Chemical Process Technology

PHOSPHORUS INDUSTRY

Fertilisers - Growth of the Nation

- It is indirectly linked to agro-business and food production.
- Also used in pesticides.
- N, P, K are the most common deficient elements in the soil.
- Fixed nitrogen from air is the major ingredient of fertilisers which make intensive food production possible.
- Main uses of nitrogen:

1. It is essential for the growth of plants at early stage to promote stems and leaves.
2. It increases protein content
3. It imparts green colour to the plants.

Main Functions of Phosphorus & Potash in Plant Growth

Posphorous

1. It stimulates early root formation
2. It stimulates rapid growth and hasten maturity
3. It accelerates the fruit formation at later stage or seeding.

Main uses of Potash:

1. It counteracts undesirable effect due to excessive supply of nitrogen.
2. It is required for the production of albuminoids.
3. It helps in the formation of carbohydrates
4. It helps to increase disease resistance.
5. It helps the development of fibrous material in plants.

Therefore, these three elements are supplied to plants in the form of chemicals as fertilisers.

PRODUCTS OF PHOSPHORUS INDUSTRY

The major source of phosphorus is from commercial deposits of phosphate rocks in the mineral form Fluorapatite [$Ca_{10}(PO_4)_6F_2$]

The products under the phosphorus industry are:

1. Phosphorus
2. Phosphoric acid
3. Ammonium phosphate
4. Calcium phosphate
5. Nitro phosphate
6. Sodium phosphate
7. Organic phosphate

Fertilizers

Phosphorus (P_4)

Types : Yellow phosphorus Red phosphorus Brown/black

Yellow phosphorus:	Red phosphorus
Mol.Wt- 123.9	123.9
MP- 44.1 °C	593°C
BP- 280°C	
Density:	More dense (polymeric material)
Solid- 1.82	2.36 gm/cc
Liquid-1.74 (45°C)	
Ignites spontaneously, stored under water	Formed by heating yellow- P
Disagreeable odour	Higher oxidation resistance and stability
Extremely toxic	

Uses of phosphorus :

Phosphorus is used to make H_3PO_4 acid, which is used to make phosphate fertilizers.

- An alloy of P called phosphor-bronze is made from P, Cu and Sn. This alloy has many applications as it is a stretchable metallic material.
- Red P is used to make match stick heads. The compound is a sulphide of red P.
- used to make smoke bombs used in wars.
- used in fireworks.
- Since it is poisonous, it is used for preparing chemicals with zinc phosphide that kill domestic pests like rats.
- It is also used in the manufacture of P- tetra chloride or P- penta chloride that are used as chlorinating agents in industries.

Method of production

Raw material :

Low grade crushed phosphate rock, coke as reductant, and sand as flux.

Chemical reactions:

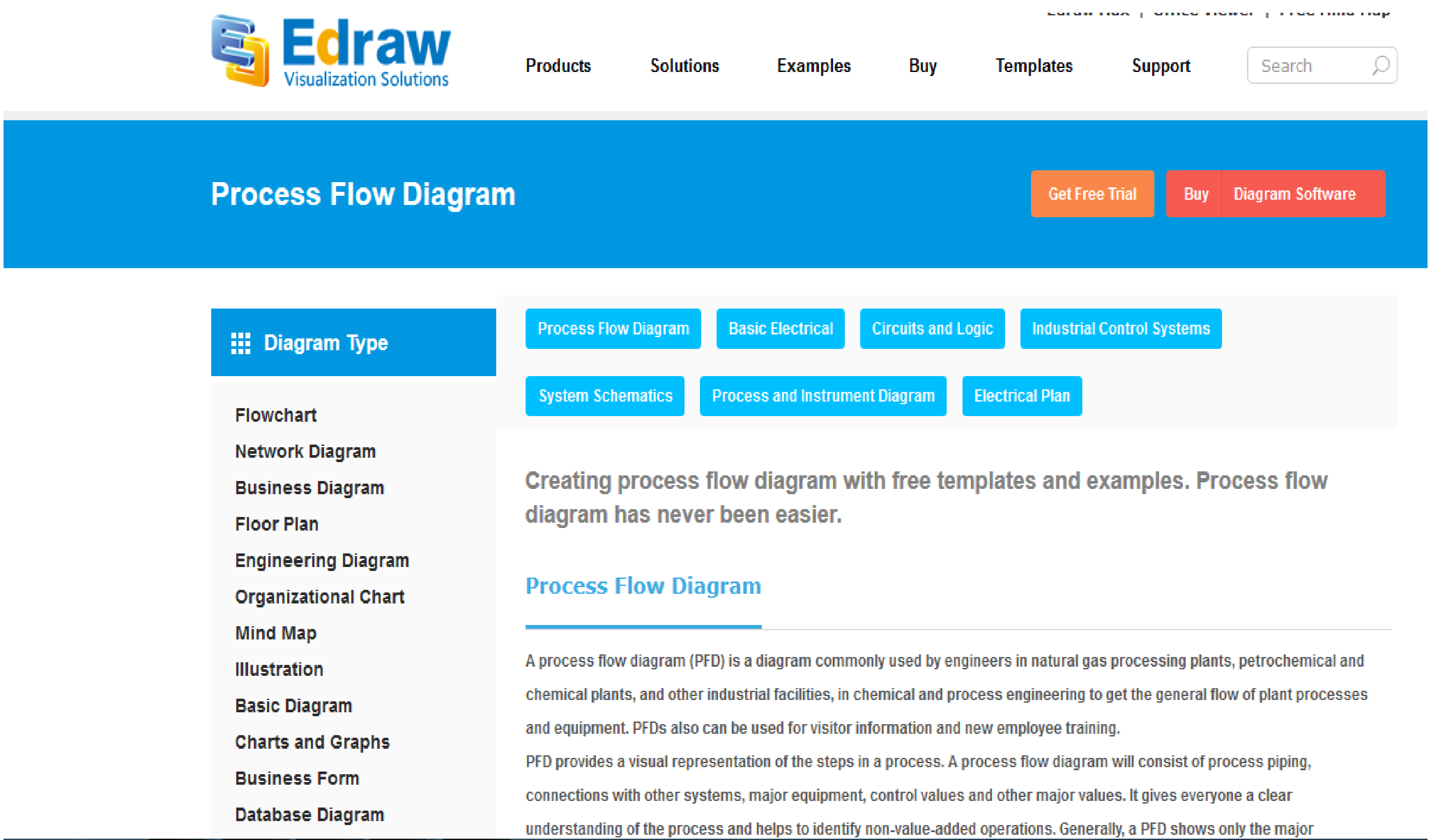
a) $2Ca_3(PO_4)_2 + 10C + 6SiO_2 \xrightarrow{1400\text{-}1450\ C} P_4 + 6CaSiO_3 + 10CO$

BPL(Bone phosphate of lime) — coke — flux — yellow Phosphorus (+ΔH = 680 kcal)

b) $P_4 \xrightarrow{250\text{-}450\ C} P_4$

yellow Phosphorus — Red Phosphorus

** Red phosphorous, which is used in the manufacture of safety matches, can be converted into white phosphorous by vaporization followed by condensation.



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Process Flow Diagram

A process flow diagram (PFD) is a diagram commonly used by engineers in natural gas processing plants, petrochemical and chemical plants, and other industrial facilities, in chemical and process engineering to get the general flow of plant processes and equipment. PFDs also can be used for visitor information and new employee training.

PFD provides a visual representation of the steps in a process. A process flow diagram will consist of process piping, connections with other systems, major equipment, control values and other major values. It gives everyone a clear understanding of the process and helps to identify non-value-added operations. Generally, a PFD shows only the major

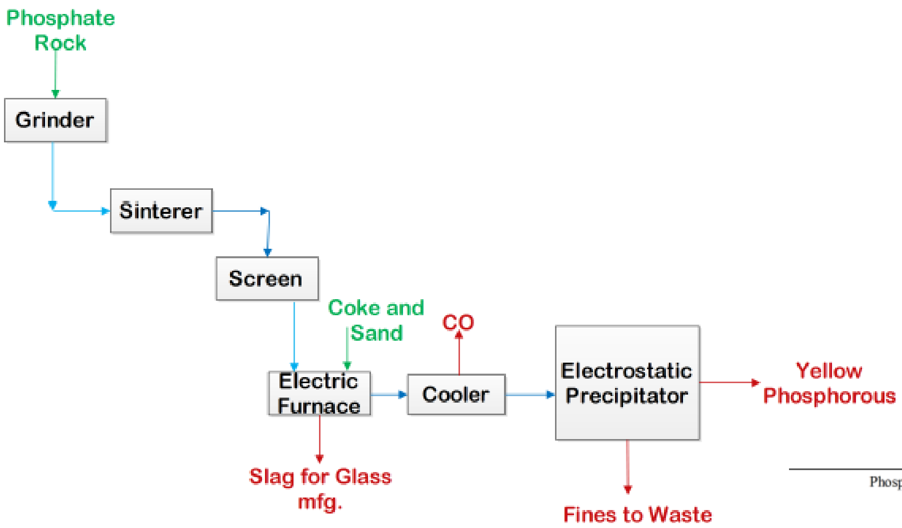
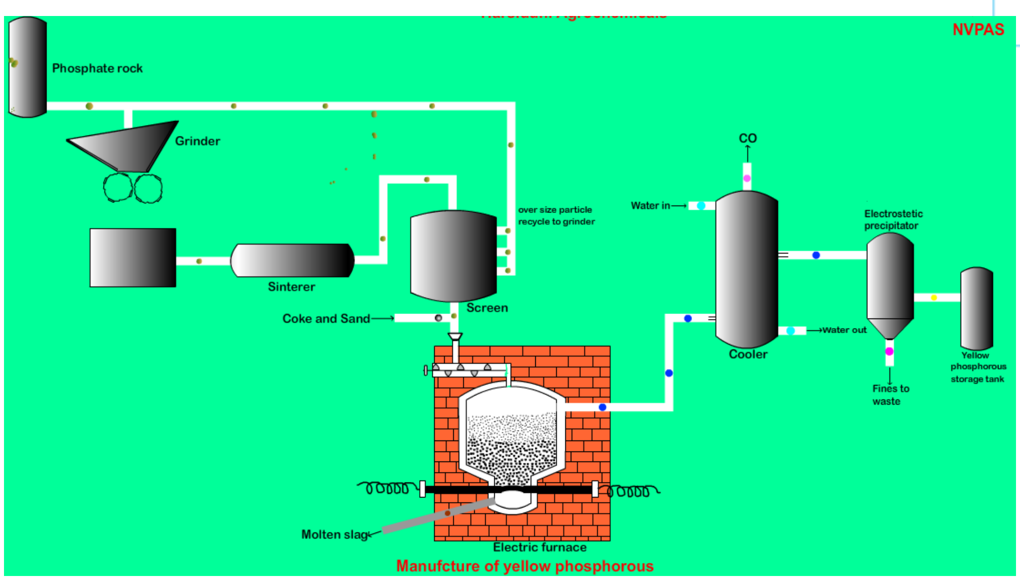


Figure: Manufacturing of Yellow Phosphorous



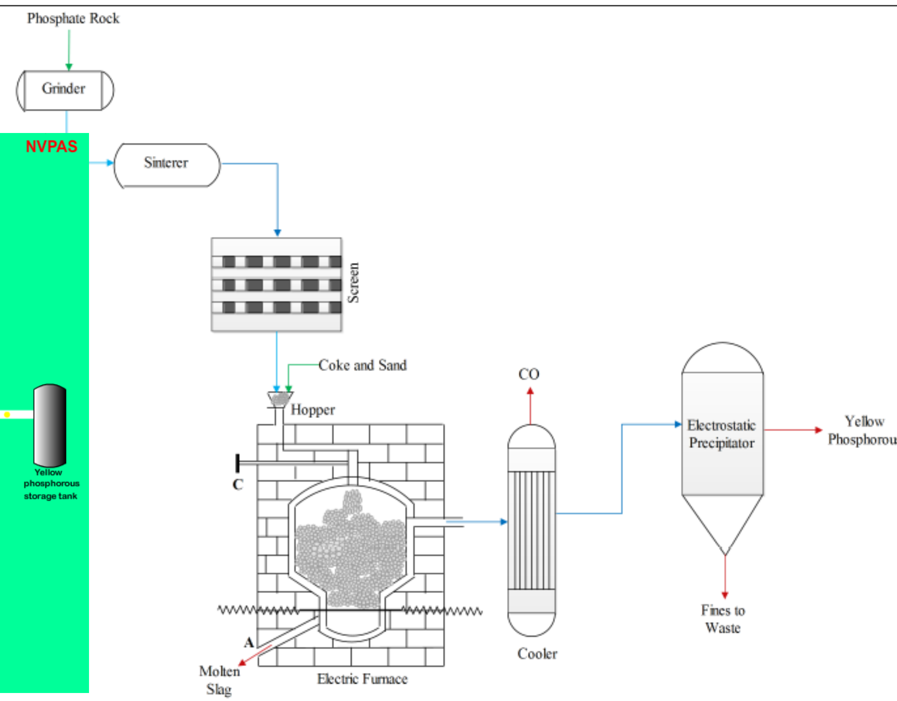
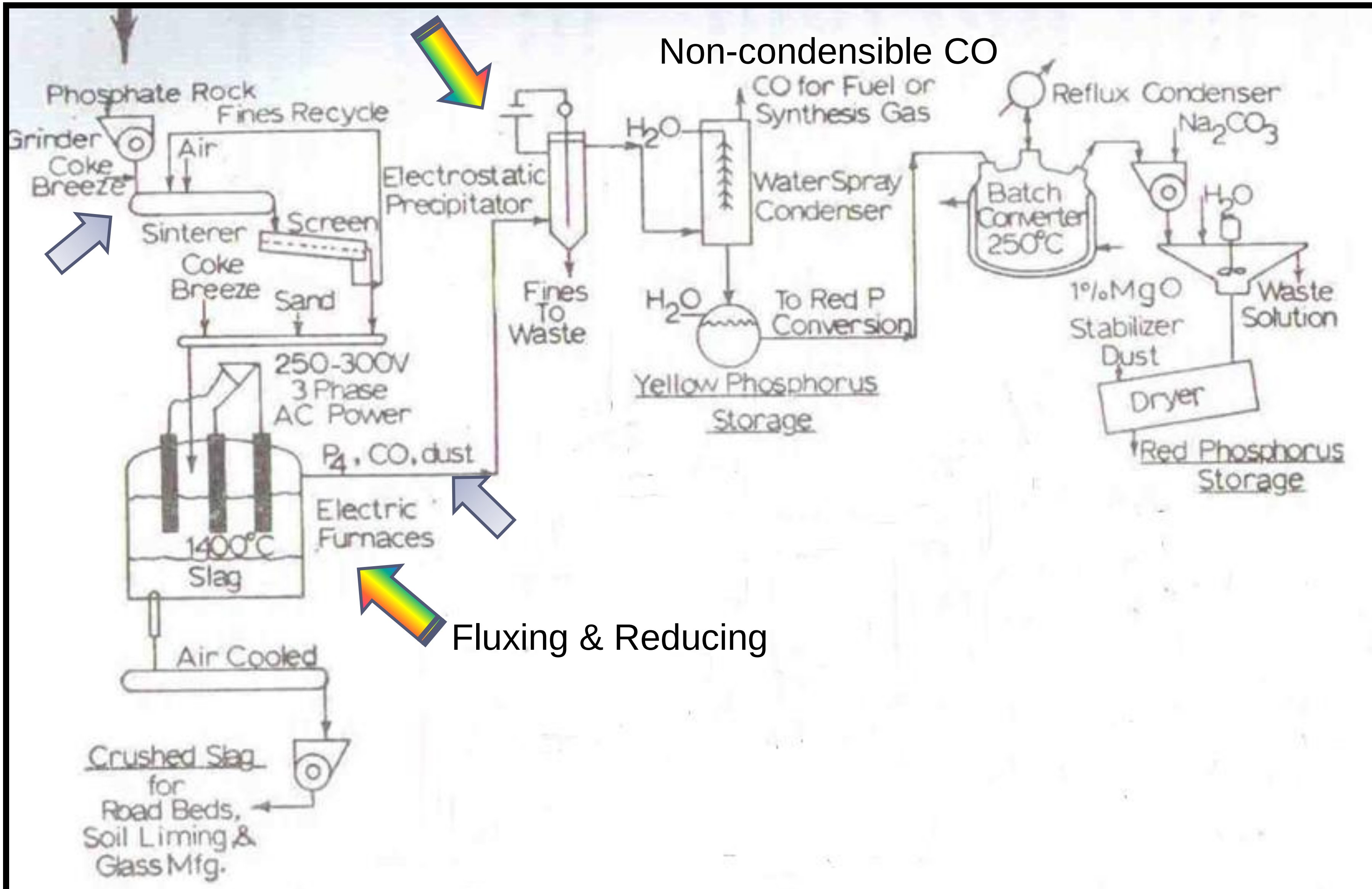


Figure: Manufacturing of Yellow Phosphorous

Flow diagram- Phosphorus



Process Description

- Phosphate grinding and sintering (at 1200-1250 ˚C)
  - BPL is sintered from sand particle size to marble size lumps
  - This step increases charge porosity to facilitate the release of P_4 & CO vapors and decreases entrained dust.
- Phosphate reduction in Electric furnace
  - Nodulized rock with silica, sand and coke is fed to phosphorus furnace (200-300V, AC-3 Phase) which heat the charge to 1400-1450 ˚ C (sufficient to fuse it and initiate the fluxing and reducing reaction, which leads the P_4 formation).
- Separation and Purification
  - CO and P_4 vapor mixture are fed to electrostatic precipitator (ESP) where entrained dust are removed when vapor are hot.
  - Next water spray condenser captures most of the liquid yellow phosphorous and separates it from non-condensible CO gas.

Phosphoric acid (H_3PO_4)

Properties-

Mol. Wt-98

MP- 42.4 ˚C

BP – Losses water of hydration at 213 ˚C

Density – 1.83 gm / cc at 20 ˚C

Completely miscible with water

Incompatibilities: Incompatible with powdered metals, strong bases, iron-containing compounds.

Method of production –

1 Wet process

a) Strong sulphuric acid leaching
b) HCl leaching

2. Electric furnace processes

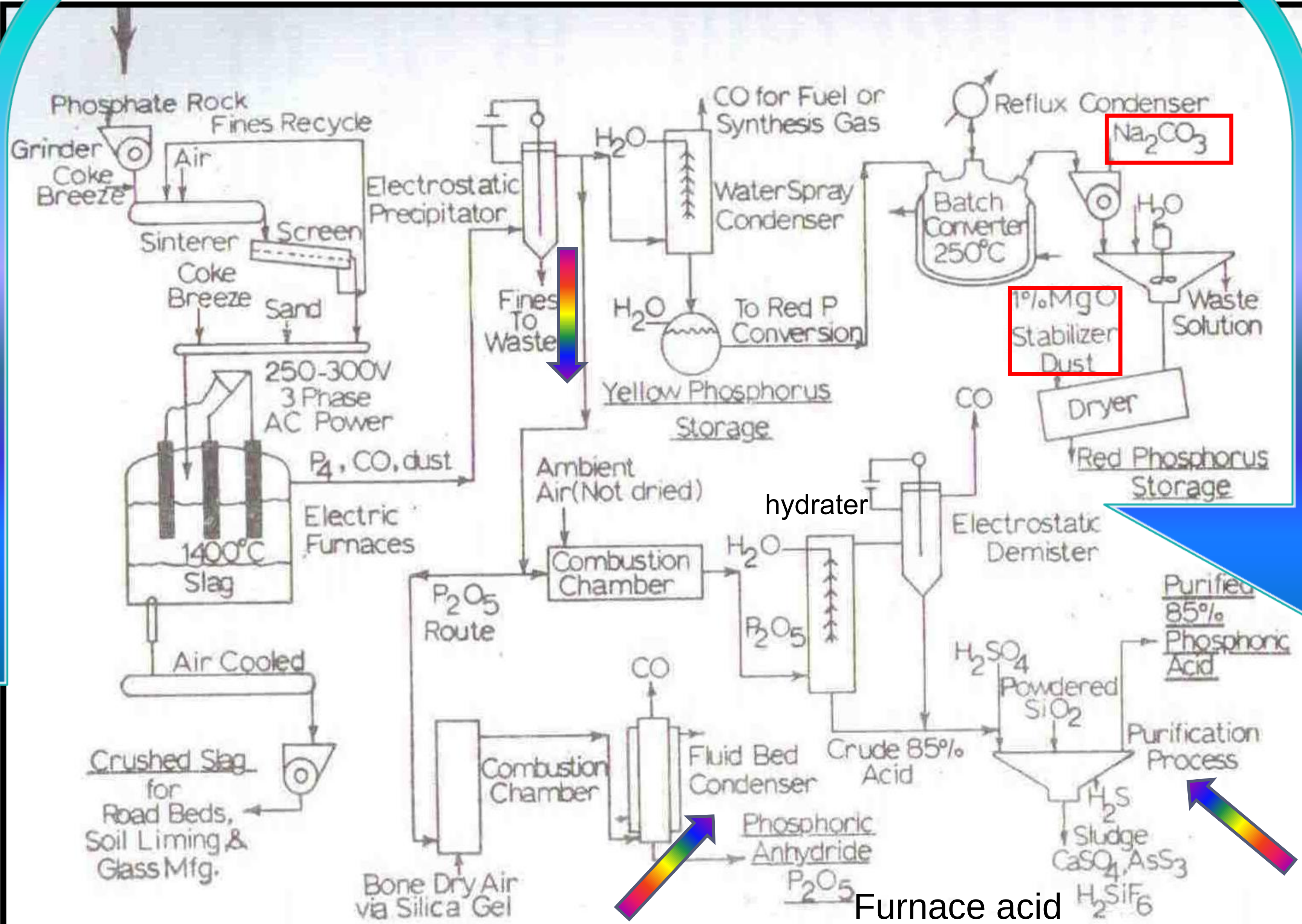
Phosphoric Acid Via Phosphorus Combustion

- One of the three routes for commercial production of phosphoric acid.
  - The 'dry process' also called 'combustion process'.
  - The other two processes operate by acidulation of phosphate rock with strong acids, and are referred as 'wet process'.

- Dry Process
  - It is obtained via combustion of yellow phosphorus in air followed by hydration of phosphorus pentaoxide product with water.

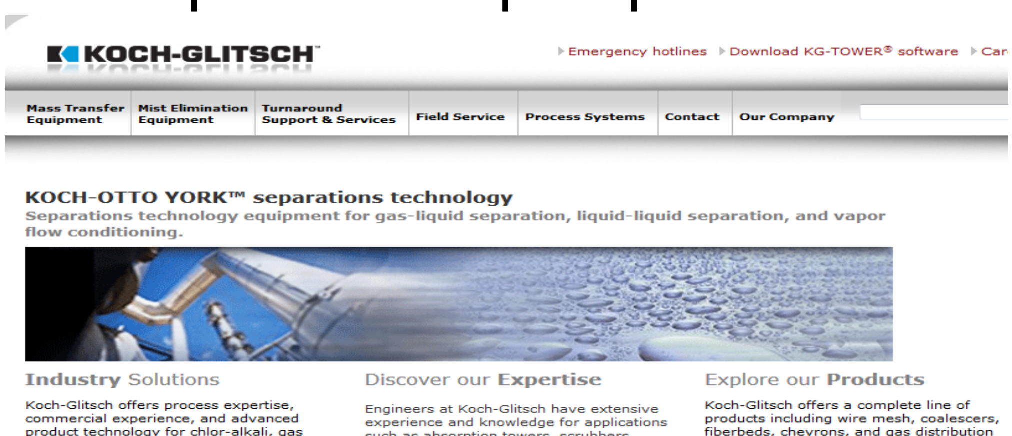
$$4P + 5\,O_2 \rightarrow P_4\,O_{10} \qquad (\Delta H = -720\text{ kcal})$$

$$P_4\,O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4 \qquad (\Delta H = -45\text{ kcal})$$


Phosphate Rock
Fines Recycle
Grinder
Air
Coke Breeze
Electrostatic Precipitator
Sinterer
Screen
Coke Breeze
Sand
250-300V 3 Phase AC Power
P_4, CO, dust
Electric Furnaces
1400°C
Slag
Air Cooled
Crushed Slag for Road Beds, Soil Liming & Glass Mfg.
Fines To Waste
H_2O
CO for Fuel or Synthesis Gas
Water Spray Condenser
H_2O
To Red P Conversion
Yellow Phosphorus Storage
Reflux Condenser
Na_2CO_3
Batch Converter 250°C
H_2O
1% MgO Stabilizer Dust
Waste Solution
Dryer
Red Phosphorus Storage
CO
Ambient Air (Not dried)
Combustion Chamber
P_2O_5 Route
hydrater
H_2O
P_2O_5
Electrostatic Demister
Purified 85% Phosphoric Acid
H_2SO_4
Powdered SiO_2
Purification Process
Crude 85% Acid
CO
Combustion Chamber
Fluid Bed Condenser
Phosphoric Anhydride P_2O_5
Bone Dry Air via Silica Gel
H_2S
Sludge $CaSO_4$, AsS_3 H_2SiF_6
Furnace acid

Process Description (Dry Process)

- Direct contact of phosphorus vapor with an air stream and then passing the phosphorus pentaoxide produced directly into a hydrater.
- The unconverted oxide plus phosphoric acid mist in the exit gases from the absorption tower are captured through an electrostatic precipitator (demister). CO is also vent off from upper section.
- Purification of furnace acid is done by the addition of sulfuric acid and silica. Impurities are precipitate out with sludge.



Major engineering problem/issues

1. **Electric furnace design:**
   - Power is a major cost component of process
   - High voltage with large reaction zone, reduce electrodes used.
   - Fossil-fueled source of heat for rotary kiln combustion to provide the energy of the endo-therm of the reaction.
2. **Control and operation of furnace:**
   - Changes in composition or ratio of blending of raw materials markedly change the yield
3. **Safety in handling phosphorus :**
   - Molten phosphorous is shipped under water and inert gas.
   - Where elemental phosphorus must be used directly as in incendiaries and matches, conversion to less poisonous red allotropic form with improved oxidation resistance is required.

What are the characteristics for fertilisers?

- Cheap and readily available
- Easily soluble in water so that it can penetrate the soil
- Its constituents readily available to plants
- It should be stable or have a longer life
- It should correct the acidity of the soil
- It should not have any tendency to deliquescence on storage.
- Fertilisers are classified into two types:

1. Direct 2. Indirect (NPK fertilisers)

Fertilisers :

Nitrogen

- Ammonia
- Urea
- Ammonium Nitrate
- Calcium Cyanamide
- Ammonium Sulphate
- Calcium Nitrate
- Calcium Ammonium Nitrate
- Potassium Nitrate
- Ammonium Chloride

Phosphatic

- Calcium phosphate
- Single Superphosphate (SSP)
- Triple Superphosphate (TSP)
- Ammonium phosphate
- Monoammonium phosphate (MAP)
- Diammonium phosphate (DAP)
- Nitrophosphate

Potash

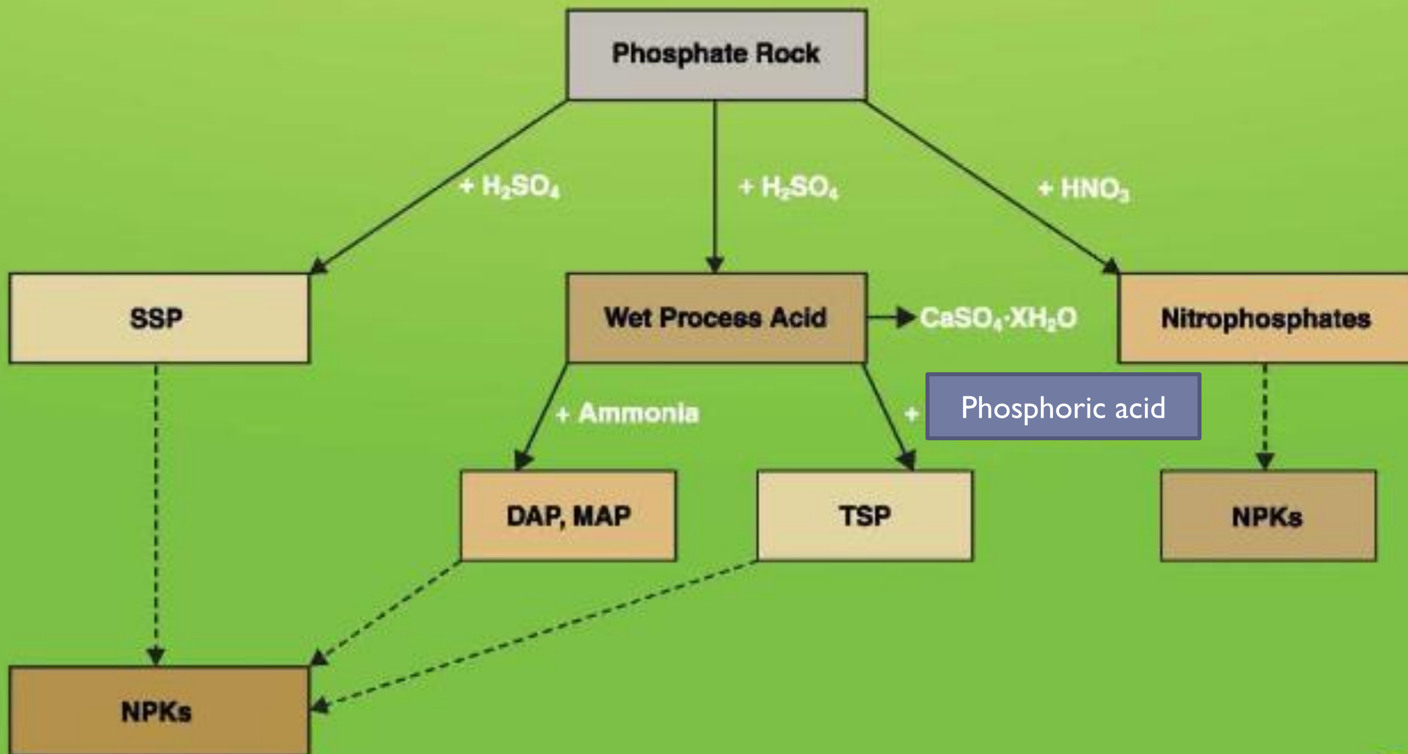
- Potassium chloride
- Potassium carbonate
- Sylvinite (mixture of KCl and NaCl)
- Carnallite
- Kainite
- Langbeinite
- Nitre or Indian Saltpetre
- Source of Potash – bitterus left over salt discovery and molasses/distellery slop.

Synthetic Fertilizers

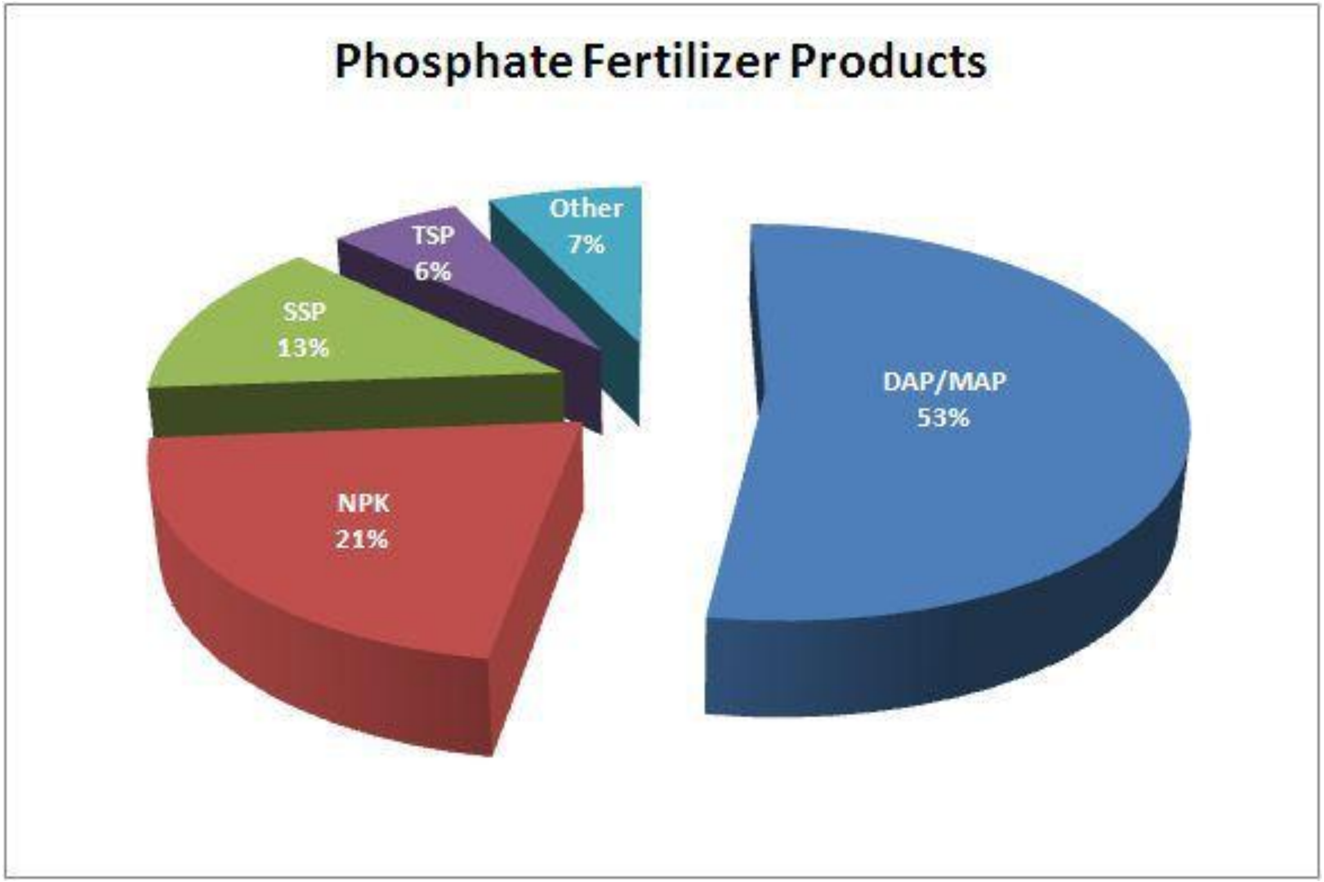
- Plant growth is required a total of nine major nutrients to proceed normally.
  - Three of these, C,H and O are obtained from air and soil(as water).
  - Another three Ca, Mg and S are present to a sufficient extent in most ordinary soils.
  - And another three N, P and K are present to a small extent but rapidly depleted from the soil with plant removal for harvesting.
  - Nitrogen contributes to early plant development and greening; Phosphorus assists with early growth and seed or fruit development; Potassium is used by plant for the production of cellulose and starches.
- For the fertilizer analysis the three principal ingredients are specified in order as follow:
  - nitrogen as %N, phosphorus as P_2O_5, and potassium K_2O as three number in sequence separated by hyphens.
  - Example: 0-20-20; 3-12-12; 5-20-20.

P Fertilizer Sources – Dry Granular

- Simplified flowchart of granular P production

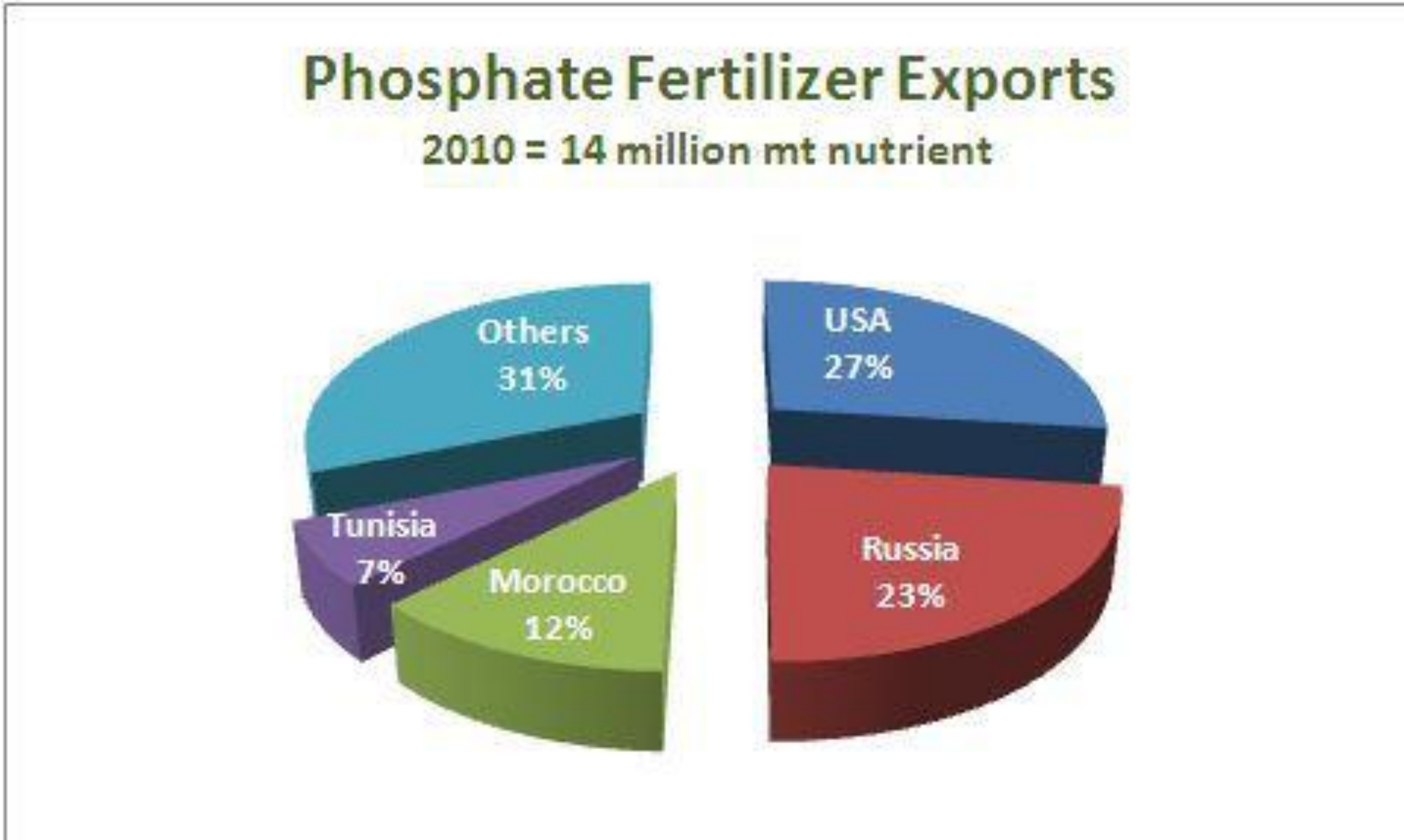


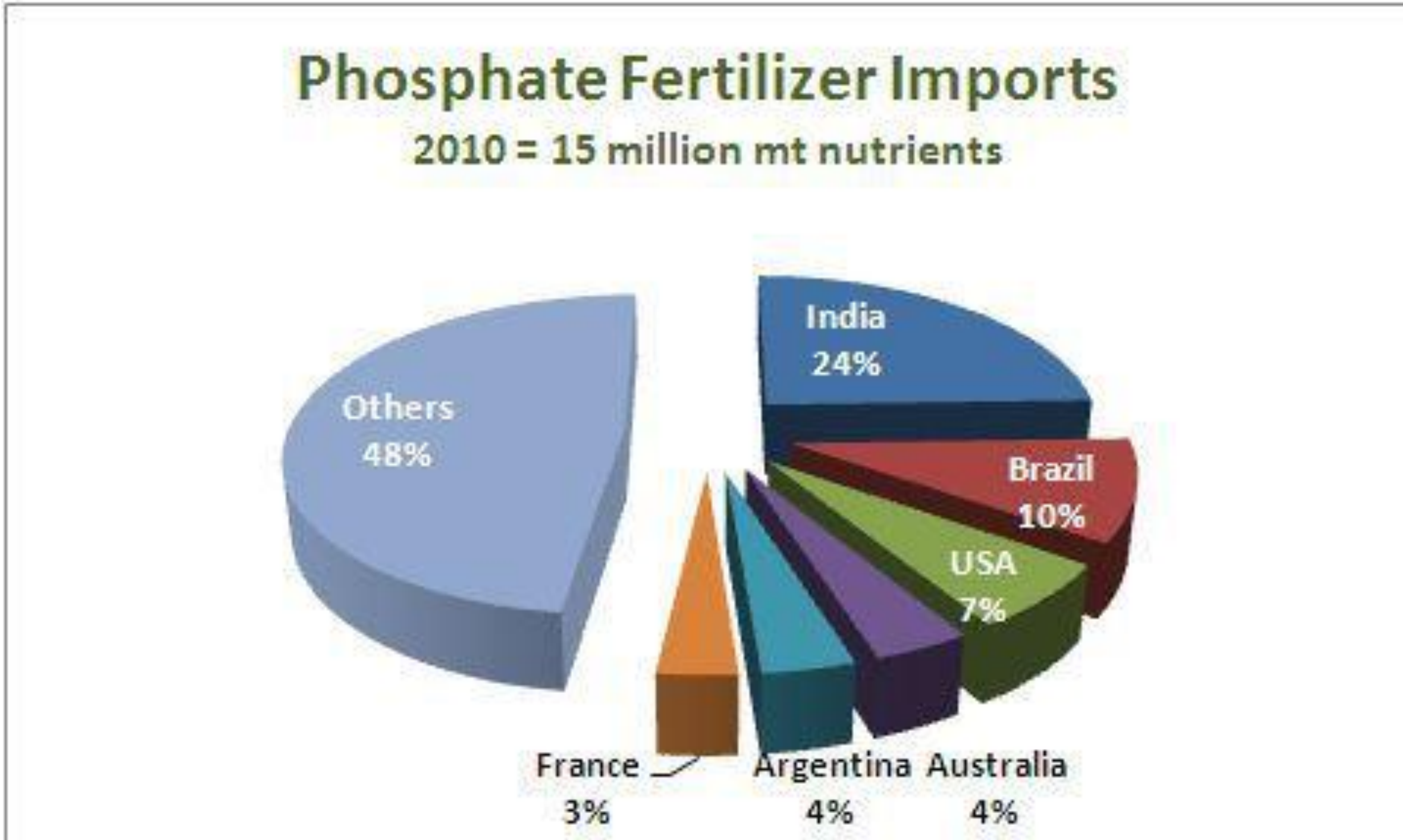
Phosphate Fertilizers


Phosphate Fertilizer Products
Other
7%
TSP
6%
SSP
13%
DAP/MAP
53%
NPK
21%


Phosphate Fertilizer Consumption
2010 = 45 million mt nutrients
Others
29%
China
37%
Brazil
7%
USA
9%
India
18%

Phosphate Fertilizers - Consumption (millions mt nutrients)						
	1970	1980	1990	2000	2010	2020
World	21,117	31,700	35,901	32,472	45,442	57,000
China	949	2,744	5,853	8,610	16,943	22,400
India	541	1,231	3,259	4,215	8,017	14,600
USA	4,346	4,930	3,811	3,862	3,883	3,000
Brazil	417	1,988	1,202	2,338	3,385	4,300
Australia	757	797	579	1,107	946	600
Pakistan	30	226	389	675	757	650
Canada	326	635	578	571	620	500
Turkey	176	619	625	629	515	450
Japan	656	690	690	583	424	400
France	1,809	1,773	1,349	795	295	300
Others	11,108	16,066	17,568	9,088	9,658	9,800


Phosphate Fertilizer Exports
2010 = 14 million mt nutrient
Others
31%
USA
27%
Tunisia
7%
Morocco
12%
Russia
23%


Phosphate Fertilizer Imports
2010 = 15 million mt nutrients
India 24%
Others 48%
Brazil 10%
USA 7%
France 3%
Argentina 4%
Australia 4%

FIPR Florida Industrial and Phosphate Research Institute

Phosphate Primer

History of Phosphate Fertilizer Production

Until the 1950s, fertilizer manufacturing facilities were relatively small and produced fertilizers tailored to the soil needs of area farmers, commonly within a 100-mile radius. Prior to 1950, only 4 million tons of primary nutrients – nitrogen (N), phosphate (P) and potassium (K) - were produced yearly. But in the late 1940s this began to change. Domestic agriculture and industry, as well as European and Western Pacific markets devastated in World War II, increasingly requested these nutrients.

In the 1960s, the Tennessee Valley Authority (TVA) and the Land Grant Colleges began to promote higher analysis fertilizers so that more phosphate could be delivered to the farmers at lower costs and changed the way fertilizers were produced. In the 1960s, more concentrated phosphates began replacing normal superphosphate as the primary fertilizer commodity, turning what had been strictly a mining business into chemical production. This was especially true in Florida, which produces approximately 75% of the phosphate rock mined in the U.S. Phosphate rock is no longer sold for fertilizer manufacture. It is exclusively used to make phosphoric acid, almost all of which is used in the production of phosphate fertilizers.

Formulation of Major Active Constitutes

- **Major Nutrients**

  Ammonia solutions, Urea, Superphosphates, Mixed fertilizers, bio fertilizers

- **Fillers and Conditioners**

  Fillers can include sand, gypsum, rock and assist in even distribution of fertilizers.

  Conditioners are used to improve soil structure. Examples are sand, specially processed wood waste , synthetic polymer (Krylium).

- **Coated Fertilizer**

  A variety of coatings have been applied to fertilizer particles to control their solubility in soil. Controlling the rate of nutrient release can offer multiple environmental, economic, and yield benefits.

http://www.e-mj.com/features/4621-chemical-beneficiation-of-phosphate-rock.html#.VMsafy5e_LU

Calcium Phosphates

- Finely ground phosphate rock ($Ca_3(PO_4)_2$) is occasionally added to fertilizer formulations as a diluent or filler. However because phosphate rock has limited water solubility its action as a phosphate nutrient is small and slow.
- Hence a more soluble form of phosphate (SSP and TSP) are made by the acidulation of phosphate rock.
- Generally known as Superphosphates.
- Two distinct grade
  - Single Superphosphate – Phosphate rock + Sulfuric acid

    P_2O_5 : 16-20 %
  - Triple Superphosphate – Phosphate rock + Phosphoric acid

    P_2O_5 : 42-50 %

Superphosphate

- Raw Materials
  - Natural or beneficiated phosphate rock
  - Dilute sulfuric acid (62- 70 % H_2SO_4)

- Acidulation

$[Ca_3 (PO_4)_2]_3 . CaF_2 + 7H_2SO_4 (aq) \rightarrow 3CaH_4 (PO_4)_2 .7Ca SO_4 + 2HF$

The product super phosphate contains the inert gypsum component as well as active calcium dihydrogen phosphate.

- SiO_2 impurity removal

$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$

$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$

$H_2SiF_6 + 2NaCl \rightarrow Na_2SiF_6 + 2HCl$

Process steps

- Mixing : Ground phosphate rock + Diluted H_2SO_4
- Aging of superphosphate in Den
- Granulation in rotary drum-granulator
- Drying and Bagging

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Birla Copper (A Copper project at Dahej, India, with Phosphate Fertiliser as a by-product).

ARMACO faced a unique challenge of improving the Birla Copper Phosphoric Acid plant facility. Birla Copper approached ARMACO to assist them with the brownfield project and improve the plant performance.

The 325tpd phosphoric acid plant was running with chronic uptime, quality, and technical efficiency problem almost in every segment of its manufacturing steps. ARMACO did performance evaluation, identified problems and devised corrections & measures to improve efficiency across some important process steps like Rock Weigh Feeder to Ball Mill, alignment of Belt Filter with respect to its Weir belt & Vacuum box, Reactor gas duct, Fluorine scrubber & its fan capacity.

It also studied and demonstrated the feasibility of fluorine effluent recovery as AlF_3 and/or as $CaSiF_6$. ARMACO also did techno-feasibility study to increase capacity of the Phosphoric Acid plant from 335 tpd to 650 tpd.

View other case studies

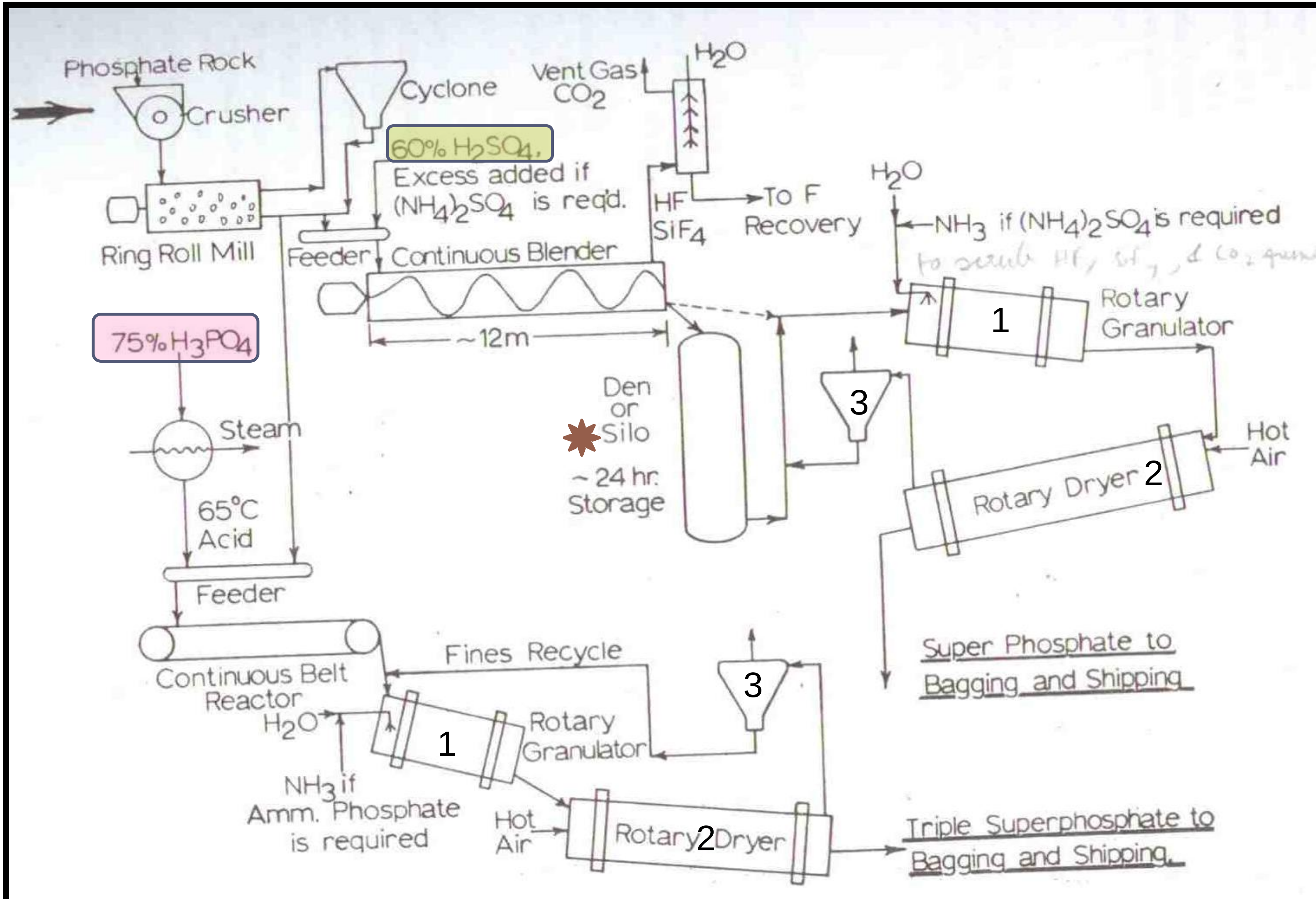
Triple superphosphate

- Much more concentrated than the ordinary superphosphate (45- 46 % of available P_2O_5).

- Triple superphosphate is manufactured by the action of phosphoric acid on phosphate rock.

- $CaF_2 . 3Ca_3 (PO_4)_2 + 14H_3PO_4 \rightarrow 10Ca (H_2PO_4)_2 + 2HF \uparrow$
  (Phosphate Rock) (Triple Superphosphate)

- Process : Very similar to SSP.



Phosphate Rock
Crusher
Ring Roll Mill
Cyclone
Feeder
60% H_2SO_4,
Excess added if $(NH_4)_2SO_4$ is req'd.
Continuous Blender
~12m
Vent Gas CO_2
H_2O
HF SiF_4
To F Recovery
H_2O
NH_3 if $(NH_4)_2SO_4$ is required
Rotary Granulator
1
Den or Silo
~24 hr. Storage
3
Hot Air
Rotary Dryer
2
Super Phosphate to Bagging and Shipping
75% H_3PO_4
Steam
65°C Acid
Feeder
Continuous Belt Reactor
Fines Recycle
H_2O
1
Rotary Granulator
3
NH_3 if Amm. Phosphate is required
Hot Air
Rotary Dryer
2
Triple Superphosphate to Bagging and Shipping.

Engineering Problem

•Sources of particulate emissions : reactor, granulator, dryer, screens, cooler, mills, transfer conveyors.
Fluorine compounds and dust particles: Silicon tetrafluoride (SiF4) and hydrogen fluoride (HF) a evolve from the reactors, den, granulator, and dryer.

•Bag houses : to control the fine rock particles generated by the rock grinding and handling
•Cyclonic scrubbers: scrubbing the effluent gas emissions from the reactor, den, and granulator
•Gaseous SiF_4 in the presence of moisture reacts to form gelatinous silica, which has the tendency to plug scrubber packings.

- use of conventional packed countercurrent scrubbers
- other contacting devices with small gas passages for emissions control is not feasible.

•Scrubber types that can be used are: (1) spray tower, (2) cyclone, (3) venturi, (4) impingement, (5) jet ejector, and (6) spray-crossflow packed.

Fig (1) Process Flow Diagram for Single Superphosphate Manufacturing

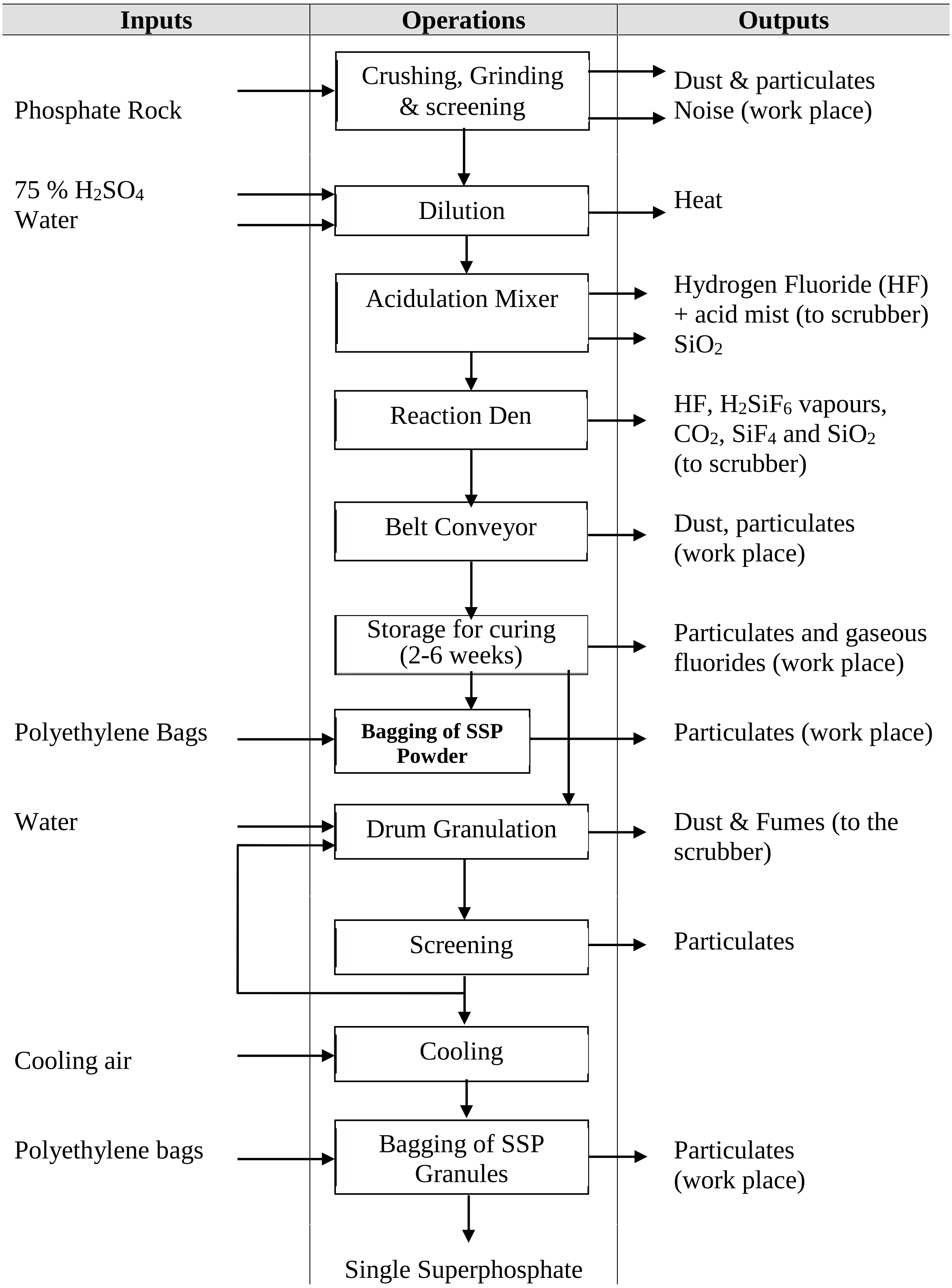
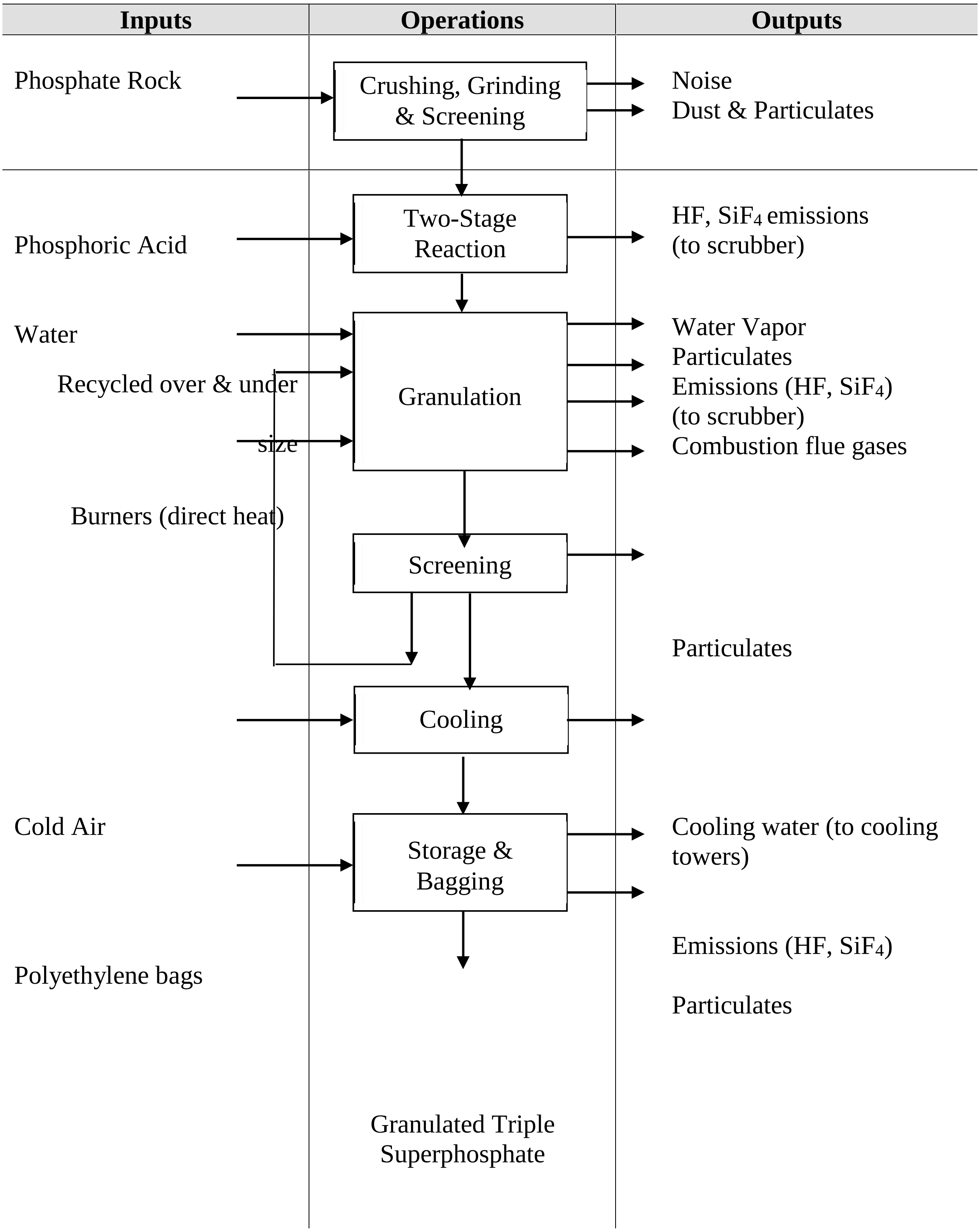


Fig (4) Process Flow Diagram for Triple Superphosphate Manufacturing



Ammonium Phosphate

Two types of Ammonium phosphate

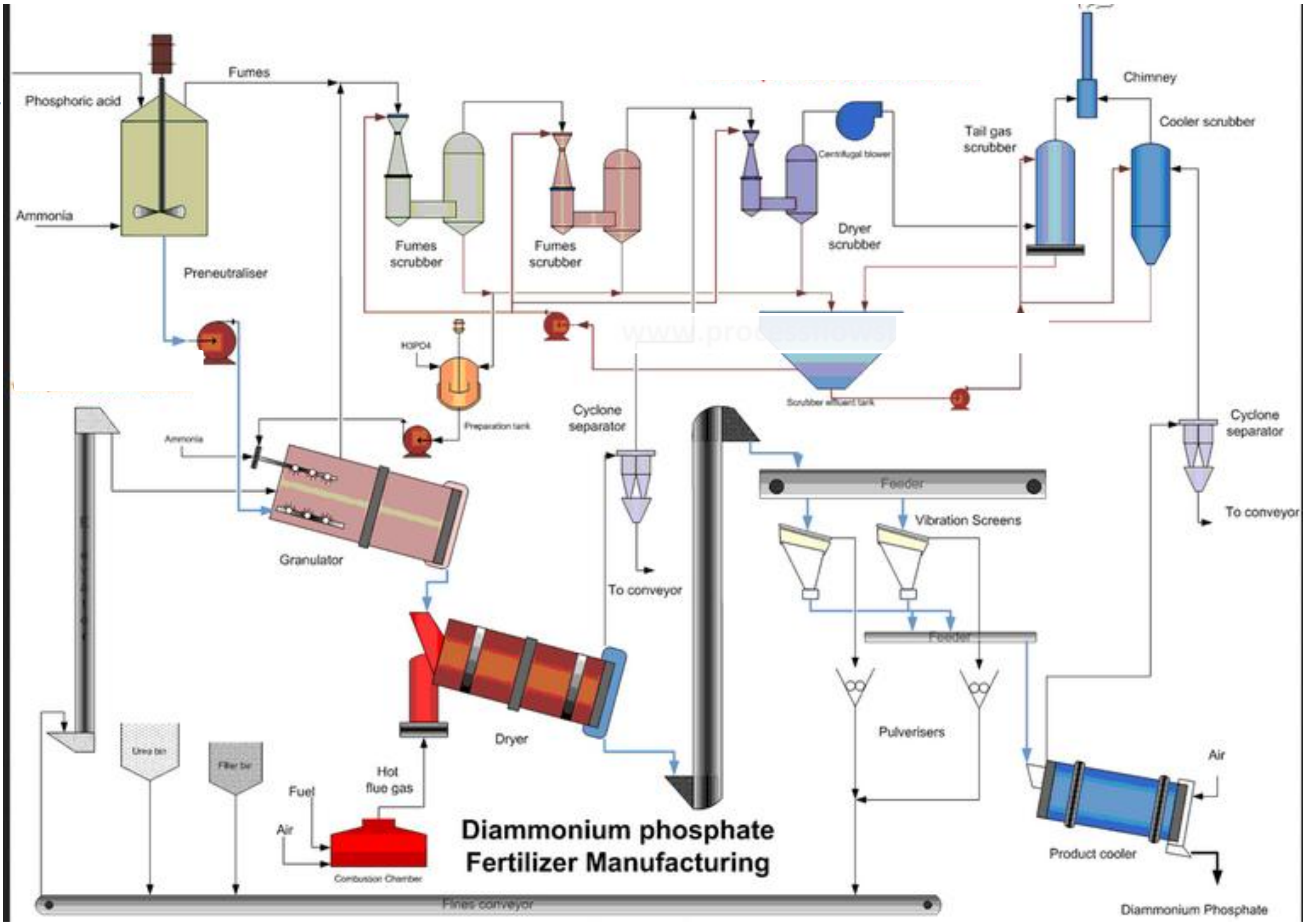
- Mono-ammonium phosphate
- Reaction Involve
  - Reacting ammonia with phosphoric acid, centrifuging and drying in a rotary dryer.

    $NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$
- Ammonia to phosphoric acid ratio is 0.6 in the pre-neutralizer and then 1.0 in the granulator

- Di-ammonium phosphate.
- Reaction Involve
  - A two-stage reactor system in order to prevent loss of ammonia.

    $NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$

    $NH_3 + NH_4H_2PO_4 \rightarrow (NH_4)_2HPO_4$
- The ratios are 1.4 and 1.0 in the pre-neutralizer and granulator respectively


Phosphoric acid
Fumes
Ammonia
Preneutraliser
Fumes scrubber
Fumes scrubber
Centrifugal blower
Dryer scrubber
Tail gas scrubber
Chimney
Cooler scrubber
H3PO4
Preparation tank
Scrubber effluent tank
Ammonia
Granulator
Cyclone separator
To conveyor
Feeder
Vibration Screens
Feeder
Cyclone separator
To conveyor
Pulverisers
Dryer
Hot flue gas
Fuel
Air
Combustion Chamber
Urea bin
Filler bin
Diammonium phosphate Fertilizer Manufacturing
Air
Product cooler
Diammonium Phosphate
Fines conveyor

Process description

- Neutralization
  - Phosphoric acid and sulfuric acid, added to 3 continuous mixed reactors.
  - Anhydrous ammonia is added in first neutralizer
- Granulation
  - Slurry from third neutralizer is mixed with KCl and feed to rotating drum granulator
  - Rotary adiabatic drier removes the moisture < 1%
- Screening
  - Dried product is separated into three fractions.

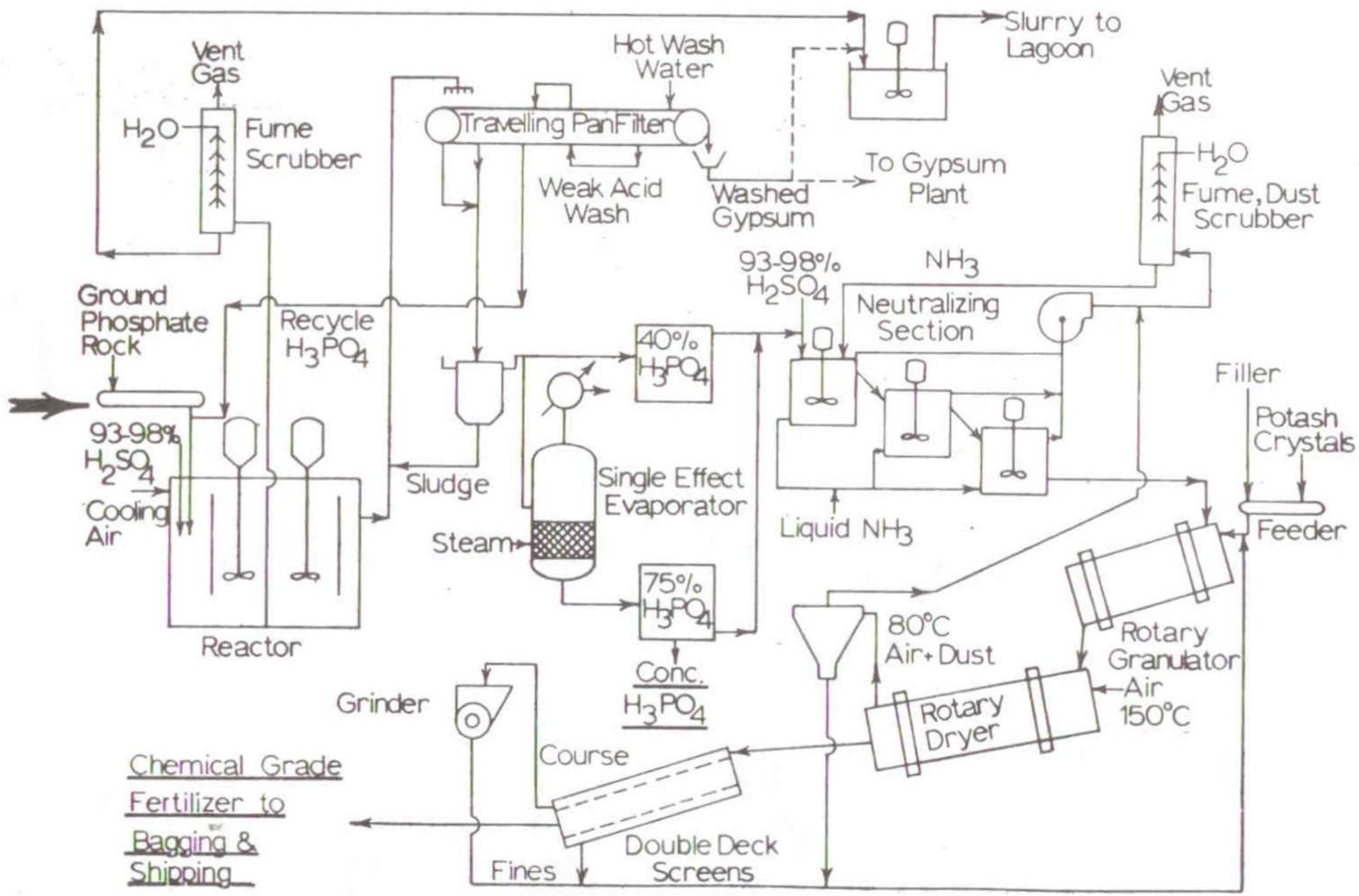


Fig. IIF-2. Production of phosphoric acid and chemical fertilizer from phosphate rock by strong acid process.

Major engineering problem

- NH_3 Losses
  - Unreacted and excess NH_3 vapor is collected from top of each tank and recharge below the liquid level.

- Corrosion
  - Use type 316 (stainless steel) for hot acid and fume ducts; carbon steel for granulation , drying and screening.

Nitrophosphates

- Mixtures of ammonium nitrate and various phosphates made by acidulation of phosphate rock with HNO_3 and/or H_2SO_4

- Chemical Reactions:
  - Nitric Acid Digestion- Ammonia Neutralization

$$Ca_3(PO_4)_2 + 6HNO_3 + 4NH_3 \rightarrow Ca(NO_3)_2 + 2CaHPO_4 + 4NH_4NO_3$$

  - Nitric Acid-Sulfuric acid Digestion- Ammonia Neutralization

$$Ca_3(PO_4)_2 + 6HNO_3 + 6NH_3 + H_2SO_4 \rightarrow 2CaHPO_4 + 6NH_4NO_3 + CaSO_4$$

  - Conversion to monocalcium phosphate

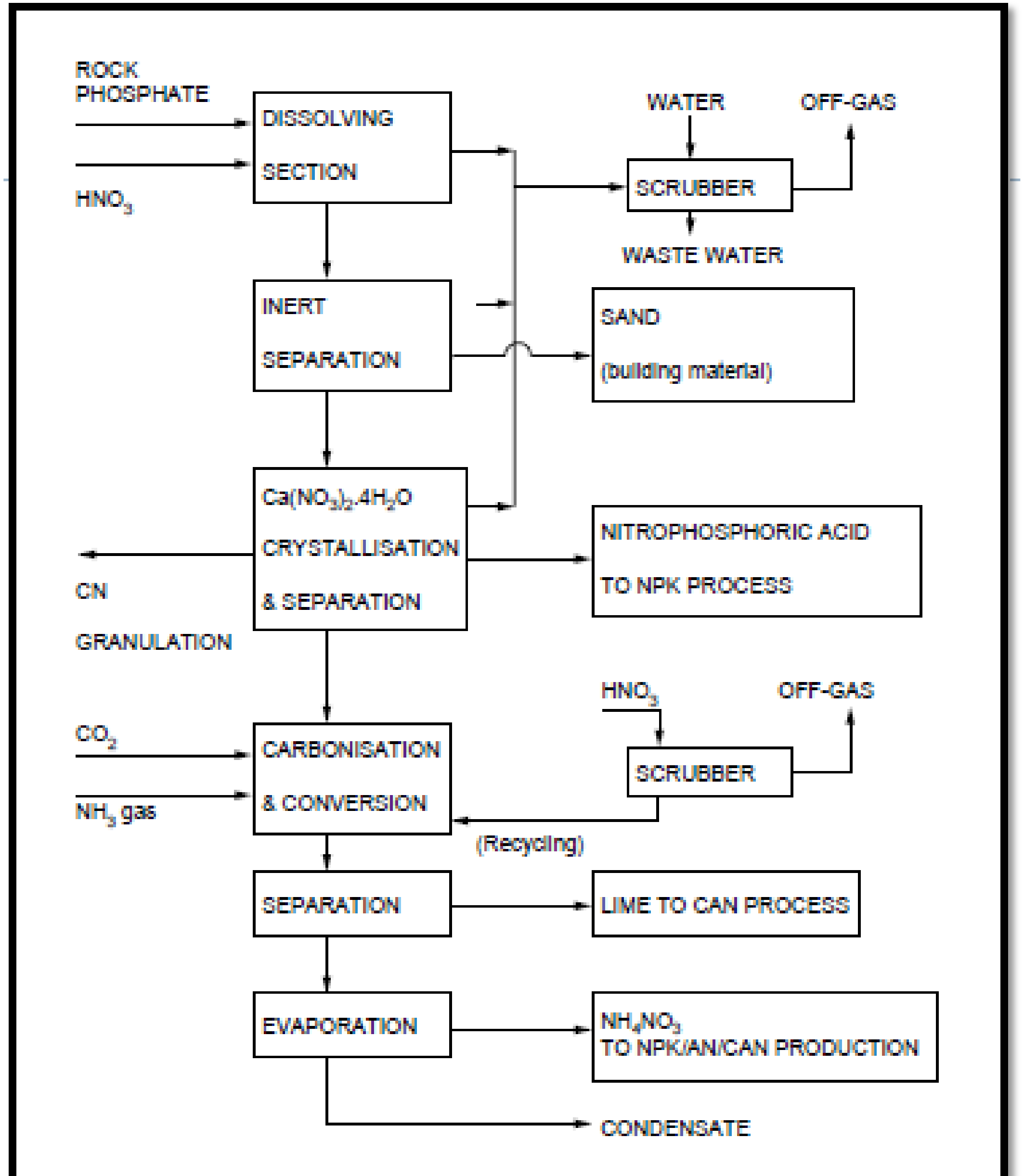
$$2CaHPO_4 + H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + CaSO_4$$

  - Carbonitric Process

$$Ca_3(PO_4)_2 + 6HNO_3 + 6NH_3 + CO_2 + H_2O \rightarrow 2CaHPO_4 + 6NH_4NO_3 + CaCO_3$$

Process description

- Pulverized phosphate rock is digested with nitric (or mixed acid)
  - Similar to wet process (Phosphoric acid)
  - Acid strength 25-40 % HNO_3
- Digested slurry is pumped to an ammoniating tank
  - Here chemical reaction completes
- Granulation and drying
  - In rotary equipments
  - Followed by screening in classifying circuit



ROCK
PHOSPHATE
HNO_3
DISSOLVING
SECTION
WATER
OFF-GAS
SCRUBBER
WASTE WATER
INERT
SEPARATION
SAND
(building material)
$Ca(NO_3)_2.4H_2O$
CRYSTALLISATION
& SEPARATION
NITROPHOSPHORIC ACID
TO NPK PROCESS
CN
GRANULATION
HNO_3
OFF-GAS
CO_2
CARBONISATION
& CONVERSION
SCRUBBER
NH_3 gas
(Recycling)
SEPARATION
LIME TO CAN PROCESS
EVAPORATION
NH_4NO_3
TO NPK/AN/CAN PRODUCTION
CONDENSATE

Major Engineering Problems

- Removal of Calcium nitrate
  - $Ca(NO_3)$ is highly hygroscopic (product to lump)
    - For HNO_3 (reaction 1) : digested liquor must be chilled to remove calcium nitrate crystals
    - Mixed acid process (reaction 2)or carbonitric process (reaction 3) : conversion to $CaSO_4$ or $CaCO_3$
- Corrosion
  - Corrosion of digestion and neutralization equipment by HNO_3 : 18-8 stainless steel.

SODIUM PHOSPHATE

- Numerous combinations of Na with P and O exist, e.g. Sodium Meta, Poly, Ortho, Pyro Phosphate.
- Ortho- and polyphosphate are made from varying ratio of carbonate, sodium hydroxides and orthophosphoric acid.

- The principal use of alkali phosphates is in detergent formulation. Other applications include metal cleaning, boiler water treatment, in foodstuffs.
  - Sodium tripolyphosphate, STPP, $Na_5P_3O_{10}$, is the main phosphate present in detergents.

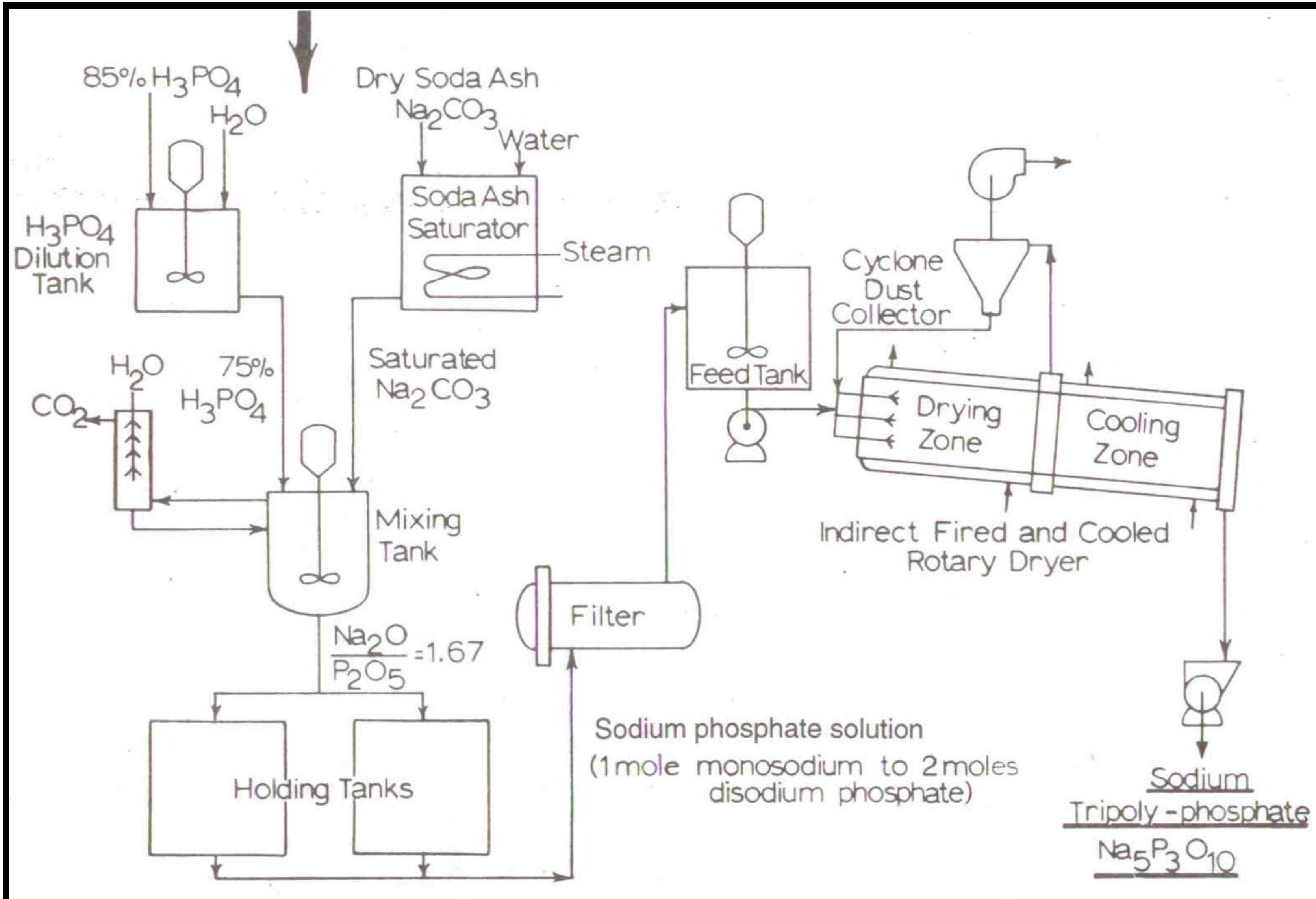
Sodium Tripolyphosphate (STTP)

- Overall reaction
  - $5\ Na_2CO_3 + 6\ H_3PO_4 \rightarrow 2Na_5P_3O_{10} + 9\ H_2O + 5CO_2$
- It is prepared from phosphoric acid by neutralisation with soda ash (sodium oxide) forming sodium hydrogen phosphates.
  - A powdered mixture of disodium hydrogen phosphate, and sodium dihydrogen phosphate is heated to 500°C to 550°C to produce the stable form of STPP

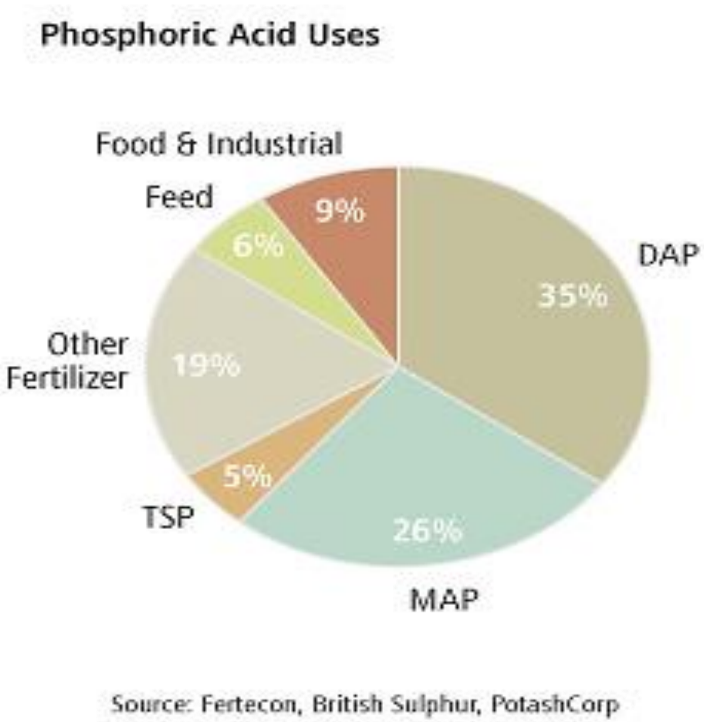
$$2\ Na_2HPO_4 + NaH_2PO_4 \rightarrow Na_5P_3O_{10} + 2\ H_2O$$

  - In a single-stage process the orthophosphate solution is converted from a liquid phase in one process step to become marketable STPP in its solid free-flowing form. The single stage process uses a rotary kiln in which granulation, drying, polycondensation and calcination of the ortho -phosphate solution to finished STPP take place in a single step.

Process Flow Sheet



CONSUMPTION PATTERN OF H_3PO_4



- By far, largest use of phosphoric acid comes in the production of fertilizers (>75%)
- It is added to foods as a preservative, acidifying agent, flavor enhancer, and clarifying agent
- It is also used in processes such as the coagulation of rubber latex, electropolishing, soil stabilization, and as a catalyst in the production of propylene and butene polymers, ethylbenzene, and cumene.

Wet process (With H_2SO_4)

Chemical reactions:

a) $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(\underbrace{CaSO_4.2H_2O}_{\text{Gypsum}})$ (ΔH=-76.4kcal)

b) Side reactions:

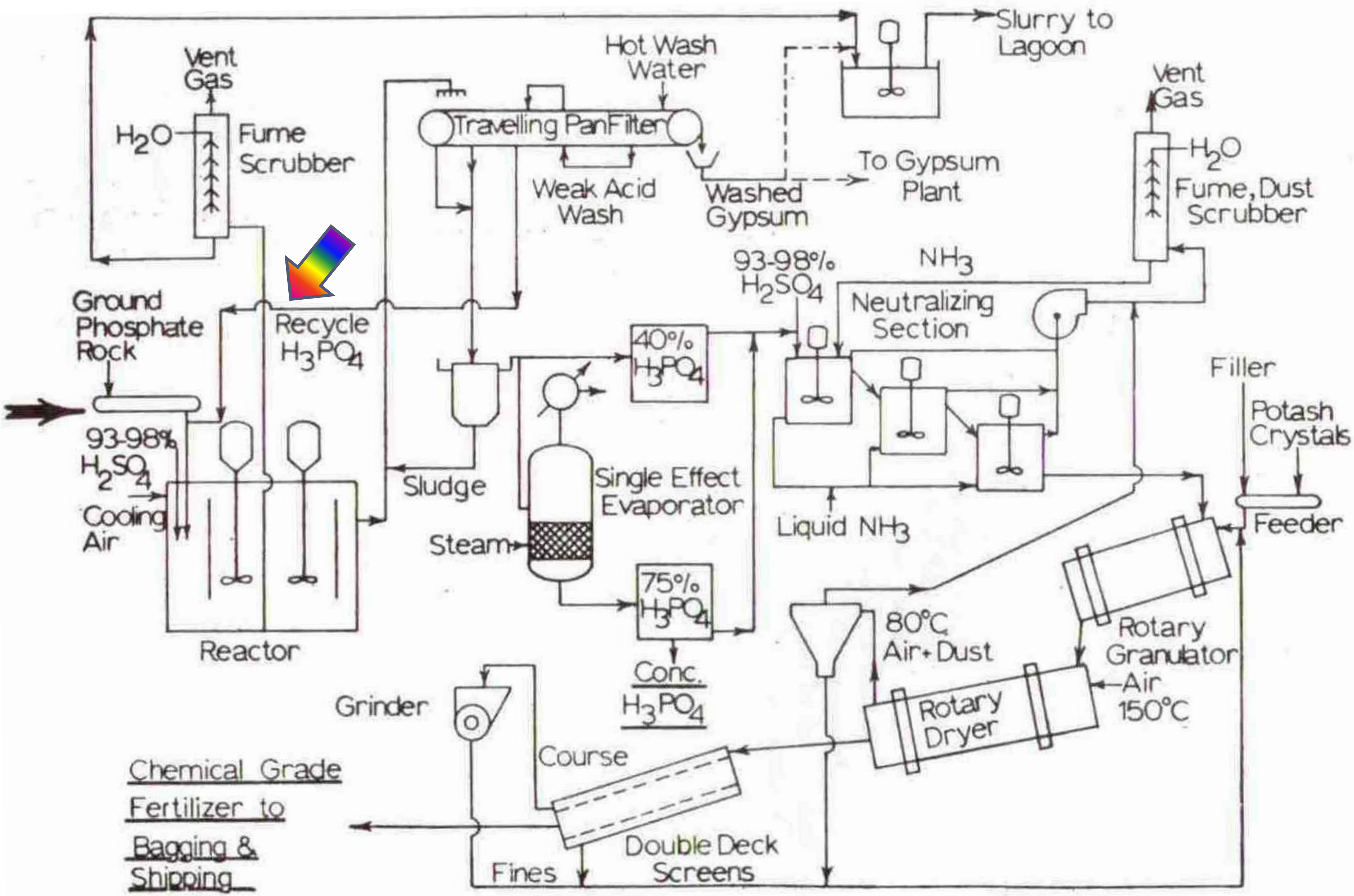
$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO_4 . 2H_2O$$

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

Raw materials:

1. The high grade of imported ore is necessary to avoid solubilization of mined rock impurities such as aluminum, silicon, iron oxides.
   - A beneficiation process can be used on low grade ore which involves milling, screening, hydroseparation, classification and flotation.
2. Other raw material is strong sulfuric acid.

Wet process (H_2SO_4)



Wet/IMI process (With HCl)

Chemical reaction:

a) $Ca_3 (PO4)_2$ + 6 HCl + 6 H_2O → $2H_3PO_4$ +3 $CaCl_2$

b) Side reaction:

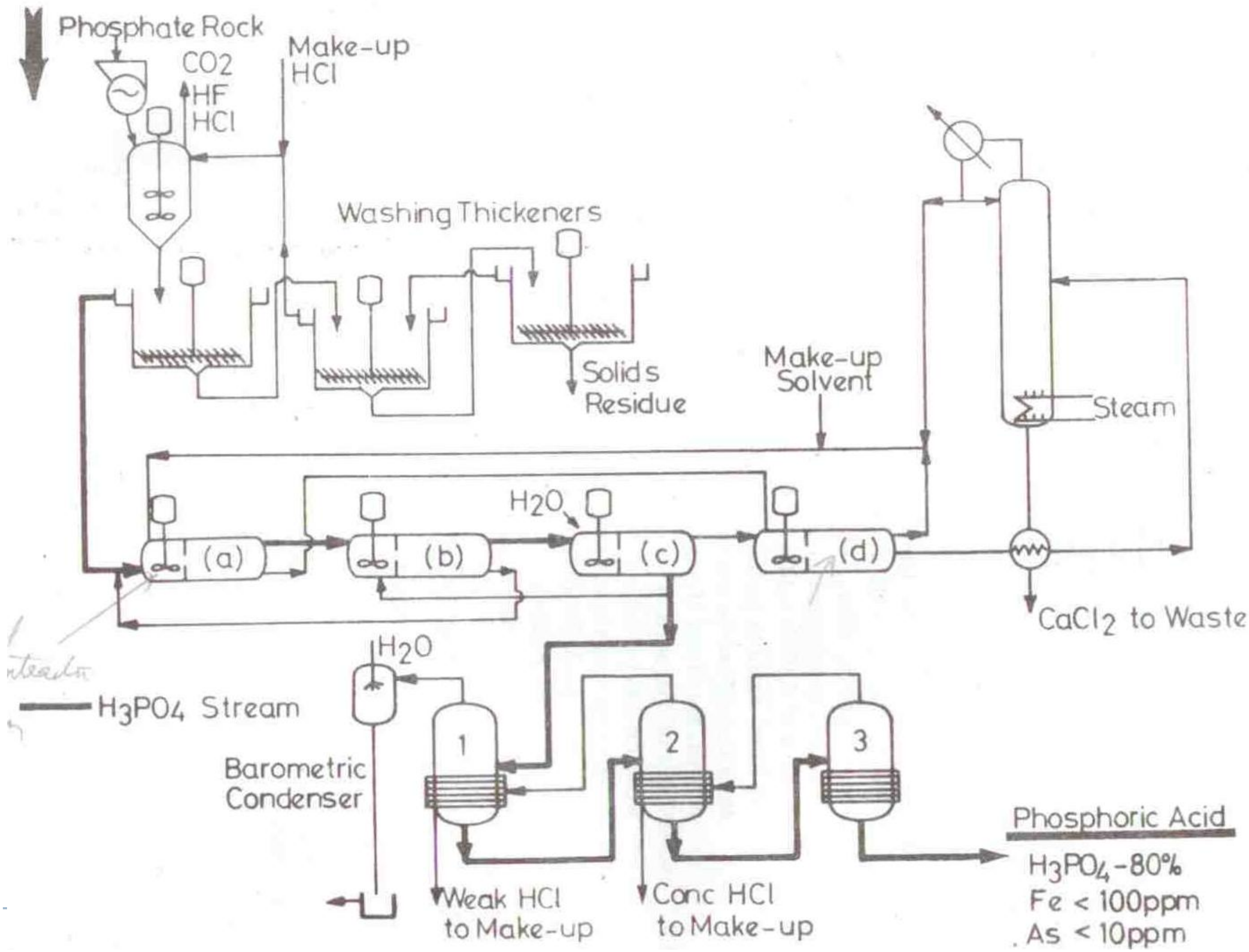
CaF_2 +2 HCl → 2HF + $CaCl_2$

6HF + SiO_2 → H_2SiF_6 + $2H_2O$

Raw Materials:

1. Phosphate rock of high P_2O_5 content (>30%) is preferred to avoid excessive acid consumption.
2. Hydrogen chloride gas or concentrated aqueous HCl (>30%) as waste or by product acid can be used.
3. Organic C_4 and/or C_5 alcohol solvents are used to extract H_3PO_4 from $CaCl_2$ solution.

Wet process (HCl)



Major Engineering Issue

- **H_2SO_4 Leaching Process**

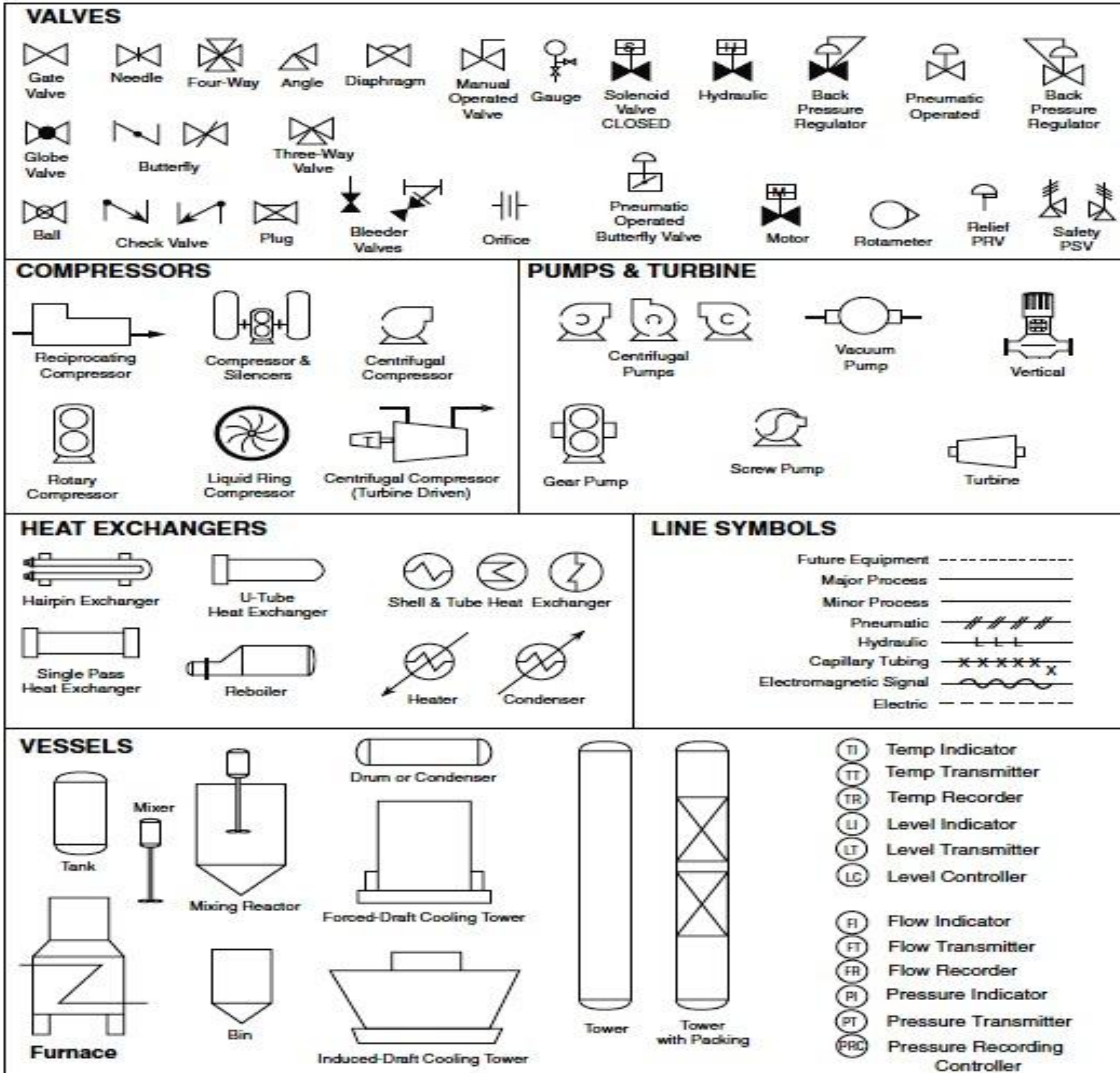
1. Process design
   - Fineness of grind
   - Undesired semihydrate and anhydrate at high T
   - Control of sulfuric acid
2. Material of construction
   - Steel and lined with acid proof brick
   - Air vent PVC coated steel
   - Storage tank rubber lined steel

- **HCl Leaching Process**

1. Solvent recovery
   - Relatively expensive solvent
   - Efficient solvent handling
2. Material of constructions
   - HCl resistance
   - PVC lined rubber lined impervious grafite
3. Waste disposal
   - $CaCl_2$ aq effleunt
   - Siliceous rock residue

Process Comparison

- The product acid from wet process using HCl is purer than sulfuric acid acidulation process, and in addition this process claimed to recover 98-99 % of the available P_2O_5 in the rock, as opposed to experience of the most efficient sulfuric acid processes.
- Trade hydrochloric acid is normally 2-3 times the price of sulfuric acid.


VALVES
Gate Valve
Needle
Four-Way
Angle
Diaphragm
Manual Operated Valve
Gauge
Solenoid Valve CLOSED
Hydraulic
Back Pressure Regulator
Pneumatic Operated
Back Pressure Regulator
Globe Valve
Butterfly
Three-Way Valve
Ball
Check Valve
Plug
Bleeder Valves
Orifice
Pneumatic Operated Butterfly Valve
Motor
Rotameter
Relief PRV
Safety PSV
COMPRESSORS
Reciprocating Compressor
Compressor & Silencers
Centrifugal Compressor
Rotary Compressor
Liquid Ring Compressor
Centrifugal Compressor (Turbine Driven)
PUMPS & TURBINE
Centrifugal Pumps
Vacuum Pump
Vertical
Gear Pump
Screw Pump
Turbine
HEAT EXCHANGERS
Hairpin Exchanger
U-Tube Heat Exchanger
Shell & Tube Heat Exchanger
Single Pass Heat Exchanger
Reboiler
Heater
Condenser
LINE SYMBOLS
Future Equipment
Major Process
Minor Process
Pneumatic
Hydraulic
Capillary Tubing
Electromagnetic Signal
Electric
VESSELS
Tank
Mixer
Mixing Reactor
Drum or Condenser
Forced-Draft Cooling Tower
Tower
Tower with Packing
Furnace
Bin
Induced-Draft Cooling Tower
TI Temp Indicator
TT Temp Transmitter
TR Temp Recorder
LI Level Indicator
LT Level Transmitter
LC Level Controller
FI Flow Indicator
FT Flow Transmitter
FR Flow Recorder
PI Pressure Indicator
PT Pressure Transmitter
PRC Pressure Recording Controller