Module: 4  
Lecture: 21  Phosphoric acid

PHOSPHORIC ACID

INTRODUCTION

Phosphoric acid (H$_3$PO$_4$), also known as orthophosphoric acid or phosphoric(V) acid, is a mineral (inorganic) acid. Orthophosphoric acid molecules can combine with themselves to form a variety of compounds which are also referred to as phosphoric acids.

Amongst the mineral acids, phosphoric acid stands an special status as it is used for specialty application including anticorrosive and food industry out of number of processes available only the latest are discussed below which includes applications of electric furnace, blast furnace and process including oxidation and hydration of phosphorous or the wet process which uses sulfuric acid and rock phosphate.

The continuous process of phosphoric acid production uses liquid white phosphorous at the boiling condition for 5 to 6hrs so that about 35 - 50 % white phosphorous is converted to red phosphorous. The hot red phosphorous is taken in a screw conveyer which along with inert gases gives a solid pure red phosphorous as product. Red phosphorous finds the application in manufacturing of matchsticks, chlorides of phosphorous as PCl$_3$, PCl$_5$, phosphorus oxide as P$_2$O$_5$ and phosphor bronze etc.

MANUFACTURE

The modern manufacturing methods of phosphoric acid are following:

1. Using phosphate rock and blast furnace
2. Using phosphate rock and electric furnace
3. Oxidation and hydration of phosphorous
4. Wet process or from sulfuric acid and phosphate rock

1. Using phosphate rock and blast furnace

The blast furnace process was widely used in the first three decades of 20$^{th}$ century. Resulting phosphoric acid can be used in manufacturing of insecticide, pesticides, detergents etc. but not for fertilizers.
Raw materials

Basis: 1000kg phosphoric acid (100%)
Phosphate rock = 2290kg
Sand (Silica) = 6800kg
Coke = 3175kg
Briquette binder = 227kg
Air = 450000ft³

Reactions

\[ \text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} \rightarrow 2\text{P} + 5\text{CO} + 3\text{CaSiO}_3 \]
\[ 2\text{P} + 5\text{CO} + 5\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 5\text{CO}_2 \]
\[ \text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4 \quad 85-90\% \text{ yield} \]

Manufacture

Phosphate rock is pulverized and mixed with coke powder and binder is compressed to 5000 psi resulting into the briquettes. Briquettes are dried and charged along with sand and additional coke powder from top of the blast furnace. The preheated air (1000 – 1100°C) is charged from bottom of the blast furnace via tuyere. A tuyere is cooled copper conical pipe numbering 12 in small furnace and up to 42 in large furnace through which hot air is blown in to the furnace. Preheated air leads to burning of briquettes giving temperature rise up to 1370°C. The coke acts

**Figure:** Manufacturing of Phosphoric acid using blast furnace

**Block diagram of manufacturing process**

**Diagram with process equipment**

**Animation**
as reducing agent as well as fuels. About 760kg of coke is consumed in reduction of phosphate rock to phosphorous and remaining generates heat by combustion with air. Reaction is completed in the furnace itself producing $P_2O_5$ and calcium silicates as slag. The product gases also contain carbon monoxide and nitrogen along with dust particles. For purification, it is passed through cyclone separator and phosphorous condenser. Thus, $P_2O_5$ and elemental phosphorous are separated out. Hot $P_2O_5$ gases are cooled in the heat exchanger. Therefore, superheated steam is produced and a part of gas is taken into regenerative blast furnace. As a result the entire phosphorous and phosphorous pentoxide is cooled and purified before taken into hydrating towers. Purification of phosphoric acid includes removal of arsenic by hydrogen sulfide treatment followed by filtration.

**Engineering aspects**

**Blast furnace**

Blast furnace is made of high temperature resistant refractories brick. Blast furnace have accessories of hot blast stove for supply of compressed preheated air having temperature 1000 – 1100°C, briquette press for preparation of briquettes of Phosphate rock and coke, dust collector (cyclone separator) for removal of dust particles from product stream. Also, two outlets for removal of slag and ferrophosphorous are provided at the bottom of the furnace.

The top of the blast furnace is closed as it operates at high top pressure. There are two different systems are used for charging of briquettes, coke and silica. One is having double bell system which is often equipped with movable throat armour and other is bell less top as shown in figure.

![Blast furnace top charging system](image)

Also, there are two construction techniques to support the blast furnace as shown in figure.
Animation

One utilized lintel or support ring at the bottom of the shaft upon which the higher level of the furnace rests. The other is free standing construction requiring and independent support for the blast furnace top and gas system. The required expansion both thermal as well as pressure for the installation is below for the lintel i.e. in bosh/belly area in lintel type furnace, while compensator for expansion in the free standing furnace is at the top.

2. Using phosphate rock and electric furnace

Raw materials

Basis: 1000kg phosphoric acid (100%)
Phosphate rock = 2225kg
Sand (silica) = 680kg
Coke breeze = 400kg
Caron electrode = 8kg
Air = 100000ft³
Electricity = 4070KWH

Reactions

\[ \text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} \rightarrow 2\text{P} + 5\text{CO} + 3\text{CaSiO}_3 \quad \Delta H = -364.8 \text{ kcals} \]
\[ 2\text{P} + 5\text{CO} + 5\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 5\text{CO}_2 \]
\[ \text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4 \quad 87-92\% \text{ yield} \quad \Delta H = -44.9 \text{ kcals} \]
Manufacture

The phosphate rock is reduced to elemental phosphorous by the action of coke and heat in the presence of sand in electric arc furnace subsequent oxidation of phosphorous gives phosphorous pentoxide which on hydration gives the product phosphoric acid.

Phosphate rock after proper grinding and primary purification is taken into sintering oven where it is nodulized and granulized so that fast oxidation of the separated phosphorous takes place. Temperature of $1095^\circ C$ is maintained in electric furnace so that maximum amount of elemental phosphorous extracted out and oxidation takes place. Since fluoride of phosphorous and calcium are the common impurity which reacts with sand giving fluorsilicates as the slag.

The gases from the furnace, phosphorous and carbon monoxide are removed by the suction process and the oxidation product $P_2O_5$ is taken into hydration column which gives $P_2O_5$ to $H_3PO_4$ at about $85^\circ C$. Purification of phosphoric acid is carried out by $H_2S$ to remove Arsenic, $H_2SO_4$ to remove calcium salts and Silica to remove fluorides. All the byproducts are removed before concentrating the acid and filtering it as final product.
Advantages of electric arc furnace over other methods

The advantage of the electric furnace process lies in its ability to use a low-grade phosphate rock, provided the major impurity is silica. Also, iron and aluminum oxides are not objectionable as in the wet process. Siliceous rocks containing 24% phosphorus as \( P_2O_5 \) are acceptable. The by-product carbon monoxide, is used as a fuel for calcination.

3. Oxidation and Hydration of phosphorous

Raw materials

- Basis: 1000kg phosphoric acid (100%)
- Phosphorus = 300kg
- Air = 46000ft\(^3\)
- Steam = variable
- Water = variable

Reactions

\[
2P + 2\frac{1}{2}O_2 \rightarrow P_2O_5
\]

\[
P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \text{ (94 – 97% yield)}
\]

Manufacture

At the locations away from phosphate rocks mines from purified elemental phosphorous is oxidized and hydrated to give phosphoric acid. In the manufacturing process molten phosphorous is sprayed into combustion chamber along with preheated air and superheated steam. Combustion of phosphorous increases the temperature up to 1980°C. Furnace design depends on the requirement with respect to quantity and quality. They are made of acid proof structural bricks, graphite, carbon and stainless steel.

Block diagram of manufacturing process

Diagram with process equipment

Animation
The gases from furnace which mainly contains \( \text{P}_2\text{O}_5 \), steam, \( \text{N}_2 \) and small quantity of oxygen is taken into a hydration column where counter current mixing of dilute phosphoric acid and the gases gives the product concentrated \( \text{H}_3\text{PO}_4 \) of 75% to 85% concentration. Remaining acid is trapped into packed column or electrostatic precipitator.

4. **Wet process or from sulfuric acid and phosphate rock**

The wet process is according to the acids (sulfuric acid, nitric acid or hydrochloric acid) used to decompose the phosphate rock. The process using sulfuric acid is the most common among all particularly for producing fertilizer grade phosphoric acid.

The wet process phosphoric acid, also called as green acid. Depending upon the hydrate forms of calcium sulfate produced during the wet process, it is classified as anhydride, hemi hydrate and dihydrate. The hydrate form is controlled mainly by temperature and acid concentration.
Anhydrite (n=0) process is not commercially viable due to high temperatures requirement and the higher rate of corrosion.

The dihydrate process is the most popular due to simplicity and ability to use a wide variety of phosphate rocks in the process. Hemihydrate processes produce phosphoric acid of a relatively high concentration without the need of the concentration step. There is also some attentiveness in the two-stage processes that involve crystallization in the hemi-hydrate form followed by recrystallization in the dihydrate form, with or without filtration or centrifugation.

**Raw materials**

- Basis: 1000kg phosphoric acid (100%)
- Phosphate rock = 1635kg
- Sulfuric acid = 1360kg

**Reaction**

\[
\text{Ca}_{10}\text{F}_2\text{(PO}_4\text{)}_6 + 10\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O} \rightarrow 10\text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{HF} + 6\text{H}_3\text{PO}_4
\]

**Manufacture**

There are two processes i.e. dihydrate and hemihydrates (CaSO₄.2H₂O and CaSO₄.1/2H₂O) are used for production of phosphoric acid.

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Dihydrate process</th>
<th>Hemihydrate process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength of sulfuric acid</td>
<td>78%</td>
<td>95%</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>Below 80°C</td>
<td>100°C</td>
</tr>
<tr>
<td>Resistance to material</td>
<td>Less</td>
<td>High</td>
</tr>
<tr>
<td>Digestion time</td>
<td>High</td>
<td>Short</td>
</tr>
<tr>
<td>P₂O₅ content in product</td>
<td>33%</td>
<td>38%</td>
</tr>
<tr>
<td>Quantity of calcium sulfate</td>
<td>High</td>
<td>Small</td>
</tr>
</tbody>
</table>

Sulfuric acid on reaction with phosphate rock along with precipitation of calcium sulfate results into the formation of phosphoric acid. The process is simple and requires grinding of phosphate rock reacting with dilute phosphoric acid so that melt is produced which in a reactor as mixed with concentrated sulfuric acid for 4 to 8hrs in the temperature range of 75-80°C. Lot of air is required to control the temperature. Resulting gases includes HF and P₂O₅ which in the absorption tower is separated and finally treated to give fluorosilicates and dilute phosphoric acid. The main product in the liquid form which is phosphoric acid and calcium sulfate is filtered and washed. Thus, gypsum and phosphoric acid are separated and after minor purification the phosphoric acid is concentrated into the evaporator.
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%.
Kinetics and thermodynamics

The average retention time in the reactor system is about eight hours. The direct contact between phosphate rock and sulfuric acid are prevented, so that maximum phosphorous is extracted from the rock and formation of easily filterable crystal of gypsum. A high concentration of free sulfuric acid would result in the formation of a coating of calcium sulfate on the phosphate rock, thereby blocking further reaction. On the other hand, a high concentration of calcium ions in the slurry would increase the amount of phosphate co-crystallized with gypsum. In order to maintain a uniform composition of slurry, the incoming stream of sulfuric acid and phosphate rock is mixed and agitated as rapidly and as completely as possible to ensure homogeneity. Most of the modern plants use about 96% pure sulfuric acid. Its mixing with dilute phosphoric acid generates heat which is used to evaporate the water and volatilize fluorine compounds (mainly SiF, and HF).

Three methods of cooling are generally in use: (a) blowing air on to the slurry, (b) blowing air across the slurry, and (c) flash cooling under vacuum.

The fumes emerging from the reactors and the digesters are sent to the fluorine recovery unit, while the suspension of the digesters are filleted in the first compartment of a continuous filter, which yields phosphoric acid containing about 33% of P_{2}O_{5}.

Engineering aspects

Selection of phosphate rock

The plant is designed in such a way that can be used for blend of rocks from different sources. The plants have extra capacity for grinding, filtration and slurry handling systems to take care of variation in the rock composition. As phosphate rock is a complex raw material that affects plant operation in numerous ways, a thorough chemical and mineralogical evaluation of the quality should be made before selecting a phosphate rock or changing the source to another. However, a trial run in a pilot plant is needed for complete evaluation of the rock. The phosphate rock used in the process is of as high a grade as possible, usually ranging from 30 to 35 % P_{2}O_{5} and 1 to 4 % iron and aluminum.

Before attack by acids, mineral must be crushed so that 60 – 70 % of it passes through 200 mesh sieve. Crushed mineral is calcined to remove organic impurities, because the presence of organic substances promotes the formation of foams which makes it difficult to filter off calcium sulfate. The purified mineral is again crushed to powder form by milling and is premixed first with recycled phosphoric acid and then fed with sulfuric acid. The recycle phosphoric acid contributes to attack on the mineral and disperse both heat of reaction and heat of dilution of H_{2}SO_{4}, thereby facilitating crystallization of the calcium sulfate. Also, these steps favours both precipitation, of readily filterable chalk consisting of minutes crystals of
CaSO\(_4\cdot2\)H\(_2\)O or CaSO\(_4\cdot1/2\)H\(_2\)O which act as crystallization nuclei, as well as digestion in suitable containers, after the attach of reaction mixture.

**Grinding of rock materials**

Wet or dry grinding of Phosphate rocks is required depending upon the raw materials. Fine grinding is required in case of multi-compartment digesters and poor sulfate control. Most of the old plants use dry grinding, and a majority of the new plants use wet grinding with a ball mill or ring roller mills having air classification. Slurry containing 62 to 70% solid is produced. Wet grinding requires about 30 to 40% less power and there is no atmospheric pollution by dust. The main disadvantages of this process are that the balls and the mill lining wear out faster, and the amount of recycled waste water that may be required in phosphoric acid production is reduced. Also, it is necessary to maintain the ratio of solids while grinding.

**Handling and storage of phosphate rock**

Phosphate rock are stored in dry conditions and protected against rain, wind and freezing weather. Relatively coarse rocks can be stored in piles. To ensure the constant supply, the storage capacity should ideally be 1.5 times the largest shipment.

**Amount of sulfuric acid**

As the by-product acid may contain some impurities, most phosphoric acid plants have on site facilities for producing sulfuric acid from sulfur or pyrites. Sulfuric acid of 93 to 98% concentration is used. The sulfuric acid requirement is calculated assuming its amount required to combine with calcium present in the rock to form calcium sulfate. Also, considering that about 15% of fluorine combines with calcium oxide to form calcium fluoride, the sulfuric acid requirement is calculated. For a high grade phosphate rock, H\(_2\)SO\(_4\) required is 2.5 tons per ton of phosphorus; and for low grade rocks, it is 3.15 tons per ton of phosphorus.

**Filtration of gypsum**

Filtration is carried out as efficiently and economically as possible. All modern plants use continuous horizontal vacuum filters. The other widely used filters are tilting pans, rotary filters, rotary table filters and belt filters. Some of the product acid is recycled to the digestion step to control the percentage of solids in the slurry, which is normally 35 to 45%.

Filters are characterized by their surface area and the rate of rotation (in a rotary filter) or the rate of travel (in a belt filter). The filtration rate is also affected by the size and shape of gypsum crystals which, in turn, are decided by the type of phosphate rock, crystal shape modifiers, control of reaction conditions, sulfate concentration, slurry re-circulation, phosphoric acid concentration, etc.
The filtration rate is also affected by temperature, concentration, viscosity of the acid, the desired recovery, the amount of vacuum, the design of the filter and insoluble impurities in the rock like clay. The normal filtration rates reported in the production are 2 to 18 tons/m²/day.

**Purification**

Phosphoric acid which is intended for use in fertilizers does not require any purification but for chemical and food products it must be purified. The block diagram of purification processes is as follows.

**Figure: Purification of Phosphoric acid**

**Sludge disposal**

The sludge usually contains gypsum, fluosilicates, iron and phosphate compounds. Acids containing sludge can be used for onsite fertilizer (triple...
superphosphate) production. Most of the phosphorus (as \( \text{P}_2\text{O}_5 \)) in the sludge is citrate-soluble but not water-soluble.

The sludge may be used in the production of non-granular mono-ammonium phosphate which is used as an intermediate in the production of compound fertilizers. There is no economical method for using sludge solids where phosphate fertilizers are sold on the basis of water solubility. Precipitation after concentration to 54% phosphorus (as \( \text{P}_2\text{O}_5 \)) is slow and never so complete as more precipitate will form on standing.

**PROPERTIES**

- **Molecular formula**: \( \text{H}_3\text{PO}_4 \)
- **Molecular weight**: 97.994 gm/mole
- **Appearance**: White solid or colourless viscous liquid above 42°C
- **Boiling point**: 158°C (decompose)
- **Melting point**: 42.35°C (anhydrous) 29.32°C (hemihydrate)
- **Density**: 1.885 gm/mL (liquid) 1.685 gm/mL (85% solution) 2.030 gm/mL (crystal at 25°C)
- **Solubility**: Soluble in water
- **Viscosity**: 147 cP (100%)

**USES**

- Used for preparation of hydrogen halides
- Used as a "rust converter", by direct application to rusted iron, steel tools, or surfaces. It converts reddish-brown iron(III) oxide, \( \text{Fe}_2\text{O}_3 \) (rust) to black ferric phosphate, \( \text{FePO}_4 \)
- Food-grade phosphoric acid is used to acidify foods and beverages such as various colas.
- Used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed.
- As an ingredient in over-the-counter anti-nausea medications that also contain high levels of sugar (glucose and fructose).
- Used in many teeth whiteners to eliminate plaque.
- Used as an external standard for NMR and HPLC
- As a chemical oxidizing agent for activated carbon production
- As the electrolyte in phosphoric acid fuel cells and is used with distilled water (2–3 drops per gallon) as an electrolyte in oxyhydrogen (HHO) generators.
- Also, used as an electrolyte in copper electro polishing for burr removal and circuit board planarization.
- As a flux by hobbyists (such as model railroaders) as an aid to soldering.
- As a common wet etching agent in compound semiconductor processing.
- Hot phosphoric acid is used in micro fabrication to etch silicon nitride (Si$_3$N$_4$). It is highly selective in etching Si$_3$N$_4$ instead of SiO$_2$, silicon dioxide.
- As a cleaner by construction trades to remove mineral deposits, cementitious smears, and hard water stains.
- As a chelant in some household cleaners aimed at similar cleaning tasks.
- Used in hydroponics pH solutions to lower the pH of nutrient solutions.
- As a pH adjuster in cosmetics and skin-care products.
- As a dispersing agent in detergents and leather treatment.
- As an additive to stabilize acidic aqueous solutions within specified pH range.