Kurdistan Region
Salahaddin University-Erbil
College of Engineering
Chemical-Petrochemical Engineering Department

# Production of Phosphoric Acid

A Project Submitted to the Chemical-Petrochemical Engineering Department
University of Salahaddin-Erbil
in the Partial Fulfillment of the Requirement for the Degree of Bachelor of Science
in Chemical-Petrochemical Engineering

Prepare By:
Zaynab Sirwan Majed
Zana Maghdid Azeez

Supervisor:
Dr. Mohammad Jawdat

2023-2024

# Abstract

This project explores the production of phosphoric acid, a vital industrial chemical with numerous applications. Beginning with a concise introduction to the significance of phosphoric acid in various industries, the study delves into the intricacies of material balance and heat balance within the production process. Material balance analysis elucidates the input-output dynamics of raw materials and products, ensuring optimal resource utilization. Meanwhile, heat balance considerations focus on the efficient management of thermal energy, essential for maintaining process integrity and sustainability. Additionally, the project investigates the design aspects of key production units, emphasizing the critical role of unit design in achieving operational efficiency and product quality. Through comprehensive analysis and design strategies, this project aims to contribute to the advancement of phosphoric acid production methodologies, fostering sustainable industrial practices and economic viability.

# Supervisor’s Certificate

I certify that the engineering project titled **"Production of Phosphoric Acid”** was done under my supervision at the Chemical-Petrochemical Engineering Department, College of Engineering - Salahaddin University–Erbil. In the partial fulfillment of the requirement for the degree of Bachelor of Science in Chemical-Petrochemical Engineering

**Supervisor**

Signature:

Name:

Date: / /

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## Chapter One

# Introduction

### 1.1 Phosphorous Acid and its History

Phosphorus, a vital element in the Earth's ecosystem, plays a crucial role in various biological and industrial processes. The focus of this engineering project research is on phosphoric acid, an essential compound derived from phosphorus. Understanding the history, production methods, and properties of phosphoric acid is vital to comprehending its significance in diverse applications. The journey into the realm of phosphoric acid begins with phosphorus, a non-metallic element classified under the nitrogen family on the periodic table. Discovered by the alchemist Hennig Brand in 1669, phosphorus has since become indispensable in various fields, including agriculture, medicine, and industry. It is crucial to acknowledge the historical evolution of phosphorus as it sets the stage for the subsequent exploration of phosphoric acid. Phosphoric acid, commonly known as orthophosphoric acid ($H_3PO_4$), is a derivative of phosphorus with a rich history dating back to the 17th century. Its synthesis involves multiple steps, with the earliest documented method being the calcination of bones, leading to the extraction of phosphorus, which could then be oxidized to form phosphoric acid. Over time, advancements in chemical engineering have facilitated the development of various production methods, each with distinct advantages and applications. One of the largest worldwide applications for phosphate rock is in the production of phosphoric acid. It is the intermediate product between beneficiated phosphate rock and other phosphate compounds where phosphorus is the key ingredient element in the form of a phosphate. The global phosphoric acid (as $P_2O_5$) production capacity in 2014 was about 55 MT. The concentration of phosphoric acid can be expressed as a percentage of phosphoric acid ($H_3PO_4$%) or a percentage of phosphorus (P%), but normally it is expressed as a percentage of phosphorous pentoxide ($P_2O_5$%). Fertilizer production accounts for about 84 – 90 % of the world market for phosphoric acid and animal feed for about 6%; the rest is used in different industrial applications. The present global phosphoric acid consumption and uses by various sectors is shown in Figure (1.1).(Toama, 2016)

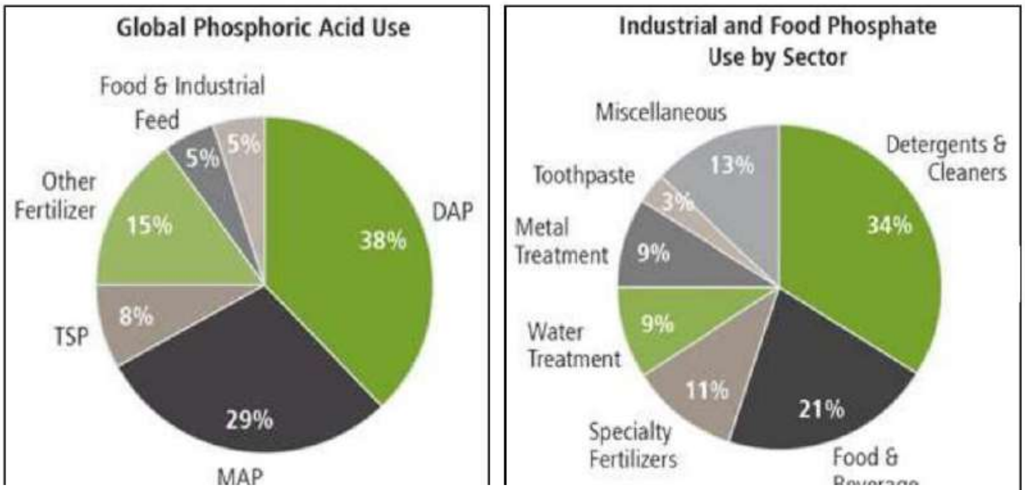


*Figure 1.1-1 Consumption and uses of phosphoric acid by sectors*

## 1.2 Physical and Chemical Properties

### 1.2.1 Physical Properties

Table 1.1(Australian Government, June 2022) shows the physical properties of phosphoric acid (pure).

| | |
|---|---|
| Molecular Formula | $H_3PO_4$ |
| Chemical Name | Ortho Phosphoric Acid |
| Common Name | Phosphoric Acid |
| Solubility | soluble in water |
| Molecular Weight | 9.994 g/mol |
| Boiling Point | 260℃ |
| Melting Point | 42℃ |
| Density | 1.88 g/mL (at 25℃) |
| Vapor Pressure | 0.03 mmHg at (20℃) |
| Vapor Density | 3.4 |

Table-1.1 Physical Properties of Phosphoric Acid

### 1.2.2 Chemical Properties

Because phosphoric acid ($H_3PO_4$) is triprotic, that is, it can contribute three protons in consecutive ionization reactions, it has special chemical features. It is a weak acid that partially ionizes in aqueous solutions to produce phosphate and hydrogen ions. Because of its acidity, it is an essential ingredient in the food processing, detergent, and fertilizer industries. The corrosion-inhibiting properties of phosphoric acid are partly attributed to its capacity to bind metal ions. It also acts as a buffer, preserving pH stability in a range of applications. The primary source of phosphor utilized in the production of phosphate fertilizers is phosphoric acid. Furthermore, phosphoric acid can irritate the skin, eyes, and mucous membranes, as well as increase the risk of ulcers.

$$3\ H_2SO_4(l) + \underset{\text{(Phosphate Rock)}}{Ca_3(PO_4)_2(s)} + 6\ H_2O\ (l) \rightarrow 2\ H_3PO_4(s) + \underset{\text{(Gypsum)}}{3\ CaSO_4.2\ H_2O(s)}$$

Side reactions:

$CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO_4.2H_2O$

$6HF + SiO_2 \rightarrow H_2SiF_4 + 2H_2O$

## 1.3 Methods of Production

Phosphoric acid may be produced using a variety of techniques, which reflects the compound's versatility in industrial processes. Phosphoric acid is created when sulfuric acid is mixed with phosphate rocks, according to the most conventional method. An alternative technique involves the thermal breakdown of phosphorus pentoxide, resulting in fuming phosphoric acid, a highly concentrated form of phosphoric acid. There are other methods as well, such the "wet process" and the "dry process," each with their own benefits and drawbacks. Phosphoric acid manufacturing methods are chosen based on a number of considerations, including cost, efficiency, and environmental effect. The sulfuric acid method, despite being a well-established and cost-effective approach, the production of gypsum as a byproduct poses environmental issues. The thermal decomposition process, on the other hand, produces a higher concentration of phosphoric acid but may present issues with energy consumption and safety.

### 1.3.1 Wet Process

Phosphoric acid is mostly produced using the wet process, which combines the hemihydrate and dehydrate processes. When phosphate rock and sulfuric acid are first combined in the dehydration process, phosphoric acid and calcium sulfate (gypsum) are produced as byproducts in the form of ($CaSO_4.2H_2O$). The reaction takes place in a series of reactors, and the liquid phosphoric acid and solid gypsum are separated by filtering the resultant slurry. Phosphoric acid is partly dried in order to transform it into a more concentrated form in the hemihydrate process. This process improves the product's purity and is especially used in the manufacturing of certain fertilizers. The byproduct, gypsum, is represented by the formula ($CaSO_4.1/2H_2O$). Several crucial phases are involved in the wet process of producing phosphoric acid, as shown in a simplified flow diagram (Figure 1.2). First, phosphoric acid and gypsum are produced by digesting phosphate rock in a reactor with sulfuric acid. The solid gypsum is subsequently separated from the liquid phase of the slurry by filtering it. The liquid proceeds through further phases of concentration and filtration now that it contains phosphoric acid. Achieving the appropriate product quality may need extra filtering and hemihydrate conversion as subsequent processes. Because of the wet process's flexibility to various sources of phosphate rock, it is a frequently used technique in the phosphoric acid business. For the production of strongest acid possible, 94% sulfuric acid is used. This plays a vital role in this process since the ratio of acid to phosphate rock entering the reactor. The heat produced in the reactor usually was removed by blowing air over the slurry surface. In modern plants, vacuum flash cooling is used. This process usually yields 26%-30% $P_2O_5$. It can be concentrated by vacuum evaporators for further applications like fertilizer production. $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4).2H_2O$

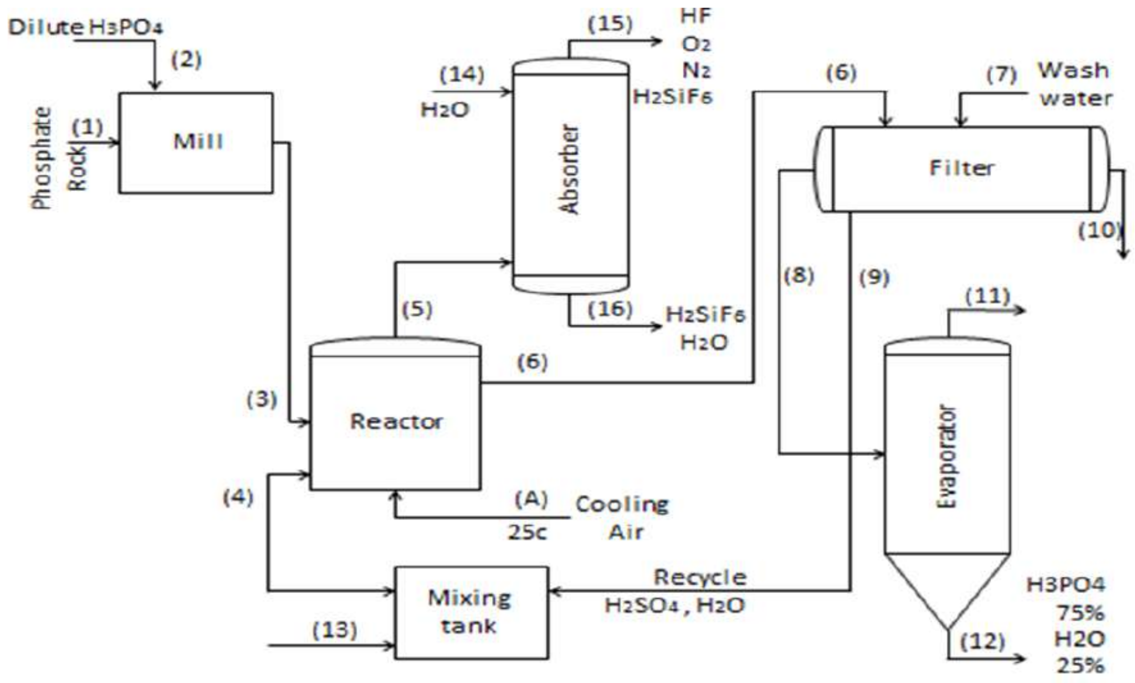


*Figure 1.1-2 Wet Process Acid Production Flow Diagram*

The present invention relates to a process for preparing phosphoric acid, which comprises: dividing raw materials which contain phosphate rock slurry and sulfuric acid into two parts, then feeding these two parts into two reactors separately. Part of the reaction solution directly flows into conversion cell and participates in the conversion reaction of dihydrate gypsum. By Such process, the recovery efficiency of $P_2O_5$ is improved and up to 99% or more. Meanwhile, good quality hemihydrate gypsum is obtained, in which $P_2O_5$ is 0.05-0.2%, water of hydration is 4-8%, and adsorptive water is about 19%. After naturally hydrating, the product can be used for producing Sulfuric acid and cement without baking dry. The coke powder as filtration-supporting agent is added to the reaction solution, which improves the filtration efficiency and reduces energy consumption. The present invention has obvious advantage in the aspect of economy and society.(Group and Company, 2001)

#### 1.3.1.1 Gypsum Disposal

Around 5 tons of gypsum are generated per ton of $P_2O_5$ produced as phosphoric acid. This represents a serious disposal problem with the individual phosphoric acid production units of over 1,000 tons per day capacity now being built.

Two methods can be used to dispose of gypsum: -

- Disposal to land
- Disposal into water

By-product gypsum contains four types of impurity that are considered to be potentially harmful: -

– Residual acidity
– Fluorine compounds
– Undesirable trace elements
– Radioactivity

#### 1.3.1.2 Disposal to water

The gypsum can be pumped through an outfall into the sea at coastal sites and estuaries. Disposal into rivers is no longer practiced, as it is not a good environmental option. Disposal of gypsum into the sea has the advantage that gypsum is more soluble in sea water than in fresh water. However, some of the impurities in the gypsum should be controlled. Clean gypsum itself ($CaSO_4$) is soluble and is not harmful to the environment. A phosphoric acid plant with high efficiency is essential for this method of disposal and only clean phosphates can be used in the plant if the pollution is to be kept within local environmental quality standards.

#### 1.3.1.3 Disposal on land

Disposal on land, under proper conditions, is the best environmental option although it is not possible everywhere because it requires space and certain soil qualities where the gypsum stack is situated. Dry gypsum from the filter in some plants is transported by belt conveyors to the gypsum storage pile. The pile area is completely surrounded by a ditch which collects the runoff water including any rain water. In other plants the filter cake is slurried with recycled pond water and pumped to special storage areas where the phosphor-gypsum eventually dries in stacks. The area receiving the phosphor-gypsum slurry is sub-divided into smaller areas, with each section being used in rotation. Slurry is discharged on top of the storage pile and the phosphor-gypsum rapidly settles out of solution. Clear water runs off and drains to the adjacent cooling ponds. The water is recycled within the system to ensure that the contaminants are kept within the plant. The phosphor-gypsum stack is completely surrounded by a ditch which can contain not only this water but also rain water and any that might spill accidentally.(2000)

### 1.3.2 Thermal Process

Air, water, and elemental phosphorus are the raw elements used in the thermal process to produce phosphoric acid. As seen in Figure 1.3, there are typically three main processes in this process: demisting, hydration, and combustion. Phosphorus pent oxide is created during combustion, which involves oxidizing liquid elemental phosphorus in ambient air inside a combustion chamber heated to between 1650°C and 2760°C. Strong phosphoric acid liquid is then created by hydrating the phosphorus pentoxide with either water or diluted $H_3PO_4$. The last phase, demisting, uses high pressure demisters to extract the phosphoric acid mist from the combustion gas stream before releasing it into the atmosphere. Phosphoric acid comprises of 75%–80%

$P_2O_5$ during this procedure. Because acid produced via the thermal process is highly concentrated and contains fewer impurities, it is generally used in more specialized industrial applications.

Reactions:

$$P_4 + 5O_2 \rightarrow 2P_2O_5$$

$$2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4$$

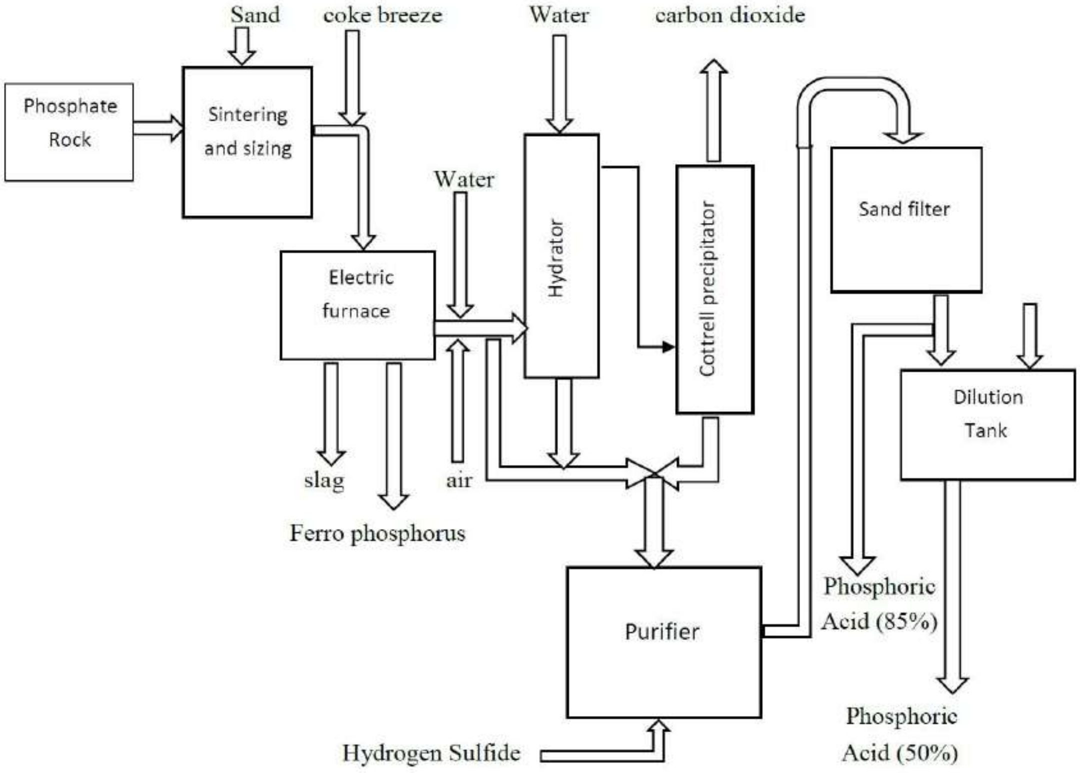


*Figure 1.1-3 Thermal Process Acid Production Flow Diagram*

## Chapter Two

# Methodology

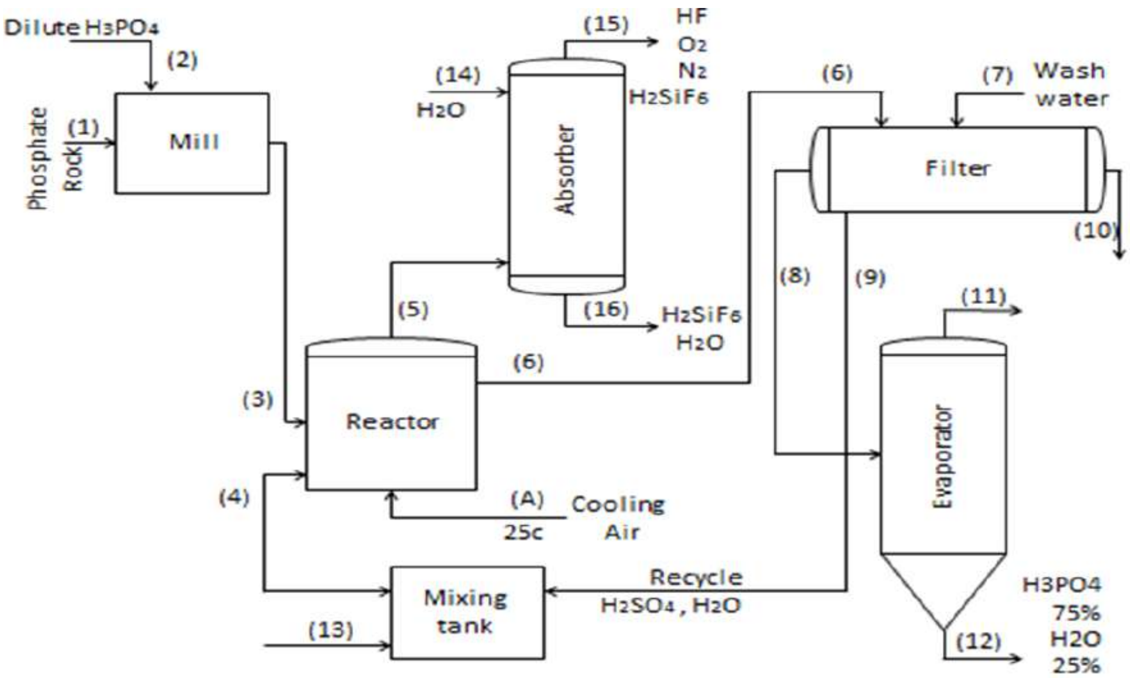
## 2.1 Material Balance

As mentioned above, wet process is more used and effective in production of phosphoric acid, hence it is our choice of material balance.

Main Reaction: -

$Ca_3(PO4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4).2H_2O$……….(1)

Side Reactions:



$CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO_4.2H_2O$……………………..(2)

$6HF + SiO_2 \rightarrow H_2SiF_4 + 2H_2O$……………………………………..(3)

Rock Analysis by weight percent:

| | |
|---|---|
| $Ca_3(PO_4)_2$ | 75 |
| $CaF_2$ | 20 |
| $SiO_2$ | 5 |

Required assumptions:

- Production of $H_3PO_4$ per year: $3 * 10^8$ kg/year = $1 * 10^6$ kg/day = 1000 ton/day
- Year = 300 days
- Yield = 95%
- $H_2SO_4$ concentration 94%
- $H_2SO_4$ excess 15%

| Components | Molecular Weight |
|---|---|
| $H_3PO_4$ | 98 |
| $H_2SO_4$ | 98 |
| $SiO_2$ | 60 |
| $CaF_2$ | 78 |
| $H_2O$ | 18 |
| $Ca_3(PO_4)_2$ | 310 |
| $CaSO_4$ | 136 |
| $CaSO_4.2H_2O$ | 172 |
| HF | 20 |
| $H_2SiF_6$ | 144 |
| $P_2O_5$ | 142 |

*Table 2-1material balance*

Production of $H_3PO_4$ = $10^6$ kg per day = 42000 kg/hr = 429 kmol/hr

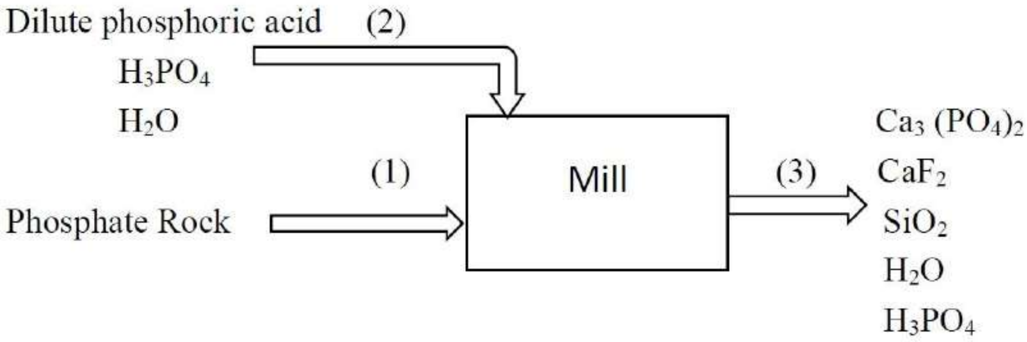
Product stream = 42000/0.75 = 56000 kg/hr

$H_2O$ = 56000*0.25 = 14000 kg/hr

From reaction (1):

$Ca_3(PO_4)_2$ = 1/2 $H_3PO_4$ = 1/2*429 = 214.5 kmol/hr = 66.5 kg/hr

Yield = $\frac{\text{Product } H_3PO_4}{\text{feed } Ca_3(PO_4)_2}$ → feed $Ca_3(PO_4)_2$ = 429/0.95 = 451.5 kmol/hr = 140000 kg/hr



Feed stream (phosphate rock) composition:

$Ca_3(PO_4)_2$ = 140000 kg/hr

Total feed=140000/0.75 = 187000 kg/hr

$CaF_2$ = 0.2*187000 = 37400 kg/hr

$SiO_2$ = 0.05*187000 = 9350 kg/hr

### 2.1.1 Material Balance on Mill

Dilute phosphoric acid stream (2), has 85% water and 15% phosphoric acid.

If the ratio of dilute phosphoric acid (2) to phosphate rock (1) is 1:2, then:

187000 * 1/2 = 93500 kg/hr of dilute phosphoric acid stream

93500 * 85/100 = 79500 kg/hr of water

93500 * 15/100 = 14000 kg/hr of phosphoric acid

| Composition | Stream 1 | Stream 2 | Stream 3 |
|---|---|---|---|
| $Ca_3(PO_4)_2$ | 140000 | | 140000 |
| $CaF_2$ | 37400 | | 37400 |
| $SiO_2$ | 9350 | | 9350 |
| $H_2O$ | | 79500 | 79500 |
| $H_3PO_4$ | | 14000 | 14000 |

*table 2-1Material Balance on Mill*

Mass in = 140000+37400+9350+79500+14000 = 280250

Mass out = 140000+37400+9350+79500+14000 = 280250

Mass in = Mass out

### 2.1.2 Material Balance on Reactor

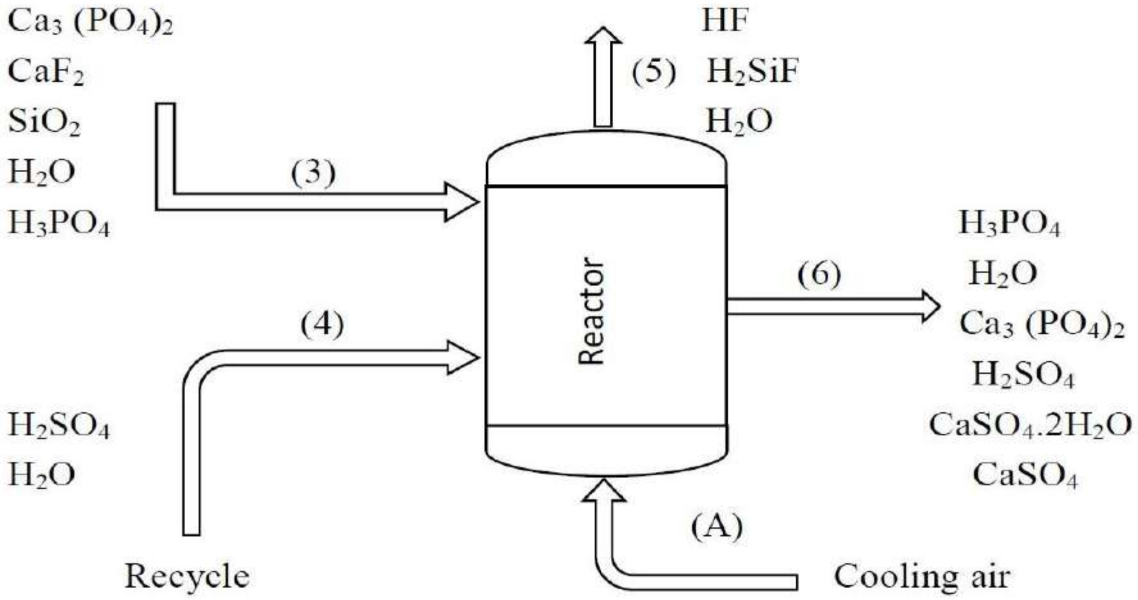


*Figure 2-2 material balance reactor*

Stream 3:

Reactions:

$Ca_3(PO4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4).2H_2O$……….(1)

$CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO_4.2H_2O$…………………….(2)

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$……………………………………..(3)

$H_3PO_4$ production = 429 kmol/hr

Reaction 1:

$Ca_3(PO4)_2$ reacted = 429/2 = 214.5 kmol/hr

Unreacted $Ca_3(PO4)_2$ = 452-214.5 = 237.5 kmol/hr

$H_2SO_4$ reacted = 3/2 * 429 = 643.5 kmol/hr

$H_2O$ reacted = 6/2 * 429 = 1287 kmol/hr

$CaSO_4.2H_2O$ produced = 3/2 * 429 = 643.5 kmol/hr

Reaction 2:

In $CaF_2$ = reacted $CaF_2$ = 480 kmol/hr

Reacted $H_2SO_4$ = 480 kmol/hr

Produced HF = 2 * 480 = 960 kmol/hr

Produced $CaSO_4$ = 480 kmol/hr

Reaction 3:

In $SiO_2$ = reacted $SiO_2$ = 156 kmol/hr

Reacted HF = 6 * 156 = 936 kmol/hr

Produced $H_2SiF_6$ = 156 kmol/hr

Produced $H_2O$ = 2 * 156 = 312 kmol/hr

Stream 4:

Total $H_2SO_4$ reacted = 643.5 + 480 = 1123.5 kmol/hr = 110000 kg/hr

Excess $H_2SO_4$ = 15% → $0.15 = \frac{\text{in}-\text{reacted}}{\text{in}} = 0.15 = \frac{\text{in}-110000}{110000}$

In = 126630 kg/hr

Non reacted $H_2SO_4$ = 126630 - 110000 = 16530kg/hr

$H_2SO_4$ concentration 94%:

$\frac{126630}{0.94} = 134700$ kg/hr

$H_2SO_4$ = 126630 kg/hr

$H_2O$ = 134700 – 126600 = 8100 kg/hr

Stream 6:

$H_3PO_4$ = 42000 + 14000 = 56000 kg/hr

$H_2O$ = 79500 + 8100 + 5600 – 23130 = 70000kg/hr

$Ca_3(PO_4)_2$ = 73600 kg/hr

$CaSO_4.2H_2O$ = 110700 kg/hr

$H_2SO_4$ = 16500 kg/hr

$CaSO_4$ = 65250 kg/hr

Stream 5:

$H_2SiF_6$ = 22450 kg/hr

$H_2O$ = assume 50% of $H_2O$ from stream 6 is vaporized:

0.5 * 70000 = 35000 kg/hr

HF = produced – reacted = 960 – 936 = 24 kmol/hr

= 480 kg/hr

Cooling air stream:

79% Nitrogen

21% Oxygen

| Component | Stream 3 | Stream 4 | Stream 5 | Stream 6 | Air Stream (%) |
|---|---|---|---|---|---|
| $Ca_3(PO_4)_2$ | 140000 | | | 73600 | |
| $CaF_2$ | 37400 | | | | |
| $SiO_2$ | 9350 | | | | |
| $H_2O$ | 79500 | 8100 | 35000 | 35000 | |
| $H_3PO_4$ | 14000 | | | 56000 | |
| $H_2SO_4$ | | 126630 | | 16500 | |
| $CaSO_42H_2O$ | | | | 110700 | |
| $CaSO_4$ | | | | 65250 | |
| $H_2SiF_6$ | | | 22450 | | |
| HF | | | 480 | | |
| $O_2$ | | | | | 21 |
| $N_2$ | | | | | 79 |

*table 2-3material Balance on Reactor*

In = 3 + 4 / Out = 5 + 6

In = 140000 + 37400 + 9350 +79500 + 14000 + 8100 + 126630 = 414980 kg /hr

Out = 35000 + 22450 + 73600 + 35000 + 56000 + 16500 + 110700 + 65250+480 = 414980 kg/hr

In = Out

### 2.1.3 Material Balance on Filter

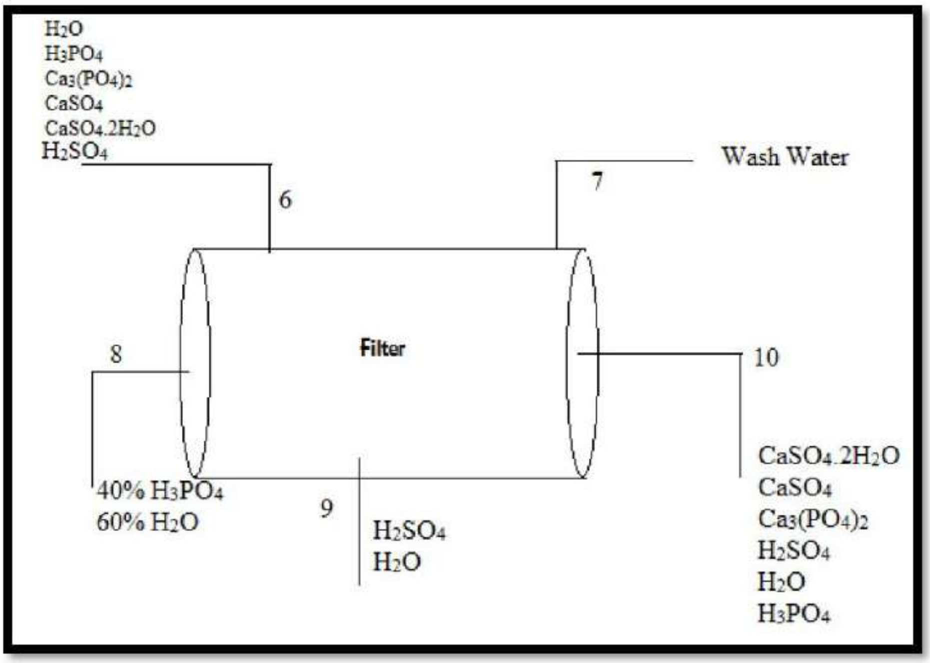


*Figure 2-3Material Balance on Filter*

Stream 10:

$H_3PO_4$ = 14000 kg/hr

Stream 8:

$H_3PO_4$ = 56000 – 14000 = 42000 kg/hr

Total stream 8 = $\frac{42000}{0.4}$ = 105000 kg/hr

$H_2O$ in stream 8 = 0.6 * 105000 = 63000 kg/hr

If we assume 1.5% of $H_2SO_4$ and $H_2O$ is allowed to go through with the gypsum for easy filtration, then:

$H_2SO_4$ in stream 10 = 16500 * $\frac{1.5}{100}$ = 247.5 kg/hr

$H_2SO_4$ in stream 9 = 16500 – 247.5 = 16252.5 kg/hr

$H_2O$ in stream 10 = 35000 * $\frac{1.5}{100}$ = 525 kg/hr

Since stream 9 recycles back to the reactor and the acid concentration needs to be at 94%, then:

Total stream 9 = $\frac{H_2SO_4}{0.94} = \frac{16252.5}{0.94}$ = 17290 kg/hr

$H_2O$ in stream 9 = 17290 * 0.06 = 1037.5 kg/hr

$H_2O$ in stream 7 = -35000 + 63000 + 525 + 1037.5 = 29562.5 kg/hr

| Component | Stream 6 | Stream 7 | Stream 8 | Stream 9 | Stream 10 |
|---|---|---|---|---|---|
| $Ca_3(PO_4)_2$ | 73600 | | | | 73600 |
| $H_2O$ | 35000 | 29562.5 | 63000 | 1037.5 | 525 |
| $H_2SO_4$ | 16500 | | | 16252.5 | 247.5 |
| $H_3PO_4$ | 56000 | | 42000 | | 14000 |
| $CaSO_42H_2O$ | 110700 | | | | 110700 |
| $CaSO_4$ | 65250 | | | | 65250 |

*table 2-4Material Balance on Filter*

In = 6 + 7 / Out = 8 + 9 + 10

In = 73600 + 35000 + 16500 + 56000 + 110700 + 65250 + 29562.5 = 386612.5 kg/hr

Out = 63000 + 42000 + 1037.5 + 16252.5 + 73600 + 525 + 247.5 + 14000 + 110700 + 65250 = 386612.5 kg/hr

In = Out

### 2.1.4 Material Balance on Evaporator

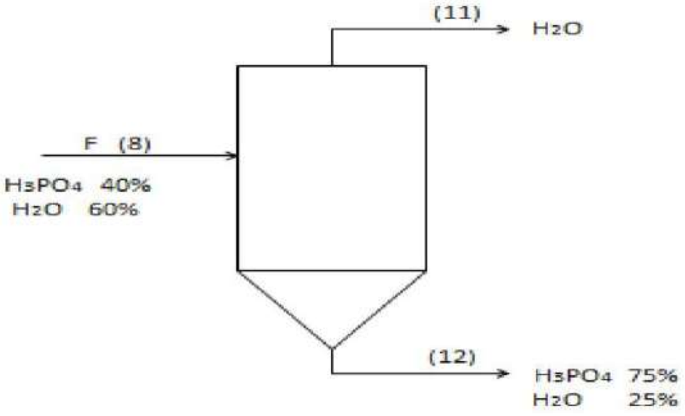


*Figure 2-4 Material Balance on Evaporator*

Stream 8(F) composition:

$H_3PO_4$ = 42000 kg/hr

$H_2O$ = 63000 kg/hr

Material balance on $H_3PO_4$:

0.4 * F = 0.75 * Stream12

0.4 * 105000 = 0.75 * Stream 12

Stream 12 = 56000 kg/hr

$H_2O$ in Stream 12 = 0.25 * 56000 = 14000 kg/hr

$H_2O$ in Stream 11 = 63000 – 14000 = 49000 kg/hr

| Component | Stream 8 | Stream 11 | Stream 12 |
|---|---|---|---|
| $H_3PO_4$ | 42000 | | 42000 |
| $H_2O$ | 63000 | 49000 | 14000 |

In = 8 / Out = 11 + 12

In = 42000 + 63000 = 105000 kg/hr

Out = 49000 + 14000 + 42000 = 105000 kg/hr

In = Out

### 2.1.5 Material Balance on Mixing Tank

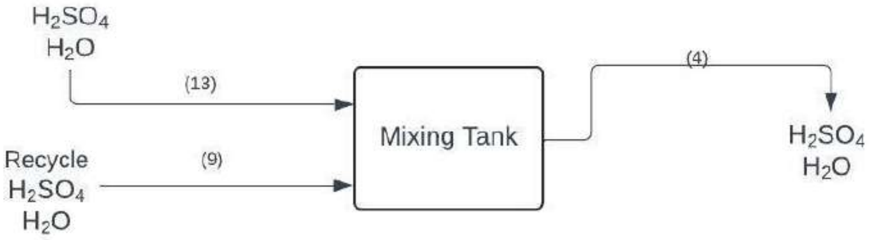


*Figure 2-5Material Balance on Mixing Tank*

Stream 4:

$H_2SO_4$ = 126630 kg/hr

$H_2O$ = 8100 kg/hr

Stream 9:

$H_2SO_4$ = 16252.5 kg/hr

$H_2O$ = 1037.5 kg/hr

Stream 13:

$H_2SO_4$ = 126630 – 16252.5 = 110377.5 kg/hr

$H_2O$ = 8100 – 1037.5 = 7062.5 kg/hr

| Composition | Stream 9 | Stream 13 | Stream 4 |
|---|---|---|---|
| $H_2SO_4$ | 16252.5 | 110377.5 | 126630 |
| $H_2O$ | 1037.5 | 7062.5 | 8100 |

*table 2-5Material Balance on Mixing Tank*

In = 9 + 13    / Out = 4

In = 16252.5 + 1037.5 + 110377.5 + 7062.5 = 134730 kg/hr

Out = 126630 + 8100 = 134730 kg/hr

In = Out

### 2.1.6 Material Balance on Absorber:

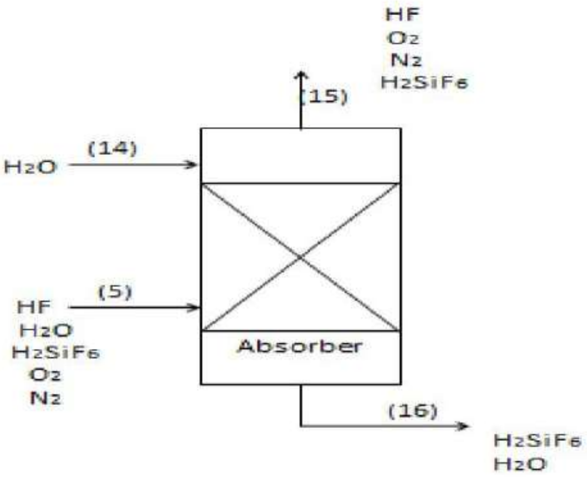


*Figure 2-6Material Balance on Absorber*

Assume 99% recovery:

$H_2SiF_6$ in stream 16 = 0.99 * 22450 = 22225.5 kg/hr

$H_2SiF_6$ in stream 15 = 22450 – 22225.5 = 224.5 kg/hr

If we assume the amount of water in stream 16 made $H_2SiF_6$ into 15%:

Total stream 16 = $\frac{22225.5}{0.15}$ = 148170 kg/hr

$H_2O$ in stream 16 = 0.85 * 148170 = 125944.5 kg/hr

$H_2O$ in stream 14 = 125944.5 – 35000 = 90944.5 kg/hr

($N_2$ and $O_2$ don't get absorbed they just enter from the bottom and leave at the top)

| Composition | Stream 5 | Stream 14 | Stream 15 | Stream 16 |
|---|---|---|---|---|
| $H_2SiF_6$ | 22450 | | 224.5 | 22225.5 |
| $H_2O$ | 35000 | 90944.5 | | 125944.5 |
| HF | 480 | | 480 | |

*Figure 2-6Material Balance on Absorber*

In = 5 + 14 / Out = 15 + 16

In = 22450 + 35000 + 480 + 90944.5 = 148874.5

Out = 224.5 + 480 + 22225.5 + 125944.5 = 148874.5 kg/hr

In = Out

### 2.1.7 Overall Material Balance

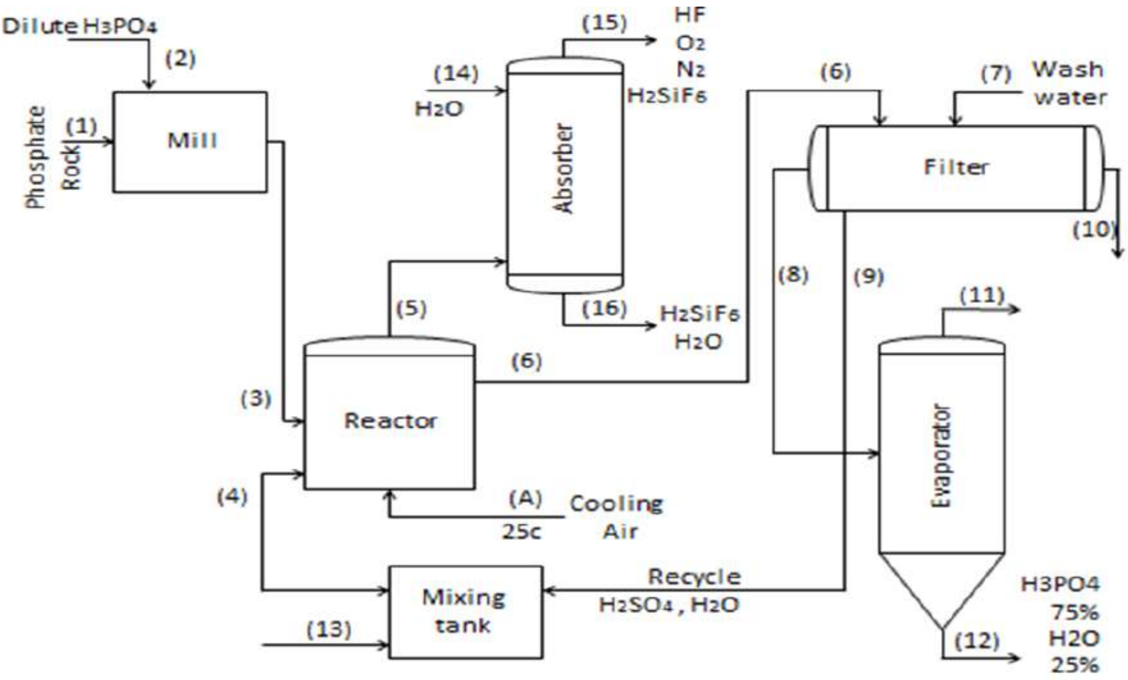
All in streams = 1 + 2 + 13 + 14 + 7

→ 186750 + 93500 + 29562.5 + 117440 + 90944.5 = 518197 kg/hr

All out streams = 10 + 11 + 12 + 15 + 16

→ 264322.5 +49000 + 56000 + 704.5 + 148170 = 518197 kg/hr

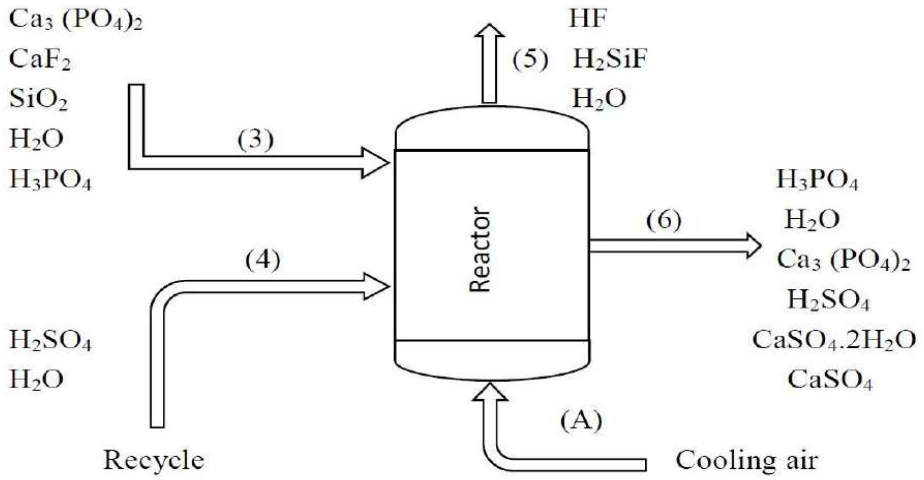
In = Out



## 2.2 Energy Balance

For the energy balance, we will be only concentrating on the reactor and evaporator since they are the main units in our process. The other units we assume no heat is lost or gained overall. Also, for easier calculations, we had a feed of 1000 tons per day, but we will only be doing the heat balance for 1 ton per day. This is to get smaller and more accurate numbers that we can deal with.

### 2.2.1 Energy Balance on Reactor



Reactions:

$Ca3(PO4)2 + 3H2SO4 + 6H2O \rightarrow 2H3PO4 + 3(CaSO4).2H2$

$O\ CaF2 + H2SO4 + 2H2O \rightarrow 2HF + CaSO4.2H2O$

$6HF + SiO2 \rightarrow H2SiF6 + 2H2$

O Operating conditions:

T = 75-80°C, P=1atm, Liquid

Phase Heat in = heat out

$$m\ Cp\ \Delta T_{Ca3(PO4)2} + m\ Cp\ \Delta T_{CaF2} + m\ Cp\ \Delta T_{SiO2} + m\ Cp\ \Delta T_{H2O} + m\ Cp\ \Delta T_{H3PO4} + m\ Cp\ \Delta T_{H2SO4} + m\ Cp\ \Delta T_{H2O} + m\ Cp\ \Delta T_{O2} + m\ Cp\ \Delta T_{N2} + \Delta Hr_{total} = m\ Cp\ \Delta T_{HF} + m\ Cp\ \Delta T_{H2siF6} + m\ Cp\ \Delta T_{O2} + m\ Cp\ \Delta T_{N2} + m\ Cp\ \Delta T_{H3PO4} + m\ Cp\ \Delta T_{H2O} + m\ Cp\ \Delta T_{Ca3(PO4)2} + m\ Cp\ \Delta T_{H2SO4} + m\ Cp\ \Delta T_{CaSO4} + m\ Cp\ \Delta T_{CaSO4.2H2O} + Q + m\ \lambda_{H2O}$$

$T_{ref} = 25°C$

We have 3 reactions: Δ

$Hr_1 = -2901.5$ kJ/kmol

$\Delta Hr_2 = 22.343$ kJ/kmol

$\Delta Hr_3$ = 770.5 kJ/kmol

$\Delta Hr_{total}$ = 0.2145kmol * -2901.5 + 0.48 * 22.343 + 0.156 * 770.5 = -490 KJ/kg

$$\frac{0.6}{20} * \Bigg[29.06(353-298) + \frac{6.611 * 10^{-4}}{2} * (353^2 - 298^2) - \frac{2.032 * 10^{-6}}{3}$$

$$* (353^3 - 298^3) + \frac{2.5 * 10^{-9}}{4} * (353^4 - 298^4)\Bigg] + \frac{31.3}{18}$$

$$* \Bigg[32.24(353-298) + \frac{1.923 * 10^{-3}}{2} * (353^2 - 298^2) - \frac{1.06 * 10^{-5}}{3}$$

$$* (353^3 - 298^3) + \frac{3.6 * 10^{-9}}{4} * (353^4 - 298^4)\Bigg] + \frac{22.32}{144}$$

$$* [0.67(353-298) + \frac{21}{32} * [28.106(353-298) + \frac{3.68 * 10^{-6}}{2}$$

$$* (353^2 - 298^2) + \frac{1.75 * 10^{-5}}{3} * (353^3 - 298^3) + \frac{1.07 * 10^{-8}}{4}$$

$$* (353^4 - 298^4)] + \frac{79}{28} * [31.15(353-298) - \frac{1.36 * 10^{-2}}{2}$$

$$* (353^2 - 298^2) + \frac{2.68 * 10^{-5}}{3} * (353^3 - 298^3)$$

$$- \frac{1.11 * 10^{-8}}{4} * (353^4 - 298^4)] + \frac{56}{98} * 185.4\,(353-298)$$

$$+ \frac{38.26}{18} * 75.3\,(353-298) + \frac{73.16}{301} * 262.9\,(353-298) + \frac{16.45}{98}$$

$$* 167.4\,(353-298) + \frac{110.4}{172} * 164.9\,(353-298) + \frac{65.28}{136}$$

$$* 236.1\,(353-298) + Q + \frac{31}{18} * 40683$$

$$= -490.765 + \frac{8.08}{18} * 75.3(304-298) + \frac{126.45}{98} * 167.4(304-298)$$

Q = -263300 Kj/hr

### 2.2.2 Energy Balance on Evaporator

Heat In = Heat Out

$m\,Cp_{H_3PO_4}\,dT + m\,Cp_{H_2O}\,dT + Q =$
$m\,Cp_{H_2O}\,dT + m\,\lambda_{H_2O} + m\,Cp_{H_3PO_4}\,dT + m\,Cp_{H_2O}\,dT$

$T_{ref} = 72°C$

$Q=(42/98)*185.4*(373-345)+(14/18)*\{4.184*(373-345)+$

$(49/18)*32.243*(373-345)+(1.9238*10^{-3}/2)*(373^2-345^2)+(1.055*10^{-5}/$

$3)*(373^3-345^3) - (3.596 * 10^{-5}/4) *(373^4-345^4)\} + (49/18)* 40683$

$Q=115700$ KJ/hr

$Q= m_s * \lambda_s$

$\lambda_s = 2113$ KJ/kg

$m_s = Q/\lambda_s = 115700/2113 = 54.76$ kg/hr.

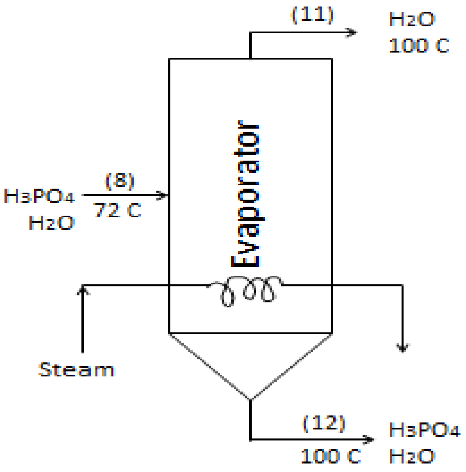


*Figure 2-7 Energy Balance on Evaporator*

## Chapter Three

# Example of Analysis and Design

### 3.1 Design of Reactor

Reactions:

$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 2H_3PO_4$

$+3(CaSO4.2H_2O)$ $CaF_2 + H_2SO_4 \longrightarrow$

$2HF + CaSO_4$

$6HF + SiO_2 \longrightarrow H_2SiF_6 + 2H_2O$

Operating Conditions T= 75 – 80C°

P= Liquid Phase

$\tau$ = 4-8hr

1atm

We have three chemical reactions.

The reaction is exothermic and temperature is maintained constant by-passing air across the reactor.
For continuous stirred tank reactor

$$\tau = V/Vo = CaoV/Fao = XaCao/(-ra) = (Cao - Ca)/(-ra)$$

| Comp. | Density Kg/m$^3$ |
|---|---|
| $H_2SO_4$ | 1153 |
| $H_2O$ | 988 |
| $Ca_3(PO_4)_2$ | 1310 |
| $CaF_2$ | 1755 |
| $SiO_2$ | 1042 |

$$\rho\ mix = \sum Xi\ \rho i$$

Where:

V° = volumetric flow rate (m$^3$/hr).

ρ = density of component (kg/m$^3$).

Mass= mass flow rate of component (kg/hr.).

| Comp. | Density (kg/m$^3$) | Mass (kg/hr) | V° (m$^3$/hr) |
|---|---|---|---|
| $H_2SO_4$ | 1153 | 126.45 | 0.11 |
| $H_2O$ | 988 | 8.08 | 0.008 |
| $Ca_3(PO_4)_3$ | 1310 | 139.5 | 0.1065 |
| $CaF_2$ | 1755 | 37.2 | 0.0212 |
| $SiO_2$ | 1042 | 9.3 | 0.009 |

*table 3-1Design of Reactor*

V° = 0.255m$^3$/hr.

Calculation the Volume of Reactor:

$$\text{Space time} = \frac{volume\ of\ reactor\ (\mathrm{m3})}{volumetric\ flow\ rate\ of\ reactor\left(\frac{\mathrm{m3}}{\mathrm{hr}}\right)}$$

V° = 0.255m$^3$/hr.

$\tau = 4 - 8$hr

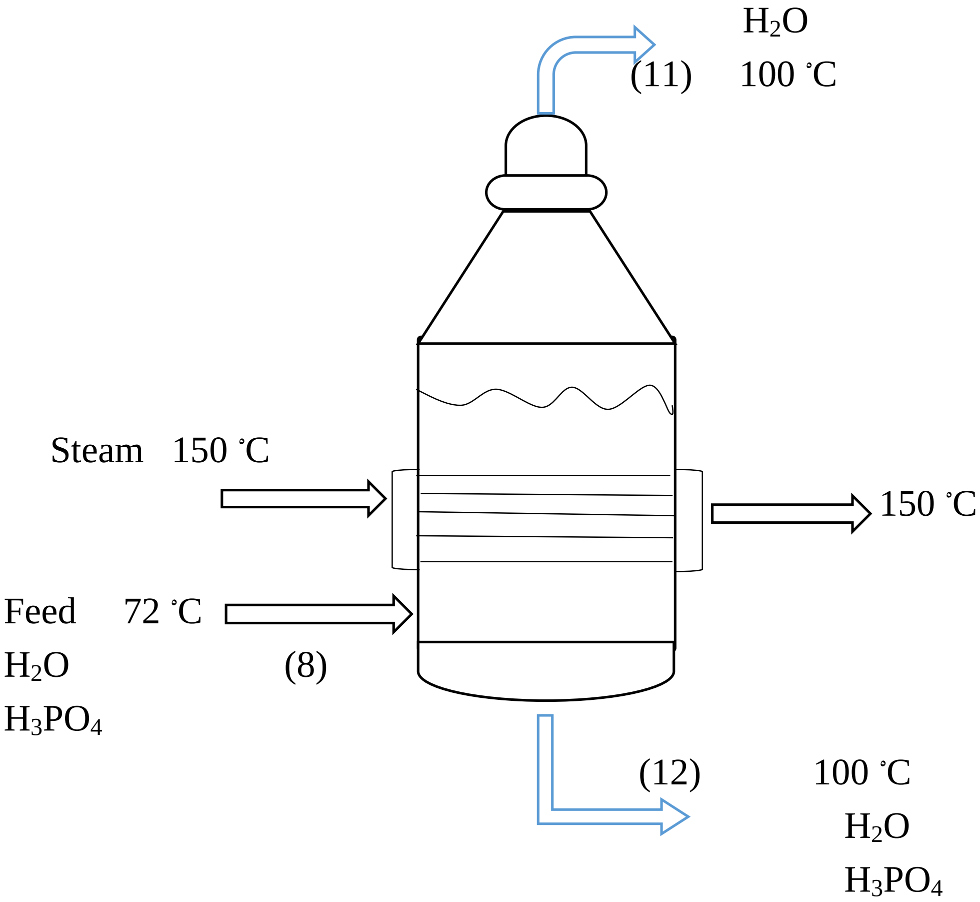
take $\tau = 6$ hr.

$$\therefore \tau = \frac{V}{V^{o}} \longrightarrow 6 = \frac{V}{0.255}$$

V= 1.53 m$^3$

∴ Volume of reactor = 1.53 m$^3$

## 3.3 Evaporator Design



| Component | Steam (8) kg/hr. | Steam (11) kg/hr. | Steam (12) kg/hr. |
|---|---|---|---|
| $H_3PO_4$ | 42 | ═ | 42 |
| $H_2O$ | 63 | 49 | 41 |

### 3.3.1 Calculation of Bundle tubes

take tube dimensions as follows (15) :-

$d_o = 16$ mm

$d_i = 14$ mm

$L = 1.5$ m

Heat flux = 2012.5 w/m$^2$ (16)

From Energy Balance

Heat load = 32.3 Kw

- Heat transfer area = Q/Heat flux

A= 32.3/2.0125 = 16 $m^2$

Area of one tube $a_\circ = \pi\ d_\circ\ L = \pi * 14*10^{-3} * 1.5 = 0.066\ m^2$

Number of tube

$N = A/a_\circ = 16/0.066 = 243$

Tubes arranged in triangular pitch one pass

$Pt = 1.25\ d_\circ$

$Pt = 1.25*16 = 20mm$

From volume (6) eq. (12.3b) P. (649)

Bundle diameter $Db = d_\circ\ [Nt/K_1]^{1/n1}$

Where $K_1$, $n_1$ constants (17)

$K_1 = 0.319$

$N_1 = 2.142$

$Db = 16\ [243/0.319]^{1/2.142} = 355$ mm

## 3.3.2 Tube side pressure drop

Temperature of steam = 150 °C

From steam table $v_g = 1.13\ m^3/kg$

$\rho_g = 1/v_g = 1/1.13 = 0.885\ Kg/m^3$

area of flow

$A_t = N_t\ (\pi/4\ d_i^2)$

$A_t = 243 * \pi/4 *(14*10^{-3})^2 = 0.0374\ m^2$

Mass flow rate $G = \rho * u_t * A_t$

$G = 0.016$ kg /s , $\rho = 0.88\ Kg/m^3$

$U_t = G/\ \rho * A_t = 0.016/0.885*0.0374 = 0.53$ m/s

Steam viscosity $\eta = 1.4*10^{-5} Ns/m^2$

$Re_t = \rho * u_t * d_t/\eta = 0.885*0.5*(14*10^{-3})/\ 1.4*10^{-5} = 442.5$

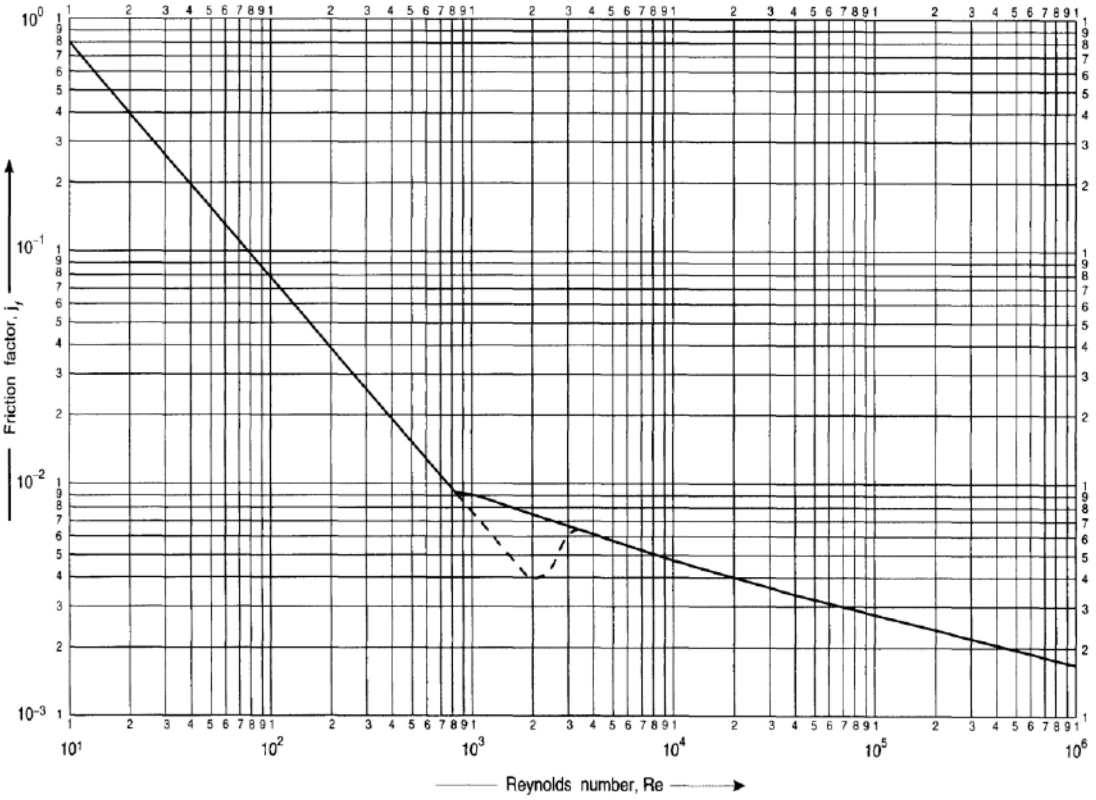


Figure 12.24. Tube-side friction factors

*Note:* The friction factor $j_f$ is the same as the friction factor for pipes $\phi(= (R/\rho u^2))$, defined in Volume 1 Chapter 3.

$j_f = 2*10^{-2}$ friction factor $^{(18)}$

$\Delta P = Np*[ 8*j_f*(L/d) *(\text{ɱ}/ \text{ɱ}_w)^{-m} + 2.5] * \rho*u_t^2/2$ $^{(19)}$

Where:

Np = number of passes

$J_f$ = fraction factor

L = tube length (m)

di = inside diameter (m)

$\rho$ = density ($Kg/m^3$)

$u_t$ =velocity (m/s)

neglect $(\text{ɱ}/ \text{ɱ}_w)^{-m} = 1$

$\Delta P = [ 8*2*10^{-2} *(1.5/14*10^{-3}) +2.5] *0.885 * (0.5)^2/2 = 2\ N/m^2$

$= 2.9*10^{-4}$ Psia

If a high-pressure drop must choose the other dimensions of the tube to get to the proper pressure drop is less than (1Psia)

## 3.3.3 Volume of evaporator

$V = 1.7261[\, e^{-p/RT} + K\,(ɱ_l/ɱ_v)^{0.2}]$ (20)

Where:

$V$= volume of evaporator ($m^3$)

$P$= pressure of evaporator ($N/m^2$)

$R$= gas constant

$T$= temperature (K)

$K$= constant depend on type of tubes bundle (steam bundle)

$K$= 2.125 for vertical tube

$K$= 1.1942 for horizontal tube

$\mu_v = 1.4*10^{-5}$ Ns/m$^2$

$\mu_l = 0.28*10^{-3}$Ns/m$^2$

take horizontal tube

operating pressure = 10 psi = 0.6 atm. = $0.69*10^5$ N/m$^2$

$V = 1.7261[\, e^{-0.69*10-5/8.314+373} + 1.1942(0.28/0.014)^{0.2}] = 5.5\ m^3$

For standard tubes diameter select shell diameter = 1.5 m

(shell diameter must be equal to tube length of steam bundle)

## 3.3.4 Length of evaporator

$V = \pi/4\ D^2 *L$

$5.5 = \pi/4\ (1.5)^2 *L$

$L = 3.114\ m = 3.2\ m$

## 3.3.5 Calculation of residence time (Ƭ)

Ƭ= $v/v_{\circ}$

Where:

$V$ = volume of evaporator ($m^3$)

$v_{\circ}$ = feed volumetric flowrate ($m^3/s$)

Ƭ= $v/v_{\circ} = \frac{5.5}{mass/\rho}$

$P_{mix.}$ = 1333.6 Kg/m$^3$

Ƭ= $\frac{5.5}{24*105/1333.6}$ = 2.9 hr. = 174 min

## 3.3.6 Mechanical Design

t= $\frac{pi*Di}{2fJ-pi}+C$ (21)

where:

t= thickness of shell (mm)

Pi = operating Pressure (N/mm$^2$)

Di= shell diameter (mm)

J = joint factor (0.8)

C= corrosion allowance (2mm)

f= design stress (N/mm$^2$)

Operating pressure = 10% above design pressure = 1.1*0.069= 0.076 N/mm$^2$

Stainless steel (18cr/8Ni) (22)

f= 150 N/mm$^2$

t= $\frac{0.076*1500}{2*0.8*150-0.076}+2=2.5\,mm=3mm$

## 3.3.7 Thickness of cover

We can use hemispherical cover thickness of cover = 0.6 * thickness of shell

t = 0.6 *3 = 1.8mm

## 3.3.8 Weight of evaporator

For stainless steel

$W_v$ = 240 $C_v$ $D_m$ ($H_v$+0.8 $D_m$)t

Where

Cv= constant (1.08)

$D_m$= mean shell diameter (m)

= (Di + t * $10^{-3}$ )= 1.503 m

H= length of vessel (m)

t = shell thickness (mm)

Wv= 240 * 1.08 * 1.503 (3.2+ 0.8 * 1.503) * 3 = 5145 N

### 3.3.9 Weight of vessel filled with water

$Ww = \pi/4\ D^2L * \rho_{H2O} * g$

$= 5.5 *1000 *9.81 = 53955\ N$

### 3.3.10 Weight of tubes

Weight of tube (1.05 Kg/m)

Weight of one tube = 1.5 * 1.05 = 1.6 Kg

Weight of tube (Wt) = 243 *1.6 * 9.81 = 3815 N

### 4.3.11 Weight of cover

$r_i = D/2 = 1.5/2 = 0.75\ m$

$r_\circ = r_i + t = 0.75 + 0.0018 = 0.7518\ m$

∴ Total height of evaporator = 3.2 + 2 * 0.7518 = 4.7 m

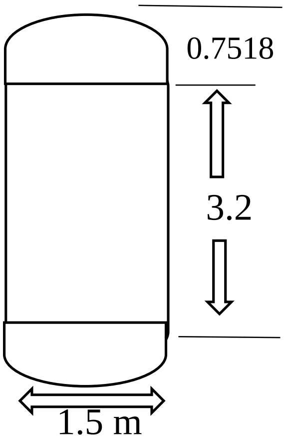
Volume of sphere ($4\pi/3 * r^3$)

∴ volume of two cover = $4\pi/3\ (r_\circ^3 - r_i)^2$

for carbon steel ($\rho = 7.7*10^{-4}\ Kg/m^3$)

$Wc = 4\pi/3[(0.7518)^2 - (0.75)^2] *7.7*10^4*9.81$

$= 8549*2 = 17098\ N$



### 4.3.12 Total weight

$W_T = W_v + W_t + W_w + W_c + W_{man}$

$W_T = 5145 + 3815 + 53955 + 8549*2 + 1500$

$W_T = 81513\ N$

$= 81.5\ KN$

## Chapter Four

# Results and Conclusion

### 4.1 Conclusion

This project explores the production of phosphoric acid, a vital industrial chemical with numerous applications. Beginning with a concise introduction to the significance of phosphoric acid in various industries, the study delves into the intricacies of material balance and heat balance within the production process. Material balance analysis elucidates the input-output dynamics of raw materials and products, ensuring optimal resource utilization. Meanwhile, heat balance considerations focus on the efficient management of thermal energy, essential for maintaining process integrity and sustainability. Additionally, the project investigates the design aspects of key production units, emphasizing the critical role of unit design in achieving operational efficiency and product quality. Through comprehensive analysis and design strategies, this project aims to contribute to the advancement of phosphoric acid production methodologies, fostering sustainable industrial practices and economic viability.

# References

1. AUSTRALIAN GOVERNMENT. June 2022. *Department of Climate Change,Energy,the Evironment and Water* [Online]. Available: https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/phosphoric-acid#daff-page-main [Accessed].
2. 2000. *Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry*, .
3. AUSTRALIAN GOVERNMENT. June 2022. *Department of Climate Change,Energy,the Evironment and Water* [Online]. Available: https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/phosphoric-acid#daff-page-main [Accessed].
4. GROUP, S. L. E. & COMPANY 2001. METHOD OF PREPARING WET PROCESS PHOSPHORIC ACID.pdf>. 5.
5. TOAMA, H. Z. 2016. WORLD PHOSPHATE INDUSTRY.pdf>.