

## Natubhai V. Patel College of Pure & Applied Sciences

### S. Y. B.Sc. (Industrial chemistry)

#### C-214: Chemical Process Industries

#### UNIT 5A

#### SYLLABUS

**PHOSPHORUS INDUSTRIES:** Raw materials, Manufacture of phosphorus, Phosphoric acid, ammonium phosphate, super phosphate

#### PHOSPHORUS INDUSTRIES

#### 5.0 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.

#### 5.1 YELLOW PHOSPHORUS

##### 5.1.1 Raw materials

Phosphorus is now manufacture from calcium phosphate obtained from bone phosphate' or phosphate rock,  $\text{Ca}_3(\text{PO}_4)_2$

##### 5.1.2 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.

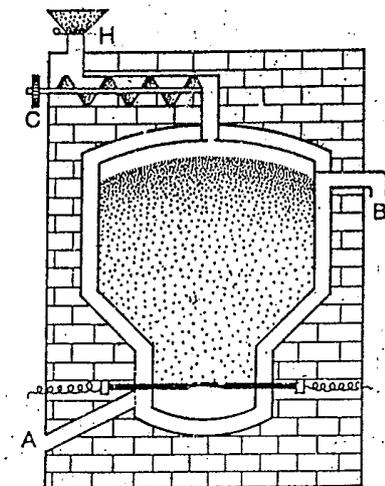
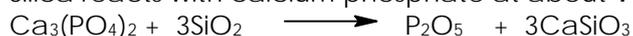
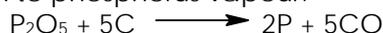


Figure: Extraction of phosphorous

Silica reacts with calcium phosphate at about **1150°C** to form  $\text{P}_2\text{O}_5$ .



When the temperature is further increased to about **1500°C**  $P_2O_5$  is also reduced by carbon to phosphorus vapour.



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 from 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.

## 5.2 RED PHOSPHORUS

### 5.2.1 Manufacture

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

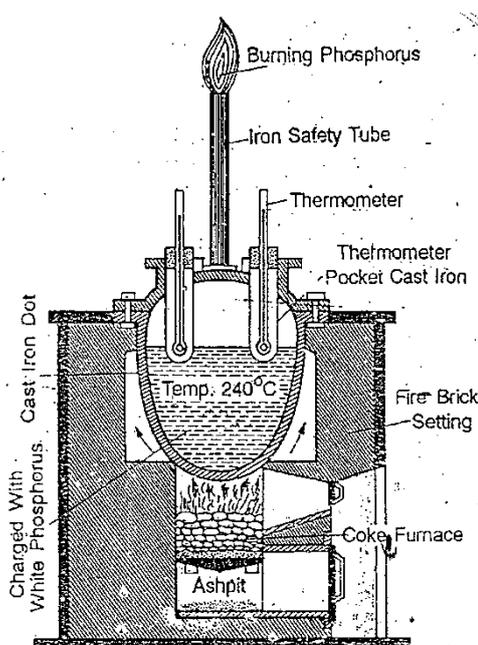


Fig. 6. Manufacture of phosphorus.

**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.

### 5.2.2 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 conveyor** 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.

### 5.2.3 Uses

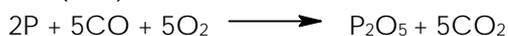
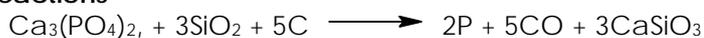
Phosphorus is used to prepare red phosphorus used in match industries. It is also used in the manufacture of  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{P}_2\text{O}_5$  and phosphorus bronze etc.

## 5.3 PHOSPHORIC ACID FROM PHOSPHATE ROCK BY ELECTRIC FURNACE

### 5.3.1 Raw materials

<b>Basis:</b> 1 ton phosphoric acid (100%) plus 4600 lb slag			
Phosphate rock(70BPL)	4900lb	Carbon electrode consumption	17 lb
Sand(silica)	1495lb	Air(minimum)	100000 cu ft.
Coke breeze	880lb	Electricity	4070 kw/hr

### 5.3.2 Reactions



### 5.3.3 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:  $\text{H}_3\text{PO}_4$  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 **2400°F**, 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.

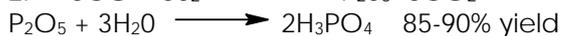
## 5.4 PHOSPHORIC ACID FROM PHOSPHATE ROCK BY BLAST FURNACE

### 5.4.1 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

### 5.4.2 Reactions



### 5.4.3 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.

Figure: Phosphoric acid from phosphate Rock by Blast Furnace

**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.

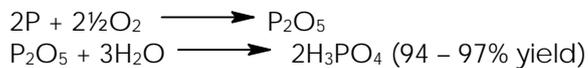
The gas containing **phosphorus**, **carbon monoxide** and **nitrogen** pass from the top of the shaft through **cyclone** dust collectors and special fume collectors. The clean gas may be split into two or three portions. **One portion** may be passed through phosphorus condensers to produce the elemental 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 preheated 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.

## 5.5 PHOSPHORIC ACID FROM PHOSPHOROUS OXIDATION AND HYDRATION

### 5.5.1 Raw materials

<b>Basis:</b> 1 ton phosphoric acid (100% $H_3PO_4$ )	
Phosphorus	655 lb
Air	46000 cu ft (STP)
Steam and water	Variable

### 5.5.2 Reactions



### 5.5.3 Manufacture

Elemental **phosphorus** 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.

Figure: Phosphoric acid from phosphorous by oxidation and hydration



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.

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.

## 5.7 AMMONIUM PHOSPHATES

### 5.7.1 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.

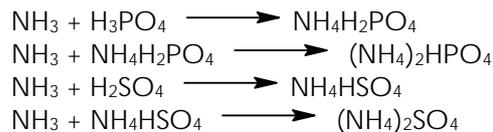
#### Quantitative Requirements

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

### 5.7.2 Chemical Fertilizer

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

### 5.7.3 Reactions



### 5.7.4 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 2<sup>nd</sup> and 3<sup>rd</sup> 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 coat 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 **150°C**. 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 fines, is

returned to the granulator. The weight ratio of recycle to product is 6: 1-15: 1 depending on the grade produced.

### 5.7.5 Uses

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

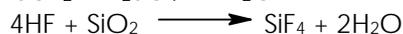
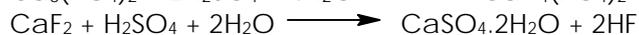
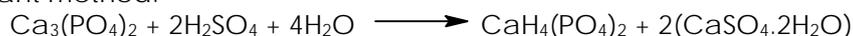
## 5.8 SUPERPHOSPHATES

### 5.8.1 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<sub>2</sub>O<sub>5</sub>**. Its main consumption, however, is as a raw material for the manufacture of phosphoric acid, superphosphate, phosphorus, and phosphorus compounds.

### 5.8.2 Reactions

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



The following is a more probable expression of the main reaction



### 5.8.3 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<sub>3</sub>**, **Fe<sub>2</sub>O<sub>3</sub>** and **CaF<sub>2</sub>**. 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<sub>2</sub>O<sub>5</sub>

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 fineness 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.

### 5.8.4 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<sub>2</sub>O<sub>5</sub> availability** acceptable for plant food. The conditions den is enclosed so that fumes do not escape into the working area. These **fumes** are scrubbed with water sprays to remove acid and fluoride before being

exhausted to the atmosphere. The scrubber water is discharged to a limestone bed to neutralize the acid.

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

#### 5.8.5 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 hygroscopic 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.

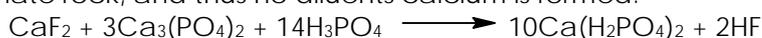
### 5.9 TRIPLE SUPERPHOSPTE

#### 5.9.1 Raw Materials

Phosphate rock  
62% Phosphoric acid  
Steam

#### 5.9.2 Manufacture

This material is a much more concentrated fertilizer than ordinary superphosphate, containing from **44 to 51%** of available **P<sub>2</sub>O<sub>5</sub>** 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.



The TVA continuous granular triple superphosphate production process is illustrated in Figure. Here the ground **phosphate rock** (75% minus 200-mesh) and **62% phosphoric acid** are metered continuously to the **granulator**, where reaction and granulation take 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 an 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.

Figure: Flowchart illustrating a triple superphosphate process.

### 5.9.3 Phosphate rock treatment processes

The most important use of **phosphate rock** is in **fertilizers**. Table is a compilation of **phosphate-rock treatment processes**. **Tricalcium phosphate** in raw and/or steamed and degreased bones and in basic slag is also used after **grinding** as a **direct phosphate fertilizer**. A small percentage of the former is sometimes treated with sulfuric acid for superphosphate or as a source, material for phosphate chemicals. Large tonnages of phosphate rock are converted to phosphorus or phosphoric acid and their derivatives.

**Table: Phosphate-rock Processing, Products and Byproducts**

Process	Raw materials and reagents	Main Products and derivatives	By- Products
Acidulation	Phosphate rock, Sulfuric acid, phosphoric acid, hydrochloric acid ammonia, potassium chloride	Superphosphate, phosphoric acid (wet process) triple super phosphate, mono ammonium phosphate, diammonium phosphate,	Fluorine compounds vanadium, uranium (limited)

Electric-furnace reduction	Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water	Phosphorus, phosphoric acid, triple superphosphate, various Na,K,NH <sub>4</sub> ,Ca salts; phosphorus pentoxide and halides, mono potassium phosphate	Fluorine compounds, CO, slag (for RR ballast aggregate, fillers, etc), ferrophosphorus, vanadium
Calcium metaphosphate	Phosphate rock, phosphorus, air or oxygen, fuel	Calcium metaphosphate	Fluorine compounds
Calcination or defluorination	Phosphate rock silica, water or steam, fuel	Defluorinated phosphate	Fluorine compounds