Minia University
Faculty of Engineering
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MANUFACTURING PROCESSES OF H_3PO_4

2019- 2020

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Introduction

-Mineral acid having Ch. Formula (H_3PO_4)

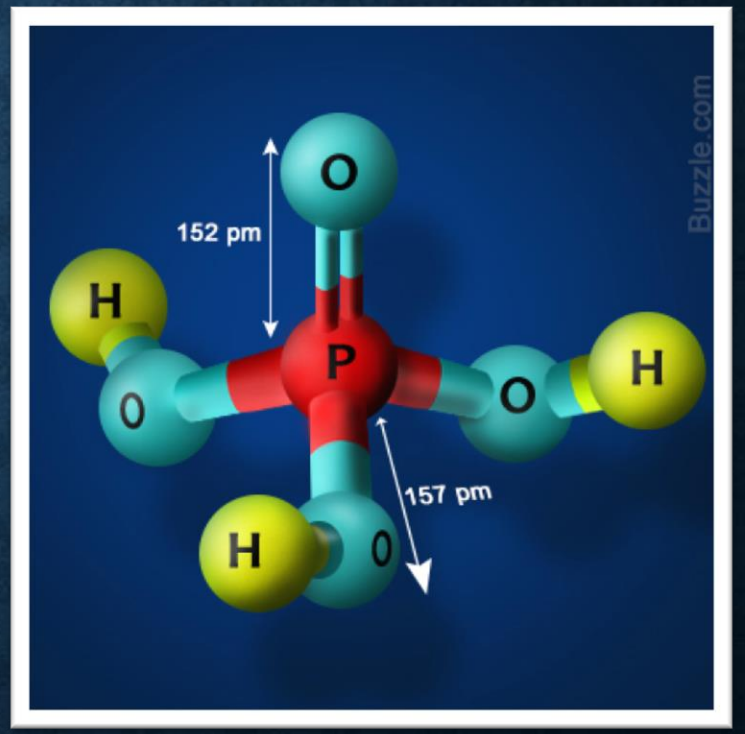
- Is the backbone of all phosphorous industrial and all other phosphoric compounds.

- 90% of phosphoric acid production is used for fertilizer production.

- phosphoric Acid is a colorless, odorless phosphorus-containing inorganic acid. Phosphoric acid is a sequestering agent which binds many divalent cations, including Fe++, Cu++, Ca++, and Mg++.
- Phosphoric acid is 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. In addition, phosphoric acid is a constituent in bone and teeth, and plays a role in many metabolic processes.
- Phosphoric acid, also known as orthophosphoric acid or phosphoric(V) acid, is a mineral acid with the chemical formula H3PO4. Alternatively, orthophosphoric acid molecules can combine with themselves to form a variety of compounds referred to as phosphoric acids in a more general way. For a discussion of these, see Phosphoric acids and Phosphates. Appears to exist only as a food additive and produced synthetically.
- PHOSPHORIC ACID is a clear colorless liquid or transparent crystalline solid. The pure solid melts at 42.35°C and has a density of 1.834 g / cm3. Liquid is usually an 85% aqueous solution. Shipped as both a solid and liquid. Corrosive to metals and tissue. Used in making fertilizers and detergents and in food processing.

Phosphorus

- Molecular formula : H_3PO_4
- Molecular weight : 98 gm/mole
- Melting point : 42.4°C
- Boiling point : 213°C



Production of H_3PO_4

There tow types of processing do produce Phosphoric Acid :-

1-Dry or electrical or thermal process

2-Wet process (strong acid process)

Raw Material

-$Ca_3(PO_4)$

-$Ca_5(PO_4)3.F$

-$Ca_{10}(PO4)6.F_2$

Sources

-Bones of animals

-Rock phosphate

-Manufactured phosphate

Production of H_3PO_4

Dry process

1)Elemental phosphorous is first produced as described before in electrical arc furnace.

2)Then P is oxidized with O2 of air to give P2O5 in a stainless steel or acid resistance bricks reactor

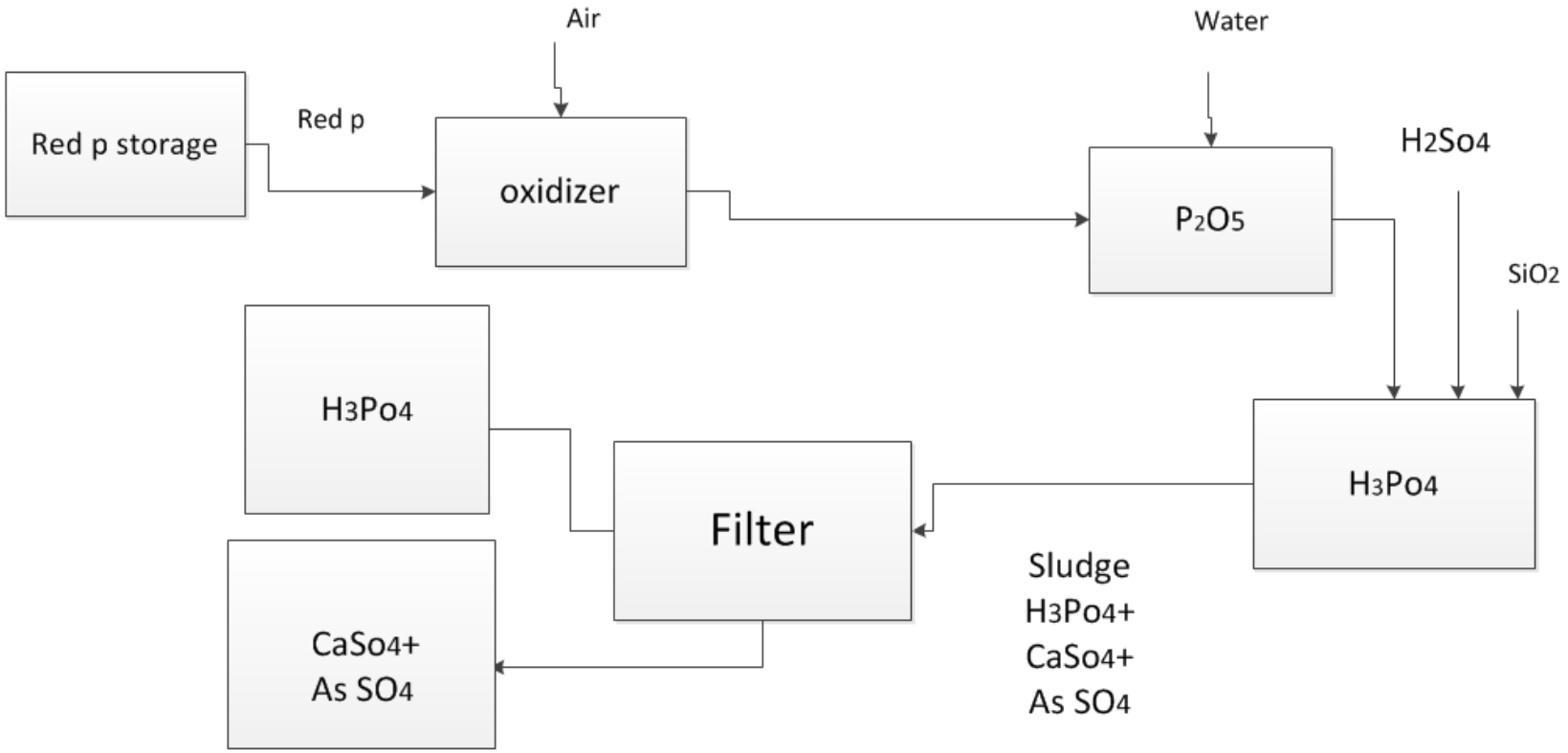
$$2P+5/2\ O_2 \longrightarrow P_2O_5$$

3) The P2O5 is removed by water spray to get (H3PO4L)

$$P_2O_5 +3H_2O \longrightarrow 2H_3PO_4$$

4) We add 85% H2SO4 to remove (Ca) as [CaSo4] We add powder silica to remove " As" as [As SO4]

5) The sludge is removed in a sand filter and acid is add such or diluted to 50% acid.


Air
Water
Red p storage
Red p
oxidizer
P2O5
H2So4
SiO2
H3Po4
H3Po4
Filter
CaSo4+
As SO4
Sludge
H3Po4+
CaSo4+
As SO4

Wet Process

1)by H_2SO_4

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 2.5H_2O \longrightarrow 3H_3PO_4 + 5[CaSO_4.0.5H_2O] + HF + Q \text{ (gypsum)}$$

First step

$$Ca_3(PO_4)_2 + 4H_3PO_4[17\%] + 4H_2O \longrightarrow 5Ca(H_2PO_4)_2 \text{ (single phosphate)}$$

Second step

$$5Ca(H_2PO_4)_2 + 3H_2SO_4 \longrightarrow 5CaSO_4.2H_2O + 2H_3PO_4 \text{ (71: 75\%)}$$

*side reactions

$$CaF_2 + H_2SO_4 + 2H_2O \longrightarrow 2HF + CaSO_4 + 2H_2O$$

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

2- by HCl

$Ca_3(PO_4)_2 + 6HCl \longrightarrow 2H_3PO_4 + 3Cacl_2$

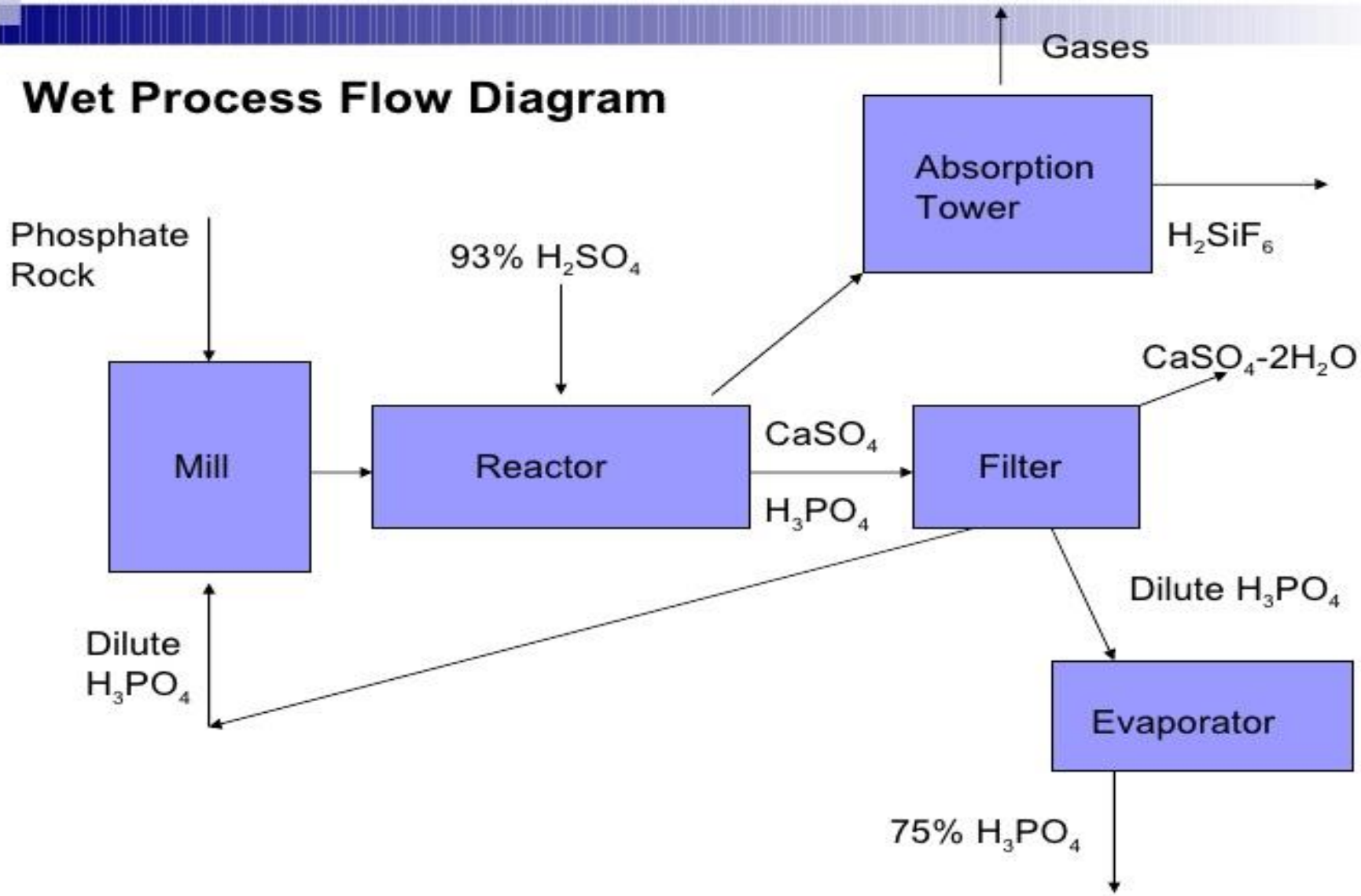
$CaF_2 + 2HCl \longrightarrow 2HF + CaCla_2$

3) by HNO_3

$Ca_3(PO_4)_2 + HNO_3 \longrightarrow 2H_3PO_4 + 3\ Ca\ (NO_3)_2$

$CaF_2 + HNO_3 \longrightarrow Ca(NO_3)_2 + HF$

Wet Process Flow Diagram



(a) Flow sheet (Fig

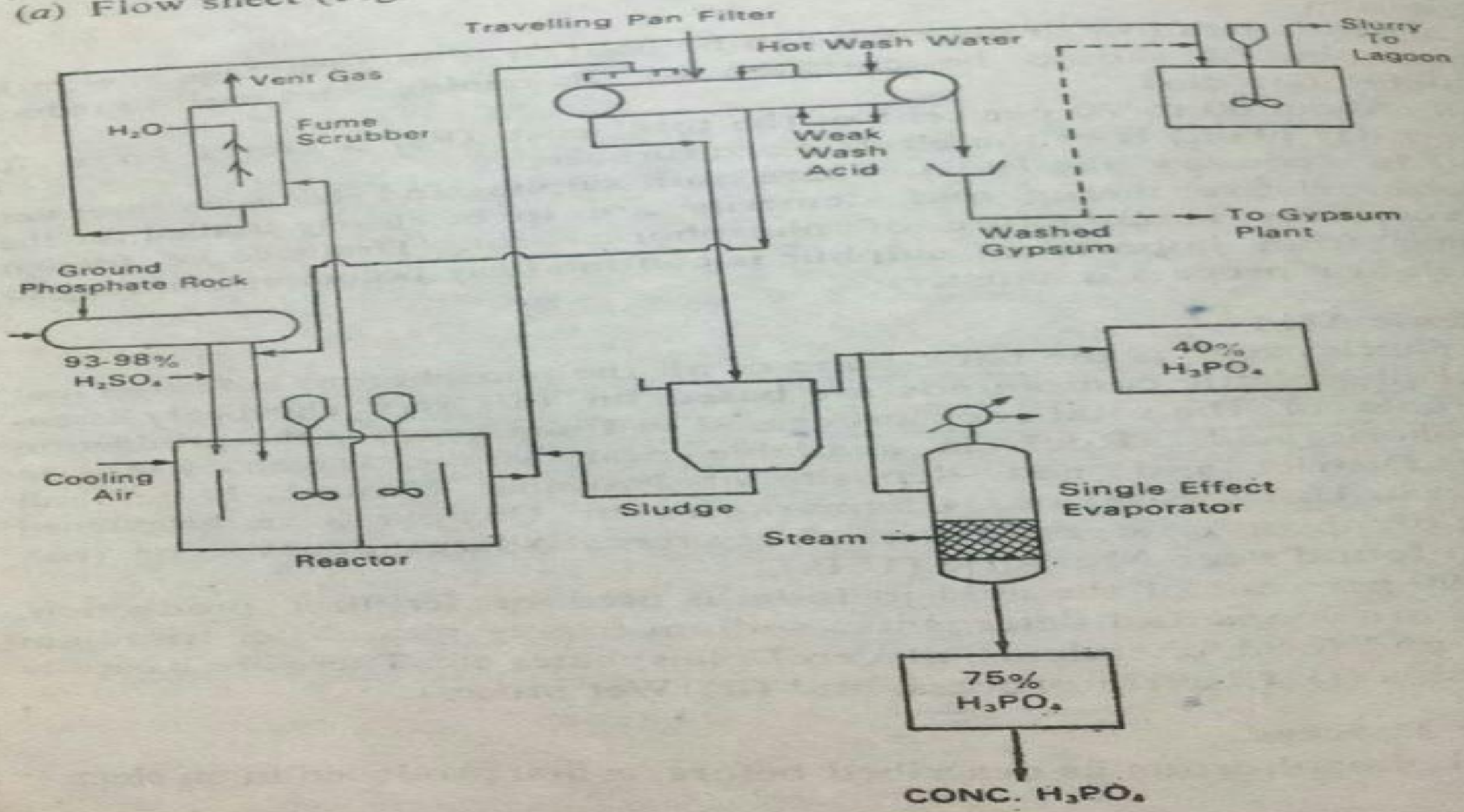


Fig. 7.17. Production of phosphoric acid.

ENGINEERING PROBLEMS

- Finess of rock phosphate is amajor importance as the whole economics depend upon this
- Fine rock give large production need large amount of power used 80 we should know the optimum particle size
- The tempraturre must be controlled as higher temp large than 100 C form $CaSO_4.0.5H_2O$ or anhydrous $CaSO_4$ which difficult to filter
- Some H_2SO_4 [1.5 Ton] is allowed to go with gypsum to take it easy to filterate

USES:

- Used for preparation of hydrogen halides
- Used as a "rust converter”.
- Food-grade phosphoric acid is used to acidify foods and beverages such as various colas.
- Used in many teeth whiteners to eliminate plaque.
- As a chemical oxidizing agent for activated carbon production
- As a cleaner by construction trades to remove mineral deposits, cementitious smears, and hard water stains.
- As a pH adjuster in cosmetics and skin-care products.

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PHOSPHATIC FERTILIZER

INTRODUCTION

Phosphoric fertilizers provide phosphorus to the plants or soil .phosphorus is required to stimulate early growth of plants and to accelerate the seed and fruit formation during the later stage of growth it also increase the resistance of plants against diseases

The various phosphatic fertilizer have different composition ,due to which they have different solubility . The two most important water soluble fertilizers are superphosphate (calcium superphosphate) $Ca(H_2PO_4)_2$ and triple phosphate (diammonia phosphate) $(NH_4)_2HPO_4$
The solubility of phosphoric salts increase with increasing acidity of the salt

Phosphate rock is found as an ore of sedimentation origin mainly in the form of fluorapatite together with various impurities .the P2O5 content of concentrated phosphate rock lies between 20 and 30 percent.
To obtain fertilizers which contain the phosphorus in a readily avaliable formed and which can be applied to any soil ,the insoluble phosphoric salts of the naturally occurring phosphate must be transformed into water soluble or avaliable salts in the technology of phosphatic fertilizers

>>The transformation of insoluble naturally occurring phosphates into solubleforms is accomplished by decomposing them with acid or base or by heating (sublimation of the phosphorus).
The technology must be aimed not only at obtaining a soluble salt but also at producing a phodphatic fertilizer with the highest possible concentration of phospjorus in it

The Manufacture of Superphosphate

The chemical industry makes two kinds of superphosphate-simple and triple superphosphates. The simple superphosphate is one of the most widely used inorganic fertilizers. It is a powder (or in the form of granules) gray in colour, which contain mainly monocalcium phosphate Ca(H,PO2 H,0 and calcium sulphate CaSO,-0.5H,0. Superphosphate also contains a number of impurities-phosphates of iron and aluminium, silica and also phosphoric acid. The manufacture of superphosphate consists essentially in decomposing naturally occurring phosphates. with sulphuric acid.

The Process of Forming Superphosphate

.The process of forming superphosphate by the interaction of sulphuric acid with calcium fluorapatite is a multiphase, heterogeneous process which is usually diffusion limited. The process can be arbitrarily divided into two stages.

The first stage

The first stage is diffusion of sulphuric acid to the apatite particles accompanied by a rapid chemical reaction on the particle surface which continues until the acid is completely consumed, and crystallization of calcium sulphate .

$$Ca5F(PO4)3+5H2SO4+2.5H20 \longrightarrow 5(CaSO4.0.5H2O)+3H3PO4+HF+Q$$

The Second Stage

The second stage is diffusion of the phosphoric acid formed into the pores of the undecomposed apatite particles; it is accompanied by the reaction $Ca5F(PO4)3+7H3PO4+5H20=5Ca(H2PO4)2.H20+HF+Q$ (b) .The monocalcium phosphate formed is initially in solution, but it begins to crystallize out when the solution becomes supersaturated. Reaction (a) ends in the superphosphate reaction chamber in 20 to 40 minutes, during the period of setting and hardening of the superphosphate pulp, which is caused by the relatively rapid crystallization of the low-solubility calcium sulphate and recrystallization of the hemihydrate to the anhydride by the reaction $2CaSO4.\ 0.5H2O=2CASO4+H20$

The next stage of the process, ageing of the superphosphate, i.ethe formation and crystallization of monocalcium phosphate, is a slow one and it ends only at the storage site (final ageing), where the superphosphate is kept from 6 to 25 days. The low rate of this stage is a result of the low rate of diffusion of the phosphoric acid through the crust of monocalcium phosphate formed on the surface of the apatite grains and of the extremely low rate of crystallization of the new solid phase $Ca(H_2PO_4)_2.H_2O$

The Factors That Determine The Optimal Conditions of The Reaction in The Reaction Den

The optimal conditions for the reaction in the reaction den are determined not only by the kinetics of the reactions and the diffusion of the acids, but by the structure of the calcium sulphate crystals formed, which effects the overall process rate and the quality of the superphosphate. The rates of diffusion and of reactions (a) and (b) can be raised by increasing the initial concentration of the sulphuric acid to an optimal value and by raising the temperature.

The Relation between The Degree of The Decomposition of The Phosphate Raw Material & The Concentration of The Initial Sulfuric Acid

How the degree of decomposition of the phosphate raw material in a given time (isochrone) de- pends on the concentration of the initial sulphuric acid is shown in Fig. 29.

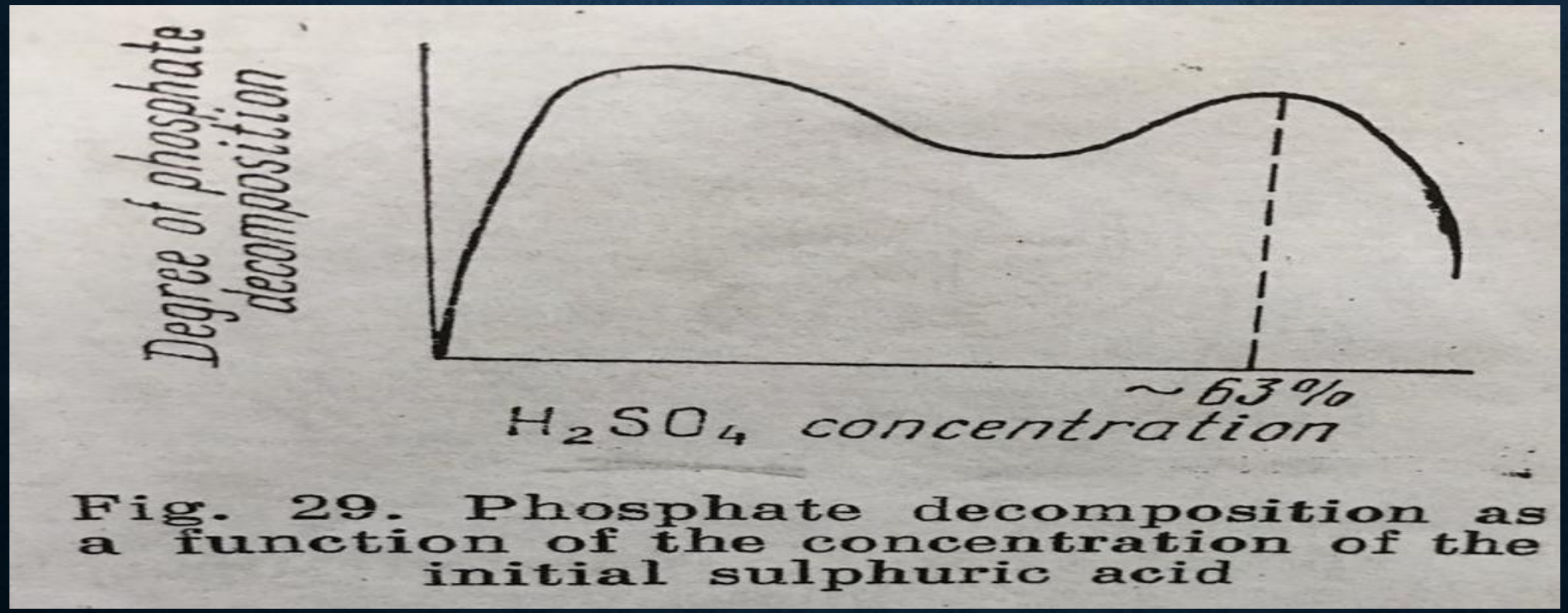

Fig. 29. Phosphate decomposition as a function of the concentration of the initial sulphuric acid

The curve has two maxi- ma. In the weak-solution region when the sulphuric acid concentra- tion is raised, and in the high-concentration region when the con- centration of the acid is lowered, the activity of the acid and, cor- respondingly, the degree of phosphate decomposition increase. an increase in the activity of the acid supersaturation of the solution with respect to calcium sulphate grows; this is accompanied by rapid crystallization and formation of a dense($CaSO_4$. $0.5H_2O$)crust on the surface of the apatite particles, which retards

diffusion of the phosphoric acid. Due to these phenomena there is a range of sulphuric acid concentrations where the rate and degree of phosphate decompositions drop; this corresponds to the minimum of the curve in fig .29.

The location and the values of the maxima of the curve depend on :

1.the nature of the raw material used

2. the S: L ratio of the pulp

3.temperature

4. residence time of the pulp in the reactor, etc.

In industrial conditions an acid concentration which corresponds closely to the second maximum of Fig. 29 is used. The range of optimal sulphuric acid concentrations for the indnstrial process lies within the limits 62-69%; in the continuous process for making superphosphate the initial sulphuric acid concentration is 68-69.5 %, At this concentration of the acid the temperature in the reaction den is approximately 110-115 °C; the rise in the temperature is a result of the heat liberated in exothermic reactions (a) and (b)

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In these conditions a friable, porous layer of calcium sulphate is formed on the phosphate particles, and diffusion of phosphoric acid into the particles takes place at a fairly high rate.

The End Product Of The Process

The P2O5-content of the end product is about half that of the raw material and amounts to 19-20% P205 for superphosphate made from apatite and 14% for superphosphate from phosphate rock. The end product still contains a certain amount of uncombined phosphoric acid, which makes the fertilizer more hygroscopic. Neutralizing admixtures are used to remove the free acid of the superphosphate, or it is treated with gaseous ammonia

These procedures improve the physical properties of the superphosphate; they lower the moisture content, the hygroscopicity and the tenden- cy to cake. If ammonia treatment is used, an additional nutritional component (nitrogen) is also introduced into the fertilizer.

Batch, semicontinuous and continuous processes are used for manufacturing superphosphate.

Only a few plants still use batch- operation dens. These have all the typical faults of batchwise opera- tions: they are of low production capacity, costs are high, the com- position and properties of the product are not constant, the air in the plant is contaminated with the gases and dust from the process, etc. At present all new plants are designed to employ a continuous- operation method and most older plants are being reconverted to such a method.

The flow diagram of a continuous-operation process for making superphosphate

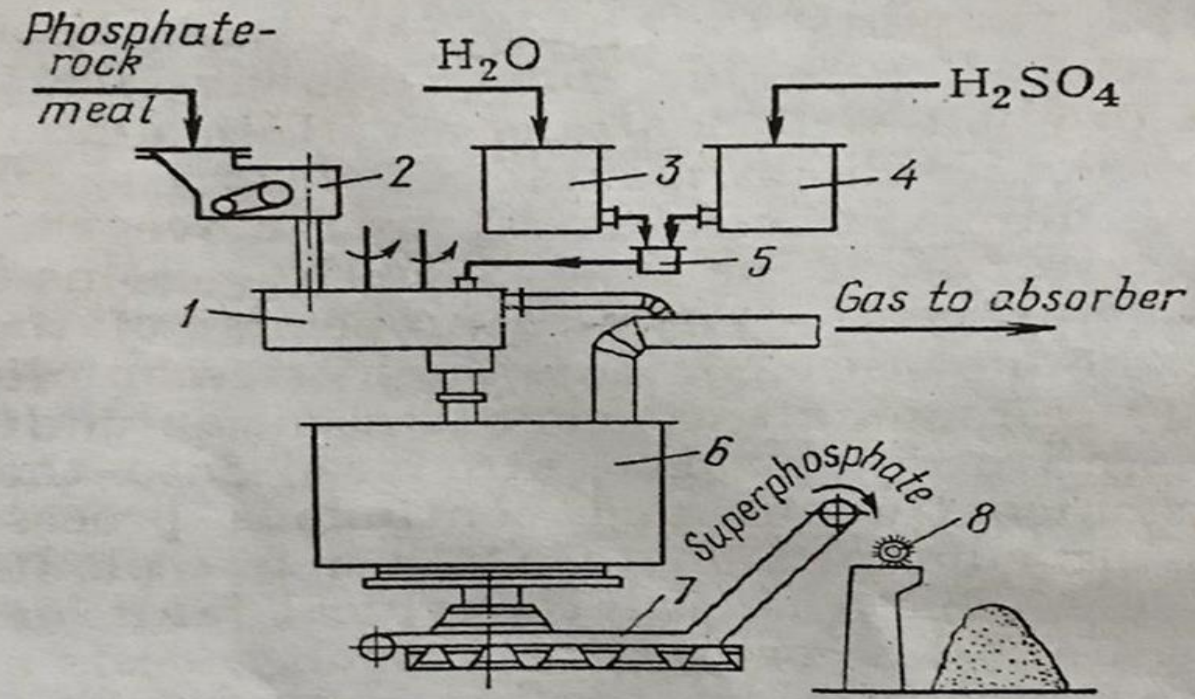


Fig. 30. Flow diagram of the continuous superphosphate-manufacturing process:
1—mixer; *2*—phosphate weigh-feeder; *3*, *4*—head tanks for sulphuric acid and water; *5*—acid measuring device; *6*—superphosphate den; *7*—superphosphate conveyer; *8*—superphosphate scatterer at the storage site

Ground apatite concentrate (or phosphate powder) by a system of belt- and screw conveyors and elevators is transported from the storage site to automatic weigh- feeder, which feeds it to a continuous-action mixer. The sulphuric acid (75%, tower H2S4) is continuously diluted with water in a batch feeder-mixer to a 68% H2So4concentration, measured by a concentration meter. and is then fed to the mixer where the phosphate raw material and the sulphuric acid are agitated mechanically. The pulp formed is transformed from the mixer to the continuous-action reaction den, where formation of the super- phosphate (setting and hardening of the pulp in the first stage of ageing of the superphosphate) takes place.

The superphosphato powder from the den is transferred for ageing by a conveyer belt located below the den to the superphosphate storage site, where it is uniformly distributed by a scattering device. To accelerate ageing the superphosphate is agitated during storage by means of a grab- bucket crane. Superphosphate is granulated in revolving drum granulators to improve its physical properties. In the granulator the powder-form superphosphate is wetted with water fed into the drum through nozzles, and rolled into granules of different size which are then dried, separated into size fractions and weighed into paper bags. During decomposition of the phosphates with sulphuric acid in the den, hydrogen fluoride evolved reacts with the silica contained in the phosphates and forms gaseous silicontetraluoride, SiF_4 .

And hydrosilicofluoric acid, H_2SiF_6. The fluorous gases, containing H,SiF, vapours, are withdrawn through an opening in the den roof and a ventilation pipe to 'an absorption unit and are utilized for making sodium fluo-silicate. The principal piece of apparatus in the manufacture of superphosphate is the superphosphate den. The mixer from which the pulp is fed to it is located directly on the den top. Mixers of a screw-conveyer type or of a chamber type with mechanical agitator are employed to provide continuous feed of the mix to the superphosphate den. Depending on the size of the chamber, one or two agitators are used.

Continuous –action superphosphate den

The most common type of continuous-action superphosphate dens is a cylindrical revolving chamber like in figure.

Fig. 31. Continuous-action superphosphate den:
1—rotating shell; 2—cutter; 3—partition; 4—stationary discharge pipe

-It is a vertical, reinforced-concrete cylinder, covered with sheet metal and with an inner lining of acid resistant diabase blocks.

-The cylinder together with reinforced-concrete bottom revolves slowly on roller supports about a stationary, hollow cast iron tube, which passes up through a seal in the den bottom and serves for removing the superphosphate from the den.

-The cutter located in the discharge zone near the partition rotates in the direction opposite to that of the den motion.

-The den makes one complete revolution in 1.5 to 2.5 hours

-During that period the superphosphate slurry solidifies and ageing begins

-Superphosphate is shaved off the solid block by the cutter blades and the shavings fall through the hollow central tube onto a transferring the superphosphate to the storehouse conveyer belt for

-The production capacity of a den 7.1 m in diameter and 2.5m high amounts its operation intensity lies to 30-50 tons of superphosphate per hour and between 550-650 kg per cu m

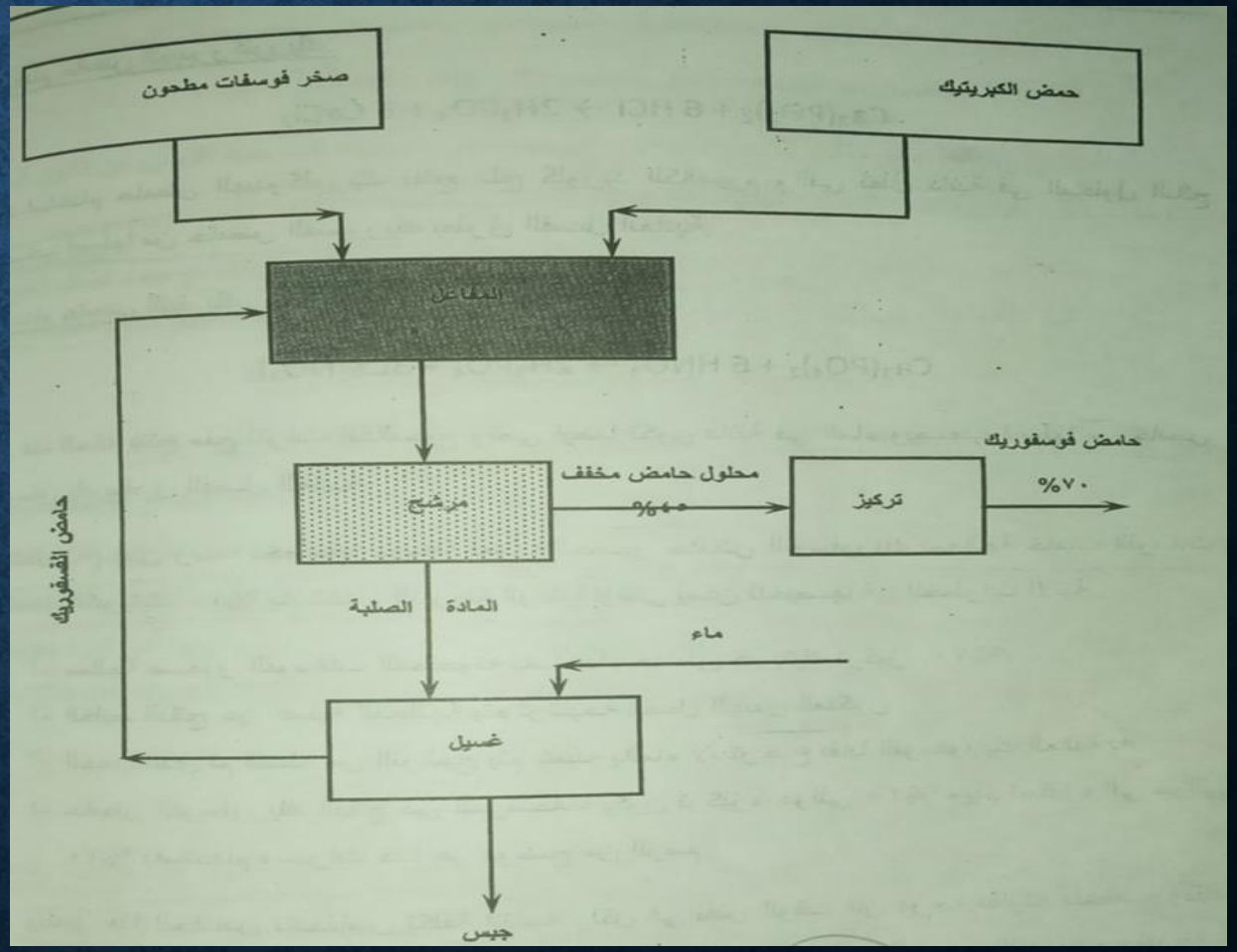
-A negative feature of simple superphosphate is its comparatively low content of the nutrient –not over 20% P_2O_5 when made from apatite concentrates ,and 15% P_2O_5 when made from phosphate rock .

obtained by -More highly concentrated phosphatic fertilizers can be decomposing the phosphate ores with phosphoric acid

The manufacture of wet-process phosphorie acid and triple super- phosphate

Phosphoric acid is an intermediate product used in manufacturing triple superphosphate, mixed concentrated fertilizers and other plhosphatic compounds. Phosphoric acid is made both by electrothermal methods and by extraction processes,

The sulphuric-acid process is the one most commonly used for manufacturing technical grade**, wet-process** phosphoric acid. The method consists in traating naturally occurring crushed phosphates with an excess of sulphuric acid to produce phosphoric acid and solid phase phosphogy psum-calcium sulphate which contains a re- mainder of undecomposed phosphate.



$$ca_3(po_4)_2+3H_2so_4+6H_2o=2H_3po_4+3caso_4.2H_2o$$

Triple superphosphate

This is produced by an action of phosphoric acid on rock phosphate
The material is a much more concentrated fertilizer than superphosphate containing about 45-50 percent P2O5

Reaction

ca3(po4)2+4H3po4+3H2o=3caH4(po4)2.H2o

Material requirement
1 ton of Triple Superphosphate
0.45 tons Rock
0.62 phosphoric acid(56 % P2O5)


Thank you!