INTRODUCTION

Phosphorus is the chemical element that has the symbol P and atomic number 15. As phosphorus was the 13th element to be discovered and can be used in explosives, poisons and nerve agents is referred as “the Devil’s element”. It is essential for life. It is a component of DNA, RNA, ATP, and also the phospholipids that form all cell membranes.

Hennig Brand discovered phosphorous during his experiment on urine in 1669. Robert Boyle was the first to use phosphorus to ignite sulfur-tipped wooden splints, forerunners of our modern matches, in 1680.

Due to its high reactivity, phosphorus is never found as a free element on Earth. Phosphorus as a mineral is present in its maximally oxidized state, as inorganic phosphate rocks from which it can be extracted out. Phosphorous which is primarily extracted from calcium phosphate rocks consider as an expensive mineral but, with the increasing demand of phosphorous products like phosphoric acid, synthetic fertilizer and phosphate salts. The situation demands modification in extraction method as well as product manufacture.

Elemental phosphorus exists in two major forms

- White phosphorus
- Red phosphorus,

White phosphorus was first made commercially, for the match industry in the 19th century, by distilling off phosphorus vapour from precipitated phosphates, mixed with ground coal or charcoal, which was heated in an iron pot, in retort. The precipitated phosphates were made from ground up bones that had been degreased and treated with strong acids. Carbon monoxide and other flammable gases produced during the reduction process were burnt off in a flare stack. This process became obsolete when the submerged arc furnace for phosphorus production was introduced to reduce phosphate rock. The electric furnace method allowed production to increase to the point where phosphorus could be used in weapons of war.
PHOSPHATE ROCK

Phosphate rock is a natural mineral found as a geological deposit on a large scale in the form of sedimentary rocks containing various amounts of calcium phosphates. India alone is estimated to have about 140 million tons of rock phosphate deposits, most of which are however, of low grade and with substantial impurities unsuitable for the production of phosphate fertilizers.

Phosphate rock is used as a phosphatic fertilizer after grinding called phosphorite or mineral phosphate, or as a primary source of phosphorus. Finely ground rock (60-100mesh size) phosphate can be applied directly to the acidic soil. For neutral or alkaline soils acid-treated rock phosphate (like superphosphate) is used. Powdered rock phosphate is free-flowing and is easily amenable to handling and storage. Crops like rubber, tea, coffee, apples and fruit plantations of oranges are suitable for direct application of rock phosphate.

Francolite (calcium carbonate-fluorapatite) of formula \([\text{Ca}_5(\text{PO}_4,\text{CO}_3)_3(\text{F},\text{OH})]\) is the most predominant mineral of phosphate. Four kinds of phosphate rocks are recognized: hard rock phosphate, soft rock phosphate, land pebble phosphate and river pebble phosphate, with the phosphorus content varying from 2 to 21%.

Phosphate rock contains phosphorus in an apatite form which is water insoluble. The citrate solubility can vary from 5 to 17% of the total phosphorus, depending on the chemical nature of the rock and the size to which it is ground.

The efficiency of the ground rock phosphate can be increased by

- Mixing with soluble phosphorus and fertilizers
- Mixing with elemental sulfur or sulfur-producing compounds
- Using phosphate solubilizing micro-organisms

More than 90% of rock phosphate is used for production of superphosphate and phosphoric acid. Less than 8% is used directly as soil fertilizer and about 2% as animal and poultry feed.

Purification

Calcium phosphate is obtained after removal of various impurities present in phosphate rock. The upgrading of ore and removal of impurities is carried out by Floatation of phosphate rock.

Clays (kaolinite, illite, smectites and attapulgite), quartz and other silicates (feldspars), carbonates (calcite and dolomite), secondary phosphates (phosphates bearing iron and aluminum) and iron oxides (geothite, hematite and magnetite) are the common impurities which are associated with phosphate rock.
Phosphate ore beneficiation is done by many methods. Froth floatation is a widely used technique in the phosphate industry. Froth floatation is generally employed with siliceous ores when other less expensive or less complicated techniques fail to produce phosphate concentrates suitable for chemical processing. Prior to its conditioning for floatation, the floatation feed of phosphate rocks is delimed.

In the floatation of phosphate ores, apatite particles are generally directly transferred to the froth fraction (direct floatation) by using anionic collectors such as fatty acids. The anionic collectors selectively attach themselves to the phosphate particles, render them hydrophobic and lift them to the surface by the froth and air bubbles formed. The mineral bearing froth may simply overflow the cells or paddles or may be skimmed off. Quartz and other silicates are removed from the bottom of the floatation cells.

A second stage of floatation may be required to remove silica from the phosphate-rich float by cationic collectors (usually amines), when silica is floated and the phosphate particles settle to the underflow.

A selective floatation of carbonates from phosphate rock is rather difficult owing to the similarity in the physicochemical properties of the carbonate and phosphate minerals. Several treatments have been proposed, including floatation, calcination, acid washing, magnetic separation and heavy media separation for the removal of free carbonates from the phosphates.

**Uses**

The most important use of phosphate rock is in fertilizers. Table is a compilation of phosphate-rock treatment processes.
Table: Phosphate-rock processing, products and byproducts

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw materials and reagents</th>
<th>Main products and derivatives</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidulation</td>
<td>Phosphate rock, Sulfuric acid, phosphoric acid, hydrochloric acid, ammonia, potassium chloride</td>
<td>Superphosphate, phosphoric acid (wet process) triple super phosphate, mono ammonium phosphate, diammonium phosphate,</td>
<td>Fluorine compounds vanadium, uranium (limited)</td>
</tr>
<tr>
<td>Electric-furnace reduction</td>
<td>Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water</td>
<td>Phosphorus, phosphorus pentoxide and halides, phosphoric acid, triple superphosphate, various Na,K,NH₄,Ca salts; mono potassium phosphate</td>
<td>Fluorine compounds, CO, slag (for RR ballast aggregate, fillers, ferrophosphorus)</td>
</tr>
<tr>
<td>Calcium metaphosphate</td>
<td>Phosphate rock, phosphorus, air or oxygen, fuel</td>
<td>Calcium metaphosphate</td>
<td>Fluorine compounds</td>
</tr>
<tr>
<td>Calcination or defluorination</td>
<td>Phosphate rock, silica, water or steam, fuel</td>
<td>Defluorinated phosphate</td>
<td>Fluorine compounds</td>
</tr>
</tbody>
</table>

**YELLOW PHOSPHORUS**

**Raw materials**

Basis: 1000kg Phosphorus
- Calcium phosphate = 6804kg
- Sand = 2018kg
- Coke = 1202kg
- Carbon electrode consumption = 22.68kg
- Electricity = 13000kWH

**Reaction**

\[
2Ca_3(PO_4)_2 + 10C + 6SiO_2 \rightarrow CaSiO_3 + P_4 + 10CO
\]

**Manufacture**

Block diagram of manufacturing process

Diagram with process equipment

Animation
Rock phosphate is crushed as fine powder, so that complete transformation to phosphorous pentoxide (P$_2$O$_5$) and finally element phosphorous is possible. The powdered rock phosphate is mixed with sand and coke powder in the required proportion and charged into electric furnace having electrodes at bottom. The base of furnace is heated with carbon blocks as the temperature increases due to electrical heating. Reaction of rock phosphate with sand starts at about 1150°C resulting into calcium silicate and P$_2$O$_5$. Further increasing the temperature to 1500°C carbon particle reacted with P$_2$O$_5$ thereby phosphorous and carbon monoxide formed which is collected from top outlet. Residual calcium silicate settles down at bottom in form of slag which is taken out time to time from the outlet provided at bottom of the furnace.

Product gases which is mixture of phosphorous and carbon monoxide is cooled in a water cooler thereby phosphorous solidify and carbon monoxide gas is separated. Purification of phosphorous is carried out by melting it and treating with chromic acid (mixture of K$_2$Cr$_2$O$_7$ and H$_2$SO$_4$). The carbon and silicon impurities are removed due to oxidation. Pure phosphorous which is pale yellow colour is washed with water before it is casted into sticks.
Recovery of the products

The fumes emerging from the furnace are first freed from any mineral and other fine reagents which may have been carried up at less than 300°C so that the phosphorous is not condensed out. The remaining gases consist of phosphorous, CO and SiF₂, are sent to a bottom of tower in which water is sprayed from two different heights. Care should be taken that temperature should not drop below 60°C. The phosphorous condenses out but does not solidify, is collected under water which reacts with the SiF₄ gas, converting into metasilicic and fluorosilicic acids.

\[ \text{SiF}_4 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6 \]

The fluorinated components are subsequently recovered from the solution. CO which is completely freed from phosphorous and fluorine compounds is then cooled, dried and subsequently used as a fuel.

The slags consisting of CaSiO₃, which are produced in the furnace and subsequently discharged from outlet provided at base of furnace, are good additives for cements, air-port runway construction and antiskid conglomerates.

The liquid phosphorous, after decolouration with activated carbon is filtered and solidify to yellow phosphorous. It is stored under water.

Kinetics and thermodynamics

It is important to ensure that three component i.e. phosphate minerals, silica and coke are thoroughly and homogeneously mixed with one another. To do this if they are obtained from flotation processes, the phosphate mineral must be agglomerated or converted into nodules after addition of a small amount of quartzite in rotating furnaces which are heated by utilizing the combustion of carbon monoxide, which is formed during the process, in conjugation with that of fuel oil.

The arc resistance furnace is responsible for providing the energy, by the conversion of electricity into thermal energy, required for the above endothermic reaction which requires 5894kcal/kg.

India has abundant supply of calcium phosphate, salt and coke, but the manufacture of phosphorus largely depends upon the production of cheap electric power.

RED PHOSPHORUS

Raw material

Yellow phosphorous
Manufacture

Block diagram of manufacturing process

Diagram with process equipment

Animation

Batch process

Yellow phosphorous obtain from earlier process is taken into iron pot provided with safety outlet and thermometer jackets. Conversion of yellow phosphorous to red phosphorous is exothermic reaction and strict maintenance of temperature in range 240°C to 250°C in required as conversion do not take place below 240°C and above 250°C accident chances are there. After complete conversion product is washed with NaOH solution as yellow phosphorous is soluble but red phosphorous is not soluble in NaOH

Continuous process

In the process liquid white phosphorous is maintained at boiling point for 5-6hrs to achieve 35 to 50% conversion. The product is taken into screw conveyer in which unreacted phosphorous vaporizes which is recrystallize and recycled. The red phosphorous is of high purity and therefore doesn’t require further purification.

PROPERTIES

- Molecular formula: P
- Molecular weight: 30gm/mole
- Appearance: White, red and black solid
- Odour: Irritating odour
- Boiling point: 280.5°C
- Melting point: 44.2°C
- Density: 2.2-2.34 gm/ml
- Solubility: Insoluble in water and soluble in carbon disulfide
- White phosphorus is a highly reactive, waxy, white-yellow, transparent solid with acrid fumes. It emits a weak green glow (luminescence) in the presence of oxygen. White phosphorus ignites spontaneously in air.

**USES**
- Red phosphorus is used in fireworks, smoke bombs and pesticides.
- Black phosphorus no significant commercial uses due to least reactivity.
- White phosphorus and zinc phosphate are mainly used as a poison for rats.
- Used in making incendiary bombs, tracer bullets and for producing smoke screen
- Used in fertilizers, which provides phosphate as required for all life and is often a limiting nutrient for crops.
- Used in the manufacture of PCl₃, PCl₅, P₂O₅ and phosphorus bronze
- Organophosphorus compounds used in detergents, pesticides and nerve agents, and matches
- Phosphorus is one of the most essential mineral in the body and is ranked second to calcium. However, the deficiency of phosphorous is relatively rare
- About 80% of all phosphorus is present in human body in the form of calcium phosphate in the teeth and bones.
- It also participates in several vital functions of the body, such as energy metabolism, synthesis of DNA and the absorption and utilization of calcium.
- Phosphorus plays a role in facilitating optimal digestion.
- It helps in the normal functioning of the kidneys and ensures proper discharge of wastes.
- Adequate levels in body is essential to maintain normal brain functions
- Phosphorus helps maintain a good hormonal equilibrium.