neutralized is mixed with **KCl** and absorbed in a bed of dry recycle fertilizer moving through a **rotating drum granulator**. This provides a tumbling action to coal recycle material with a slurry film.

A **rotary adiabatic drier** reduces the moisture to less than **1%**, with a **10 minute** contact time with air initially at **150⁰C**. Dried product is separated into three fractions on a double deck screen. A portion of the product from the deck of the lower screen (-6 + 12) is sent to bagging operations. The balance, together with pulverized oversize and lines, is returned to the granulator. The weight ratio of recycle to product is 6: 1-15: 1 depending on the grade produced.

1.12.5 Uses

The only major use is for chemical fertilizers. Minor uses are in fire-retardants, nutrient yeast culture, ammoniated gentrifies.
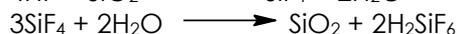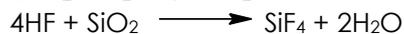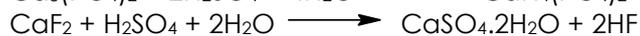
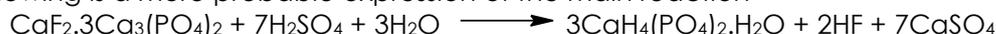## 1.13 SUPERPHOSPHATES

1.13.1 Raw Materials

Phosphate rock, when very **finely pulverized** has **limited use** as a **fertilizer** itself, chiefly because of the relatively **slow availability** of the **P_2O_5**. Its main consumption, however, is as a raw material for the manufacture of phosphoric acid, superphosphate, phosphorus, and phosphorus compounds.

1.13.2 Reactions

The **acidulation of phosphate rock** to produce superphosphate has been the most important method.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \longrightarrow CaH_4(PO_4)_2 + 2(CaSO_4.2H_2O)$$
$$CaF_2 + H_2SO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + 2HF$$
$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$

The following is a more probable expression of the main reaction

$$CaF_2.3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O \longrightarrow 3CaH_4(PO_4)_2.H_2O + 2HF + 7CaSO_4$$

1.13.3 Manufacture

The **hydrofluoric acid** reacts as shown above forming **fluosilicic acid** but with incomplete removal fluorine. An excess of **sulfuric acid** is consumed by such impurities in the phosphate rock as $CaCO_3$ Fe_2O_3 and CaF_2.The product increase in weight over the **70-75°C** bone phosphate of line by phosphate rock used as much as 70%, resulting in superphosphate with 16 to 20% available P_2O_5

The **manufacture** of superphosphate involves **four steps**
1. Preparation of phosphate rock
2. Mixing with acid
3. Curing and drying of the original slurry by completion of the reactions
4. Excavation, milling, and bagging of the finished product.

Although newer plants use **continuous processes**, some plants still conduct these operations stepwise. All plants first pulverize the rock with modern pulverizing and air-separation equipment, most rock is ground to an average finesse of 70 to 80% through a 200mesh screen, with the following benefits
➢ The reaction rate is faster
➢ More efficient use is made of the sulfuric acid and consequently less acid is needed
➢ A higher grade of product in better condition is obtained.

1.13.4 Manufacture of normal superphosphate by a continuous-den process

This is depicted by figure where ground **phosphate rock** (90% minus 100) is fed by a weigh feeder into a **double-conical mixer** (TVA), where it is thoroughly mixed with metered quantities of **sulfuric acid**. The sulfuric acid is dilute with water in the cone to a concentration of 51°Be. The heat of dilution serves to heat the sulfuric acid to proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The **rate of water addition** and **acid concentration** may be varied to control product **moisture**. The acid and

water are fed into the **cone mixer** tangentially to provide the necessary mixing with the phosphate rock. The fresh superphosphate is discharged from the cone mixer into a **pug mill**, where additional mixing takes place and the reaction starts. From the pug mill the **superphosphate** drops onto the **den conveyor**, which has a very low travel speed to allow about **1 hr** for solidifying before reaching the cutter. The **cutter** slices the solid mass of crude product so that it may be conveyed to pile storage for **"currying"** or completion of the chemical reaction, which takes **10 to 20 day** to reach P_2O_5 **availability** acceptable for plant food. The conditions den is enclosed so that fumes do not escape into the working area. These **fumes** are scrubbed will water sprays to remove acid and fluoride before being exhausted to the atmosphere. The scrubber water is discharged to a limestone bed lo neutralize the acid.
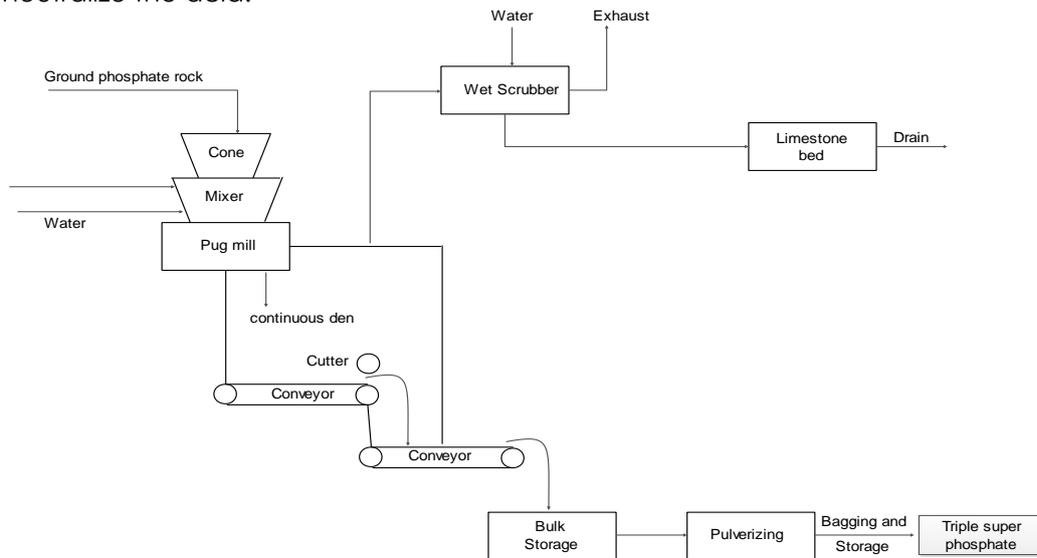

Figure: Flowchart for the manufacture of superphosphate by the continuous-den process.

1.13.5 Nitric and **mixed acid acidulation of phosphate rock**

Europe probably first used **nitric** and mixed acid **acidulation** of **phosphate rock**. The substitution of **nitric for sulfuric acid** is desirable, since **nitrogen** has an essential value as plant food and can be resold at its purchase price. Also, this **saves sulfur**. Simple acidulation of phosphate rock with nitric acid produces a hydroscopic superphosphate, since it contains calcium nitrate. The TVA and other have studied and recommended **commercial processes**. **In one**, the phosphate rock is extracted by mixed nitric and sulfuric acids, followed by ammoniation drying and the addition of potassium chloride (optional). Another features mixed nitric and phosphoric acidulation followed by the conventional steps and **others use** nitric acid alone for acidulation. These processes, as well as conditioning against moisture absorption as practiced for ammonium nitrate, have led to an extension of this acidulation with nitric acid. **Nitrophosphate** is also gaining in Europe. **Phosphate rock** is decomposed with nitric acid plus small amount of phosphoric acid. The resulting slurry is ammoniated and carbonated and, if desired, combined with potassium salts and spray-dried to yield a uniform palletized product.

1.14 <u>TRIPLE SUPERPHOSPHTE</u>

1.14.1 Raw Materials
Phosphate rock
62% Phosphoric acid
Steam
1.14.2 Manufacture
This material is a much more concentrated fertilizer than ordinary superphosphate, containing from **44 to 51%** of available P_2O_5 or nearly **three times** the amount in **regular**

superphosphate. Triple superphosphate is made by the action of phosphoric acid on phosphate rock, and thus no diluents calcium is formed.

$$CaF_2 + 3Ca_3(PO_4)_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF$$

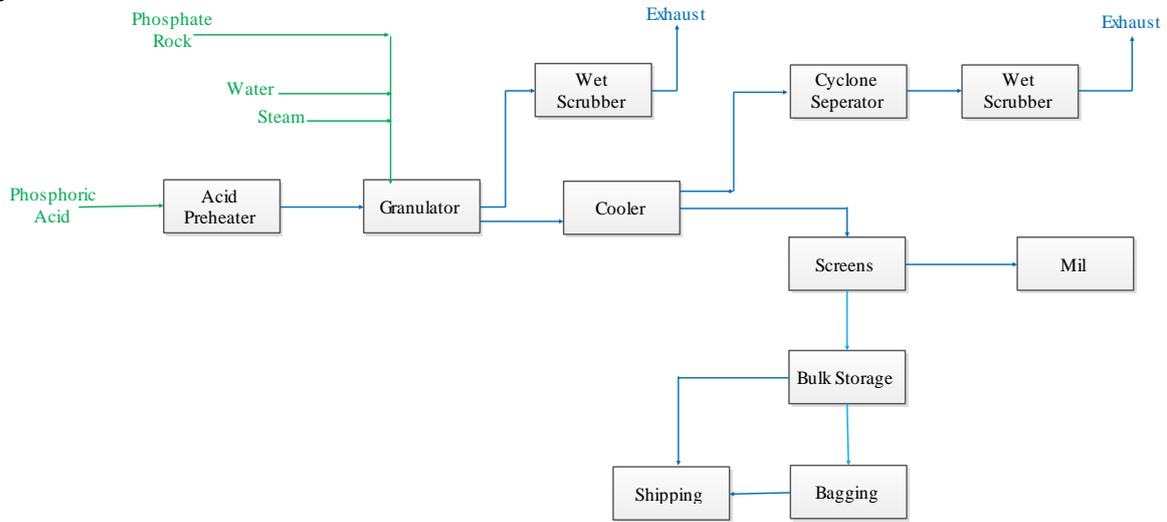The TVA continuous granular triple superphosphate production process is illustrated in Figure.

Figure: Flow diagram of manufacture of triple superphosphate

Here the ground **phosphate rock** (75% minus 200-mesh) and **62% phosphoric acid** are metered continuously to the **granulator**, where reaction and granulation lake place. Fines from the product screen are recycled to the granulator, and the **moisture and temperature** required for proper granulation are maintained by addition of **water and/or steam**. The granulator is a cylindrical vessel rotating about a horizontal axis and has in overflow dam at the discharge end. The **phosphoric acid** is fed uniformly under the bed of material through a perforated pipe. When **wet-process phosphoric acid** is used, it is also necessary to provide an **acid pre-heater**. The granules overflow the dam into a **rotary cooler**, where they are cooled and dried slightly by a counter current flow of air. The exhaust gases from the cooler pass through a **cyclone**, where dust is collected and returned to the granulator as recycle, the cooled product is screened, the coarse material being milled and returned, along with the fines, to the granulator. The product is then conveyed to bulk storage, where the material is cured 1 to 2 weeks, during which a further reaction of acid and rock occurs, which, increases the availability of P_2O_5 as plant food, the exhaust gases from the granulator and cooler are scrubbed with water to remove silicofluorides. The cost per unit of P_2O_5 in this concentrate as compared with ordinary superphosphate is higher, because of greater capital investment and additional labor and processing. However, this is offset to a great extent by the ability to use a lower-grade, cheaper phosphate rock to make the phosphoric acid which is reacted with higher-grade rock. There are also substantial savings on handling, bagging, shipping, and distributing. The production of concentrated superphosphate has grown in short tons in terms of 100% available phosphoric acid (APA). Normal superphosphate production has dropped slightly.

INDUSTRIAL CARBON

1.15 SYNTHETIC GRAPHITE

Graphite mixed with impurities is found in nature and is known as **natural graphite**. Natural graphite is found in Siberia, Sri Lanka, USA, Canada and Czechoslovakia. In India it occurs in small amounts at Visakhapatnam, Travancore, Rajasthan and Orissa. The **artificial graphite** was first prepared by **A. G. Acheson** by heating amorphous carbon with certain catalysts, such as SiO_2 or Al_2O_3 in an electric furnace at a temperature of about 3000°C. It is known that the industrial process converts amorphous carbon directly to artificial or synthetic

graphite in an electric furnace.

1.15.1 Raw Materials

The raw material for the manufacture of artificial graphite is petroleum coke or anthracite or pitch coke. All these contain small amount of ash (SiO_2) which acts as a catalyst. The reaction for the allotropic change is

$$C \text{ (amorphous)} \xrightarrow{3000^0C} C \text{ (graphite)} \ \Delta H = -2.5 \text{ k.cals}$$
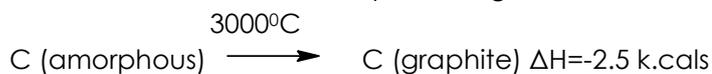
1.15.2 Manufacture

The furnace used for the manufacture of artificial graphite is an **open top resistance furnace** and consists of a core of the coke being graphitised. The front, back and the floor of the furnace are made **mainly of concrete**, with **cooling coils** in the ends in order to reduce the temperature of electrodes in contact with air to prevent them from burning. The side walls of the furnace are built of loose **refractory blocks and plates** which are torn down during unloading. Several **graphite or carbon rods** are inserted through the front and back walls. The core of **coke** to be graphitized is also surrounded by a layer of **sand, coke and raw dust**. The **raw dust acts as insulation**. The resistance of the charge increases the temperature of the furnace to **3000°C**, at which amorphous carbon is converted into graphite and voltage decreases from **200 to 40 volts**,   because of lowered resistance. Some heat is generated due to exothermic reaction but bulk of the heat is generated by the resistance provided by the charge to the flow of electricity. At a temperature of 3000°C, any silicon carbide that may be present also decomposes into graphite and silicon. The latter volatilizes off at this temperature leaving graphite in the furnace. After cooling the furnace is torn down and graphitized carbon taken out. The insulating sand, coke and silicon carbide mixture is again fed to the furnace to be utilized again. Power rating is 6000-10000 Kw-hr per tonne of finished graphite. The **complete cycle** of the furnace consist of: loading: 1 day; heating-5-6 days; cooling 15 days and unloading 2 days. Hence about **23 days are required** from charge to charge.

1.15.3 Properties

Graphite has a two dimensional structure and series of layer. In graphite only 3 valance electrons of each carbon atom are involved. Thus each carbon atom makes use of sp^2 hybrid orbital forming three covalent bonds and three other carbon atoms in the same plane. The fourth valence electron remains unpaired or free. This makes graphite a good conductor of electricity. The C-C covalent distance is 1.42^0A and the distance between two successive layers is 3.34^0A. The sheets or layers are held together by weak Vander Waal's forces. Lead of lead pencils contain graphite and variable quantities of clay depending upon the hardness required.

Some of the **unusual characteristics of graphite** are.

➢ Extremely high fusion point under pressure
➢ Low density
➢ High resistance to chemical and mechanical corrosion
➢ Strong resistance to mechanical shocks
➢ Strong resistance to temperature fluctuations
➢ Good electrical conductivity
➢ High sublimation temperature (3600^0C)
➢ High arc plasma temperature ($>5000^0C$)
➢ High degree of insolubility in molten salt

1.15.4 Uses

Natural graphite has widely been used in the manufacture of clay-graphite crucibles, lead pencils and as a lubricant. It is, however, not suitable for the manufacture of graphite electrodes which are extensively used in the manufacture of large number of electrochemical and electro-thermal products (such as aluminium, magnesium, caustic

soda, chlorine etc). This is probably due to the impurities associated with natural graphite.

 Artificial graphite can be substituted for any of the use of the natural product **except** in the production of **clay-graphite crucibles**, although several crucibles and trays have also been manufactured from artificial graphite. For **lubricating purposes**, it is suspended in water or oil and placed in contact with moving parts. In **electrical industries**, graphite is used for electrodes, brushes, contacts and electronic tube rectifier elements.

1.16 ARTIFICIAL ABRASIVES

 Formerly natural products, such as diamonds, garnet, quartz, rouge, kieselguhar, emery and corundum were used as abrasives. In 1891, Acheson produced the **first man made abrasive**, known as **silicon carbide** in a homemade electric arc furnace. Later on various other abrasives, such as fused aluminium oxide, boron carbide, boron nitride and calcium carbide were also prepared commercially in the **electric thermal furnace**.
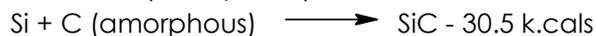
1.17 SILICON CARBIDE OR CARBORUNDUM

 Silicon carbide is one of the most important abrasive and was first discovered by Acheson(1891) while attempting to harden clay in a homemade electric furnace.
When carbon was dissolved in molten clay it was assumed to be mixture of carbon and fused alumina called **corundum** and hence the name **carborundum**.

1.17.1 Raw Materials

 Silicon carbide (SiC) is now manufactured by making use of sand or silica and carbon. The sources of carbon are coke, pitch, petroleum cokes and anthracite. The sand contains pure silica (98 to 99.5%) SiO_2

1.17.2 Reactions

 The various reactions involved in the manufacture of silicon carbide are

$SiO_2 + 2C$ (amorphous) $\longrightarrow$ $Si + 2CO + 144.8$ k.cal

$Si + C$ (amorphous) $\longrightarrow$ $SiC - 30.5$ k.cals

$\overline{\phantom{SiO_2 + 3C \text{(amorph)} \longrightarrow SiC + 2C0 + 114.3 k.cals}}$

$SiO_2 + 3C$ (amorph) $\longrightarrow$ $SiC + 2C0 + 114.3$ k.cals

 The temperature is maintained at 2000°c. Higher temperature is prevented as Sic is decomposed into graphite at high temperature.

1.17.3 Manufacture

 Special type of open top indirect heating **resistance furnace** is used for manufacture of SiC. The furnace consists of a permanent bed of curved cast iron pieces lined with fire brick on which the charge is placed. The charge is built up in the furnace around a heating core of granular carbon. The 30-50 ft long furnace is provided with about 60 carbon electrodes which are one metre long and 8 cm. in diameter and the central core of iron connects these electrodes. The ends of the furnace are permanent and the sides are built up every time with the charge. Excessive heat loss does not take place because the outside unreacted charge acts as an insulator. The sides are pulled down after the completion of the process to take out the product. The charge which is a mixture of 53.5% SiO_2, 40% coke, 5% saw dust and 1.5% salt is added to furnace until it is full. **Saw dust increase the porosity of the charge to permit the circulation of vapours and the escape of carbon monoxide formed**, CO burns at the top of the furnace. **Salt is added as a flux.** A typical initial current between the electrodes is 6000amps at 250 volts, but its resistance gradually decreases as the reaction proceeds and the final current becomes 20000 amperes at 75 volts. After about 2 hours, the current increases rapidly from 6000 to 20000 amps and remains steady during the whole run of 36 hours. The **temperature at the core is 2200°C** amps and remain steady during the whole run of **36 hour** until the reaction is complete. The product is then cooled for 24hour and

crystals of silicon are removed from the furnace. The **yield** is about **6-8 tonnes** per furnace. The **black crystals** are broken and then treated successively with sulphuric acid and sodium hydroxide solution. It is dried in a kiln and graded through a screening or sieving system into, the powders of various degrees of fitness.

It should be noted that the temperature of the core should not exceed 2200°C. **Higher temperature** leads to the **decomposition of silicon carbide into graphite** with the volatilization of silicon. The graphite formed in this manner is called **artificial graphite**. The outer unreacted part of the charge is combined with the next charge for the furnace and next to the core some graphite formed as a result of decomposition of SiC is obtained. After complete run, which takes about 36+24=60 hours, the graphite can be separated as a byproduct from silicon carbide and converted to desired shapes. A part of the core used in the furnace can be made of coke suitable for graphite manufacture.

A **good yield** of carborundum can be obtained by taking the following points into consideration.

➢ Silica or sand used should be of about 98% purity.
➢ The carbon used may be petroleum coke, metallurgical coke, anthracite etc. having low ash and sulphur contents.
➢ Fe_2O_3 and Al_2O_3 in silica should be as low as possible as they catalyse the decomposition of SiC. The carbide undergoes decomposition at 2830°C.
➢ The temperature of formation of silicon carbide is about $1840°C \pm 30°C$
➢ 100 parts by weight of finest grade sand, 60 parts by weight of coke and 19 parts by weight of saw dust is the charge composition for a good yield of SiC. Saw dust increases the porosity of the charge or escape of CO and other volatile matter during SiC formation.

1.17.4 Properties

Silicon carbide has **high thermal conductivity** due to which it is resistant to shock because of temperature fluctuations. Its **conductivity** lies between those of metals and non-metals or insulators and so it **acts as semiconductor**. Its **radiation resistance** is much higher than pure silicon. It is exceptionally stable to most chemicals at low temperatures but reacts at high temperatures.

1.17.5 Uses

The most notable property of silicon carbide is its hardness. It is almost **as hard as diamond** and is used for making grinding machines, grinding stones, crushers, for giving edge to cutting tools (razors, knives, swords etc.). On account of its **refractory nature** and **higher heat conductivity**, it is also used for making crucibles. It has also been used as a refractory material, both in the form of bricks and as loose material. Silicon carbide has also been used as an abrasive for making the modern grinding tools, which are used as in fabricating the metal parts of modern automobiles, tanks, engines, rifles, aeroplanes and other machines. It is also used for carbon rods in resistance heaters.

1.18 CALCIUM CARBIDE

1.18.1 Raw Materials

Calcium carbide is commercially manufactured from carbon and quick lime at 2000-2200°C in a specially designed calcium carbide electric furnace.

$$CaO + 3C \text{ (amorphous)} \longrightarrow CaC_2 + CO \quad \Delta H = +103 \text{ k.cals}$$

The carbon is obtained from coke, anthracite or petroleum coke. Coke has, however, widely been used. The coke must be compact and have low ash content, low ignition point and high electrical resistivity (or low electrical conductivity) so that the bulk of the furnace charge may be highly resistant to the flow of energy. As a result, the energy becomes concentrated in the charge rapidly producing high temperature required for the reaction to

take place and to go for completion. The coke should also be free from phosphorus, because it forms a phosphide, which is converted to poisonous phosphine (PH_3), when acetylene is formed by the action of water on carbide. The presence of phospine may even causes serious explosion. The coke must contain low ash contents (about 3% or less) otherwise the carbide formed will be viscous and therefore, will create difficulty during tapping from the furnace.

The quicklime is obtained by during limestone containing about 97 percent $CaCO_3$.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Magnesia, silica and iron oxides present in the form of impurities hamper production and give less pure carbide. These impurities should, therefore, be properly controlled before the charge is fed to the furnace.

Basis: 1 tone of Calcium carbide

Lime: 1900lbs.   Coke: 1300lbs

Electrode paste: 35lbs   Energy: 3000kw/hr

1.18.2 Manufacture

A typical three phase furnace of 25000 kilowatts-hr produces about 200 tonnes of 85% carbide per day is as shown in figure.
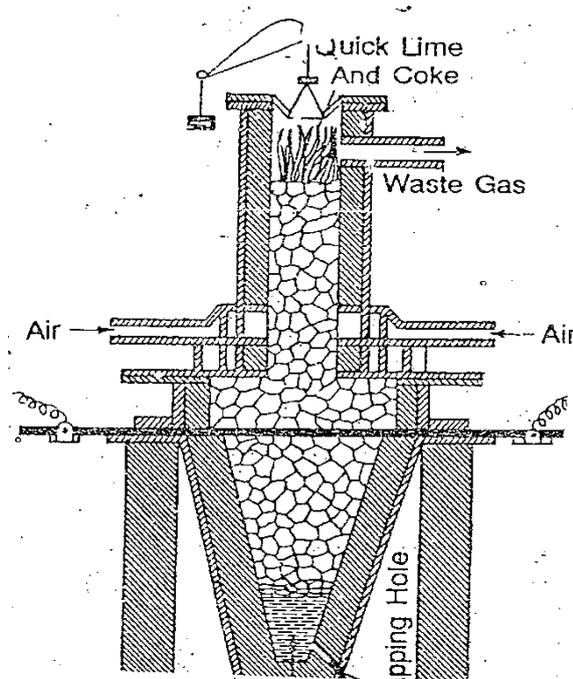
Carbide furnaces fall in the class of combined resistance and direct arc heating, since some of the heat is due to the resistance of the raw material, but most part of it is due to sparking across the charge. The furnaces consists of a steel shell 10 X 3 meter in area or more with the side walls lined with refractory material and the bottom covered with carbon block, or anthracite to with stand extremely hot alkaline conditions. Most of the **recent large furnaces** have closed top (where almost all the CO evolved during the reaction is collected and utilize) and three phase electric current i.e. they have three vertical electrodes suspended in the shell and the each is connected to one of the low tension bars. The electrodes are made up of graphite, fitted and bound. They may be as long as 10 X 2ft and may be round or oval in the cross section. They are also provided with arrangement for lowering because they are consumed.

Recently Soderberg Continuous Self Baking Electrodes have been used in place of prebaked electrodes, since the former permit large capacity furnaces. The electrodes are dipped in the charge which almost fills the furnace. The layer of carbon or anthracite in the

bottom acts as the bottom electrode. The charge consisting of 60% calcium oxide and 40% coke is fed from the top. Before it reaches the region of high temperature (2000°C) provided by the furnace, it gets heated by the burning of carbon monoxide (liberated in the reaction) in air. The latter is pumped through side tubes in the middle of the furnace. Calcium carbide is formed at the bottom as a result of reaction of calcium oxide and coke. The molten calcium carbide is periodically tapped out of the furnace and fresh charges added into cast iron chilled pots of about 5 tones capacity each. The carbide is cooled, crushed and sized.

Commercial calcium carbide thus obtained is generally black, reddish black or reddish brown, depending upon the presence of iron or other constituents.

1.18.3 A good yield of calcium carbide is obtained when
- Lime is prepared from lime stone of about 96-97% purity.
- MgO content of lime should not excess 1%. Higher amount may cause reduction of fluidity of molten CaC_2 creating difficulty in tapping.
- Al_2O_3 should be as small as possible, because it also creates the same problem as created by MgO.
- SiO_2 should not exceed 1.25%
- Fe_2O_3 + Al_2O_3 should not exceed 0.5%, because Fe_2O_3, if present reacts with SiO_2 and produce ferrosilicon. The latter settles down below CaC_2 and attacks the refractory material of the furnace.
- Impurities of phosphorus and sulphur in lime should not be more than 0.1% because they would produce Ca_3P_2 and CaS which in their turn produce PH_3 and H_2S during water treatment of the carbide.
- Metallurgical coke, petroleum coke and soft coke with low ash content and volatile matter should be used. Petroleum coke is most commonly used because of its low ash content and high resistivity.
- The moisture content of coke used should not exceed 2%.
- 60 parts of CaO and 40 parts by weight of coke are used.
- The electrodes may be prebaked, square of rectangular made from amorphous carbon, graphite or continuous self backing type made from calcined anthracite and coal and pitch as binder.

1.18.4 Uses
Today calcium carbide is used as an abrasive and for the manufacture of acetylene which is used in oxyacetylene blow pipes acetylene lamps and as starting material for the preparation of many compounds, such as CH_3CHO, CH_3COCH_3, CH_3COOH, $CH_3COOC_2H_5$. It is also used in the manufacture of calcium. A small amount or the calcium carbide is used as reducing agent in some metallurgical processes and as a drying agent.

In India calcium carbide is manufactured at various places. Imports have already been stopped in 1961.

Some **leading manufactures** are
- Birla Jute Manufacturing CO. Ltd. Birlapur   (W.Bengal)
- Calico Mills Tromday,   Bombay.
- Industrial Chemicals Ltd. Talaiyuthu, Tamil Nadu (Madras)

Carbon black

Silicon

Lime

Gypsum