FERTILIZERS TECHNOLOGY

CHEM 0905554

Spring Semester 22/23

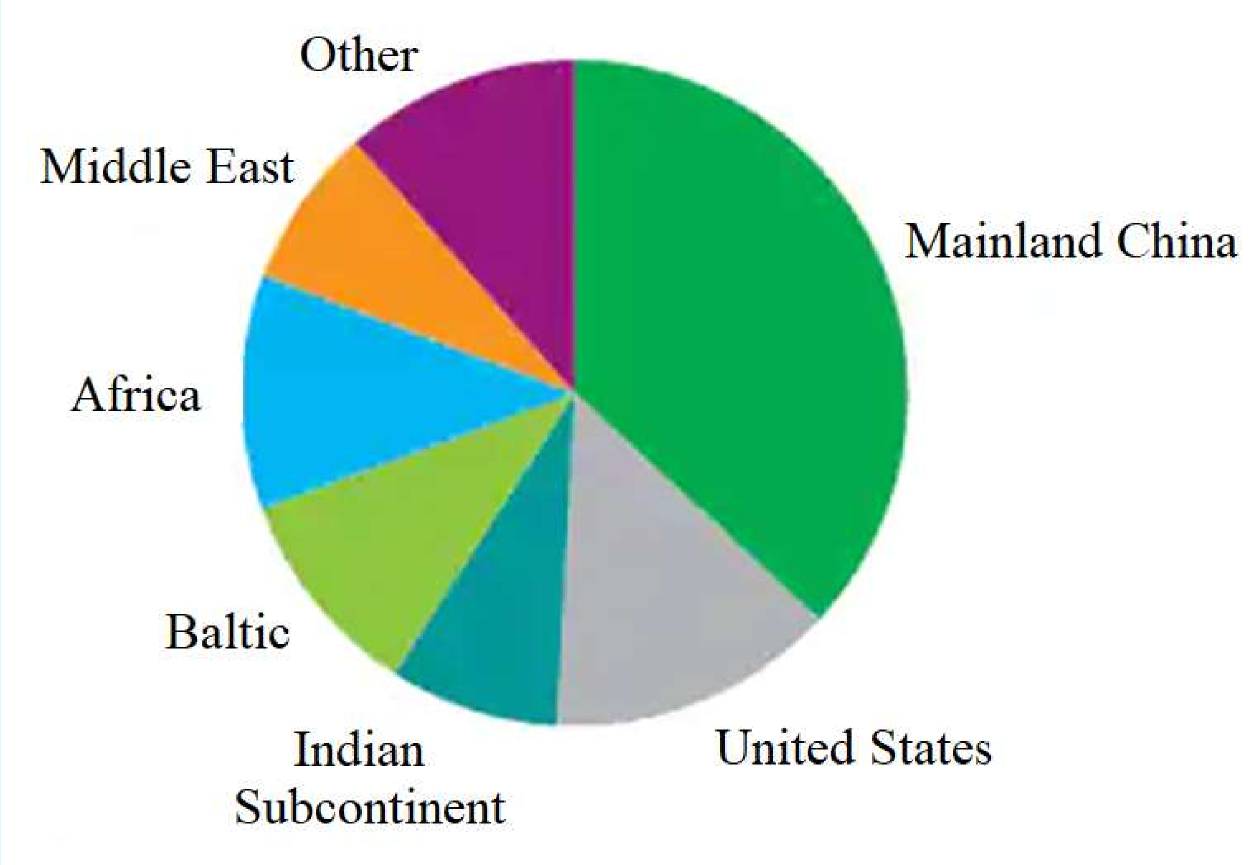
CHAPTER 6

PHOSPHORIC ACID PRODUCTION

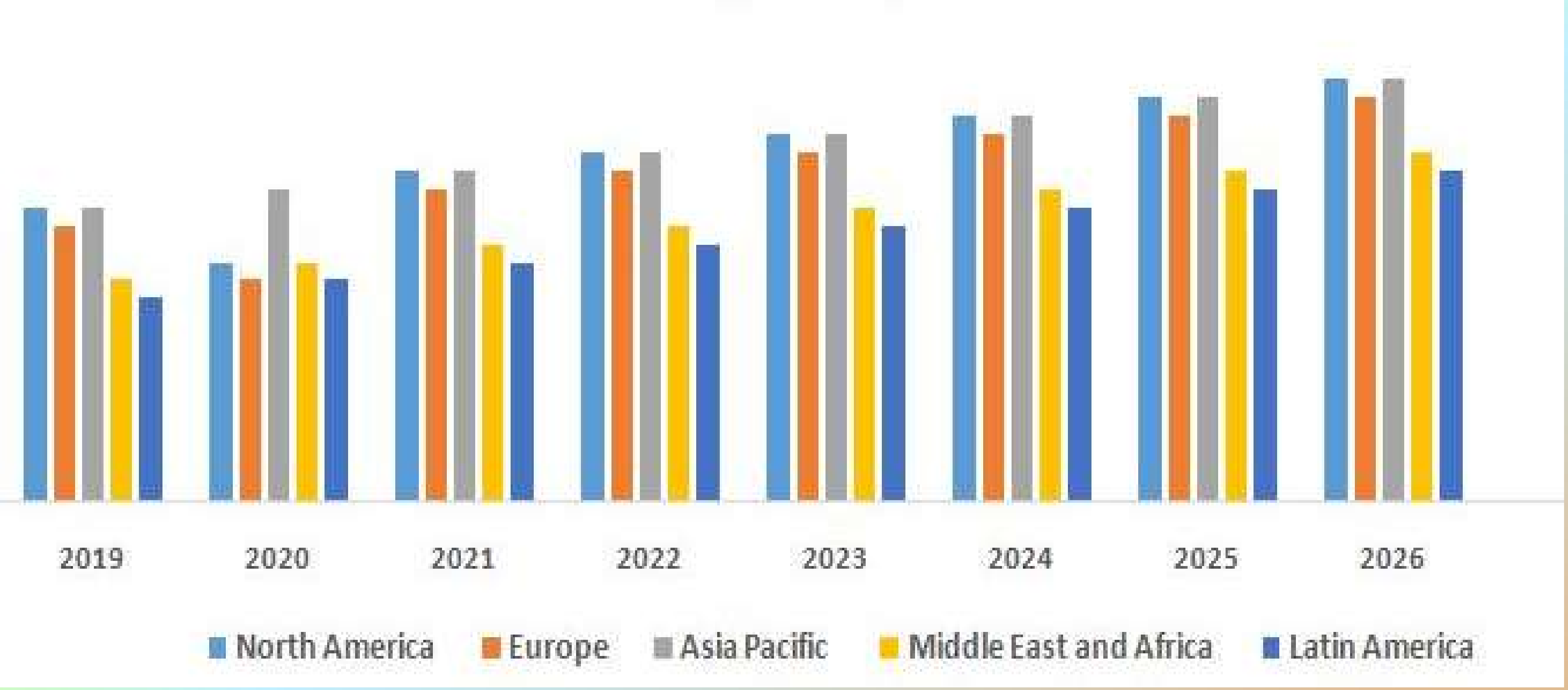

磷酸
Phosphoric Acid


CAUTION
KEEP OUT OF REACH OF CHILDREN
READ SAFETY DIRECTIONS BEFORE OPENING OR USING
Bosca Chemicals
And Cleaning Supplies
PHOSPHORIC
ACID
85%
CORROSIVE
BOSCATRADING.COM.A

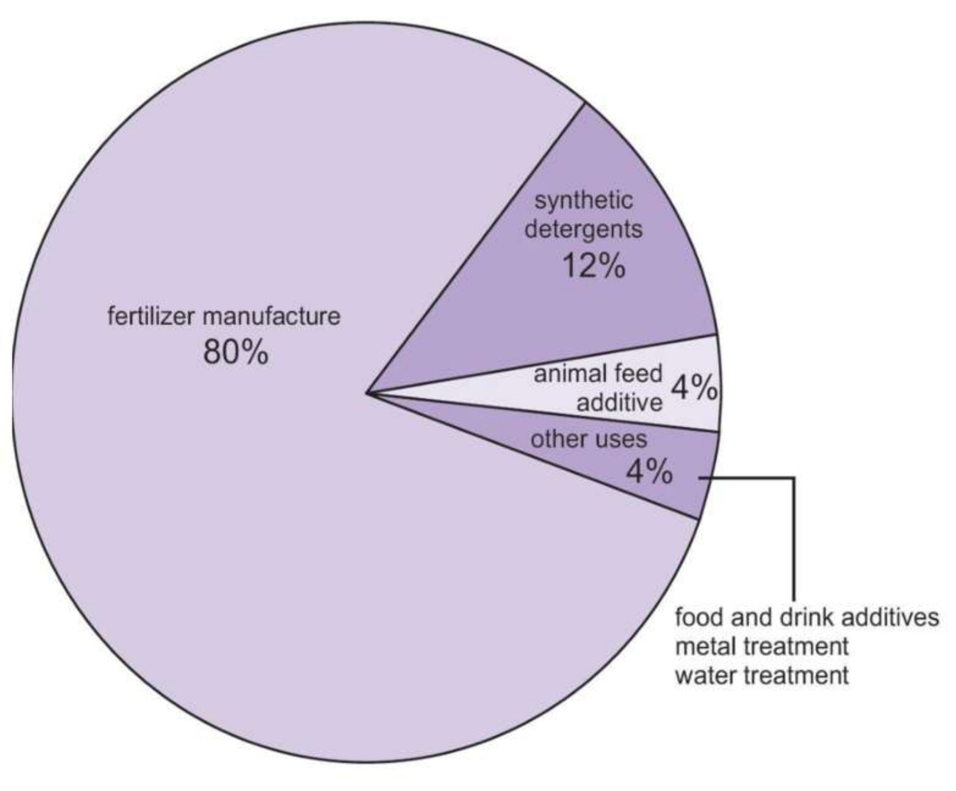
WORLD CONSUMPTION OF PHOSPHORIC ACID

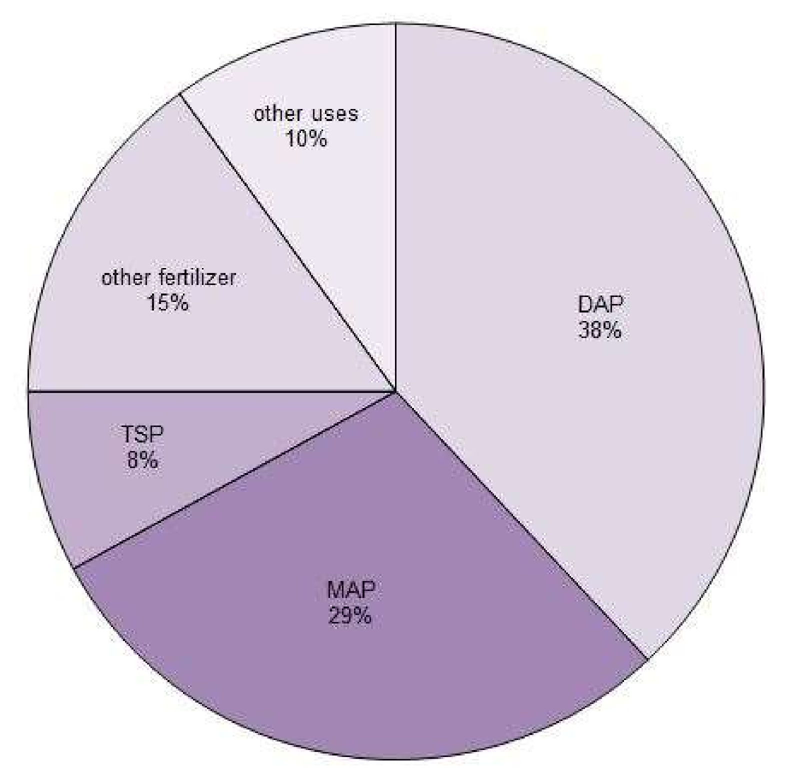


GLOBAL PHOSPHORIC ACID MARKET – BY REGION

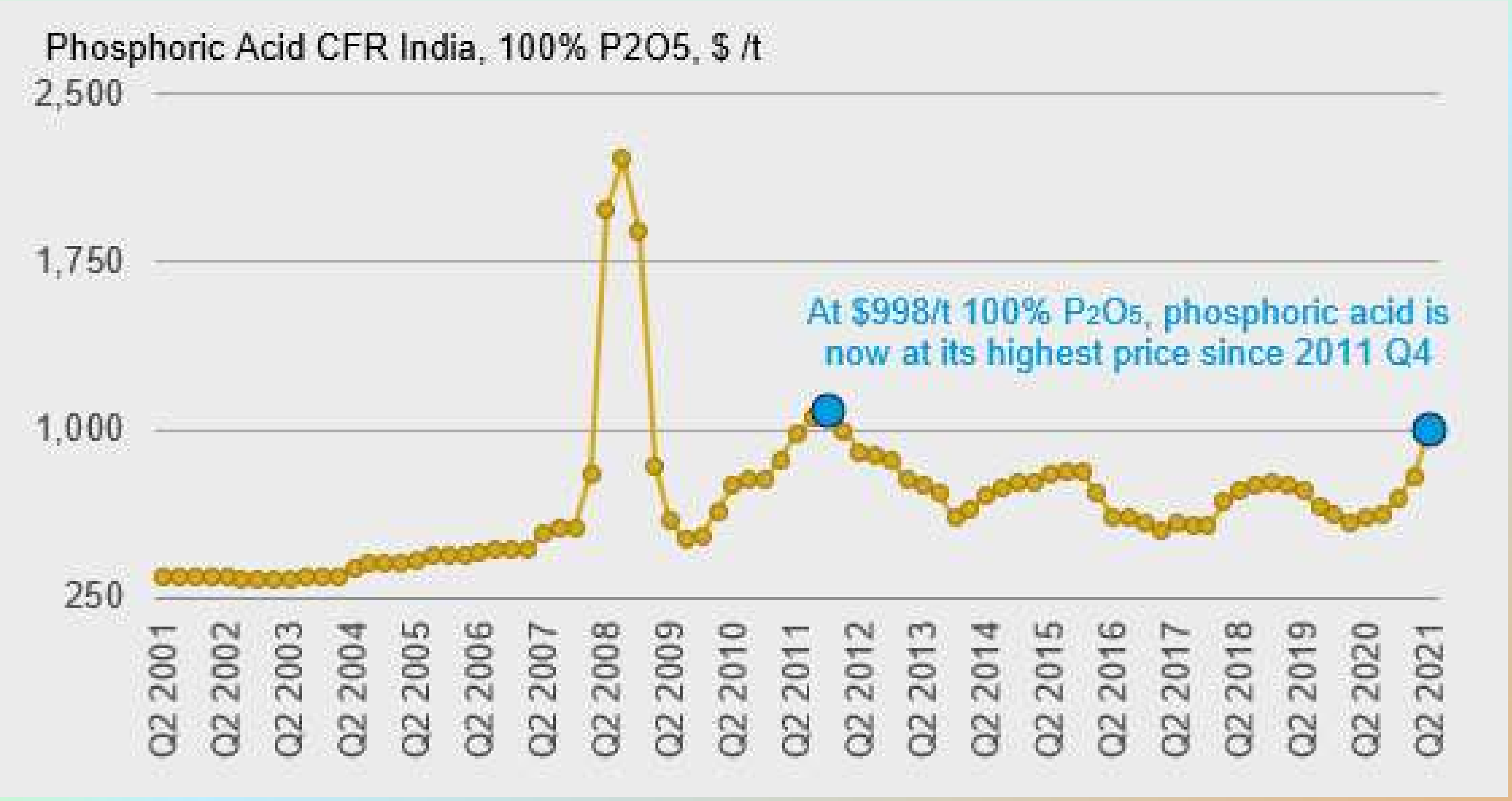


GLOBAL PHOSPHORIC ACID MARKET SHARE





PHOSPHORIC ACID PRICES



INTRODUCTION

- Processes with different raw materials are used in the manufacture of phosphoric acid.
- The process is known as "thermal" when the raw material is elemental phosphorus.
- This process has been abandoned because of the amount of energy which is needed.
- The processes that use phosphate minerals which are decomposed with an acid, are known as "wet processes" and they are the only economic alternative way to produce phosphoric acid.

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INTRODUCTION

- Three possible subgroups of wet processes depending on the acid that is used for the acidulation.
- This may be nitric, hydrochloric or sulfuric acid.
- The sulfuric acid route is the process normally used in the production of fertilizers.
- There are three types of sulfuric acid process, according to the condition of the calcium sulfate produced, since it can be obtained in the form of:

1. Anhydrite ($CaSO_4$)
2. Hemihydrate ($CaSO_4.0.5H_2O$)
3. Dihydrate ($CaSO_4.2H_2O$)

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- Bones used to be the principal natural source of phosphorus, but phosphoric acid today is produced from phosphatic ores mined in various parts of the world.
- Phosphate ores are of two major geological origins:

1. Igneous as found in South Africa, Brazil, etc.
2. Sedimentary as found in Morocco, Algeria, Jordan, U.S.A., etc.

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are:
  1. Fluorapatite $Ca_5(PO_4)_6F$
  2. Francolite $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$
- Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks.
- The most easily mined phosphate deposits are found in the great sedimentary basins.

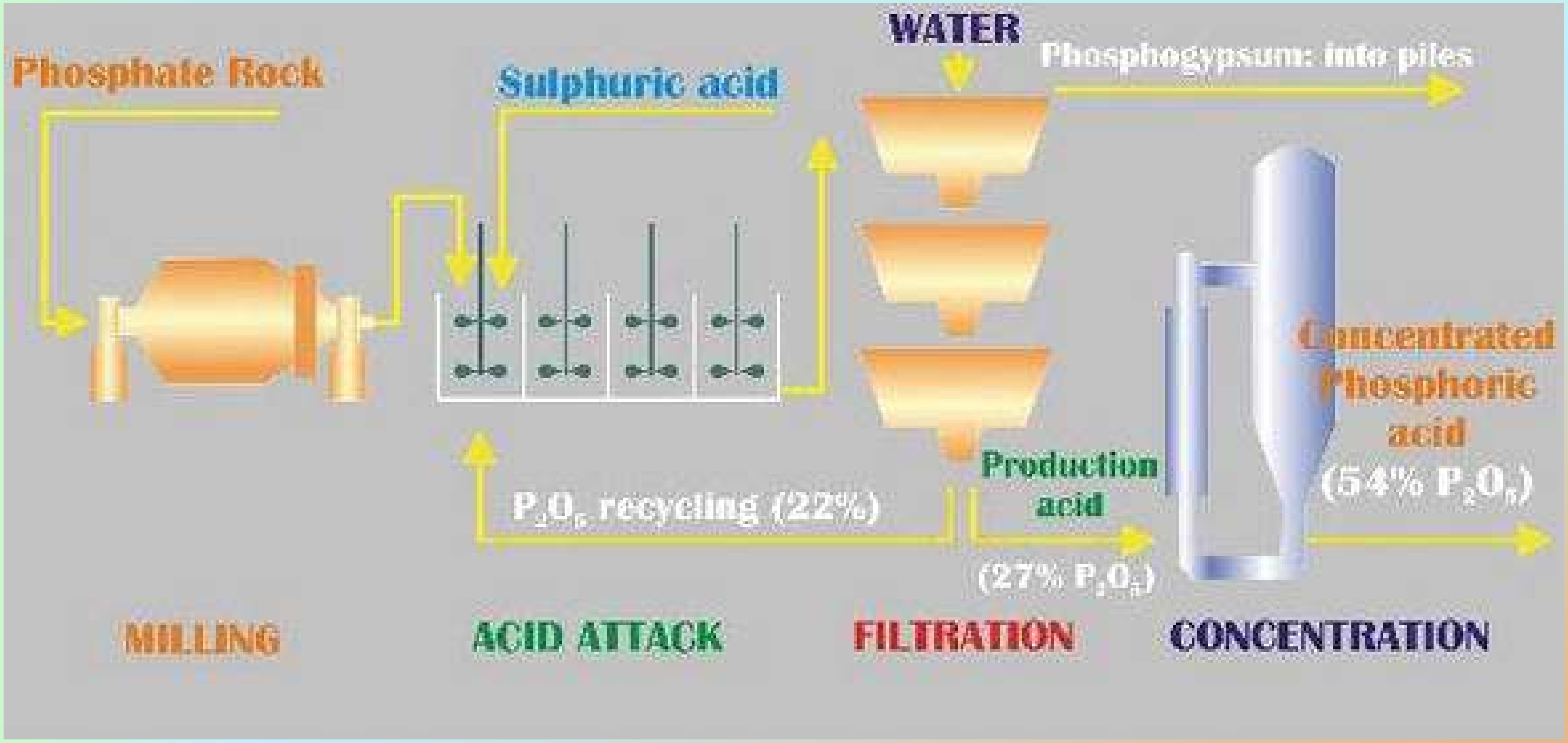
RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- These sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds.
- These phosphates are interposed with sedimentary strata of the waste materials interpenetrated by gangue minerals and thus sedimentary phosphate ores have differing compositions within the same source.
- Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market.

RAW MATERIALS FOR PHOSPHORIC ACID PRODUCTION

- Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities.
- This gives rise to further variations in the finished ore concentrate product.
- Phosphoric acid technology, having to rely on raw materials of great variety, has to readapt itself constantly.

PHOSPHORIC ACID PRODUCTION



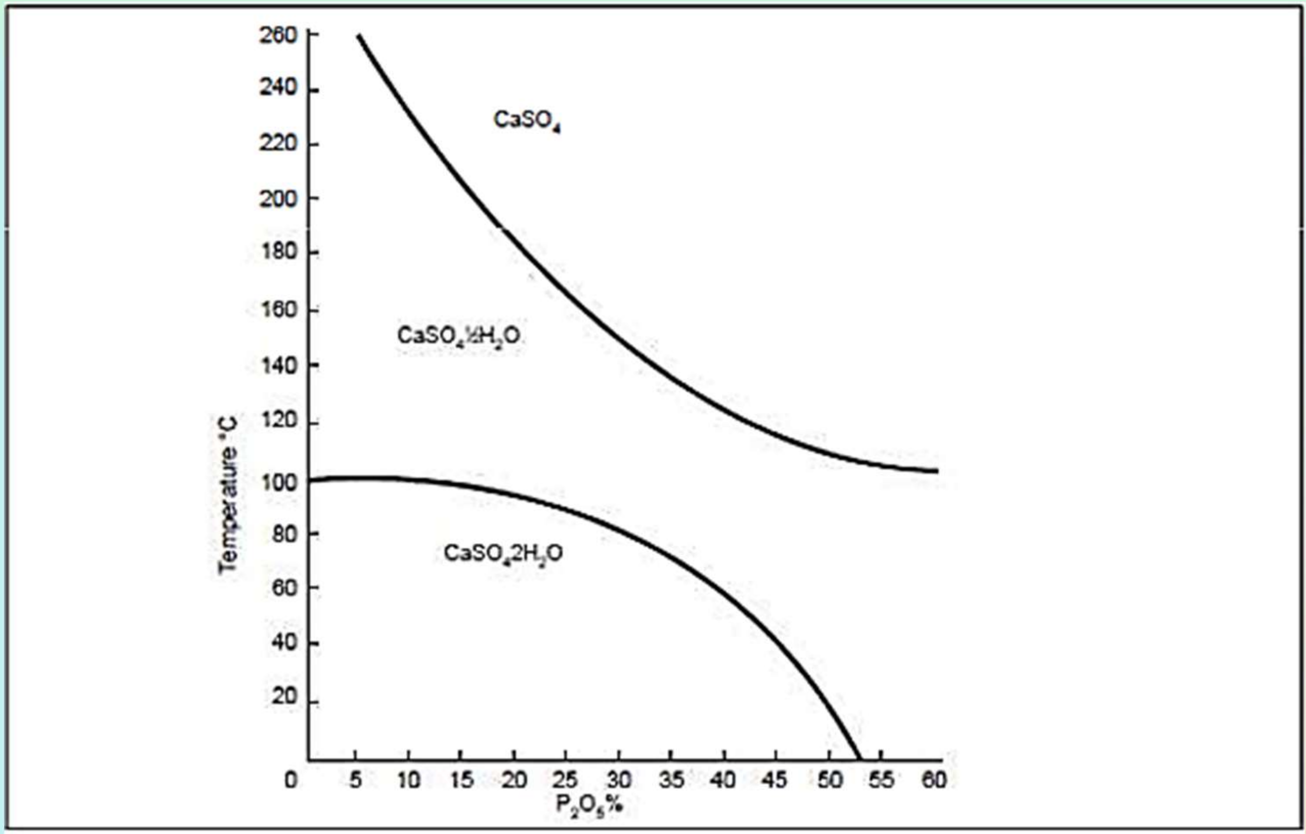
PRINCIPLES OF THE PROCESS

- The basic chemistry of the wet process is exceedingly simple.
- The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulfuric acid into phosphoric and the insoluble salt calcium sulfate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

- The insoluble calcium sulfate is then separated from the phosphoric acid, most usually by filtration.
- Calcium sulfate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulfate content.

PRINCIPLES OF THE PROCESS



Dependance of Calcium Sulphate Hydrate Crystallisation on Temperature and P_2O_5.

- The operating conditions are generally selected so that the calcium sulfate will be precipitated in:
  1. The dihydrate.
  2. Or the hemihydrate form.
- 26 - 32% P_2O_5 at 70 - 80 °C for dihydrate precipitation.
- 40 - 52% P_2O_5 at 90 - 110 °C for hemihydrate precipitation.

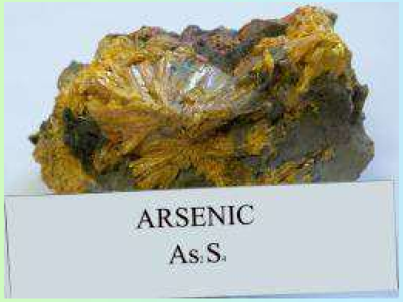


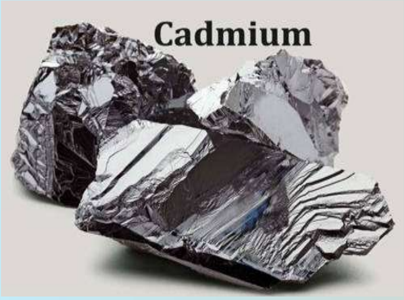
IMPURITIES

- There are many impurities in phosphate rock, the amounts and proportions of which are very variable.
- Fluorine is present in most phosphate rocks to the extent of 2 - 4% by weight.
- This element is liberated during acidulation, initially as hydrogen fluoride but in the presence of silica this readily reacts to form fluosilicic acid, H_2SiF_6.
- Other components such as magnesium and aluminum can also react with HF to form compounds ($MgSiF_6$ and H_3AlF_6).

IMPURITIES

- Emphasis must also be placed on another group of impurities such as arsenic, cadmium, copper, lead, nickel, zinc and mercury, which are present in most phosphate rocks, and which may pass into the acid during acidulation.
- Impurities such as iron, aluminum, sodium, potassium, chlorine, etc have some influence during the production of phosphoric acid and on the quality of the acid produced.





HEMI-HYDRATE WET PROCESS ACID PRODUCTION

- The Hemi-hydrate phosphoric acid production is the new invented technology at which it is being applied in many phosphoric acid production plants.
- In this process phosphoric acid can be produced directly with a concentration of 40 - 52% with consequent valuable saving in energy consumption and that is what make this process the leading process in wet phosphoric acid production

DI-HYDRATE WET PROCESS ACID PRODUCTION

- The Dihydrate processes for phosphoric acid production are still the most popular one until now.
- Many plants for phosphoric acid production nowadays still operate using this process due to its ease and simplicity, the major advantage of this process is its flexibility and reliability.
- It has high adaptability to phosphorus ore, and it accepts any kind of phosphorus ore.
- More moisture is allowed and permissible in the phosphate feed, and there is more acceptance to the use of weak sulfuric acid since the overall water balance in the dihydrate system is not so critical

DI-HYDRATE WET PROCESS ACID PRODUCTION

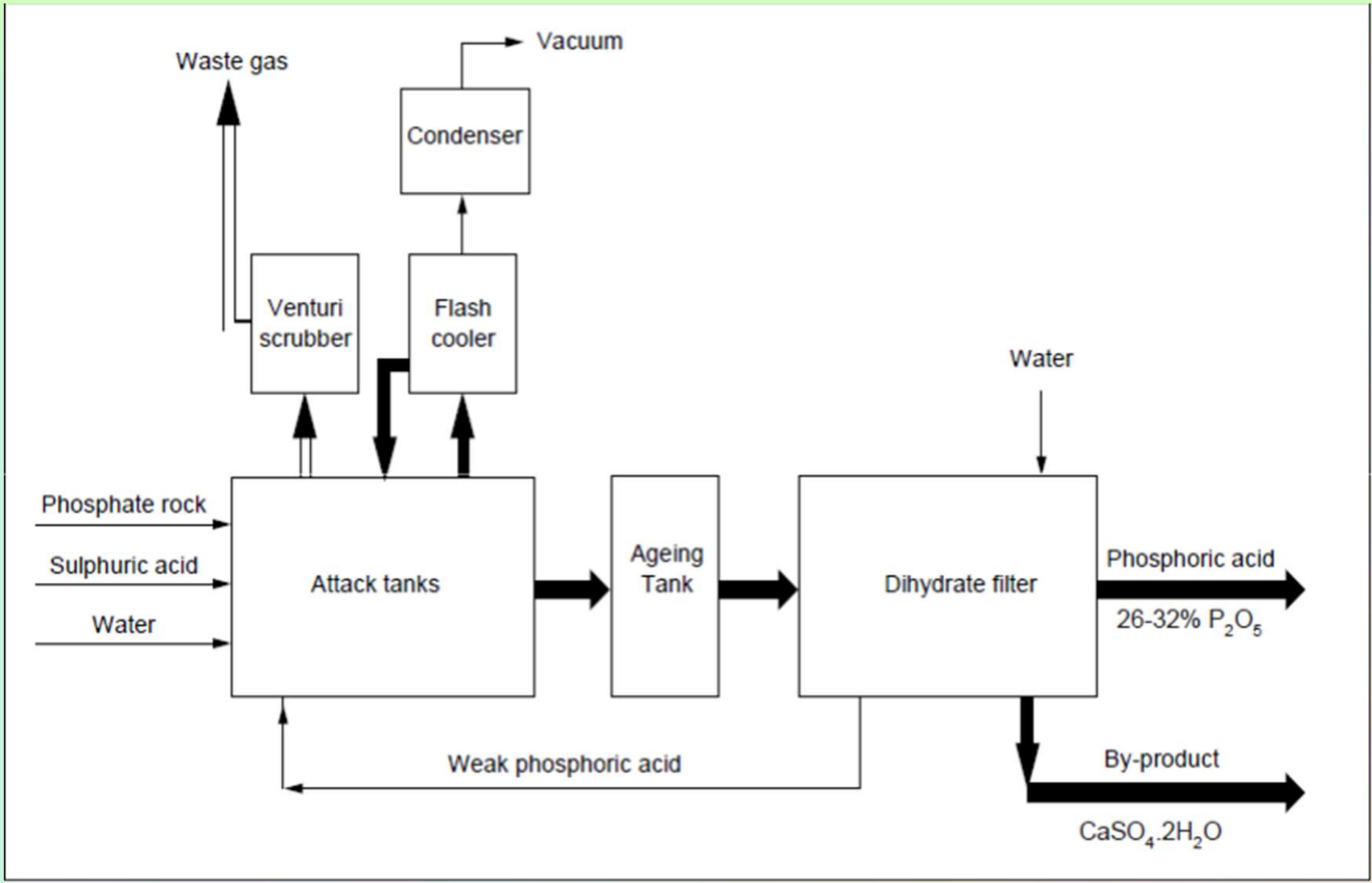
- Drawbacks of the di-hydrate process include:
  - ✓ Relatively low acid concentration produced which is about (28 – 30% P_2O_5) and
  - ✓ Higher energy consumption than other processes,
  - ✓ 4 - 6% P_2O_5 losses, most of them co-crystallized with the calcium sulfate
- Despite these drawbacks, the process is considered:
  - ✓ Simple startup and shutdown operation, and
  - ✓ Easy scalability

and these make the di-hydrate process the most widely used technique for phosphoric acid production

ADVANTAGES OF THE DIHYDRATE PROCESS

This is the most diffused process and the advantages of dihydrate systems are:

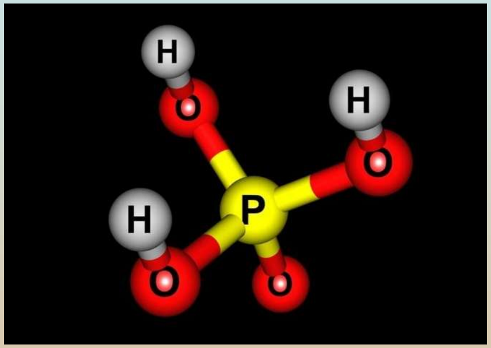
1. There is no phosphate rock quality limitation
2. Operating temperatures are low
3. Start-up and shut-down are easy
4. Wet rock can be used (saving drying costs)


Waste gas
Vacuum
Condenser
Venturi scrubber
Flash cooler
Water
Phosphate rock
Sulphuric acid
Water
Attack tanks
Ageing Tank
Dihydrate filter
Phosphoric acid
26-32% P_2O_5
Weak phosphoric acid
By-product
$CaSO_4.2H_2O$

PHOSPHORIC ACID PRODUCTION IN JORDAN

PHOSPHORIC ACID PRODUCTION IN JORDAN

- The Phosphoric Acid plant in the Industrial Complex (Aqaba) was designed to produce 1250 Ton/day of 54% P_2O_5 concentration.
- The main row materials for phosphoric acid plants are:

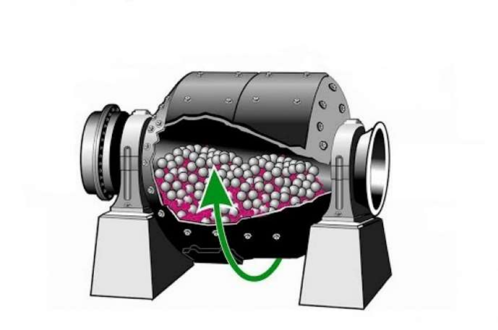


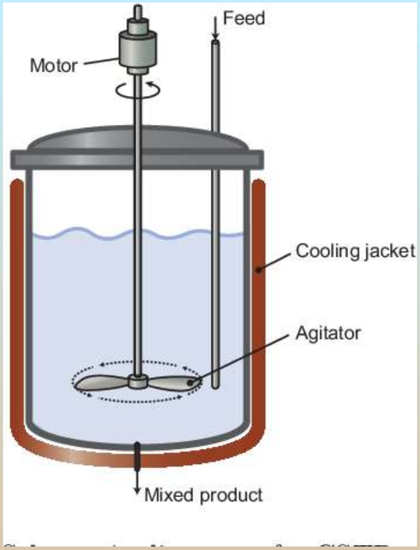
1. Phosphate rock.
2. Sulfuric acid of 98.5% by weight H_2SO_4.
3. Caustic soda 3% NaOH.
4. Pond and industrial water.
5. Steam used at the start up and used for warming up the process water.

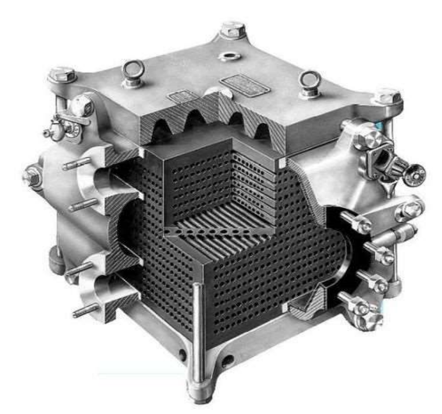
PHOSPHORIC ACID PRODUCTION IN JORDAN

The process of producing phosphoric acid consists of the following sections:

1. Grinding of the phosphate rock.
2. Attack and filtration.
3. Concentration.







GRINDING OF THE PHOSPHATE ROCK

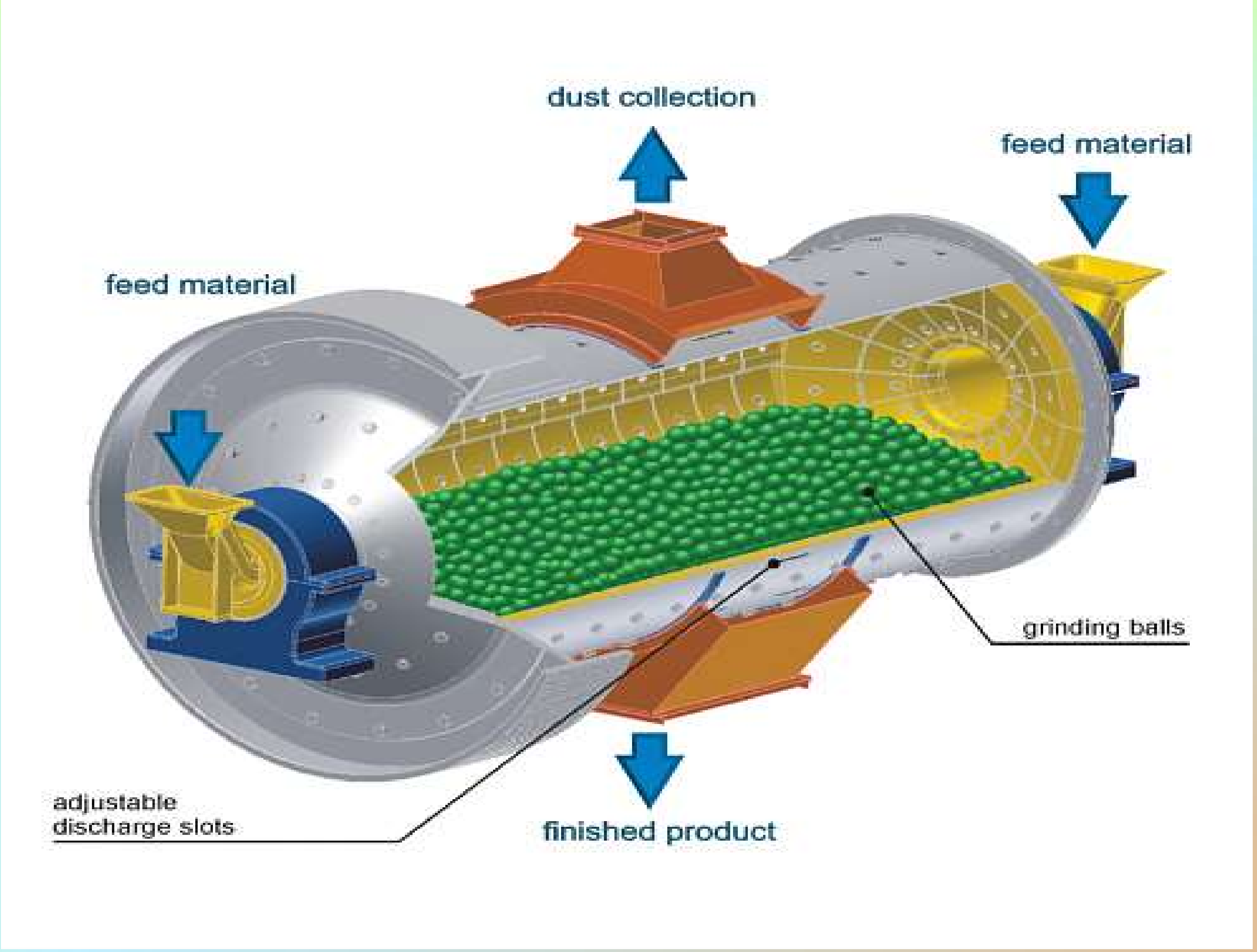
- The raw phosphate has the following analysis.

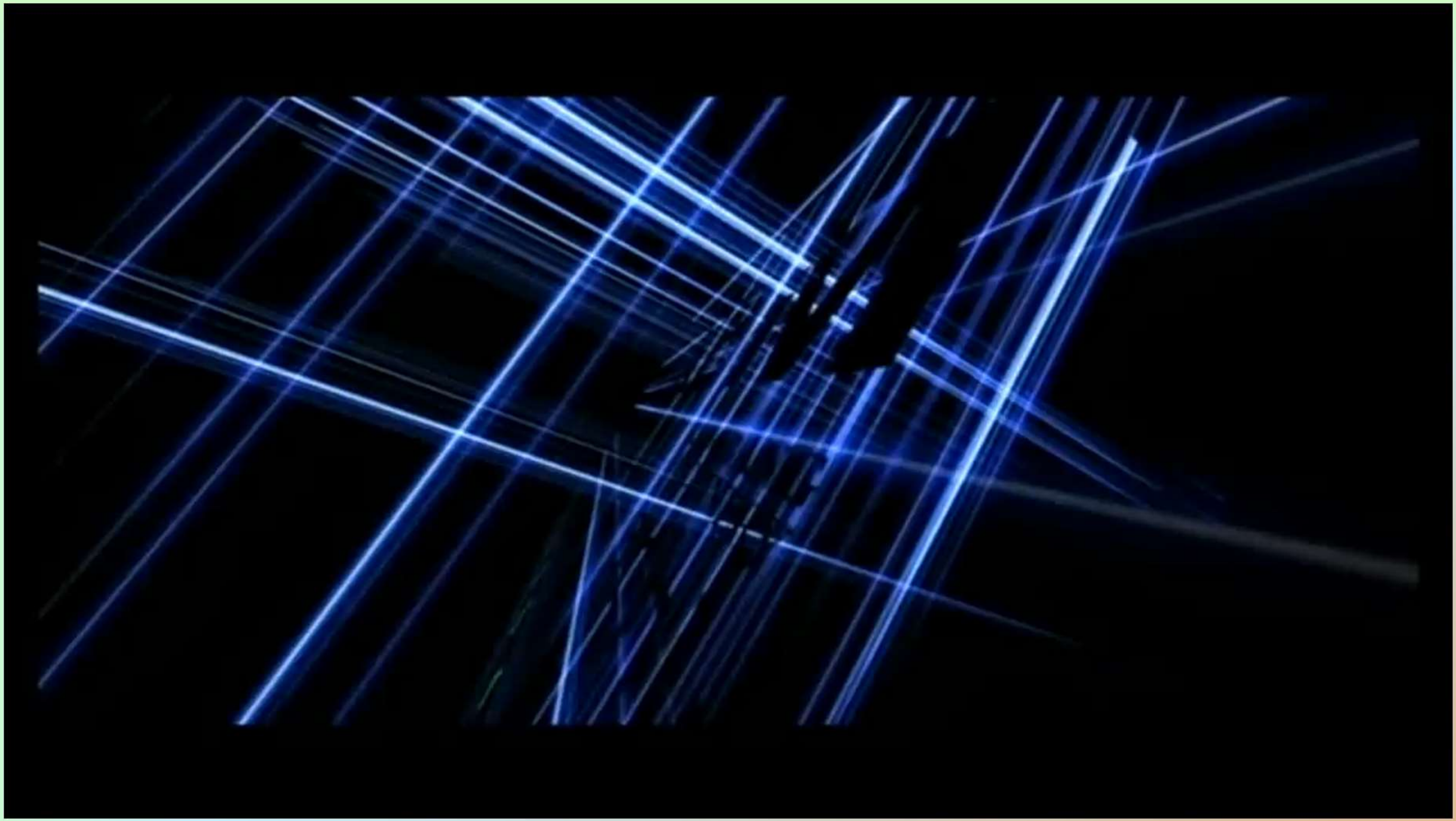
H_2O by weight	1.5 – 3 % max
Sizing	0 – 6 mm
Density	1.2 – 1.4 Ton/m^3
Temperature	Ambient

- In the H_3PO_4 plant the phosphate rock needs to be ground because the bigger the specific surface is the more product surface is submitted to acid attack and the best the plant efficiency will be.

GRINDING OF THE PHOSPHATE ROCK

- Phosphate rock is transported from storage area to the grinding system using a grinding mill with a capacity of 175 ton/h.
- Phosphate rock enter a hopper above the mill then to chain feeder.
- From the chain feeder the rock is poured into the feed duct from which it falls into the mill.
- The mill is a big cylindrical shell coated with steel sheets from the inner.
- Inside the mill there is 240 Ton of the balls have been placed.


dust collection
feed material
feed material
grinding balls
adjustable discharge slots
finished product



GRINDING OF THE PHOSPHATE ROCK

- Ground phosphate drops out of the mill by overflow while a screen keeps the balls inside the mill.
- At the mill outlet the product is taken away by an air flow which brings to the classifier in order to get fine particles.
- A classifier with wide diameter is used to decrease the speed of air which carry the coarser particles which will fall down to the classifier bottom and then to the mill to re-crush.
- In the classifier there is a turning plates equipped with blades; their adjustable rotation speed will create a centrifugal force that will throw the coarser particles against the walls.

GRINDING OF THE PHOSPHATE ROCK

- The higher the rotation speed of plates the smaller the particles to the cyclones and the fineness is increased and fineness increases by the increase of ball load and decrease of mill sweep.
- In order to collect the fine particles, the flow from the classifier is conveyed by the air flow to the cyclone where they deposit under centrifugal effects and fall into the silo.
- The air from cyclone still contain some dust and the phosphate particles contained in the air collected by the filter bags and the air leaves the filter clean from dust.
- To clean the bags a compressed air injects to the filter and the dust is then sent to the silo.

GRINDING OF THE PHOSPHATE ROCK

- If the phosphate contains a percent of moisture, we should use hot gases coming from furnace to make the phosphate dry and prevent clogging of the mill.
- The final grinded phosphate has the following analysis:

H_2O (by weight)	<= 1%
Finesses	98 % < 315 μm
Temperature	65/80 °C

GRINDING PARAMETERS

The grinding unit operation parameters are:

1. The phosphate rock flow controlled mainly by the feeder speed.
2. The product fineness controlled mainly by the classifier efficiency
3. The grinding efficiency controlled mainly by the grinding medium quantity.
4. The air process and flows in the circuit controlled by the various valves.

- The circuit pressure caused by fans in the system can be controlled with various valves and depend on classifier speed mill throughput.
- Fans used to produce a vacuum system in order to transfer the product from equipment to another because we handle with solid which is difficult to be pumped by pumps.

ATTACK AND FILTRATION

- The 30 % P_2O_5 acid unit includes two main parts:

1. An attack section contains agitated reactor and reactor cooling system, a gas scrubbing system with possibly a sulfuric acid dilution and cooling stage, grinded phosphate handling.
2. A filtration section including a pumping system, a vacuum unit and gypsum handling facilities.

- Phosphoric acid and gypsum are obtained as a result of the attack of a raw phosphate and H_2SO_4 as follows.

$$Ca_3(PO_4)_2+6H_2O+3H_2SO_4 \longrightarrow 3(CaSO_4.2H_2O) + 2H_3PO_4$$

- Five tones of gypsum are generated for every tone (P_2O_5) of product acid produced.

REACTION OPERATING PARAMETERS

The main operating parameters which must be kept constant are:

1. Concentration of strong acid.

The acid has to be concentrated with a good attack of the phosphate and good filtration; the chosen concentration may have a range of (27 - 30) % P_2O_5 .

2. Sulfuric acid content of slurry.

Below (20 g/l) filtration becomes bad and above (30 g/l) sulfuric acid consumption becomes undue.

REACTION OPERATING PARAMETERS

3. Solid content of slurry.

The best solid content is (30-40) % because increasing the solid ratio leads to:

- ✓ Slurry is more difficult to filtrate.
- ✓ Attack – ratio falls.
- ✓ Slurry is more difficult to pump.

4. Temperature of slurry.

The higher the temperature is more complete the attack and the better the filtration will be (75-90 ^{o}C).

REACTION OPERATING PARAMETERS

- The sulfuric acid must be diluted with industrial water before entering the reactor from 98.5% to 80%.
- Since the dilution process is exothermic then sulfuric acid cooled in a carbon block heat exchanger to 50 ^{o}C.
- Then sulfuric acid introduced to the reactor by surface agitator and phosphate introduced to the bottom of the reactor in order to give the reaction a good residence time to complete the reaction before the overflow sent to the filter.
- The time needed for this reaction is approximately 15 minutes.

REACTION OPERATING PARAMETERS

- Because the attack reaction of the phosphate by sulfuric acid is exothermic, the heat quantity is removed by forced circulation of air.
- This air carries off the emitted gases due to the reactions and mainly formed of water-steam, carbonic gas, and fluorine compounds.
- Fluorine polluting substance and removed from the gases by water absorption system and the overflow is collected to be used in filtration washing process, and a cleaned gases leave the column to the atmosphere.
- The absorption system consists of a primary washing tower using water for absorption and a secondary washing tower using water with caustic soda (NaOH).

REACTION OPERATING PARAMETERS

- The overflow slurry from the reactor is pumped to a vacuum filter cloth to separate the gypsum from the acid, the filter consists of six parts.
- The first part is fed continuously with the slurry and the liquid of the first part flow to the vacuum box and then to a separate tank and mixed with the medium acid return to the reactor.
- From the second part the acid (30% P_2O_5) is filtered and collected in the multi compartment separator, then pumped to the desaturation acid tank.

- In the fourth part a weak acid is filtered and collected in a multi-stage separator then pumped to the sixth section where after removing the gypsum by the screw a small thickness of the cake is washed counter-currently by high pressure water mixed with the weak acid from the fourth part and the filter from this stage is pumped to the fifth part where a very weak acid is filtered and pumped to the fourth section.
- The makeup of the water cycle comes from the overflow water of the absorption tower for gas washing because this water contains some acid.
- The vacuum in the filter is caused by a big fan.
- The acid coming from the attack-filtration section is warm and loaded with gypsum and fluosilicate.

REACTION OPERATING PARAMETERS

- These solids cause quick sealing of the concentration circuit especially the heat exchanger, to avoid this phenomenon the diluted acid from the attack and filtration section is kept in a stirred aging tank not more than (24 h).
- The acid thus desupersaturated is then decanted before being stored for use in the concentration section and the sludge formed in this tank is removed by a screw and pumped to the reactor.
- The 30% P_2O_5 slide from the decanted tank to the settled acid storage tank.
- All gases from the storage tank of 30% P_2O_5 are passes through a water absorption tower to remove these gases and the air leaves the tower cleaned.

CONCENTRATION UNITS

- P_2O_5 concentration section consist of three identical lines having similar operating conditions.
- Every line designed for the concentration of 450 Ton/day of P_2O_5 from 30% to 54% and the purpose of the concentration section is to evaporate the water in excess.
- In the concentration section in order to get the evaporation at lower boiling temperature the evaporation takes place under vacuum and the pressure is approximately (70mm Hg).
- At this pressure 54% P_2O_5 acid boils at about 80ºC and the heat load is obtained by low pressure steam 3.5 bar.

CONCENTRATION UNITS

- Saturation takes place in a carbon block heat exchanger in which the acid to be concentrated passes by means of forced circulation in order to prevent scaling and to increase the heat transfer, since water under 70 mm Hg boils at 42ºC then superheated steam and fluorine are observed in the gases let out form the evaporator and chlorine with some P_2O_5 carried off as fine droplets in the gaseous flow so it is necessary to forecast a demister.

CONCENTRATION UNITS

- In order to concentrate the phosphoric acid from 30% to 54%, a carbon block heat exchanger is used.
- To raise the temperature of the phosphoric acid from 80ºC to 88.5ºC to introduce it in a vacuum boiler evaporator with a temperature of 87ºC.
- So, 30% P_2O_5 acid with a temperature of 38-40ºC is mixed with the acid leaving the heat exchanger with 88.5ºC and the two streams gives a temperature of 87ºC which enters the vacuum evaporator.
- The heating medium in the carbon block heat exchanger is low pressure steam used counter currently with circulated phosphoric acid enters from the bottom and leaves from the top comes from the basket filter.

CONCENTRATION UNITS

- In the vacuum evaporator the other compounds such as $H_2O.H_2SiF_6$ and traces of H_3PO_4 leaves as gases and the 54% H_3PO_4 remains in the bottom of the boiler and the product is drain from the boiler at a height of 90 cm from the bottom of the boiler, at this stage the acid sent to the acid production pump to storage tanks.
- Below this height the flow is taken to the basket filter then to the circulation pump which send it to the carbon block heat exchanger.
- The droplets of the acid with steam of gases passes through the demister in order to remove the H_3PO_4 traces and drain to the acid production pump which pumped it to storage tanks as 54% H_3PO_4.

FLUORIDE

- During the reaction of phosphate ore and sulfuric acid, silicon tetrafluoride (SiF_4) and HF are formed as byproducts.
- These gases are usually scrubbed with water, forming fluorosilicic acid, H_2SiF_6 (FSA) as a waste stream.
- The process used is the absorption under vacuum of the fluorine by water addition.
- Gases flows to the demister to remove any traces of H_3PO_4, and the gases leaves the demister at 80^oC and enters a primary vacuum fluorine absorber using industrial circulating water as absorbent.
- Then gases leaves to the secondary fluorine absorber with temperature of 47^oC.

FLUORIDE

- After these two processes the water gases leaves with temperature of $43^{o}C$ from the secondary absorber and enters a vacuum condenser.
- The Flosilicic acid is produced from the primary absorber with 20% H_2SiF_6 and sent to storage tanks.
- These are the equations takes place in the vacuum absorber

$$4HF+SiO_2 \overset{\text{Heat}}{\rightleftharpoons} SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \rightleftharpoons H_2SiF_6$$

GYPSUM DISPOSAL

- Around 5 tones of gypsum are generated per tone of P_2O_5 produced as phosphoric acid.
- This represents a serious disposal problem.
- Two methods can be used to dispose of gypsum:
  1. Disposal to land
  2. Disposal into water
- By-product gypsum contains four types of impurity that are considered to be potentially harmful:
  1. Residual acidity (P_2O_5)

GYPSUM DISPOSAL

2. Fluorine compounds

These are only harmful if disposal is into fresh water because disposal into sea water results in the formation of insoluble calcium fluoride.

3. Undesirable trace elements

4. Radioactivity

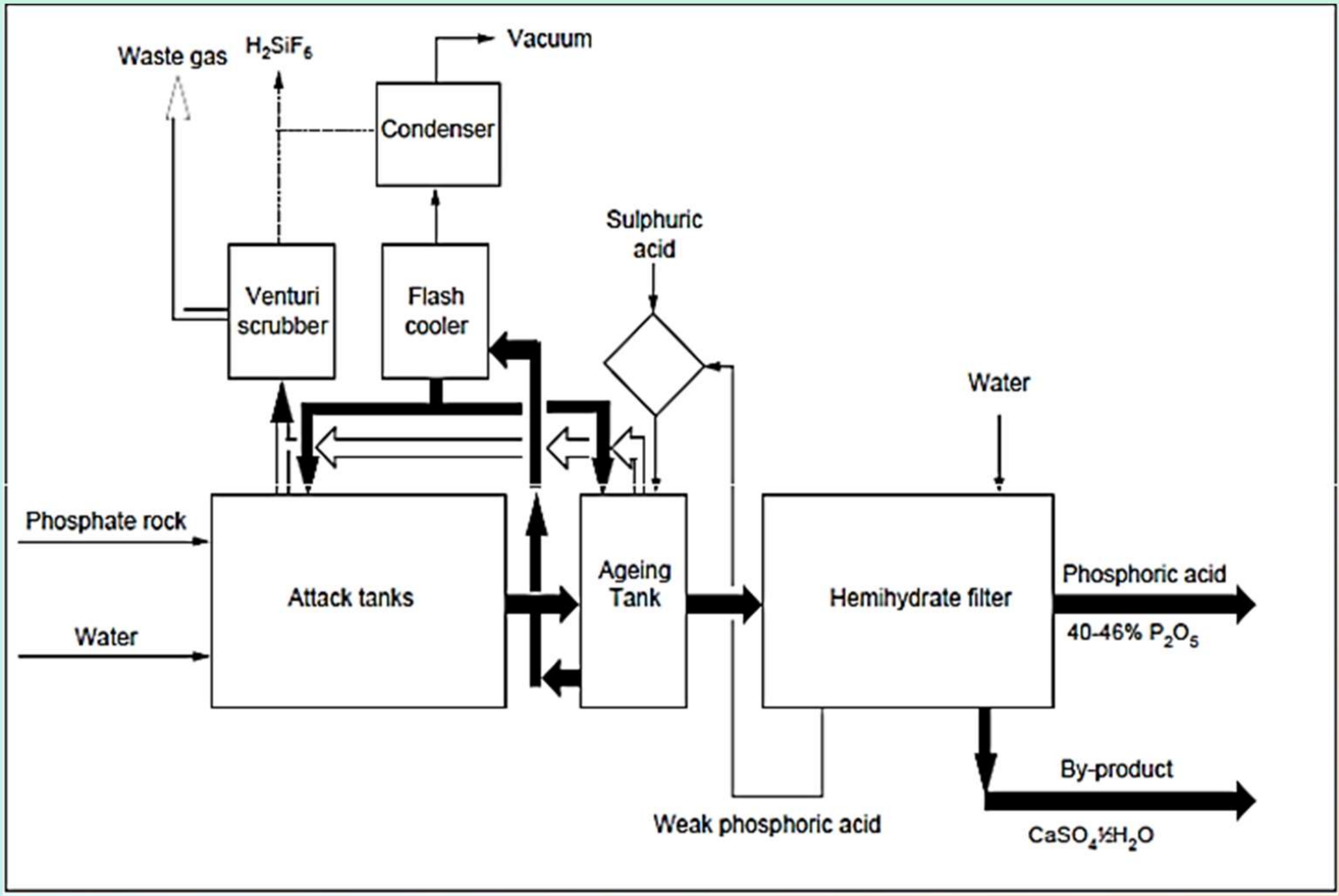
- Disposal on land, under proper conditions, is the best environmental option although it is not possible everywhere because it requires space and certain soil qualities where the gypsum stack is situated.

GYPSUM DISPOSAL

HEMIHYDRATE (HH) PROCESS

- Operating conditions are selected in this process so that the calcium sulfate is precipitated in the hemihydrate form.
- It is possible to produce 40-52% P_2O_5 acid directly, with consequent valuable savings in energy requirements.
- The figure shows a simplified flow diagram of a HH process.
- The stages are similar to those of the dihydrate process, but grinding may be unnecessary.

HEMIHYDRATE (HH) PROCESS



ADVANTAGES OF THE HH PROCESS

- The main advantages of this process, apart from the reduction or elimination of evaporation heat requirement, are:

1. Capital savings.
2. Purer acid: acid from the HH process tends to contain substantially less free sulfate and suspended solids and lower levels of aluminum and fluorine than evaporated dihydrate process acid of the same strength.
3. Lower rock grinding requirements: a satisfactory rate of reaction can be achieved from much coarser rock than in the dihydrate process, because of the more severe reaction conditions in the HH process.

DISADVANTAGES OF THE HH PROCESS

1. Lower Filtration rate.

   - Hemihydrate crystals tend to be small and less well formed than dihydrate crystals and thus, hemihydrate slurries tend to be more difficult to filter than dihydrate slurries unless
   - Crystal habit modifiers are used to suppress excessive nucleation.
   - With a good HH process however, there is no need to use crystal habit modifiers. There are examples of phosphate rocks that produce hemihydrate crystals achieving higher filtration rates than obtained with dihydrate crystals.

DISADVANTAGES OF THE HH PROCESS

2. Phosphate losses.

- Water balance considerations restrict the amount of wash water that can be used.
- At the same time, the amounts of both soluble and insoluble P_2O_5 remaining in the filter cake are greater because of the higher P_2O_5 concentration of the slurry being filtered.
- Nevertheless, the simplicity of the HH plant and the absence of silicofluoride scaling in the HH filter, may compensate for the higher insoluble P_2O_5 loss via HH cake.

DISADVANTAGES OF THE HH PROCESS

3. Scaling.

- Hemihydrate is not a stable form of calcium sulfate and there is a tendency for it to revert to gypsum even before the acid has been filtered off.
- The conditions are even more in favor of rehydration during washing.
- In a good HH plant there is no conversion in the reactor.
- A small quantity of anti-scale agent may be required in a single-stage HH plant filter to avoid scaling.

DISADVANTAGES OF THE HH PROCESS

4. Filter cake impurity.

- The cake is more acidic than gypsum filter cake because of the extra P_2O_5 losses and it also contains more fluorine and cadmium.

5. Corrosion.

- The demands on susceptible items of equipment, particularly agitators and slurry pumps, are increased because of the higher temperature (100°C) and acid concentration (40 - 50% P_2O_5) compared to a dihydrate plant.