UTKALMANI GOPABANDHU INSTITUTE OF ENGINEERING, ROURKELA



LECTURE NOTES

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SUBJECT- CPI-I

DEPARTMENT OF CHEMICAL ENGINEERING

SESSION-(2021-22)

Unit Operations

- A unit operation is defined as a process which does not involve any chemical reaction. Unit operations only deal with physical changes of the materials involved in the process. They are equipments which cause the materials to undergo physical changes.
- The physical changes are carried out for variety of purposes. Generally unit operations steps are carried out before subjecting the materials to chemical reactions so that chemical reactions happen smoothly.
- The physical changes can imply phase changes such as; evaporation, condensation, crystallization etc. Thus Distillation is a unit operation step because condensation and evaporation happens inside the column. Evaporators, and crystallisers are also unit operations equipment.
- Unit operation equipments are also responsible for mechanical operations which involves size reduction, physical separations, mixing, and grinding. The mass transfer, heat transfer process all may happen together. Chemical reaction doesn't happen.
- The unit operations are classified in the following manner:

1. Fluid flow operations: Pumping, compression, and fluidisation.
2. Mechanical operations: Size reduction, size enlargement, mixing, agitation, blending, filtration, classification-separation, etc.
3. Mass transfer: Distillation, evaporation, crystallization, leaching, absorption, adsorption, extraction, etc.
4. Heat transfer: When materials are handled the heat transfer can take place by any fundamental mechanism; conduction, convection, or radiation. Usually two fundamental mechanisms occur simultaneously.

Unit Process

- Chemical reaction is at the heart of the unit processes. A chemical reactor is an equipment which falls under the category of unit processes.
- Literal chemical change takes place inside the equipment wherein the the chemical structure of the material changes and it transforms and forms an entirely new material.
- All kinds of chemical reactions carried out in industrial equipments comes under this category.
- Some examples of such chemical reactions are; sulphonation, nitration, halogenation, alkylation, hydrolysis, hydrogenation, polymerization, oxidation, reduction, etc. The examples can be innumerable as there can be innumerable compounds which can be formed by reaction of two or more materials or by decomposition of the material itself. Thus classification can be similarly endless.
- Most of the chemical reactions are irreversible in nature. A chemical reaction step in a process forms the heart of the process, often governing the economics of the entire process. Thus the unit processes are often subject of optimization.
- Often unit operations have to be carried out before unit processes to give proper shape to the materials so that they will be able to react optimally.
- Also unit operations are often needed even after the chemical reaction has happened, they are needed for the purpose of separation of the primary product from the secondary or tertiary products.

- All the unit operation processes wherein chemical reaction is made to take place to improve the efficiency of the equipment also falls under unit processes. For example, reactive distillation, reactive extraction, reactive absorption, etc.

Batch and continuous process

Particulars	Batch Process	Continuous Process
Definition	Batch process refers to a process that consists of a sequence of one or more steps that should be performed in a defined order. A finite quantity of the product is produced at the end of the sequence, which is repeated in order to produce another product batch.	A continuous process refers to a processing that involves moving a single work unit at a time between every step of the process without any breaks in time, substance, sequence or extend. As the name suggests, the flow of product or material is continuous.
Co-ordination between the equipments	The equipments may or may not be coordinated. The time between to equipments is maintained by scheduling.	Every machine operates in a steady state and performs a certain processing function.
Quantities Produced	Small quantities of products are obtained. Production rate is usually less than $5x10^5$ kg/year.	Large quantities of products are obtained.
Fouling	If fouling expectations is large than Batch Processes are preferred.	If fouling can be eliminated than continuous process is chosen.
Product Life Span	Short, 1 – 2 years.	Larger Product Life expectancy.
Cost of factory equipment	Low cost equipments. (Even if special equipments are constructed.)	High Cost of equipments
Controlling	Easier to control and maintain Process	Difficult to control, requires sophisticated control system.
Shut Down Times	Often	Rare
Workforce	Small Work force needed	Large Work force is needed. (If not fully automated).
Examples	Pharmaceuticals, Specialty Chemicals.	Petroleum Industry, Fertilizer Industry.

Manufacturing process of Hydrogen from propane with a flow sheet

Electrolytic Process for Hydrogen gas

Pure hydrogen along with oxygen is manufactured by electrolytic process. It is also obtained as a by-product in the production of caustic soda by electrolysis of aqueous solution of sodium chloride. Heavy water may be prepared on a large scale by burning deuterium separated from hydrogen obtained by electrolysis.

Reactions

In acidulated water

H_2SO_4 $2H^+ + SO_4^{-2}$

At cathode

$2H^+ + 2H_2O$ $2[H_3O]^+$

[H3O]+ + e- H+ + H2O
H+ + H+ H2
At anode
SO4-2 SO4 + 2e-
SO4 + H2O H2SO4 + O-2
O-2 + O-2 O2

In KOH solution

KOH K+ + OH^-
At cathode
K+ + e- K
K + H2O KOH + H+
H+ H+ H2
At anode
2OH^- H2O + O-2
O-2 + O-2 O2

In Ba(OH)2 solution

Ba(OH)2 Ba+2 + 2OH^-
At cathode
Ba+2 + 2e- Ba
Ba + H2O Ba(OH)2 + H2
At anode
2OH^- 2OH + 2e-
2OH^- O-2 + H2O
O^{2-} +O^{2-}----O_2

Manufacture

Construction

Both unipolar and bipolar cells are used for electrolysis. In case of unipolar cells, iron elsheets and nickel coated iron sheets are used as cathodes and anodes respectively. Both anodes and cathodes are placed close to one another to prevent the loss of voltage. Asbestos diaphragm is placed between anode and cathode compartment.

In case of bipolar cells the same sheet act as both anode and cathode as the electrodes are connected in series. The cell is partitioned by vertical iron sheet; the anode side of the sheet is electroplated with nickel. Vertical asbestos sheet as diaphragm is placed between the anode side and cathode side of former sheet. The same sheet acts as anode of one cell and cathode of the cell behind it. The anode and cathode compartments are connected to two separate horizontal pipes by means of standpipes, to lead away oxygen and hydrogen respectively. 250 cells are connected in series, and current of 10000amp is passed to operate the cells. The purity of H2 and O2 are 99.95% and 99.6% respectively.

Working

Pure hydrogen can be manufacture by electrolysis of brine or water. Since water is non-conductor of electricity and can be made conductor by addition of small quantities of pure H2SO4 or KOH or Ba(OH)2. 2:1 volume of H2(g) and O2(g) are simultaneously liberated at cathode and anode respectively

Produced hydrogen contains small quantity of oxygen, which can be removed by passing the gas over the catalyst gently heated palladium asbestos. The gas obtained by electrolysis is very pure and used for hydrogenation of oils.

Engineering aspect

The energy consumption is high due to resistance cause by the bubbling. This is somewhat mitigated by conducting electrolysis under pressure. The decomposition voltage is 1.23 volts, so that the evolution of 2gms of hydrogen 53.6amp.hour is necessary. Hence to generate

1000litre of H2 at 180C and 1atm pressure 2.8KWH are required because of overvoltage of the electrode and ohmic resistance of the electrolyte and diaphragm.

LEAD CHAMBER PROCESS OF SULPHURIC ACID MANUFACTURING

- In 1746 John Roebuck developed the *lead chamber* process for the manufacture of sulfuric acid.
- Prior to this time, sulfuric acid had been produced in glass bottles several pounds at a time. But the lead chamber process could produce sulfuric acid by the ton.
- In the lead chamber process hot sulphur dioxide gas enters the bottom of a reactor called a Glover tower where it is washed with nitrous vitriol (sulphuric acid with nitric oxide, NO, and nitrogen dioxide, NO_2, dissolved in it) and mixed with nitric oxide and nitrogen dioxide gases;
- Some of the sulphur dioxide is oxidized to sulphur trioxide and dissolved in the acid wash to form tower acid or Glover acid (about 78% H_2SO_4).
- From the Glover tower a mixture of gases (including sulphur dioxide and trioxide, nitrogen oxides, nitrogen, oxygen, and steam) is transferred to a lead-lined chamber where it is reacted with more water.
- The chamber may be a large, boxlike room or an enclosure in the form of a truncated cone.
- sulphuric acid is formed by a complex series of reactions; it condenses on the walls and collects on the floor of the chamber.
- There may be from three to twelve chambers in a series. The acid produced in the chambers, often called chamber acid or fertilizer acid, contains 62% to 68% H_2SO_4.
- After the gases have passed through the chambers they are passed into a reactor called the Gay-Lussac tower where they are washed with cooled concentrated acid (from the Glover tower);
- The nitrogen oxides and unreacted sulphur dioxide dissolve in the acid to form the nitrous vitriol used in the Glover tower.
- Remaining waste gases are usually discharged into the atmosphere.
- The Glover tower serves two functions: concentration of the chamber acid and Stripping of nitrogen oxides from the liquid to the gas or denitration, Concentration of the chamber acid (62% to 68% H_2SO_4) is achieved by the hot gases entering the tower which evaporate water from the acid.

The reactions occurring in the lead chamber are:

- $NO + ½\ O_2$ -----> NO_2
- $NO_2 + NO + H_2O$ -----> $2\ HNO_2$
- $SO_2 + H_2O$ -----> H_2SO_3
- $2\ HNO_2 + 2\ H+$ -----> $2\ NO + 2\ H_2O$
- H_2SO_3 -----> $HSO_3^- + H^+$
- $NO+ + HSO_3^-$ -----> $NOSO_3^- + H^+$
- $NO+ + NOSO_3^-$ -----> $2NO + SO_3$
- $SO_3 + H_2O$ -----> H_2SO4
- Overall Reaction: $SO_2 + ½\ O_2 + H_2O$ -----> H_2SO_4
- Product acid at a concentration of 78% H_2SO_4 is drawn from the cooled acid stream that is circulated from the Glover tower to the Guy-Lussac tower.
- Nitrogen losses are made up with nitric acid which is added to the Glover tower.

Chemistry

- Sulfur dioxide is generated by burning elemental sulfur or by roasting pyritic ore in a current of air:

$$S_8 + 8\ O_2 \rightarrow 8\ SO_2$$
$$4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$$

- Nitrogen oxides are produced by decomposition of niter in the presence of sulfuric acid or hydrolysis of nitrosylsulfuric acid:

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + NO + NO_2 + O_2$$

$$2\ NOHSO_4 + H_2O \rightarrow 2\ H_2SO_4 + NO + NO_2$$

- In the reaction chambers, sulfur dioxide and nitrogen dioxide dissolve in the reaction liquor.
- Nitrogen dioxide is hydrated to produce nitrous acid (HNO_2) which then oxidizes the sulfur dioxide to sulfuric acid and nitric oxide (NO).
- The reactions are not well characterized but it is known that nitrosylsulfuric acid is an intermediate in at least one pathway. The major overall reactions are:

$$2\ \ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$SO_2\ (aq) + HNO_3 \rightarrow NOHSO_4$$

$$NOHSO_4 + HNO_2 \rightarrow H_2SO_4 + NO_2 + NO$$

$$SO_2\ (aq) + 2\ HNO_2 \rightarrow H_2SO_4 + 2\ NO$$

- Nitric oxide escapes from the reaction liquor and is subsequently reoxidized by molecular oxygen to nitrogen dioxide. This is the overall rate determining step in the process:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

- Nitrogen oxides are absorbed and regenerated in the process, and thus serve as a catalyst for the overall reaction:

$$2\ SO_2 + 2\ H_2O + O_2 \rightarrow 2\ H_2SO_4$$

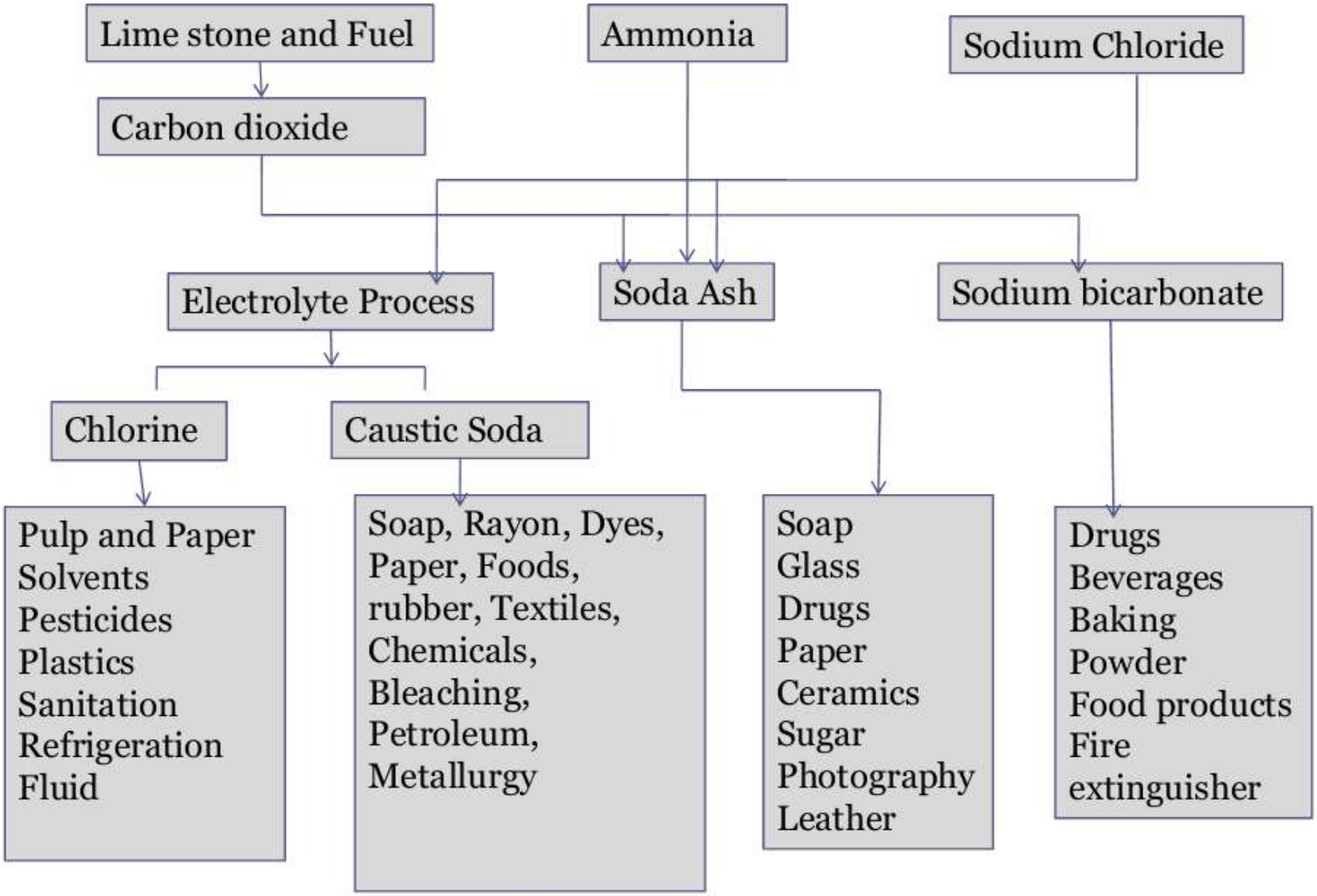
CHLORO–ALKALI INDUSTRY

PREPARED BY-SATARUPA SAHU

Electrolysis

Electrolysis is a unit process in which chemical change results from electron transfer reactions across the electrode/solution interfaces. A voltage applied between the two electrodes in an electrolytic cell drives these reactions. A schematic of an electrolytic cell for the manufacture of Cl2and NaOH is shown in Figure. The feedstock is aqueous NaCl brine, fed to the anolyte compartment between the anode and a cation permeable membrane. **Chloride** is oxidized to chlorine gas at the **anode** surface and water is reduced to **hydrogen** gas and **hydroxide ion at the cathode**. In order to maintain charge balance, migration of ions must occur, and the membrane is designed to allow the passage of only Na+ from anolyte to catholyte. As a result, **sodium hydroxide** is formed in the **catholyte compartment**. Also, in order to preserve charge balance, the rate of transfer of electrons at the two electrodes must be equal –therefore for each mole of chlorine formed, two moles of sodium hydroxide must also be produced.

Chlor-Alkali Industry



Manufacture of Chlorine and Caustic Soda

Sodium Hydroxide:

- White, solid material that picks up moisture from air.
- If put in water, it produces a large amount of heat.
- Very corrosive and can cause severe burns

Caustic Soda and Chlorine Processes

- Sodium Chloride solution (brine)is electrolytically decomposed to **elemental chlorine** (in the anode compartment), and **sodium hydroxide solution and elemental hydrogen** (in the cathode compartment) in all the processes
- The overall reaction for the electrolytic production of caustic soda and chlorine is:

$$2\,NaCl\,(aq) + 2\,H_2O = Cl_2\,(gas) + H_2\,(gas) + 2\,NaOH\,(aq)$$

Anode | Cathode

Manufacture of Chlorine and Caustic Soda cont'd

Reactions:

$$NaCl + H_2O = NaOH + \tfrac{1}{2} H_2 + \tfrac{1}{2} Cl_2$$

Decomposition Voltage and voltage efficiency:

$$E = \frac{-J\Delta H}{nF} + \frac{T\,dE}{dT}$$

Where, E= Theoretical decomposition voltage

ΔH= enthalpy change of reaction

J= electrical equivalent of heat

T= absolute temperature

F= Faraday constant

n= number of equivalents involved

Manufacture of Chlorine and Caustic Soda cont'd

Decomposition Voltage and voltage efficiency (cont'd):

- The ratio of theoretical voltage to that actually used is the **Voltage efficiency** of the cell(ranges from 60-75%).
- The ratio of the theoretical to the actual current consumed is defined as the **Current efficiency**(ranges from 95-97%).
- The product of voltage efficiency and current efficiency is the **energy efficiency** of the cell.

Manufacture of Chlorine and Caustic Soda cont'd

Methods of manufacture

1. Chemical: Lime soda Process
2. Electrochemical: Chloro Alkali Process

- **Diaphragm Cell**
- **Mercury Cell process**
- **Membrane cell process**

Electrochemical methods of manufacture

Diaphragm cell process:

- This process uses a steel cathode, and the anode area is separated from the anode area by a permeable diaphragm.
- A diluted caustic brine leaves the cell.
- The caustic soda must usually be concentrated to 50% and the salt removed.

Mercury cell process:

- Sodium metal forms an amalgam at a mercury cathode.
- This sodium is then reacted with water to produce NaOH.

Membrane cell process:

- This process is similar to the diaphragm cell process.
- Here a Naflon membrane is used to separate the cathode and the anode reactions. Only sodium ions and a little water pass through the membrane.
- It produces a high quality of NaOH.
- Of the three processes , it requires the lowest consumption of electric energy and the amount of steam needed for the concentration of the caustic soda is relatively small.

Electrochemical methods of manufacture cont'd

Chlor/alkali manufacturing process

Electrochemical and chemical reactions occurring in mercury cells

[1] $2Cl^- \Longrightarrow Cl_2 + 2e^-$ (anodic reaction)

[2] $2Na^+ + 2Hg + 2e^- \Longrightarrow 2Na\,(in\ Hg)$ (cathodic reaction)

[3] $2Cl^- + 2Na^+ + 2Hg \Longrightarrow Cl_2 + 2Na\,(in\ Hg)$ (overall cell reaction)

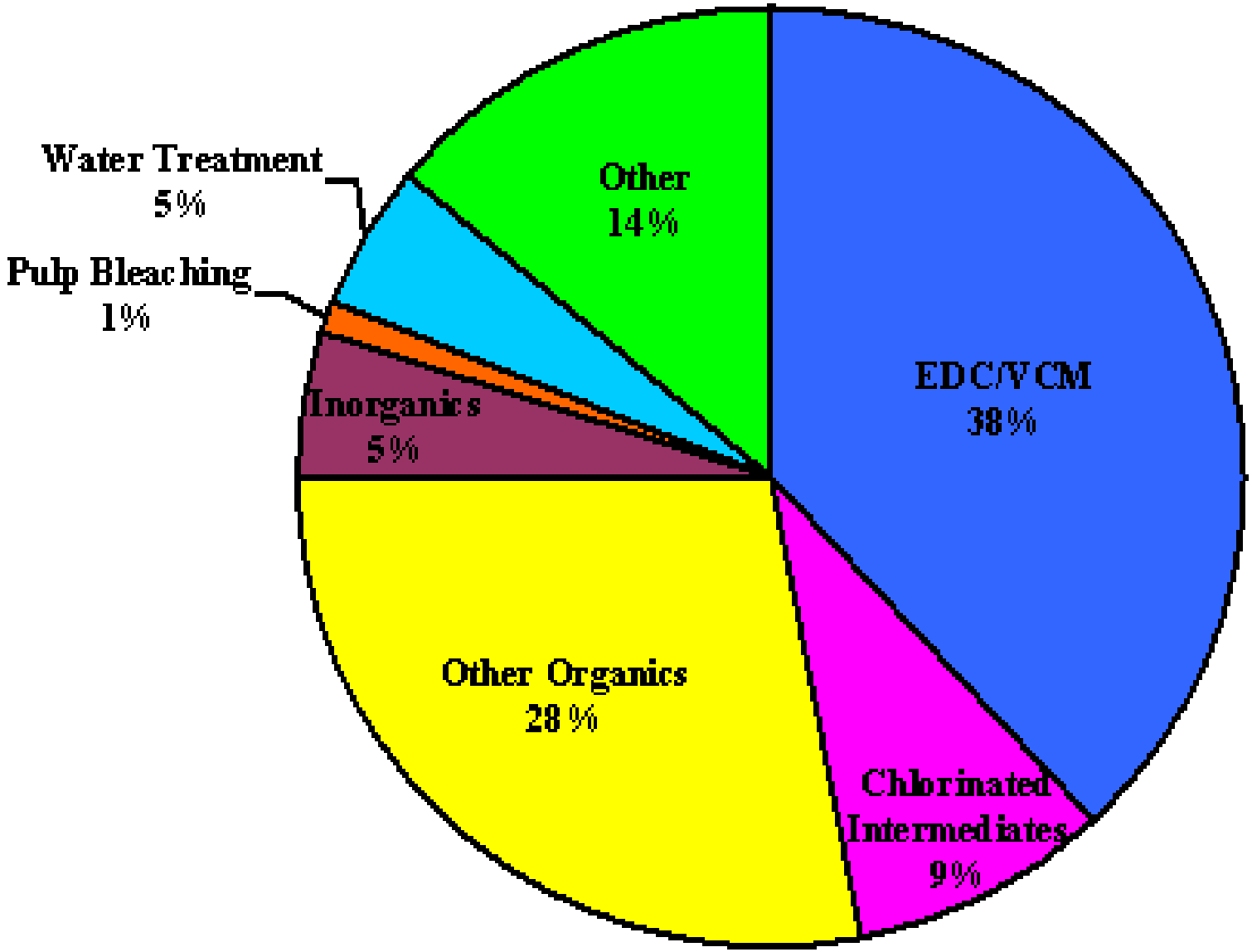
[4] $2Na\,(in\ Hg) + 2H_2O \Longrightarrow H_2 + 2NaOH + Hg$ (decomposer reaction)

[5] $2NaCl + 2H_2O \Longrightarrow Cl_2 + 2NaOH + H_2$ (overall process reaction)

Advantages and Disadvantages of Electrochemical methods of manufacture

Process	Advantages	Disadvantages
Diaphragm Process	•Use of well brine • Low electricity consumption	•Use of asbestos •High steam consumption •Low purity caustic •Low chlorine quality
Mercury Process	•50% caustic direct from cell •High purity chlorine and hydrogen •Simple brine purification	•Use of mercury •Expensive cell operation •Large floor space •Costly environment protection
Membrane Process	•Low energy consumption •Low capital investment •High purity caustic •Insensitivity to cell load variations and shutdowns	•Cost of membrane •Use of solid salt, high purity brine •High oxygen content in chlorine

Uses of Caustic Soda



Other Chlor Alkali Products

Liquid Chlorine

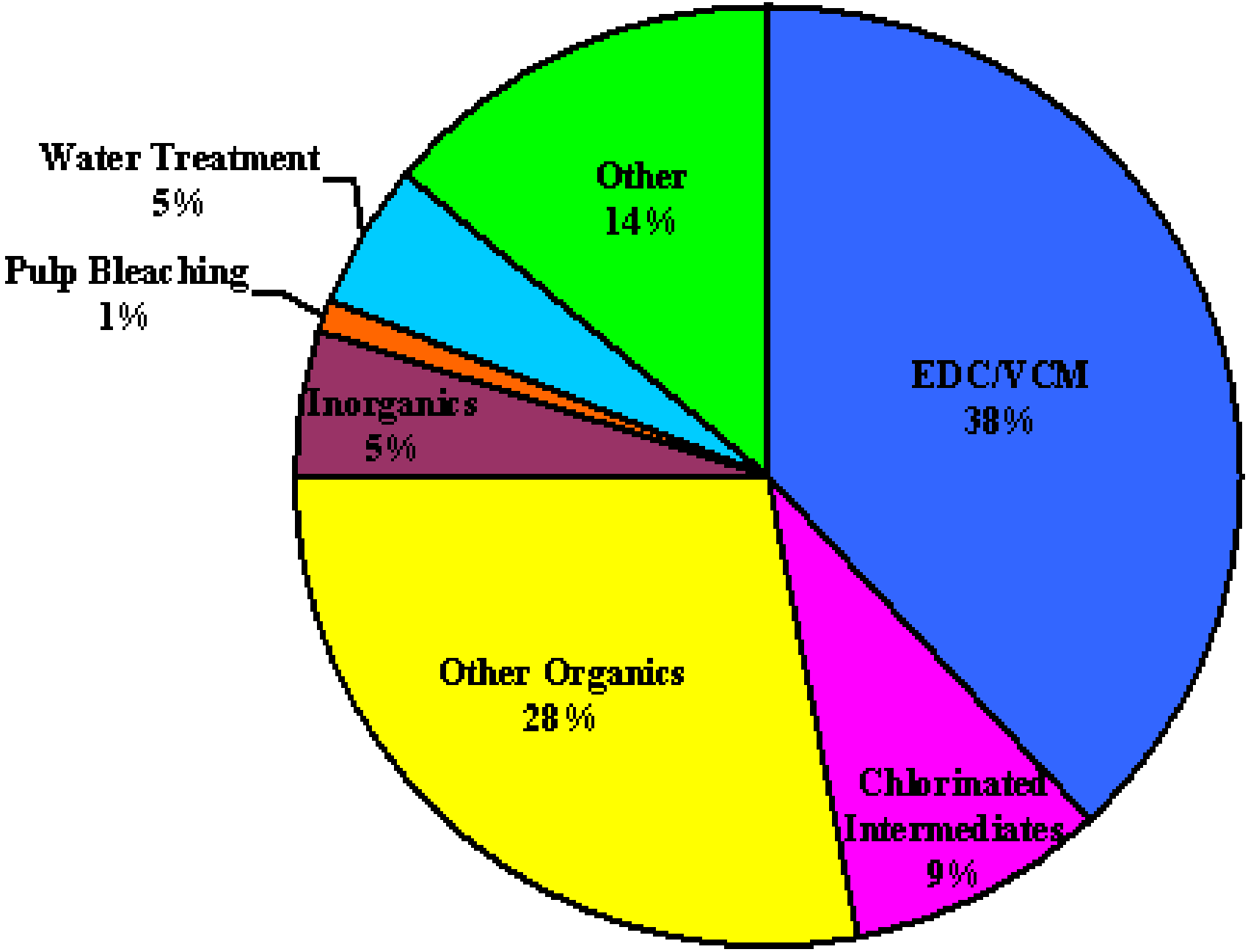
Chemical Formula: Cl_2

Appearance: Clear amber color

Product Quality: Cl_2 purity 99.5%

Uses:

- Manufacture of various chemical compounds e.g., carbon tetrachloride, chlorinated lime, PVC, HCl, etc.
- Water purification, manufacture of metallic chlorides, chlorinated lime, chlorobenzene, etc.
- Shrink proofing wool, in flame-retardant compounds, manufacture of trichloroethylene, neoprene etc.
- Processing of meat, fish, vegetables and fruit, in special batteries (with lithium or zinc)


Water Treatment
5%
Pulp Bleaching
1%
Other
14%
EDC/VCM
38%
Inorganics
5%
Other Organics
28%
Chlorinated
Intermediates
9%

- Molecular formula : Cl_2
- Molecular weight : 70.906gm/mole
- Appearance : Yellow green gas
- Odour : similar to house hold bleach
- Boiling point : -34^0C
- Melting point : -101^0C
- Vapour density : 2.48 (v/s air)
- Vapour pressure : 4800mmHg (20^0C)
- In upper atmosphere, chlorine containing molecules such as chlorofluoro-carbons have been implicated in ozone depletion.
- Elemental chlorine is extremely dangerous and poisonous for all life forms

- It is necessary to most forms of life, including humans, in form of chloride ions.
- It is the only acidic gas which turns damp blue litmus red and bleaches it to white.
- It is two and a half times heavier than air. It becomes a liquid at −34 °C.
- The affinity of chlorine for hydrogen is so great that the reaction proceeds with explosive violence in presence of light

Uses

- Used for producing safe drinking water.
- Chlorinated compounds are used mostly for sanitation, pulp bleaching and textile processing.
- Used for the manufacture of chlorates and it is important in organic chemistry, forming compounds such as chloroform, carbon tetrachloride, polyvinyl chloride, and synthetic rubber.
- Used in dyestuffs, petroleum products, medicines, antiseptics, insecticides, foodstuffs, solvents, paints and plastics.
- As an oxidizing agent and in substitution reactions.
- In paper and pulp, solvents, explosives, plastics, pesticides and sanitation
- As a common disinfectant, chlorine compounds are used in swimming pools to keep them clean and sanitary.

Hydrochloric acid

Chemical Formula: HCl

Product quality: 30-32% HCl

Appearance: Colorless or slightly yellow fuming liquid

Uses:

- Metal picking and cleaning, industrial acidizing, boiler scale removal
- Processing of bone in gelatin manufacturing industry, food processing (corn syrup, sodium glutamate).
- Manufacture of dyestuffs, casein, pharmaceuticals, synthetic rubber, laboratory reagent etc.
- Effluent treatment and the regeneration of ion-exchange resin in water treatment.

Sodium Hypochlorite

Chemical Formula: NaOCl

Product quality: Available Cl2

Appearance: Pale greenish liquid

Uses:

- Disinfection, odor control, specification, bleaching.
- Chlorination of drinking and process water, oil refineries, petroleum refineries.
- Textile industry, pulp and paper industry, soap manufacturing, food processors, wood processing.
- Elimination of slime and algae in swimming pool and boiler water.

Stable Bleaching Powder

Chemical Name: chlorinated lime

Chemical Formula: Ca(OCl)Cl

Product quality: 30-32% HCl

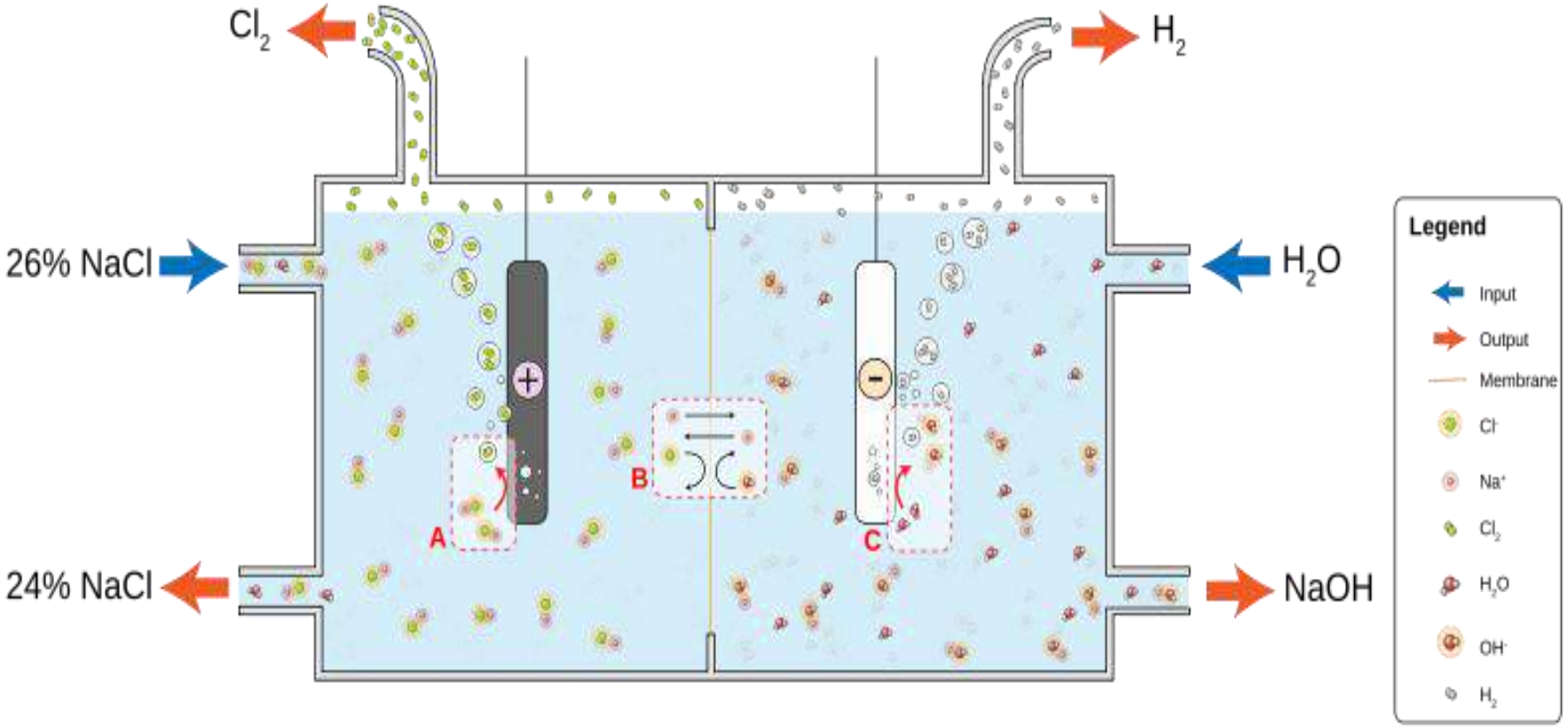
Appearance: Dry free flowing dull white powder

Product quality: Available chlorine conc. 35-37% min

Uses:

- Sewage disposal, odor control, BOD reduction and removal of poisonous matter.
- Potable water purification, mosquito control, control of epidemic etc.
- Bleaching agent (paper & textile), algaecide, bactericidal and deodrant.
- Elimination of algae and slime in swimming pool, sanitation and general hygiene.

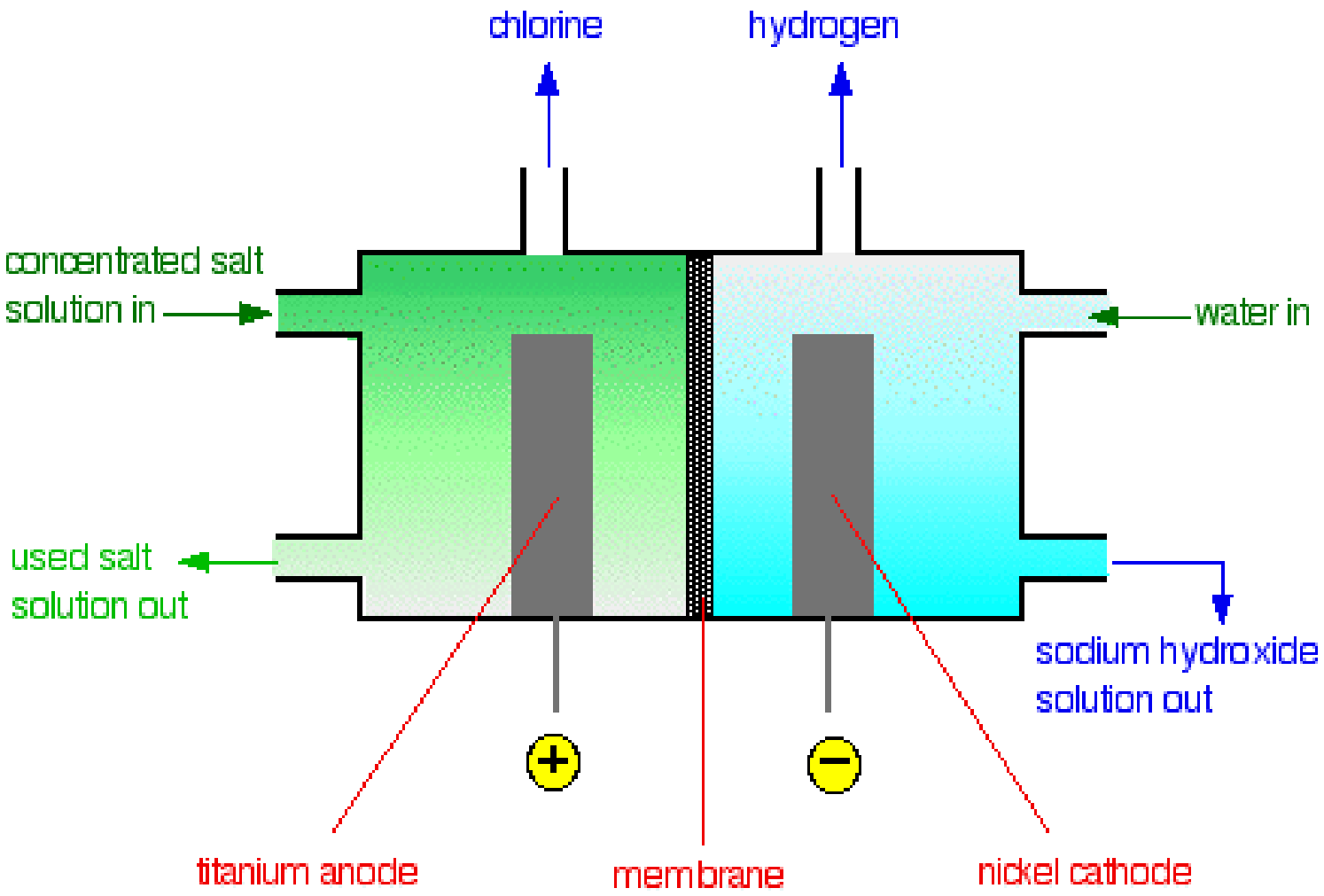
Electrolysis



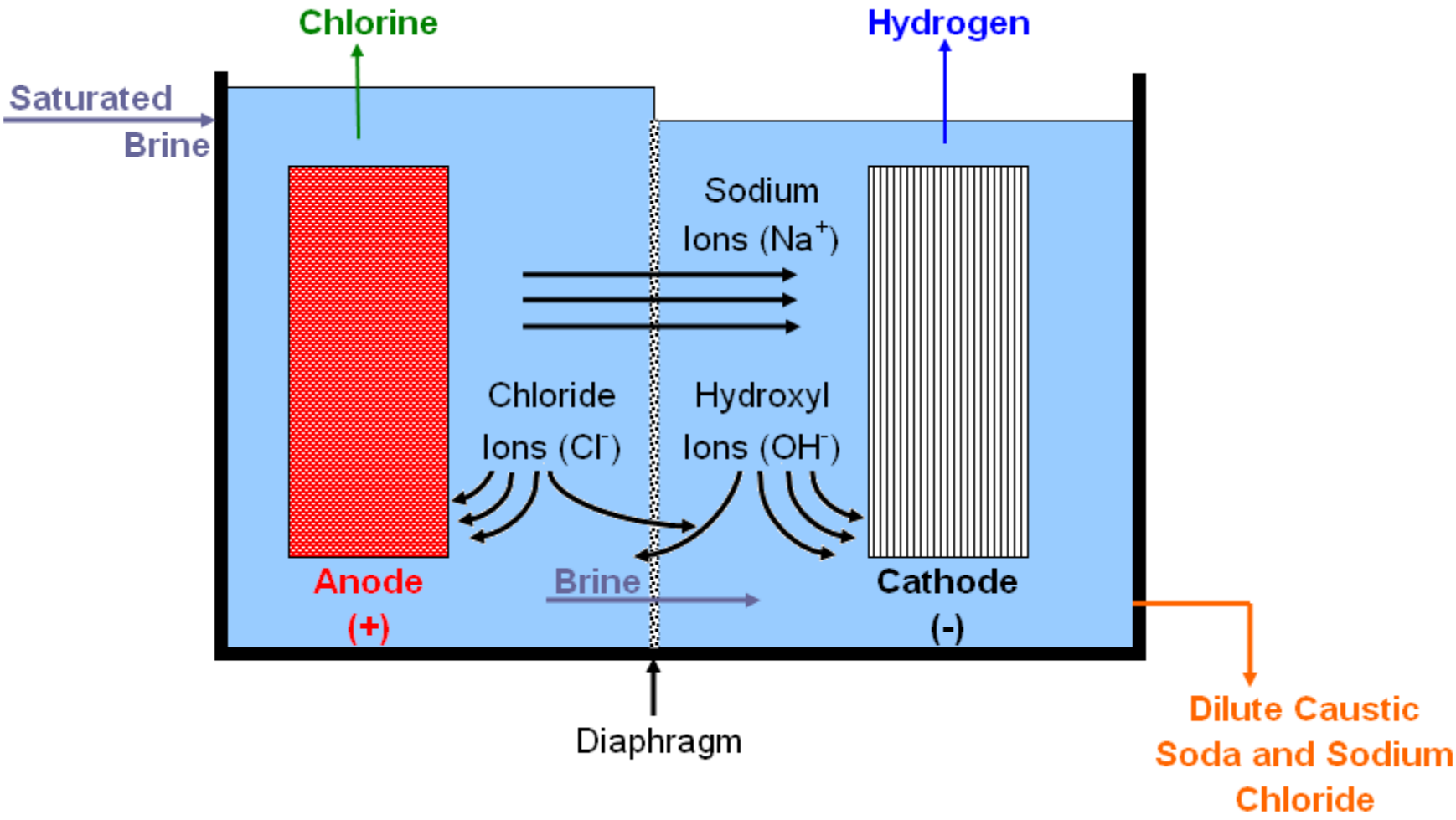
Membrane Cell



Membrane


chlorine
hydrogen
concentrated salt solution in
water in
used salt solution out
sodium hydroxide solution out
titanium anode
membrane
nickel cathode

Diaphragm Cell

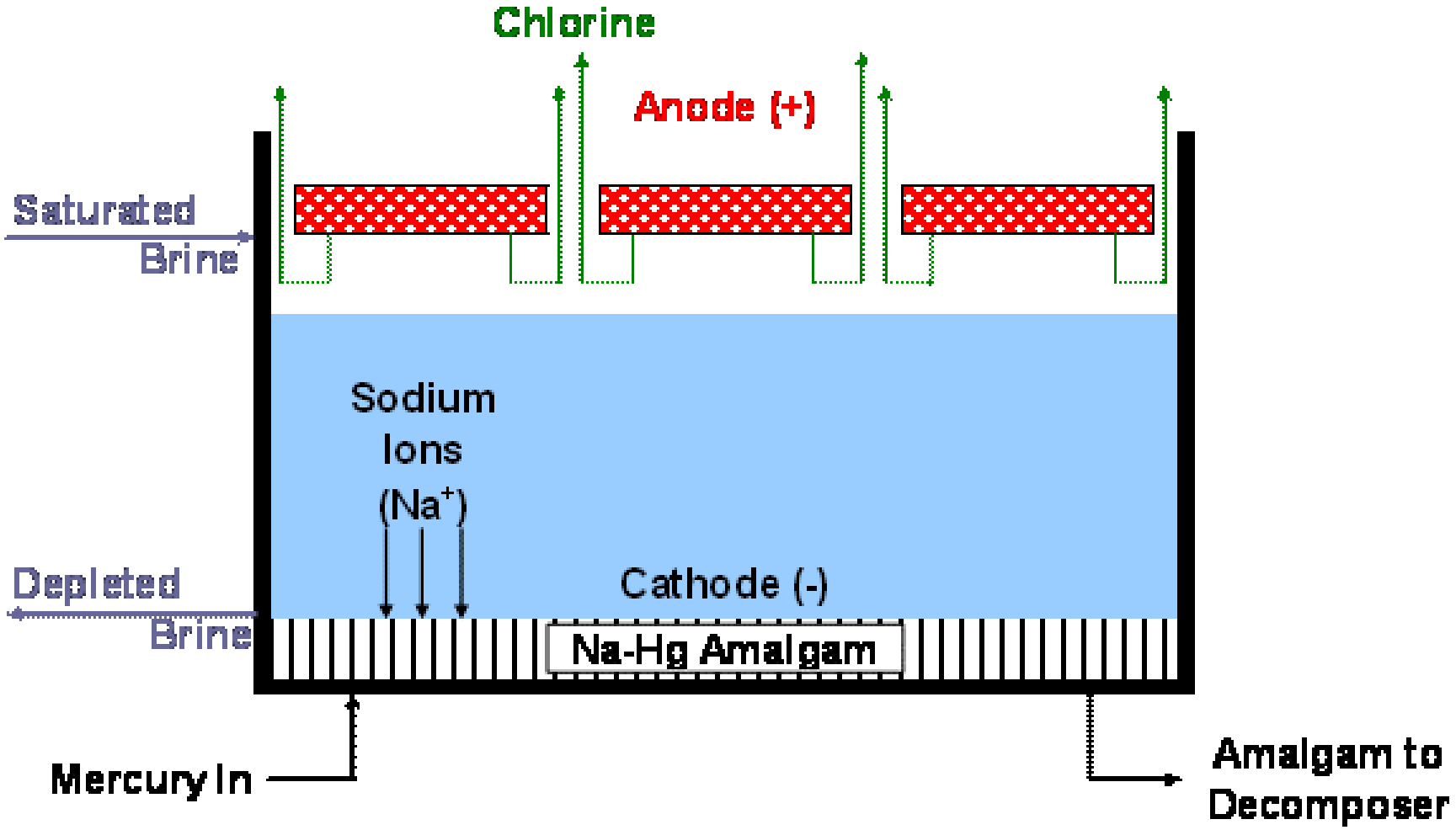


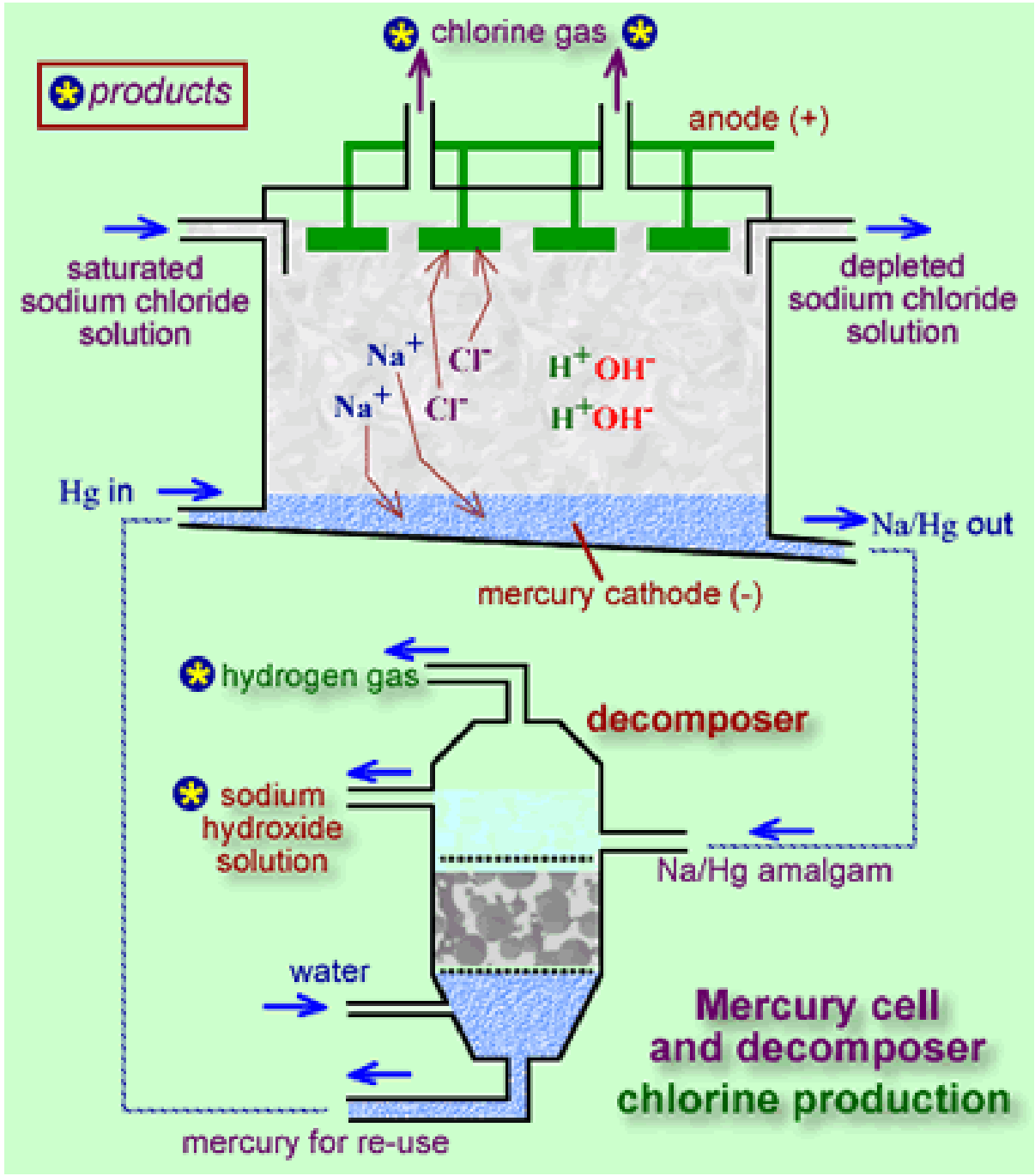
Anode – Titanium
Cathode-Steel

- The diaphragm cell is a rectangular box with metal anodes supported from the bottom with copper-base plates, which carries a positive current.
- The cathodes are metal screens or punch plates connected from one end to the other end of the rectangular tank.
- Asbestos, dispersed as a slurry in a bath, is vacuum deposited onto the cathodes, forming a diaphragm.
- Saturated brine enters the anode compartment and the chlorine gas liberated at the anode during electrolysis, exits from the anode compartment.
- It is saturated with water vapor at a partial pressure of water over the anolyte.

- The sodium ions are transported from the anode compartment to the cathode compartment, by the flow of the solution and by electromigration, where they combine with the hydroxyl ions generated at the cathode during the formation of the hydrogen from the water molecules.
- The diaphragm resists the back migration of the hydroxyl ions, which would otherwise react with the chlorine in the anode compartment.
- In the cathode compartment, the concentration of the sodium hydroxide is ~12%, and the salt concentration is ~14%.
- There is also some sodium chlorate formed in the anode compartment, dependent upon the pH of the anolyte.

Mercury Cell




products
chlorine gas
anode (+)
saturated sodium chloride solution
depleted sodium chloride solution
Na+
Cl-
Na+
Cl-
H+OH-
H+OH-
Hg in
Na/Hg out
mercury cathode (-)
hydrogen gas
decomposer
sodium hydroxide solution
Na/Hg amalgam
water
mercury for re-use
Mercury cell and decomposer chlorine production

Chlorine Processing

- The chlorine gas from the anode compartment contains moisture, by-product oxygen, and some back-migrated hydrogen. In addition, if the brine is alkaline, it will contain carbon dioxide and some oxygen and nitrogen from the air leakage via the process or pipelines.
- Chlorine is first cooled to 60°F (16°C) and passed through demisters to remove the water droplets and the particulates of salt and sodium sulfate.
- The cooled gas goes to sulfuric acid circulating towers, which are operated in series. Commonly, three towers are used for the removal of moisture.
- The dried chlorine then goes through demisters before it is compressed and liquefied at low temperatures. The non-condensed gas, called snift gas, is used for producing hypochlorite or hydrochloric acid.
- If there is no market for hydrochloric acid, the snift gas is neutralized with caustic soda or lime (calcium hydroxide) to form hypochlorite. The hypochlorite is either sold as bleach or decomposed to form salt and oxygen.

Hydrogen Processing

- The hydrogen gas from the chlor-alkali cells is normally used for the production of hydrochloric acid or used as a fuel to produce steam.
- Hydrogen from mercury cells is first cooled to remove the mercury, which is then returned to the cells.
- Occasionally, a secondary treatment is used to remove the trace levels of mercury in the hydrogen via molecular sieve columns.
- The hydrogen gas is then normally compressed.
- If a customer needs nearly pure hydrogen containing low amounts of oxygen, some plants will heat the hydrogen over a platinum catalyst (to remove the oxygen by reacting it with the hydrogen to form water), cool, and compress the diaphragm or membrane cell hydrogen, before supplying it to the customer.
- The heat value in the hydrogen cell gas can be recovered in a heat exchanger via heating the brine feed to the cells.

PULP & PAPER INDUSTRY

PREPARED BY-SATARUPA SAHU

PAPER

- Paper is a sheet material made of fibers which are held together by hydrogen bonds. In wet process, fiber suspension in water is made and it is then made into sheet and dried. Paper making process is generally done on Fourdrinier machine.
- Type of paper:

1.Wrapping paper: bag paper, grease proof paper

2.Tissue paper: cigarette, toilet, towel, napkin

3.Book paper: textbook, lithograph offset

4.Writing paper: bond weight, linen paper

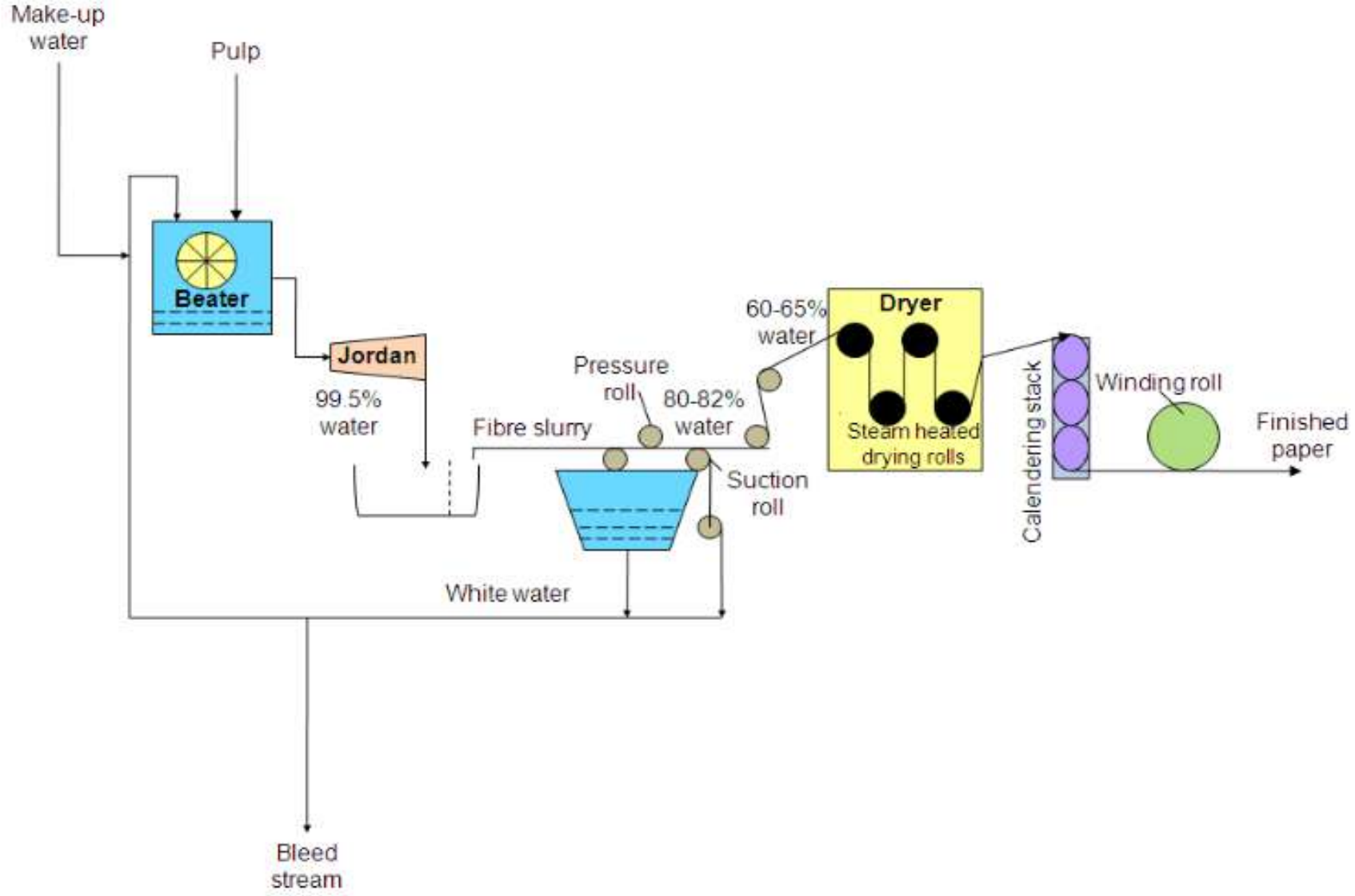
5.Ground wood printing paper: catalog, newsprint, tablet

6.Paperboard: laminated paper stock

- Raw material:

Fibrous raw material:

1. Paper pulp
2. Re-use pulp ------ newspaper, paper board
3. Cellulose pulp----- straw, linen, cotton, rag



Other materials added.

- Inorganic raw material: clay, titanium dioxide, zinc sulfide
- Organic raw material: rosin, glue, waxes, glycerol, dyestuffs

(a) Beater

- Beater mechanically disintegrates the pulp fibers to make paper stronger, uniform, dense, opaque etc.
- It consists of metal blades attached with rotating drum.
- Finely ground fillers (to increase brightness, flexibility, softness and weight) and coloring agents are also added.

(b) Jordan

- It is a conical refiner or Jordan engine.
- Metal bars and stones are set inside.
- Here, pulp is deformed, defibered and dispersed.

(c) Web forming

- 99.5% water fiber slurry are made to run on an endless belt at a speed of 50m/min to 500m/min.
- Pulp fibers are arranged into web. Water is drained out by gravity.
- Shaking motion is provided for better interlocking of fibers on mat.
- White water is collected and it is reused to conserve water and additives and to avoid pollution.

(d) Pressing

- Free water is removed by pressing with pressure roll, water mark roll and suction roll.
- Water content is reduced to 60-65% water.

(e) Drying

- Additional water is removed by smoothing rolls and series of steam- heated metal drying rolls.
- Water is reduced from 60-65% to 5-6%.

(f) Finishing

- Here paper is passed through a series of calendaring rolls for producing smooth paper.
- It is wounded on a large winding roll.

1. How are environmental issues taken care in pulp and paper production?

Ans:• Chip dust is burnt in the boiler to eliminate environmental problems associated with chip dust disposal.

- Bleaching of pulp with chlorine produce dioxins and other undesirable products.So chlorine is replaced by hydrogen peroxide.
- White water is collected and is reused to conserve water & additives and to avoid massive pollution.
- In pulp production process, hot water which is added in second filter is reused in first filter to conserve water.
- Waste-water treatment involving incineration is usually associated with the paper and pulp manufacturing plant. This solves both environmental and energy issues of the pulp and paper plant.

2. What is white water ?

Ans: White water consists of flour (minute fibers) that drains from the wire part of the paper manufacturing machines. It consists of about 0.5 % of pulp.Since beyond a desired viscosity the pulp + water mixture would not provide good quality paper for fixed choice of other operating parameters of the paper manufacturing process, white water needs to be bleed out.

4. Explain how dryer performance can be controlled to obtain good paper quality in quantity ?

Ans: The dryer needs to operate in such a way that the temperatures of different rolls and their speeds be optimized. This is due to the fact that paper with about 60 % water enters the dryer and leaves with about 5 % moisture in the paper. In summary, there exists trade-offs with respect to the roller speed and roller temperature. Subsequently, the roller temperature is controlled using steam flow rate. In other words, both steam flow rate and roller speed contribute towards the dryer efficiency and providing required quality control for the manufactured paper.

5. Why is web forming process supported by the endless belt ?

Ans: A slurry of 99.5 % cannot withstand its own weight and disperses away. Therefore, the endless belt would act as a support system to gradually form the web as the solution progresses ahead.

6.Discuss the economics of paper industry ?

Ans: 1.Shortage of fibrous raw material

2. High price and shortage of chemicals

3. Procurement of plants and equipment

PULP PREPARATION

PREPARED BY-SATARUPA SAHU

Introduction

- Indian paper industry is more than 100 yr old.
- India was the first country in world to use bamboo as a basic raw material for making paper.
- Due to limited forest resources, other raw materials like bagasse, straw, jute etc were identified and are now extensively used.
- Indian paper industry is classified into six group of manufacturing units.

1. Large integrated paper and paperboard unit(based on convectional materials like bamboo, wood etc)
2. Small paper industry (based on non-convectional resources such as bagasse, wheat, rice straw along with the imported pulp)
3. Small paper unit based on waste paper
4. Paper units set up as a part of large integrated sugar complex.
5. Large integrated newsprint manufacturing units
6. Hand-paper producing unit using cotton rags, jute waste, cotton linters etc.

This is under the control of Khadi and Village Industries Commision (KVIC) and produced about 4000 tons of paper in 1989-90.

Raw materials:

Softwood(coniferous and non-coniferous)
Grasses and reeds(lemon, panni, bagasse, barley,reed)
Straws(rice, wheat, barley)
Cotton linters
Hardwoods(accacia, pinus,eucalyptus etc)
Kenaf and mesta

Requirements of Cellulose raw materials

- Ample supply
- Available to pulp mill through out the entire year
- Should not deteriorate in storage
- High yield of quality fiber
- Cost of conversion to paper must be low.
- Quality of paper must be competitive
- Must not have high priority use.

Pulping:

Paper production requires a disintegration of the bulky fibrous materials to individual or small agglomerate fibers. This is called pulping. The ideal fiber should be high grade ,long, high in cellulose content and low in lignin content.

Pulp manufacturing

There are mainly three modes of production of pulp:

(a) Mechanical (b) Chemical (c) Semi chemical

1.Mechanical :

- The ground-wood pulping process grinds wood by pressing it against a rotating surface to grind off small pieces.
- Mainly used for production of newsprint, toilet paper, cheap paper
- Strength and ease of bleaching is not important.

2.Chemical:

- Remove non-cellulose components leaving intact the cellulose fiber.
- Yields somewhere between 45 and 65% of the wood mass.
- Two methods: kraft (sulfate) and sulfite processes.
- Kraft process is applicable to all types of wood species.
- Strength and ease of bleaching is important.

3.Semi-chemical:

- Wood chips are given mild chemical treatment with dilute mixture of sulfite, sulfate, caustic soda, soda ash reagent to soften it for mechanical separation.
- High yield of (65-90)% achieved.

Chemical reactions involved

(i) Digestion (hydrolysis and solubilization of lignin)

R-R’ + NaOH--R”COONa + ROH

R-R’ + Na_2S ----Mercaptans

(ii) Chemical recovery from black liquor

(a) Smelting

2NaR + air----Na_2CO_3 + CO_2 (lignin)

Na_2SO_4 + 2C----Na_2S + 2CO_2 (from R)

(b) Causticizing

Na_2CO_3(aq) + $Ca(OH)_2$(s)---2NaOH(aq) + $CaCO_3$(s)

$CaCO_3$---CaO + CO_2

CaO + H_2O ---$Ca(OH)_2$

Quantitative requirements:

Basic: 1 ton of pulp

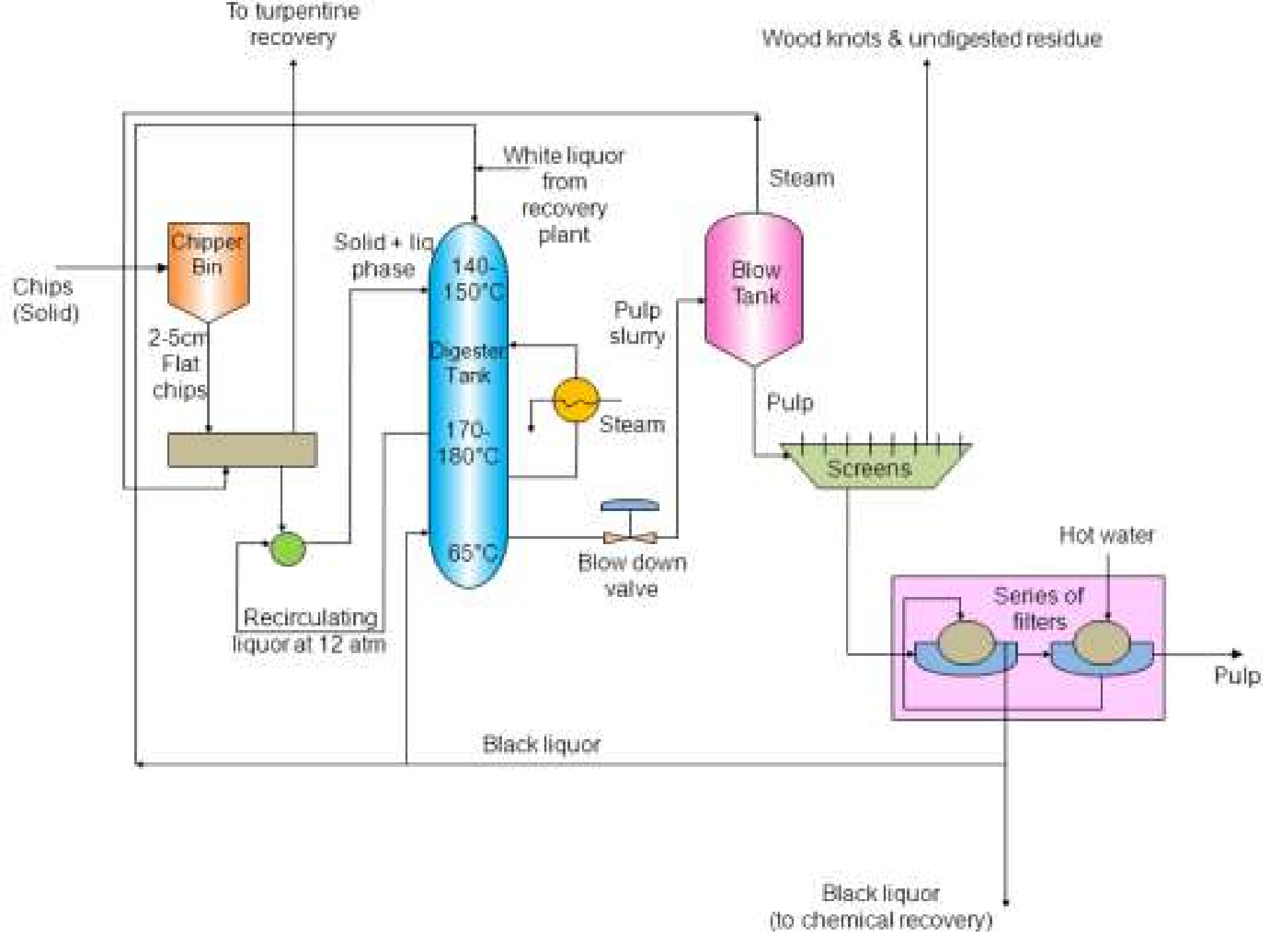
Bamboo or wood---- 2.2-2.5 ton

Lime make up--------- 18 kg

Salt cake make up----- 50 kg

Sulfur---------- 8 kg

Plant capacity ----------100-700 tons/day


To turpentine recovery
Wood knots & undigested residue
White liquor from recovery plant
Steam
Chipper Bin
Chips (Solid)
Solid + liq phase
140-150°C
Digester Tank
170-180°C
65°C
Blow Tank
Pulp slurry
2-5cm Flat chips
Steam
Pulp
Screens
Hot water
Blow down valve
Recirculating liquor at 12 atm
Series of filters
Pulp
Black liquor
Black liquor (to chemical recovery)

(a) Chipper bin:-

Chips are fed in this device.

- Cut logs are conveyed to the chipper where rotary disks with heavy knives reduce the wood to size 2-5cm flat chips.
- Size reduction is done to maximize penetration of process chemicals.

(b) **Digester tower:-**

- Continuous digester tower is 25–30m tall.
- Chips are preheated with volatilizing turpentine and non-condensable gases.
- For controlling digestion temperature, cooking liquor is withdrawn as side streams and circulated through heat exchanger.
- Digestion is done to free lignin and other non-cellulosic content.
- Cooking time is about one and a half hours at 170°C.
- To avoid mechanical weakening of fibres, digested chips are cooled with recycled black liquor.
- Temperature is maintained at 140-180°C and pressure at about 10 atm.
- Bottom temperature is maintained at 65°C

(c) **Blow down valve**:-

- This valve reduces the pressure of the stream from 10atm to 1atm before entering blow tank.

(d) **Blow tank**:-

- When hot pulp slurry is passed to the blow tank, heat is recovered in the form of steam.
- The chips are preheated with this recovered steam.
- The blow tank has high concentration of pulp and low concentration of water.

(e) **Screens**:-

- Pulp is screened so as to remove wood knots and undigested residues.

(f) **Series of filters**

- Pulp is filtered to separate black liquor for chemical recovery plant.
- Black liquor is also recycled back to digester for cooling the digested chips.
- Hot water is added to second filter for better filtration.

Modified process for bagasse:

- Bagasse based raw material contains both dirt and pith. The bagasse based raw material is thin walled and short cells which make poor paper fiber..
- The depiting method by strong mechanical shredding and grinding method made the pith fine powder and fibrous material into small size chips.

Bleaching of pulp

- To produce white paper, the pulp is bleached.
- The chemicals used to bleach pulp must be environment friendly.
- Bleaching with chlorine produces dioxins and other undesirable products.
- So, nowadays pulp is bleached with hydrogen peroxide, ozone, chlorine dioxide, oxygen etc.
- Most commonly hydrogen peroxide with sodium hydroxide which activates peroxide in order to stabilize the peroxide production sodium silicate is used.
- The objective of bleaching is to remove small fractions of lignin that remains after digestion.

Finishing operation of the pulp:

If the plant is of captive paper type ,it should be sent to beater operation which is the first step of paper manufacturing.

Dewatering is done by:

1.Hydro-pressing the pulp at 200-300 atm to form wet lap sheet.

2.Vacuum flash drying of mechanically dewatered pulp to produce a dry fluffy material

3.Extrusion in form of easily handed noodles or pellets containing 30-40% solids for conveying short distance or dried to 90% solid for longer range shipping

Recovery of chemicals:

- Black liquor from blow tank contains (98-99)% of the digestive chemicals which must be recovered in order to avoid water and air pollution.
- Multi-effect evaporator using 5-6 stages of calendria equipment followed by disk evaporator concentrate the liquor from (15-18)% solid to the point where combustion can be substained in a smelting waste heat boiler to 60% solid.
- Organic carbon burned and gives CO2 to produce molten smelt.
- The molten smelt is sent to dissolver where it react with alkali supplied by Na2SO4 to yield green colour liquor solution.
- The insoluble impurities such as unburned carbon are settled out and clear liquid causticized by adding lime. The filtration gives calcium carbonate and white liquor which is sent back to digester.

Byproduct:

Gum(live coniferous tree):Research applications

Tail oil: resin and plastic fields (epoxy resins)

Tarpentine: camphor

Lignin: little use providing steam.

Use of soda process:

- Small tonnage plants involves hydrolysis with NaOH and Na_2CO_3 in 4:1 ratio. This process eliminate the sulfur requirement but increases the cost. Inferior quality product is formed.

What is the technical difference between Sulfate(Kraft) Process and Sulfite Process?

i)Sulfate process is an alkaline process where asthe Sulfite process is an acidic process.

ii) The pulp has to be bleached more in the Sulfate Process as compared to the Sulfite process.

iii) For Sulfate process, digestion time is 1-1.5hrs at temperature 170-176°C and pressure 660-925kPa whereas for Sulfite process, time required is 6-12hrs at temperature 125-160°C and pressure 620-755kPa.

iv) Raw materials are less significant and fibers have better strength properties in Sulfate process.

Why does the black liquor enters at various sections of the digester ?

i)Black liquor is recycled to the base of digester tower for cooling digested chips so as to avoid mechanical weakening of fibres.

ii)It is withdrawn as side stream from digester and circulated through heat exchanger to reheat and control the digester temperature.

iii)It is also used along with white liquor to adjust solid -liquid ratio in the digester entry section. Thereby, desired operating conditions of the digester are met.

Pulping Process	Typical Composition of Fresh Pulping (Cooking) Liquor	Waste organic Products Of Pulping
Kraft (Sulfate, Alkaline)	• 12.5 wt% Solution of NaOH, Na_2S, Na_2CO_3 - NaOH 58.6% - Na_2S 27.1% - Na_2CO_3 14.3%	• Lignin & Lignin-derived Products, e.g., - Alcohols - Acids - Mercaptans
Sulfite (Acid)	• 7 wt% Solution of SO_2 As: - H_2SO_3 (4.5 wt%) - $Mg(HSO_3)_2$ (2.5 wt%) ($Mg(OH)_2$, (Na+), NH_4OH, $Ca(HSO_3)_2$ can also be used)	• Lignin & Lignin-derived Products, e.g., - lignosulfonic acids and metal (e.g., Mg, Ca) salts thereof

CEMENT MANUFACTURING

It involves the following steps

1. Mixing of raw material
2. Burning
3. Grinding
4. Storage and packaging

1. Mixing of raw material

Mixing can be done by any one of the following two processes

(a) Dry process

Lime stone or chalk and clay are crushed into gyratory crusher to get 2-5 cm size pieces. Crushed material is ground to get fine particle into ball mill or tube mill. Each material after screening stored in a separate hopper. The powder is mixed in require proportions to get dry raw mix which is stored in silos (storage tank) and kept ready to be fed into the rotary kiln. Raw materials are mixed in required proportions so that average composition of the final product is maintained properly.

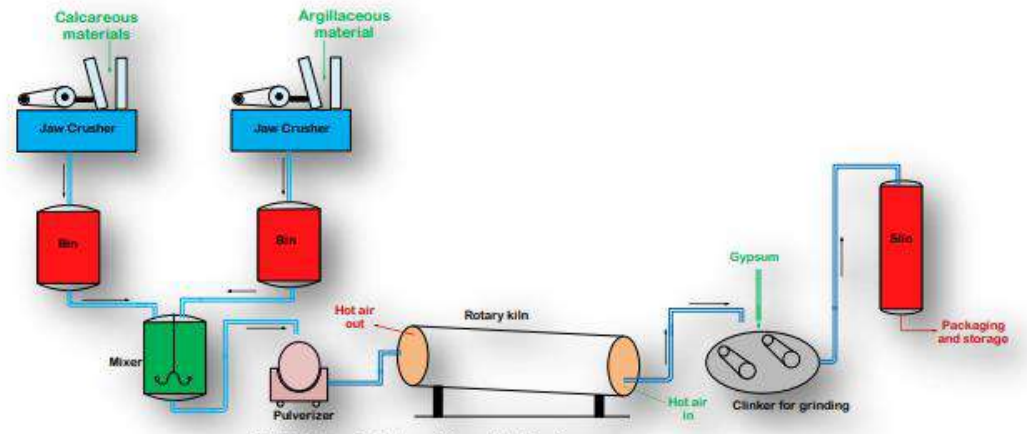


Figure: Manufacturing of Cement by Dry Process

(b) Wet process

Raw materials are crushed, powdered and stored in silos. The clay is washed with water in wash mills to remove adhering organic matter. The washed clay is stored separately. Powdered lime stone and wet clay are allowed to flow in channel and transfer to grinding mills where they are intimately mixed and paste is formed known as slurry. Grinding may be done either in ball mill or tube mill or both. Then slurry is led to correcting basin where chemical composition may be adjusted. The slurry contains 38-40% water stored in storage tank and kept ready for feeding to a rotary kiln.

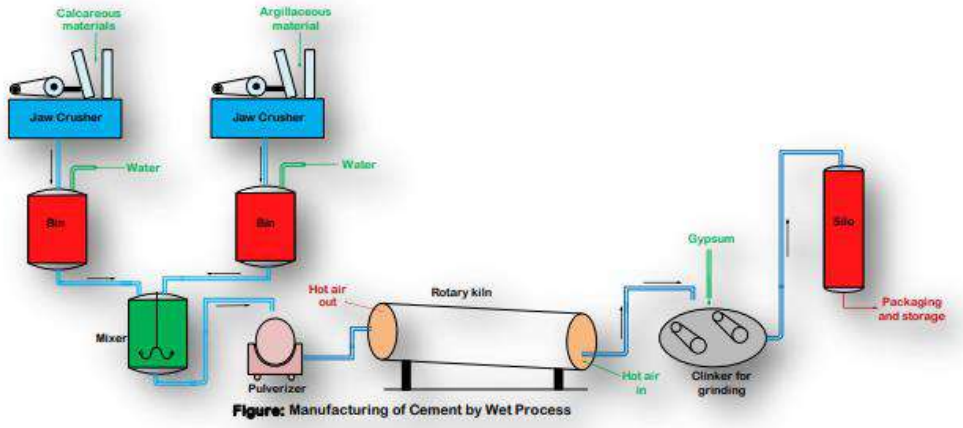


Figure: Manufacturing of Cement by Wet Process

2. Burning:

Burning is carried out in rotary kiln which rotating at 1-2 rpm at its longitudinal axis. Rotary kiln is steel tubes having diameter in between 2.5-3.0meter and length varies from 90-120meter. The inner side of kiln is lined with refractory bricks. The kiln is rested on roller bearing and supported columns of masonry or concrete in slightly inclined position at gradient of 1 in 25 to 1 in 30. The raw mix or corrected slurry is injected into the kiln from its upper end. Burning fuel like powdered coal or oil or hot gases are forced through the lower end of the kiln so long hot flame is produced. Due to inclined position and slow rotation of the kiln, the material charged from upper end is moving towards lower end (hottest zone) at a speed of 15meter/hour. As gradually descends the temperature is rises. In the upper part, water or moisture in the material is evaporated at 4000C temperature, so it is known as drying zone. In the central part (calcination zone), temperature is around 10000C, where decomposition of lime stone takes place. After escapes of CO2, the remaining material in the forms small lumps called nodules.

$CaCO_3 \rightarrow CaO + CO_2$

The lower part (clinkering zone) have temperature in between 1500-17000C where lime and clay are reacts to yielding calcium aluminates and calcium silicates. This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as clinkers. The size of the clinker is varies from 5-10mm.

$2CaO + SiO_2 \rightarrow Ca_2SiO_4$ (dicalcium silicate (C2S))

$3CaO + SiO_2 \rightarrow Ca_3SiO_5$ (tricalcium silicate (C3S))

$3CaO + Al_2O_3$ $Ca_3Al_2O_6$ (dicalcium aluminate (C2A))

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10}$ (tetracalcium aluminoferrite(C4AF))

As clinkers are coming from burning zone, they are very hot. The clinkers are cooled down by air admitting counter current direction at the base of rotary kiln. Resulting hot air is used for burning powdered coal or oil and cooled clinkers are collected in small trolleys or in small rotary kiln.

3. Grinding

Cooled clinkers are ground to fine powder in ball mill or tube mill. 2-3% powdered gypsum is added as retarding agent during final grinding. So that, resulting cement does not settle quickly, when comes in contact with water. After initial set, cement - water paste becomes stiff, but gypsum retards the dissolution of tri-calcium aluminates by forming tricalcium sulfoaluminate which is insoluble and prevents too early further reactions of setting and hardening.

$3CaO.Al_2O_3 + xCaSO_4.7H_2O \rightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$

4. Storage and packaging

The ground cement is stored in silos, from which it is marketed either in container load or 50kg bags.

Constituents of cement

Components	Content in clinker	Content in raw meal	Impurity limits
	Wt. %	Wt. %	Wt. %
CaO	63.8-70.1	~43	
SiO_2	19.7-24.3	~14	
Al_2O_3	3.8-6.8	~4	
Fe_2O_3	1.3-1.6	~5	
MgO	0.0-4.5		5
SO_3	0.2-2.1		4.5
K_2O	0.3-1.8		0.8 as $(NaO_2)_e$*
Na_2O	0.0-0.3		0.8 as $(NaO_2)_e$*
Mn_2O_3	0.0-0.7		0.5
TiO_2	0.2-0.5		
P_2O_5	0.0-0.3		0.2
CO_2	0.0-0.8		
H_2O	0.0-1.1		
Cl_2			0.1
LOI	0.1-1.6	~34	3

*$(NaO_2)e$, the effective amount of alkali, is calculated as $0.658(\%K_2O) + \%Na_2O$.

Table :1 Composition of Portland cement clinker and raw meal and impurities limit

Additives used in cement industries

- Cement-modification improves the properties of certain silt clay soils that are unsuitable for use in subgrade construction. The objectives may be to decrease the soil‘s cohesiveness (plasticity), to decrease the volume change characteristics of expansive clay, to increase the bearing strength of a weak soil, or to transform a wet, soft subgrade into a surface that will support construction equipment.
- Tricalcium Silicate (C_3S): Hardens rapidly and is largely responsible for initial set and early strength. In general, the early strength of Portland cement concrete is higher with increased percentages of C_3S.
- Dicalcium Silicate (C_2S): Hardens slowly and contributes largely to strength increases at ages beyond 7 days.
- Tricalcium Aluminate (C_3A): Liberates a large amount of heat during the first few days of hardening and together with C_3S and C_2S may somewhat increase the early strength of the hardening cement. It affects setting time.
- Tetracalcium Aluminoferrite (C_4AF): Contributes very slightly to strength gain. However, acts as a flux during manufacturing. Contributes to the colour effects that makes cement gray.



UNIT-III
FERTILIZERS

PREPARED BY-SATARUPA SAHU

Nutrients

- There are 35 nutrients for a plant growth, but out of them 16 elements are highly essential for plant growth.

Natural nutrients (3)

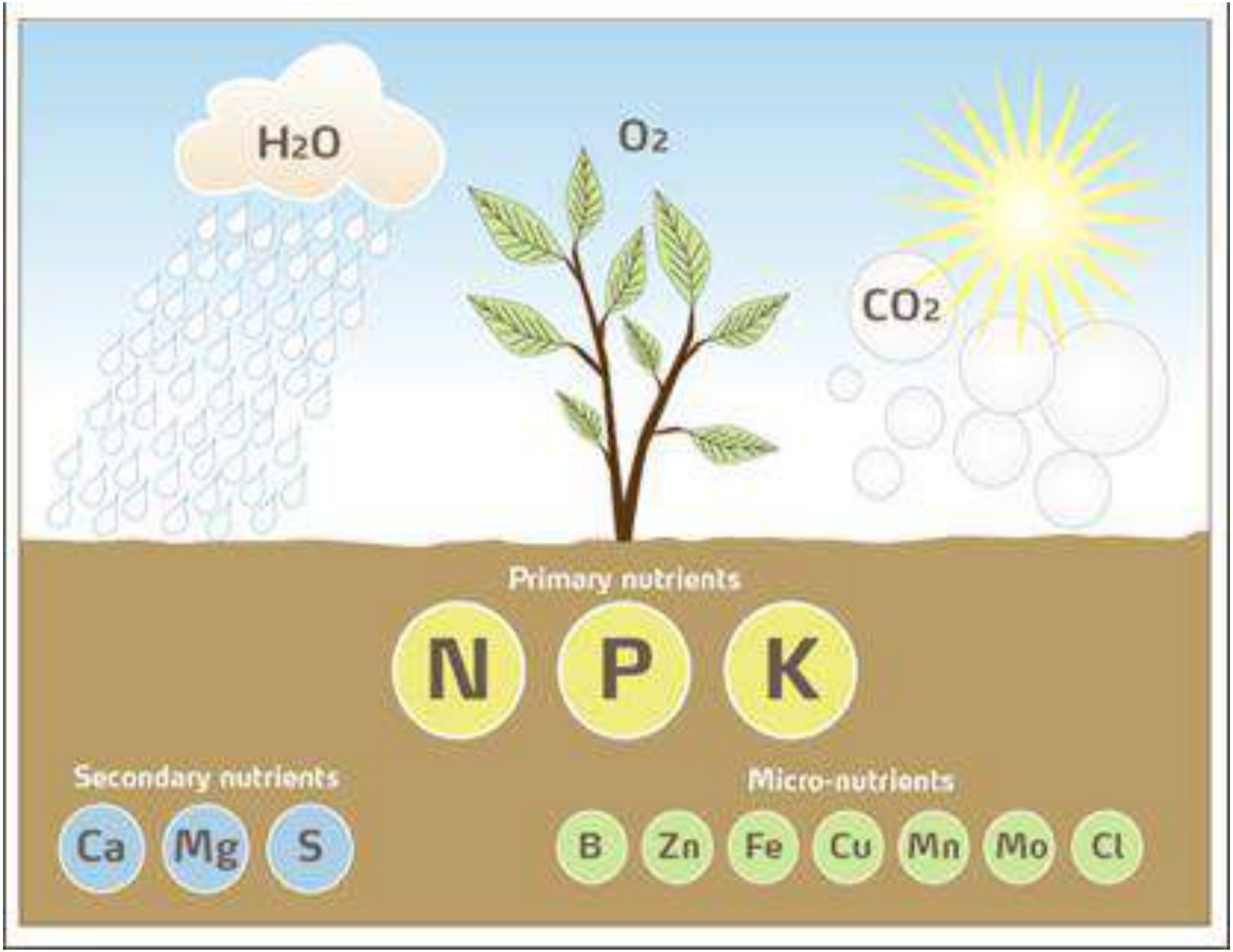
- Provided by air and water
- C,H_2,O_2

Micro nutrients (7)

- Provided by soil
- Mn, Mo, Cu, B, Zn, Fe, Cl .
- Required in minute quantity.

Macro nutrients (6)

- Provided by soil, required in large quantity
- Primary: N_2,P,K.
- Secondary: Ca,Mg,S


H2O
O2
CO2
Primary nutrients
N
P
K
Secondary nutrients
Ca
Mg
S
Micro-nutrients
B
Zn
Fe
Cu
Mn
Mo
Cl

- There are several other nutrients required in minute quantities such as Ru, St, Cr, Ni, As etc.
- These are called potential or beneficial micro nutrients.

Function of these nutrients

- Stimulate process of metabolism
- Growth of plant
- Increase the content of valuable plant components such as starch of potato, sugar of beet, fruits, berries etc.
- Increase the resistance to frost, drought, disease.

Why Fertilizers

- After repeated cultivation, a stage occurred where the productivity of soil is too much reduced due to deficiency of nutrients.
- So in order to preserve the productivity, we need to add elements in form of compounds which are known as fertilizers.
- The need for fertilizing a land:

1. To supplement what has been eaten up by the plant.
2. To supply them an additional tonic and good food for their growth.
3. To maintain the pH of the soil in the vicinity of 7-8 and thereby facilitate optimum growth and health.

Fertilizers were in the elemental form

They would be difficult to handle:

Elemental nitrogen (N)–a colorless inert gas that could drift off into the air.

Elemental phosphorus (P)–catches fire spontaneously when exposed to the air. It is actually poisonous to plants in concentrated forms.

Elemental potassium (K)–placed in contact with water it will catch fire, explode and decompose into a strong caustic solution.

Nitrogen (N)

1. Promotes rapid vegetative growth (leaf and stems) hastening recovery after mowing and imparting vigor to the turf.
2. A vital element in the formation and function of chlorophyll–the key ingredient imparting dark green color.
3. Synthesizes amino acids which in turn form protein.
4. Regulates the uptake of other nutrients.
5. Basic ingredient of vital compounds - Nucleic acid and enzymes.

Excess

1. Delay ripening
2. Leaves become thick and leathery and in some case crinkled.
3. Detoriates the quality of food.
4. Delay the reproductive growth.

Deficient

1. Yellow and light green colour, remain stunted
2. Leaves, young fruits drop prematurely.
3. flower bud becomes pale.
4. Delay growth rate, reproductive growth.

Phosphorus (P)

1. Stimulates early root formation and growth–gets plants off to a good start and forms a root filter system in the soil to efficiently pick up the other available plant nutrients and water. Improves the strength and stamina of the plant.
2. Hastens maturity (conversion of starch to sugar).
3. Stimulates blooming and seed development.
4. Causes energy transformation and conversion processes in which sugars are converted to hormones, protein and energy to grow new leaves and fruit.
5. Forms nucleic acids (DNA and RNA).
6. Vital for photosynthesis (greening for plants).
7. Essential for cell division.

Excess

1. Profuse root growth
2. Leaves become thick and leathery and in some case crinkled.
3. Causes trace elements deficiency like Zn, Fe
4. Unlike N_2, it is not harmful in excess.

Deficient

1. Root and shoot growth is restricted.
2. Tillering of cereal crop decreases as a result of low yield.
3. Potato tubers have shown brown lessions.
4. Premature ripening of crops.

Potassium (K)

1. Aids in the development of stems and leaves.
2. Increases disease resistance and hardiness which helps wearability.
3. Strengthens cell walls, causing grass to stand up and reduces lodging.
4. Affects water intake by plant cells–plants with inadequate potassium may wilt in the presence of ample moisture.
5. Acts as a catalyst in Iron uptake.
6. Essential to the formation and translocation of protein, starches, sugar and oil–improving the size and quality of fruit, grains and tubers.

Deficiency

- Causes cholosis i.e yellowing of leaves and leaf scorch.
- Dying back tips of shoots, the older leaves show the symptoms first.
- Potato shows an abnormal dark green colour of folliage followed by brownish.
- Blackening of tuber and decrease of the photosynthesis process.

Secondary plant nutrients

- **Calcium (Ca)**

1. Calcium is an essential part of cell wall structure and must be present for the formation of new cells.
2. Deficiency of calcium causes weakened stems and premature shedding of blossoms and buds.

- **Magnesium (Mg)**

1. Essential for photosynthesis (greening of plant).
2. Activator for many plant enzymes required in growth process.

- **Sulfur (S)**

1. A constituent of three amino acids and is therefore essential in the formation of protein.
2. Helps maintain green colour in plants.
3. Improves alkaline soils.
4. Helps compacted soils–making them loose and allowing better water penetration.

Micro nutrients

- Iron (Fe)

1. Yellowing of grass (Iron Chlorosis) is often due to iron deficiency. Iron is required for the formation of chlorophyll in the plant cell.
2. It serves as a catalyst for biological processes such as respiration, symbiotic fixation of nitrogen and photosynthesis.
3. Applications of iron can correct iron deficiency, but it may be temporary in high pH soils, due to tie up with calcium.

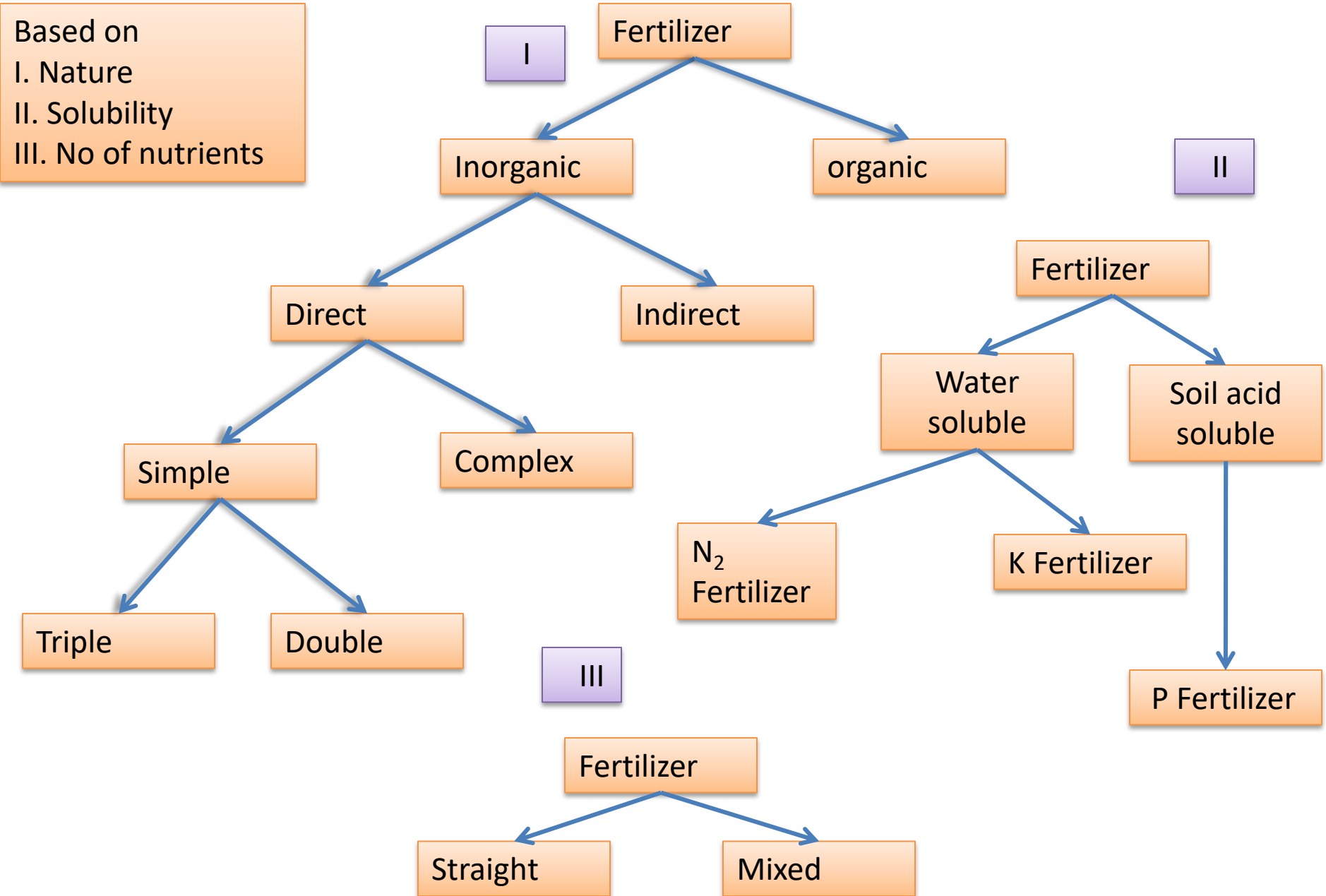
- Zinc (Zn)

1. It is a part of auxins and controls the synthesis of indoleacetic acid which regulates growth compounds.
2. Zinc also affects the intake and efficient use of water by plants.

- Manganese (Mn)

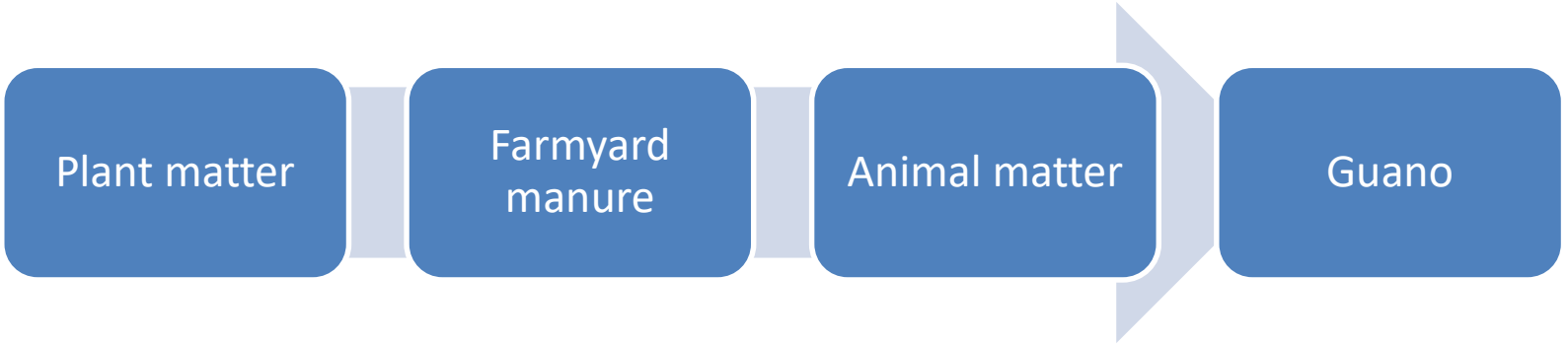
1. Manganese serves as an activator for enzymes in plants. Without Manganese, the plants cannot use the iron which they have absorbed.
2. It assists the iron in chlorophyll formation which causes yellowish turf to green up.

Classification of fertilizers

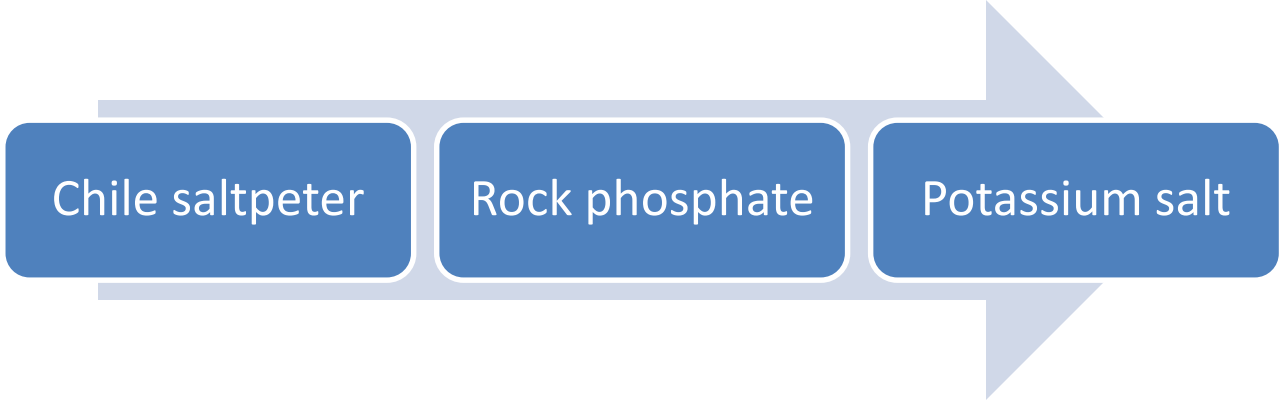


Sources of fertilizer

ORGANIC	1.Cotton seed meal 2.Lineseed meal 3.Caster cake	1.Cow dung 2.Sheep dung 3.Human excretion	1.Powdered dry fish 2. Dry blood from slaughter house	Mixture of bird excretion fish refuge

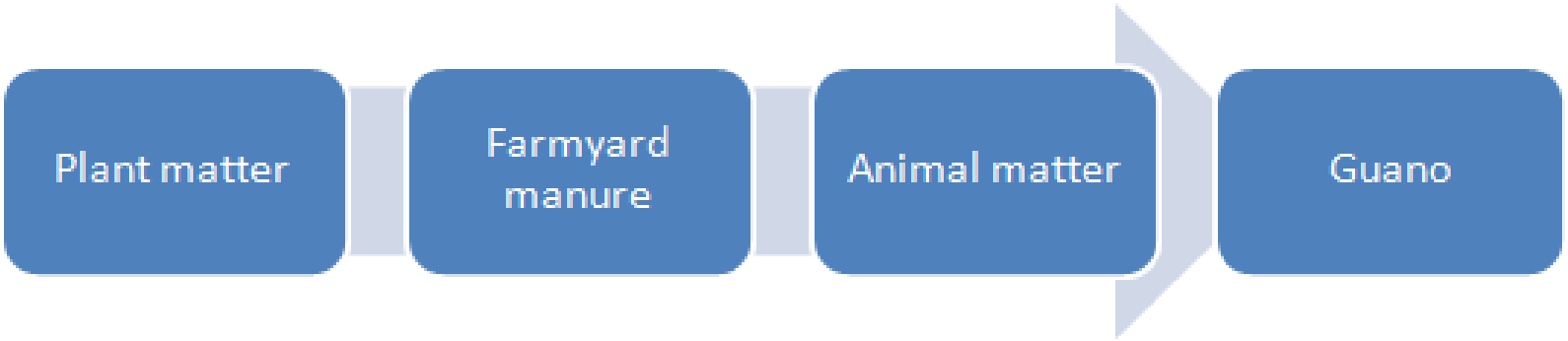


IN-ORGANIC

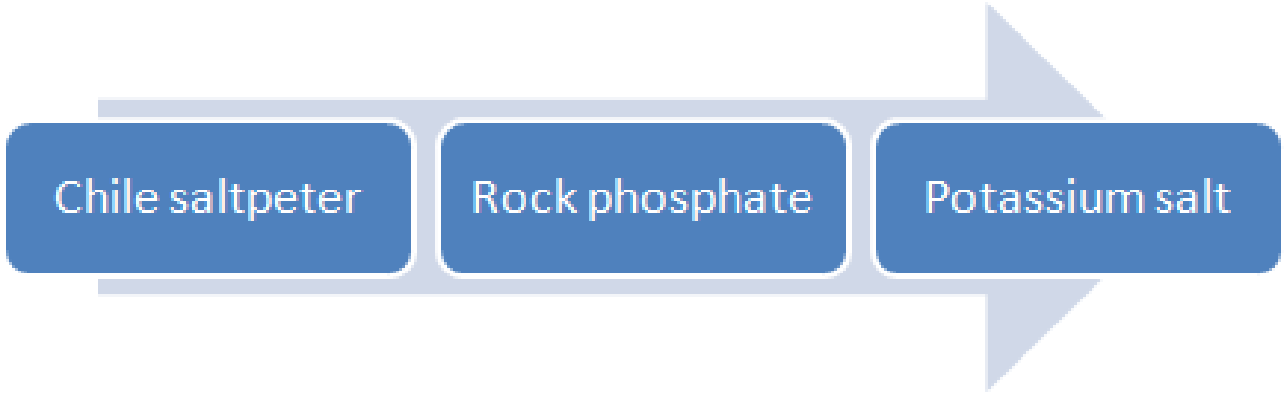


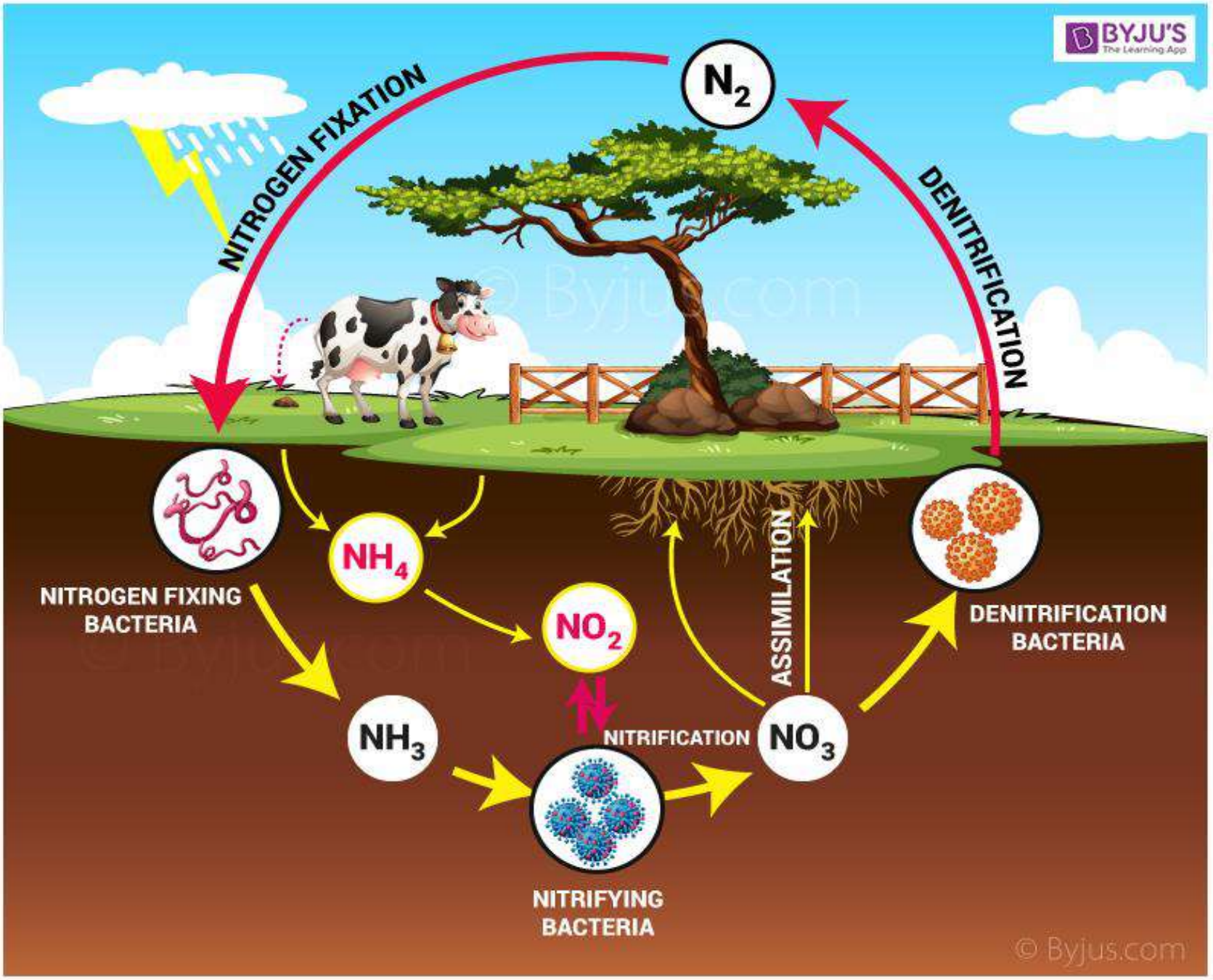
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IN-ORGANIC





Nitrogen Fixation

Fertilizers

There are basically six different types of nitrogen fertilizers:

1.Ammonium Nitrate
2.Ammonium Chloride
3.Ammonium Phosphate
4.Ammonium Sulphate
5.Urea

There are basically two different types of phosphate fertilizers:

1.Rock phosphate
2.Superphosphate

- **1.Single superphosphate** containing 16 to 20% phosphoric acid
- **2.Dicalcium phosphate** containing 35 to 38% phosphoric acid
- **3.Triple superphosphate** containing 44 to 49% phosphoric acid.

There are basically two different types of potassium fertilizers:

1.Muriate of potash (Potassium chloride)
2.Sulphate of potash (Potassium sulphate).

Ammonium Nitrate

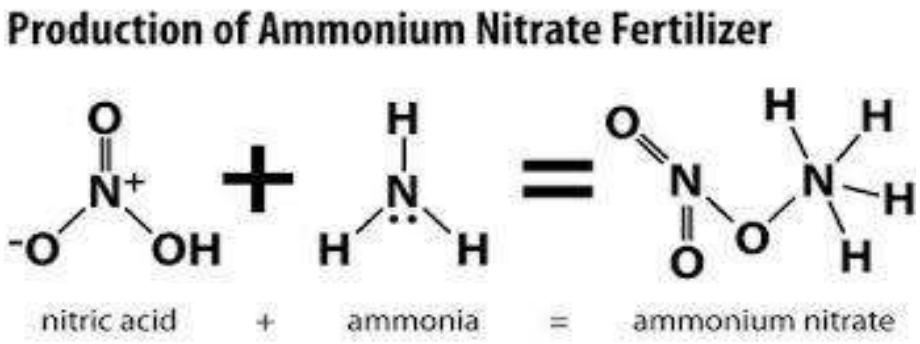
- Ammonium Nitrate is in the first place a nitrogenous fertilizer representing more than 10% of the total nitrogen consumption worldwide.
- It is more readily available to crops than urea. In the second place, due to its powerful oxidizing properties is used with proper additives as commercial explosive.

Property:

Percent of N_2		33.5 %	
Solubility, g/100g		118 at 32^o F, 843 at 212^o F	
Melting point, ^{o}C		170.4	
Particle size		95%- 6 mesh, 5%-16 mesh	
Hygroscopic point		59.4	
Sp.gravity,20/4 ^{o}C		1.725	
Bulk density,lb/ft^3		40-62	
Crystal state	**State**	**Temp, ^{o}C**	**System**
	1	170 to 125	Cubic
	2	155 to 84	Tetragonal
	3	84 to 32	Rhombic
	4	32-18	Rhombic
	5	Below 18	Tetragonal

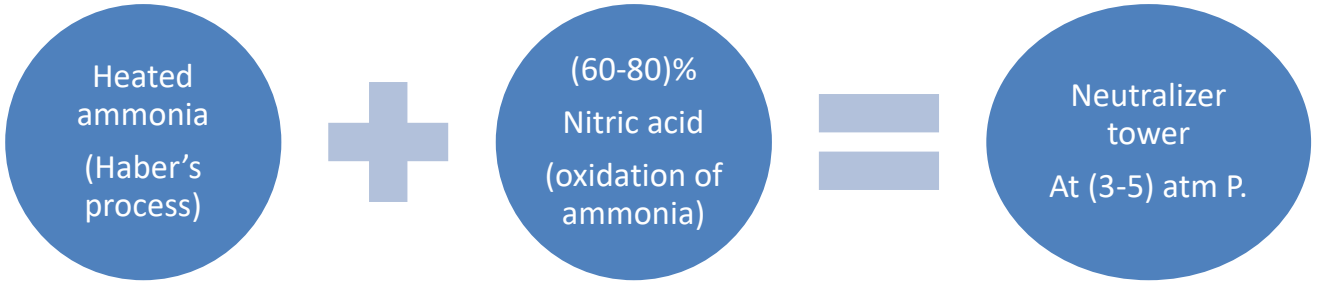
Method of production

1. Crystalisation
2. Flaking
3. Prilling (latest and important method)
    1. Neutralisation
        2. Evaporation
            3. Prilling
                4. Drying and Finishing
                    a. Short tower prilling
                        b. Stengel process
                            c. Bamag process



- Practically all nitric acid made by oxidising ammonia and absorbing the resultant nitrogen oxides in water.
- Modern plants make acid of (60-70)% concentration. Older plants are still using a concentration of about 45%.
- **Raw material**: Ammonia and Nitric acid

1.Neutralisation:



The neutralisation reaction is exothermic and provide a higher yield of heat of reaction because of preheating of reactants before mixing, efficient utilization of heat of Rx^n.

2.Evaporation:

Solution obtained contained about **83%** ammonium nitrate is sent to **heater** followed by **vacuum evaporator** where the concentration is increased to 95% from 83%.

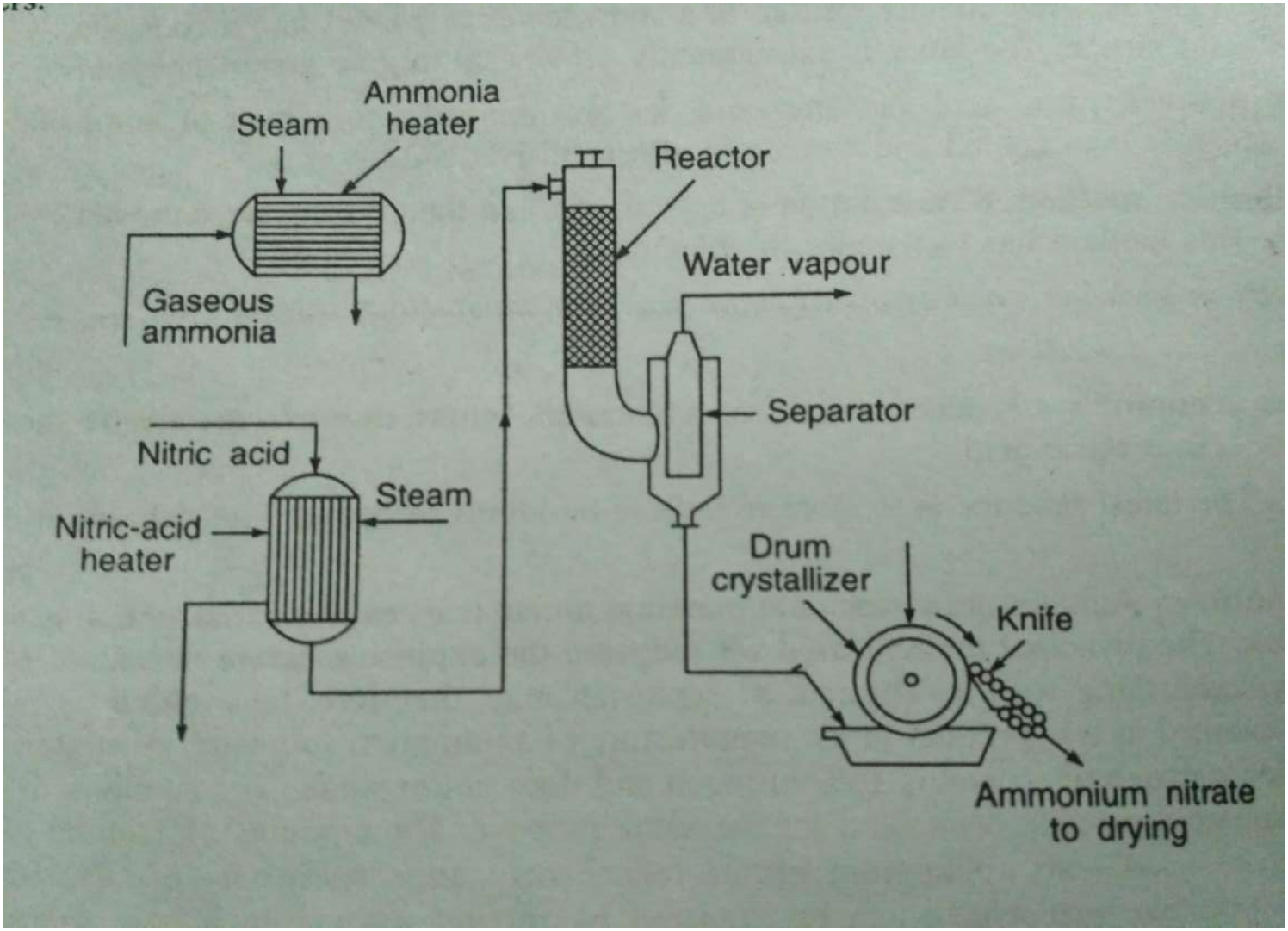
3. Prilling:

The concentrated solution is sprayed through the spray nozzle into the prilling tower(up to 185 ft height) in such as a way that the **liquid is broken into drops of uniform size** and ultimately cooled and solidified at the bottom of the tower.

4.Drying and finishing:

The drying temp should be low in order to avoid melting. One method is to cooled it to 90^oF and then remaining moisture is removed in second dryer.

1.Short tower prilling: Conc of 99.5% can be achieved by usual method without using dryer, but using strong solutions. The quality is reduced.



Flow sheet of anmmonium nitrate no evaporation manufacturing process

2.Stengel process: Super heated ammonia vapour (145^{o} C) and Conc nitric acid(170^{o}C) are reacted in *packed tower*, followed by the separation of stream in a *cyclone*. The remaining water can be removed from melt by using the *short prilled tower* or througha *cold steel*.

3. Bamag process: nitric acid and ammonia gas are pumped into a top of a distillation chamber where ammonium Nitrate at about 150^{o} C which is then converted into ammonium nitrate granules.

Crystallisation:

83% solution is crystallised and crystals are removed by centrifuging and then dried. There are two disadvantages such as poor physical conditions and difficulty in growing of crystals of adequate size.

Explosive nature:

The main chemical hazards associated with ammonium nitrate are fire, decomposition and explosion. So it is mixed with $CaCO_3$ or ammonium sulphate. Mixture of ammonium nitrate and calcium carbonate is called as the nitrochalk.

Hydroscopic nature of NH_4NO_3 make cakes when exposed to air. So calcium and magnesium nitrate ,phosphate are added to prevent this condition.

Ammonium Chloride

Percent of N_2	26 %
Solubility, g/100g	Solubility in water, alcohol
Melting point, ^oC	338^0C (decomposes)
Molecular weight	53.491gm/mole
Hygroscopic point	59.4
Sp.gravity,20/4 ^oC	1.725
Bulk density	1.527gm/ml
Appearance	White solid, hygroscopic
NATURE	Acid forming fertilizer

- **Sal ammoniac** is a name of the natural, mineralogical form of ammonium chloride.
- The mineral is commonly formed on burning coal dumps, due to condensation of coal derived gases.
- It is also found around some types of volcanic vent

Comparison with other Fertilizers

- Ammonium chloride contains 26% nitrogen, where as ammonium sulfate contains 20.5%.
- Ammonium chloride is relatively cheaper than ammonium sulfate and available as a by-product from important industries such as the Solvay soda industry and potassium sulfate industry.
- Nitrification of ammonium chloride is less rapid than that of urea or ammonium sulfate. Therefore, nitrogen losses are lower and yields, higher.
- However, ammonium chloride is a highly acid forming fertilizer and the amount of calcium carbonate required to neutralization.
- Further, it has lower nitrogen content and higher chloride content compared to urea and ammonium nitrate, making it harmful to some plants such as chilies, potatoes and tobacco .
- The corrosive action due to high degree of hydrolysis and cake forming tendency made it difficult to store.

Uses

- As fertilizer.
- Producing low temperatures in cooling baths. Ammonium chloride solutions with ammonia are used as buffer solution.
- Ingredient in fireworks, safety matches and contact explosives.
- As electrolyte in zinc carbon batteries.
- As a thickening agent in hair shampoo, and as glue in plywood.
- Textile and leather industry as dyeing, tanning, printing ingredients.
- As flux in preparing metals to be tin coated, galvanized or soldered.
- As a flux by cleaning the surface of work pieces by reacting with the metal oxides at the surface to form a volatile metal chloride.
- As food additive.

Manufacturing

Manufactured by two processes

- Direct reaction
- Duel salt process

1. Direct reaction : This process is not widely used.

Raw materials

Basis: 1000kg Ammonium chloride

Ammonia = 323kg Hydrochloric acid (50%) = 215kg

Reaction : $NH_3 + HCl$ --------- NH_4Cl

Manufacture

- Gaseous ammonia is bubbled into 30 % hydrochloric acid solution in a reactor.
- The reaction is controlled by addition of water.
- The resulting solutions are then reacted with ammonia.
- The slurry from the saturator is centrifuged and the crystals are washed with water and dried with warm air in a manner to that used in ammonium sulfate.

Engineering aspects

- It is necessary to ensure that the reactors have an acid resistant lining and they must not be operated above certain temperatures during the drying phase as NH_4Cl to tends dissociate. In practice, the salt is dried by circulating air or under low pressure.

Duel salt process

Raw materials

Basis: 1000kg of ammonium chloride

Ammonia (30%) = 1000kg CO_2 = 840kg NaCl = 1115kg Water = 350kg

Reaction

- $NH_3 + H_2O + CO_2$ ---------- NH_4HCO_3
- $NH_4HCO_3 + NaCl$ ---------- $NaHCO_3 + NH_4Cl$

Process:

- The most widely used process for producing ammonium chloride is the salting out process for soda ash manufacture or modified Solvay's process.
- In the process, ammonia(30%) is treated with carbon dioxide in a carbonating tower to form ammonium bicarbonate.
- The ammonium bicarbonate reacts with sodium chloride to give sodium bicarbonate and ammonium chloride.
- The bicarbonate is separated by filtration, washed and calcined to produce sodium carbonate.
- In the modified Solvay‘s process, ammonium chloride in the solution, after separation of the sodium bicarbonate, is salted out by ammoniating the solution, cooling below 15^0C and adding washed sodium chloride.

- The precipitated ammonium chloride is centrifuged, washed and dried to about 0.25% free moisture in a rotary drier at 105^0C form fine crystals by roll compaction.
- Large ammonium chloride crystals of 2 to 3 mm size have been developed by cooling, nucleation and crystallization, under closely controlled conditions in specially designed vessels.
- After the removal of ammonium chloride, the liquor is reammoniated to start a new cycle of operations.
- As the demand for soda ash is comparatively lower than that for nitrogen fertilizers, ammonium chloride from this source is not likely to meet the nitrogen fertilizer needs.

Handling and storage

- Crystalline ammonium chloride is free flowing and non-abrasive and does not have any problem in handling and storage.
- As it is susceptible to caking at high humidity and has slightly acidic reaction, ammonium chloride has to be bagged in HDPE or jute bags lined with polyethylene film.

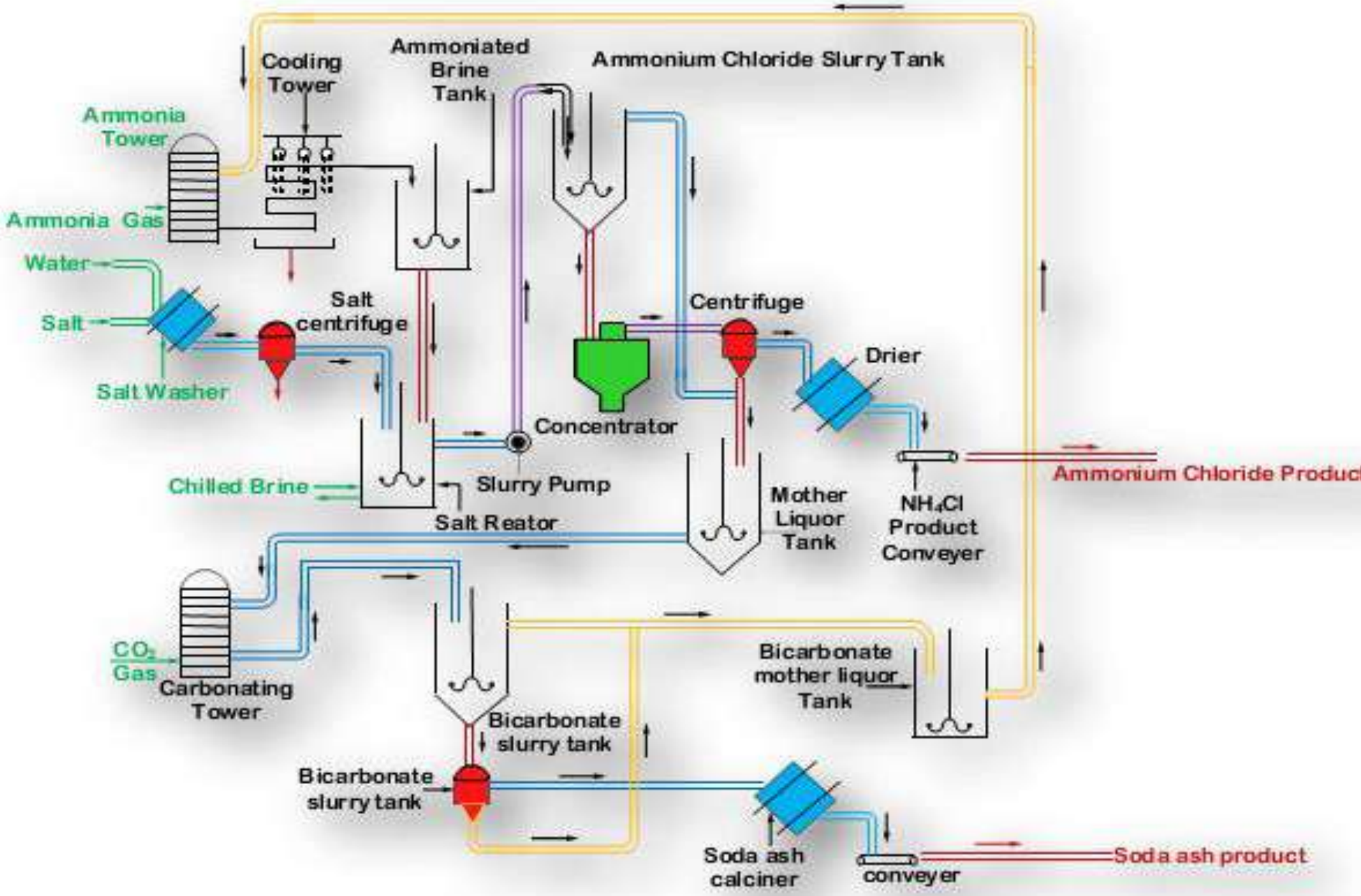


Figure: Manufacturing of Ammonium Chloride by dual salt process

AMMONIUM PHOSPHATE

Percent of N_2	26 %
Solubility, g/100g	Solubility in water
Melting point, ^oC	190^0C (decomposes)
Molecular weight	115.03gm/mole
Odour	oderless
Bulk density	1.803gm/ml
Appearance	White crystal
pH	4-4.5
Grades	Monoammonium phosphate (MAP, $NH_4H_2PO_4$) Diammonium phosphate (DAP, $(NH_4)_2HPO_4$)

- The standard commodity grade of diammonium phosphate is 18-46-0.
- Pure and completely soluble ammonium phosphates are used mainly as liquid fertilizers.
- DAP is unstable at temperatures above 150^0C while monoammonium phosphate remains stable even at much higher temperatures.

Uses:

- Used as a high effective non-chloride N, P compound fertilizer in agriculture. It contains totally 73% fertilizer elements ($N+P_2O_5$).
- In flame-proofing, plant nutrient solutions
- Used in manufacturing of vinegar, yeast foods, bread improvers.
- Used in buffer solutions and in analytical chemistry
- Used as a fire prevention agent for fabric, timber and paper
- As a fermentation agent, nourishment agent.

Types of ammonium phosphate:

1.Monoammonium phosphate (MAP, $NH_4H_2PO_4$)

2.Diammonium phosphate (DAP, $(NH_4)_2HPO_4$)

- Mono-ammonium phosphate is manufacture by reacting **ammonia** with **phosphoric acid**, centrifuging and drying in a rotary dryer.
- Diammonium phosphate requires two-stage reactor system in order to prevent loss of ammonia. The granulation process followed by neutralization is completed in rotary dryer, which is heated by a furnace using fuel.

1. Mono-ammonium phosphate (MAP)

- Anhydrous ammonia added to liquid phosphoric acid gives mono ammonium phosphate (MAP).
- It is a fertilizer or fertilizer intermediate with high P_2O_5 content of about 55% and nitrogen content 11-12%.

2. Diammonium phosphate (DAP)

- With more ammonia, technical grade diammonium phosphate (DAP) containing 16 to 18% nitrogen and 20 to 21 % phosphorus (46% P_2O_5) is formed.

MANUFACTURE

Raw Materials

Basis: 1000kg of Diammonium phosphate

Ammonia= 200kg , Phosphoric acid = 465kg , Electricity = 200MJe ,Fuel = 525MJ

Reactions

- $NH_3 + H_3PO_4$ ---------- $NH_4H_2PO_4$
- $NH_3 + NH_4H_2PO_4$ ---------- $(NH_4)_2HPO_4$

The two principal steps are

a) Neutralization

b) Granulation

Manufacture

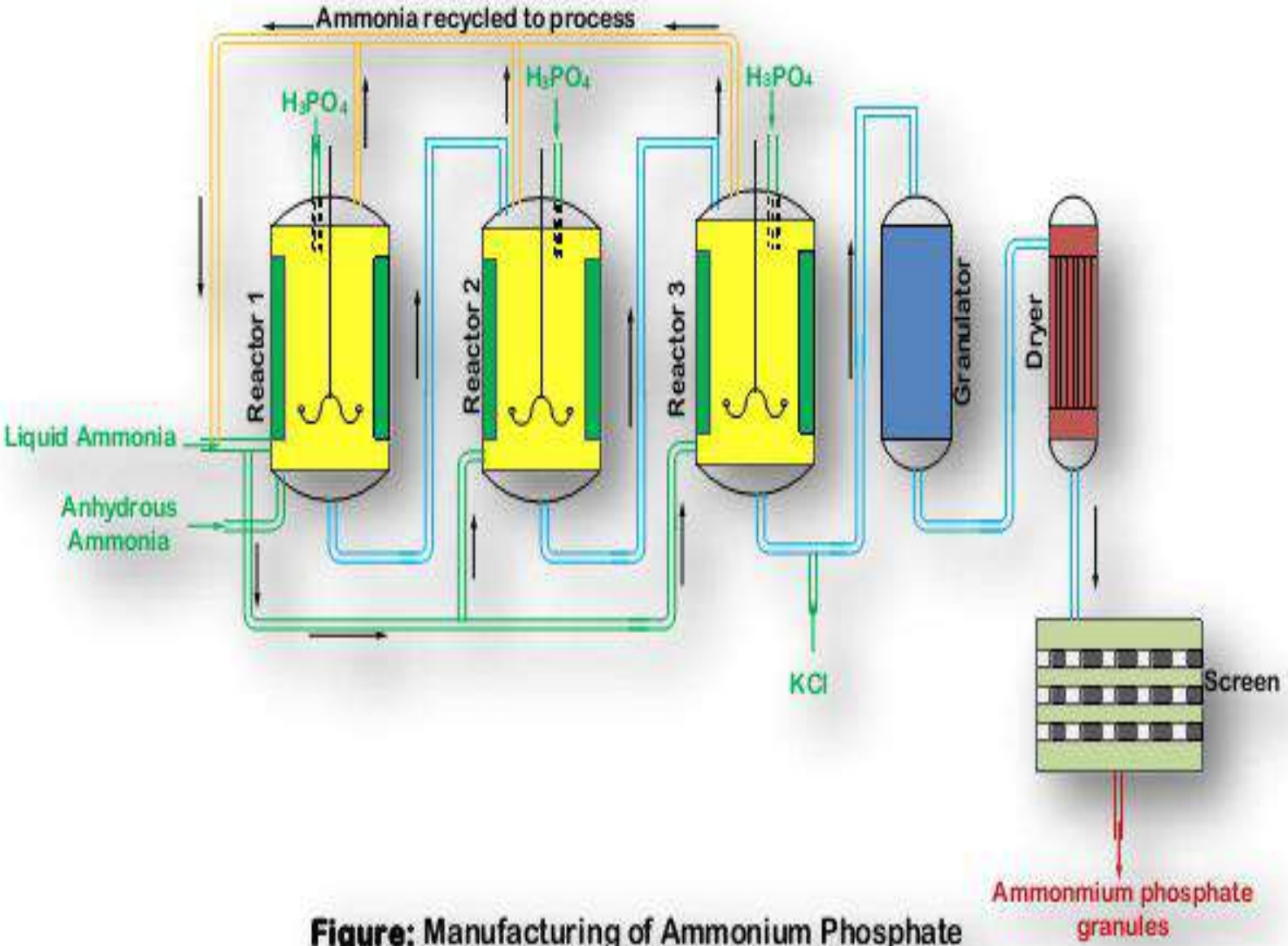


Figure: Manufacturing of Ammonium Phosphate

a)Neutralization

- MAP: NH_3/H_3PO_4ratio =0.6(neutralizer),1.0 (granulator).
- DAP: NH_3/H_3PO_4ratio =1.4(neutralizer),1.0 (granulator).
- Phosphoric and ammonia are added to the first of three continuous mixed reactors,
- Anhydrous ammonia is added beneath the slurry level in the first tank for MAP. Further ammonia is added in the 2^{nd} and 3^{rd} tanks to obtain conversion of DAP.
- The exothermic reaction heats the slurry nearly to the boiling point (130°C).
- **Top product**: Un-reacted and excess NH_3 vapor which is recharged below the liquid level for reducing NH_3 losses (less than 3%).
- **Bottom product**: Hot slurry containing about 16 to 20% water is pumped into the granulator to which ammonia is added to increase the molar ratio to approximately 2.0.

b) Granulation

- Slurry from the third neutralized is mixed with KCl and absorbed in a bed of dry recycle fertilizer moving through a rotating drum granulator.
- A rotary adiabatic drier reduces the moisture to less than 1%, with 10 minute contact time with air initially at 150^0C.
- Dried product is separated into three fractions on a double deck screen.
- A portion of the product from the deck of the lower screen is sent to bagging operations. The balance, together with pulverized oversize and fines, is returned to the granulator.
- The weight ratio of recycle to product is 6: 1-15: 1 depending on the grade produced.

- **Powder ammonium phosphate :** Powdered ammonium phosphate is still in use because of its high phosphorus content (as P_2O_5).
- In addition, a group of fertilizers, such as ammonium phosphate-sulfates, ammonium phosphate-chloride and ammonium phosphate-nitrate are produced by a number of processes involving the neutralization of ammonia with a mixture of phosphoric acid and plant waste acids like sulfuric acid, nitric acid or hydrochloric acid.
- These fertilizers are free flowing and non-hygroscopic (or less hygroscopic) compared to the individual components, and have been successfully used in many types of soils.

Major Engineering Problem

- Ammonia losses : Ammonia loss should be kept below 3%. It can be achieved by using multistage reactors along with efficient recycling mechanism of collecting the vapour of ammonia from top of the neutralization tower and recycle back to the process.
- Corrosion : Use of corrosion resistance material like SS316 for hot acid and fumes ducts, carbon steel for granulation, drying and screening

Ammonium Sulphate

- It contains 21% nitrogen and can be obtained from byproduct of steel industry, various chemical and metallurgical industries.
- Raw material: Ammonia and Sulphuric acid.
- Sulphuric acid may be obtained as a byproduct of alcohol manufacture, nitrating process, alkylation in petroleum refining and benzene production. The acid obtained by such processes is called as spent acid.
- Property:

Percent of N_2	(20-21) %
Solubility, g/100g	70.6 at 32^o F, 103.8 at 212^o F
Melting point, ^{o}C	513
Particle size	28 %, +16 mesh, 70%, -16 mesh, +60 mesh (**Standard**) 20%, +10 mesh (**Large crystal**) 80%,-10mesh,+20 mesh Over 90%, -6mesh,+ 16 mesh (**Granular**)
Hygroscopic point	59.4
Sp.gravity,20/4 ^{o}C	1.769
Bulk density,lb/ft^3	50

PHOSPHORIC ACID

Molecular formula	H_3PO_4
Solubility, g/100g	In water
Boiling point	158^0C (decompose)
Melting point, ^{o}C	42.35^0C (anhydrous), 29.32^0C (hemihydrate)
Viscosity	147cP (100%)
Molecular weight	97.994gm/mole
Sp.gravity,20/4 ^{o}C	1.769
Bulk density, gm/ml	1.885gm/ml (liquid) 1.685gm/ml (85% solution) 2.030gm/ml (crystal at 25^0C)

Two grades of phosphorous

1.White phosphorous 2. Red phosphorous

- The continuous process of phosphoric acid production uses liquid white phosphorous at the boiling condition for 5 to 6 hrs so that about (35-50) % white phosphorous is converted to red phosphorous.
- Red phosphorous finds the application in manufacturing of matchsticks, chlorides of phosphorous as PCl_3, PCl_5, phosphorous oxide as P_2O_5 and phosphor bronze etc.

Uses

- Used for preparation of hydrogen halides
- Used as a "rust converter", by direct application to rusted iron, steel tools, or surfaces. It converts reddish-brown iron(III) oxide, Fe_2O_3 (rust) to black ferric phosphate, $FePO_4$
- Food-grade phosphoric acid is used to acidify foods and beverages such as various colas.
- Used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed.
- An ingredient in anti-nausea medications which contain high levels of sugar (glucose and fructose).
- Used in many teeth whiteners to eliminate plaque.
- Used as an external standard for NMR and HPLC
- As a chemical oxidizing agent for activated carbon production
- As an electrolyte in copper electro polishing for burr removal and circuit board planarization.
- As a flux by hobbyists (such as model railroaders) as an aid to soldering.
- As common wet etching agent in compound semiconductor processing,
- Hot phosphoric acid is used in micro fabrication to etch silicon nitride (Si_3N_4). It is highly selective in etching Si_3N_4 instead of SiO_2, silicon dioxide.
- As a cleaner by construction trades to remove mineral deposits, cementitious smears
- As a chelant in some household cleaners aimed at similar cleaning tasks.
- Used in hydroponics pH solutions to lower the pH of nutrient solutions.
- As a pH adjuster in cosmetics and skin-care products.
- As a dispersing agent in detergents and leather treatment.
- As an additive to stabilize acidic aqueous solutions within specified pH range

Raw materials

Basis: 1000kg phosphoric acid (100%)

Phosphate rock = 2290 kg Sand (Silica) = 6800 kg Coke= 3175 kg

Briquette binder = 227 kg Air = 450000 ft^3

Reactions

- $Ca_3(PO4)_2 + 3SiO_2 + 5C$ ----- $2P + 5CO + 3CaSiO_3$
- $2P + 5CO + 5O_2$ ---------- $P_2O_5 + 5CO_2$
- $P_2O_5 + 3H_2O$ ---------- $2H_3PO_4$ (85-90)% yield

MANUFACTURE

The modern manufacturing methods of phosphoric acid are :

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

1. Using phosphate rock and blast furnace

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

Manufacture

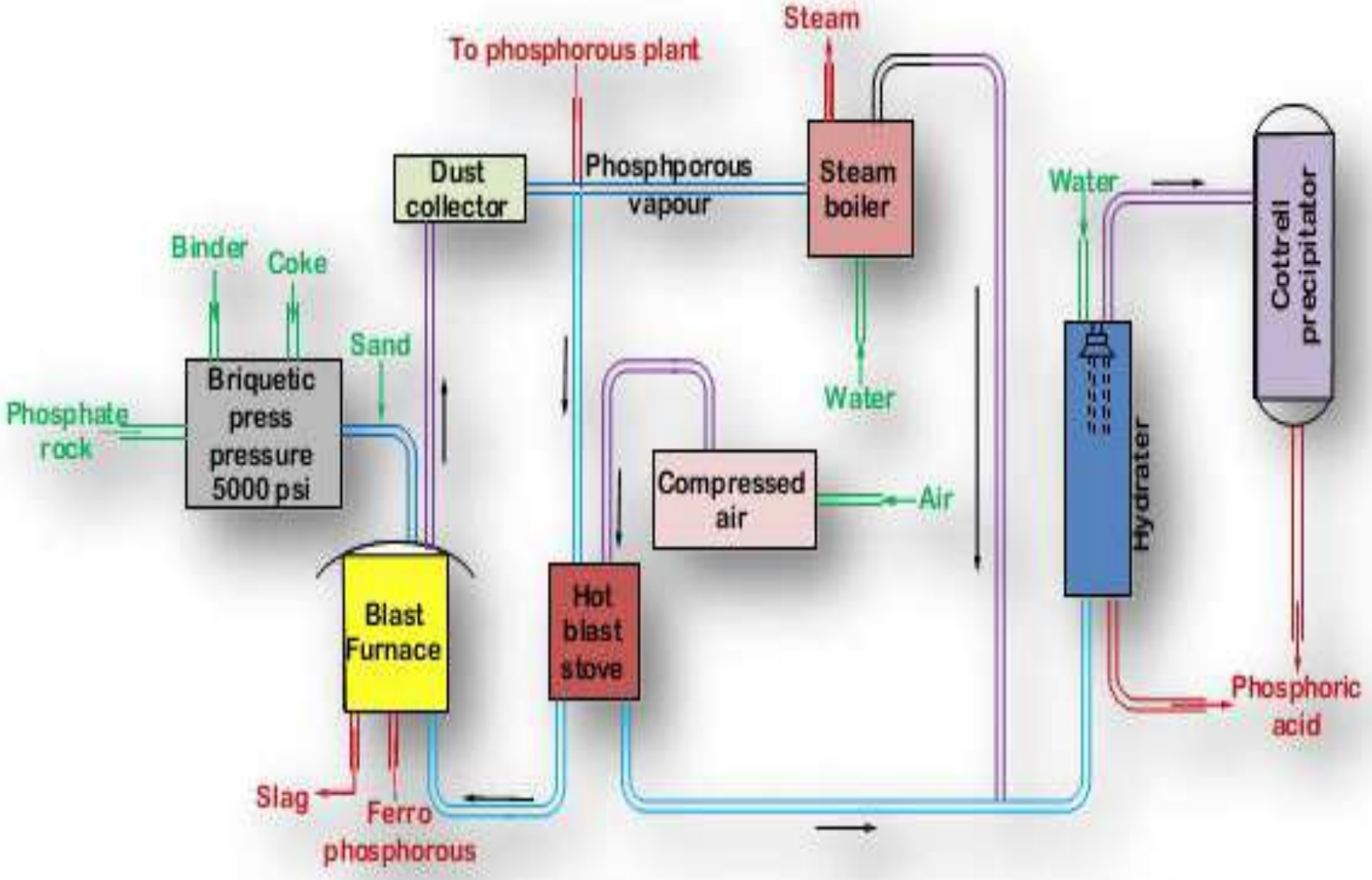


Figure: Manufacturing of Phosphoric acid using blast furnace

- Reaction is completed in the furnace itself producing P_2O_5 and calcium silicates as slag.
- The product gases also contain carbon monoxide and nitrogen along with dust particles.
- For purification, it is passed through cyclone separator and phosphorous condenser. Thus, P_2O_5 and elemental phosphorous are separated out. Hot P_2O_5 gases are cooled in the heat exchanger. Therefore, superheated steam is produced and a part of gas is taken into regenerative blast furnace.
- As a result the entire phosphorous and phosphorous pentoxide is cooled and purified before taken into hydrating towers.
- Purification of phosphoric acid includes removal of arsenic by hydrogen sulfide treatment followed by filtration.
- Phosphate rock is pulverized and mixed with coke powder and binder is compressed to 5000 psi resulting into the briquettes.
- Briquettes are dried and charged along with sand and additional coke powder from top of the blast furnace.
- The preheated air (1000 – 1100^0C) is charged from bottom of the blast furnace via tuyere. A tuyere is cooled copper conical pipe numbering 12 in small furnace and up to 42 in large furnace through which hot air is blown in to the furnace.
- Preheated air leads to burning of briquettes giving temperature rise up to 1370^0C.
- The coke acts as reducing agent as well as fuels. About 760 kg of coke is consumed in reduction of phosphate rock to phosphorous and remaining generates heat by combustion with air.

2. Using phosphate rock and electric furnace

Raw materials

Basis: 1000kg phosphoric acid (100%)

Phosphate rock= 2225 kg Sand (silica)=680 kg Coke breeze = 400 kg

Caron electrode= 8 kg Air= 100000 ft^3 Electricity = 4070KWH

Reactions

- $Ca_3(PO_4)_2 + 3SiO_2 + 5C$ ----- $2P + 5CO + 3CaSiO_3$ ΔH = - 364.8 kcals
- $2P + 5CO + 5O_2$ ---------- $P_2O_5 + 5CO_2$
- $P_2O_5 + 3H_2O$ ---------- $2H_3PO_4$ ΔH = - 44.9 kcals 87-92% yield

Process

Proper grinding and primary purification | **Sintering oven for nodulization and granulation** | **Electric arc furnace**

- The phosphate rock is reduced to elemental phosphorous by the action of coke and heat in the presence of sand in electric arc furnace
- Oxidation of phosphorous gives phosphorous pentoxide which on hydration gives the product phosphoric acid.
- Temperature of 1095^0C is maintained in electric furnace for extraction of maximum amount of elemental phosphorous.

Manufacture

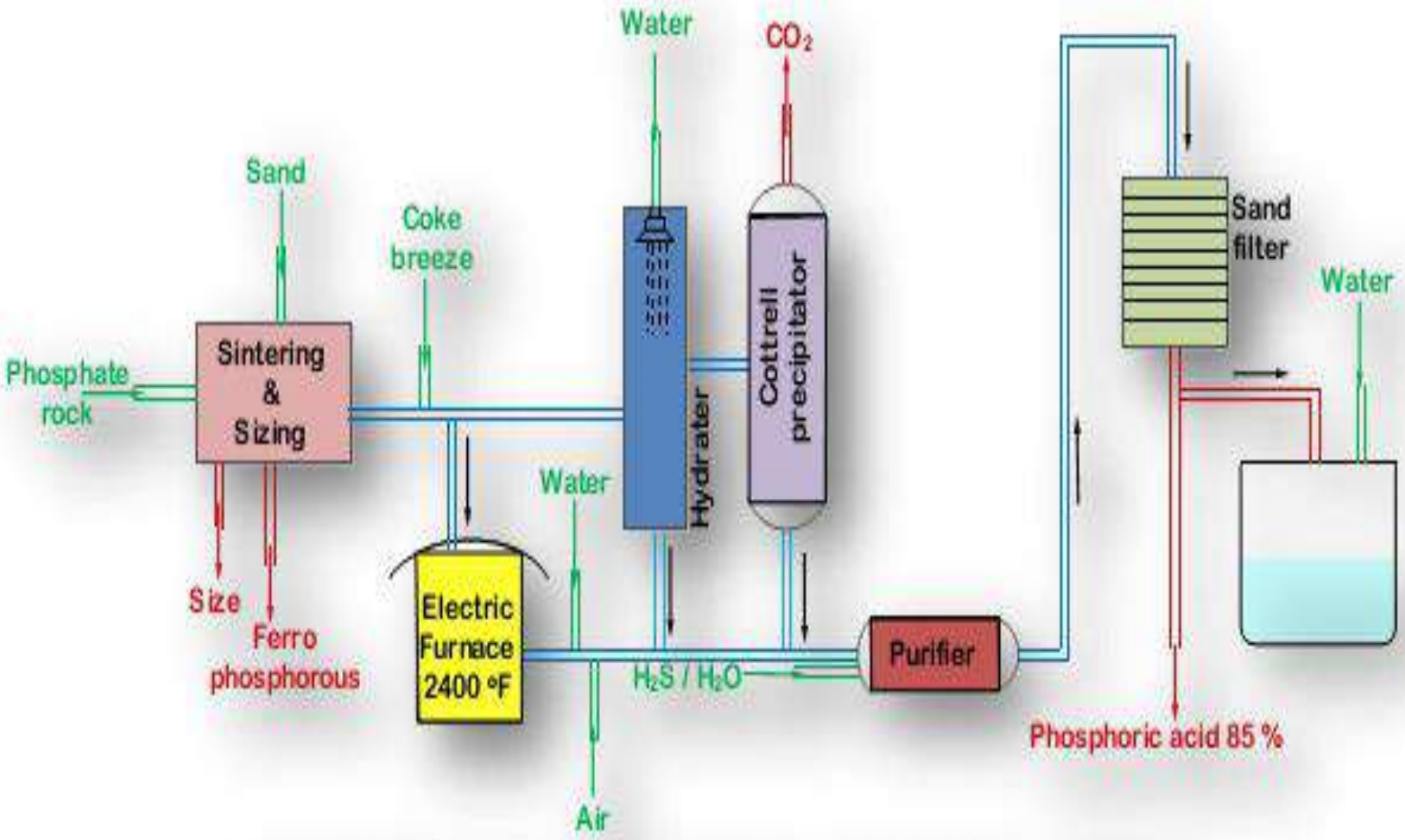


Figure: Manufacturing of Phosphoric acid using Electric furnace

- **Impurities** such as: Fluoride of phosphorous and calcium which reacts with sand giving flourosilicates as the slag.
- **Gases**: Phosphorous and carbon monoxide are removed by the suction
- **Oxidation product** P_2O_5 : To hydration column to form H_3PO_4 at 85^0C.
- Purification of phosphoric acid by

H_2S	Removal of Arsenic
H_2SO_4	calcium salts
Silica	fluorides

Advantages of electric arc furnace over other methods

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

3. Oxidation and Hydration of phosphorous

Raw materials

Basis: 1000kg phosphoric acid (100%)

Phosphorus = 300 kg Air = 46000 ft^3 Steam = variable Water = variable

Reactions

- $2P + 2½O_2$ ---------- P_2O_5
- $P_2O_5 + 3H_2O$ ---------- $2H_3PO_4$ (94 – 97% yield)

Manufacture

- Molten phosphorous is sprayed into combustion chamber along with preheated air and superheated steam.
- Combustion of phosphorous increases the temperature up to 1980^0C.
- Furnace are made of acid proof structural bricks, graphite, carbon and stainless steel.
- Gases from furnace: P_2O_5, steam, N_2 and small quantity of oxygen
- Gases are sent to hydration column

> counter current mixing of dilute phosphoric acid and the gases

- Final product H_3PO_4 is concentrated of 75% to 85% concentration.
- Remaining acid is trapped into packed column or electrostatic precipitator.

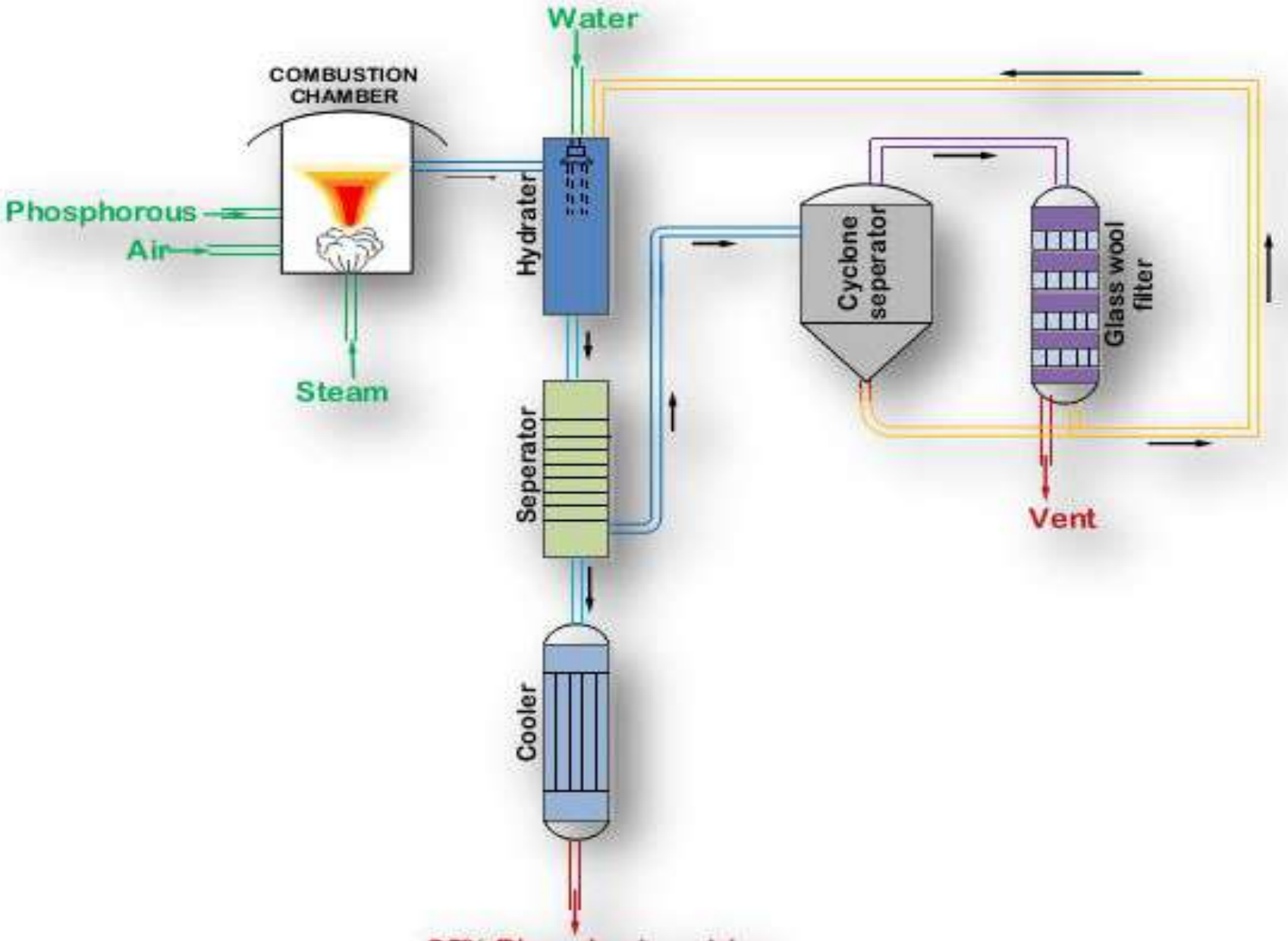


Figure: Manufacturing of Phosphoric acid by Oxidation and Hydration

Clay swelling

- A type of damage in which formation permeability is reduced because of the alteration of clay equilibrium.
- **Clay swelling** occurs when water-base filtrates from drilling, completion, workover or stimulation fluids enter the formation.
- Clay swelling can be caused by ion exchange or changes in salinity. However, only clays that are directly contacted by the fluid moving in the rock will react; these include authigenic clays, some detrital clays on the pore boundaries and unprotected clay cement.
- The nature of the reaction depends on the structure of the clays and their chemical state at the moment of contact.
- The most common swelling clays are smectite and smectite mixtures that create an almost impermeable barrier for fluid flow when they are located in the larger pores of a reservoir rock.
- In some cases, brines such as potassium chloride [KCl] are used in completion or workover operations to avoid clay swelling.

POTASSIUM SULFATE

Molecular formula	H_3PO_4
Solubility, g/100g	In water
Boiling point	158^0C (decompose)
Melting point, ^{o}C	42.35^0C (anhydrous), 29.32^0C (hemihydrate)
Viscosity	147cP (100%)
Molecular weight	97.994gm/mole
Sp.gravity,20/4 ^{o}C	1.769
Bulk density, gm/ml	1.885gm/ml (liquid) 1.685gm/ml (85% solution) 2.030gm/ml (crystal at 25^0C)

- Potassium sulfate contains 48 to 54% potassium (as K_2O) and supplies 17-20 % of sulfate

USES

- As fertilizer particularly in chloride sensitive crops like tobacco, grapes and potato which require chloride free potassium fertilizers.
- For best results, potassium sulfate should contain at least 50 % potash by weight.
- As a flash reducer in artillery propellant charges.
- It reduces muzzle flash, flareback and blast overpressure
- The crude salt is also used in the manufacture of glass.

MANUFACTURE

1. Mannheim process
2. Recovery from natural complex salts

1. Mannheim Process

- **Raw materials :** Potassium chloride; Sulfuric acid

Reaction

$KCl + H_2SO_4$ ---------- $KHSO_4 + HCl$

$KHSO_4 + KCl$ ---------- $K_2SO_4 + HCl$

- Originally developed for **sodium sulfate** production. For making potassium sulfate, sodium chloride is replaced with potassium chloride.
- Potassium chloride reacts with sulfuric acid in the gas heated **Mannheim furnace** consisting of cast iron muffle with rotating plough which helps to agitate the mixture.

Manufacture

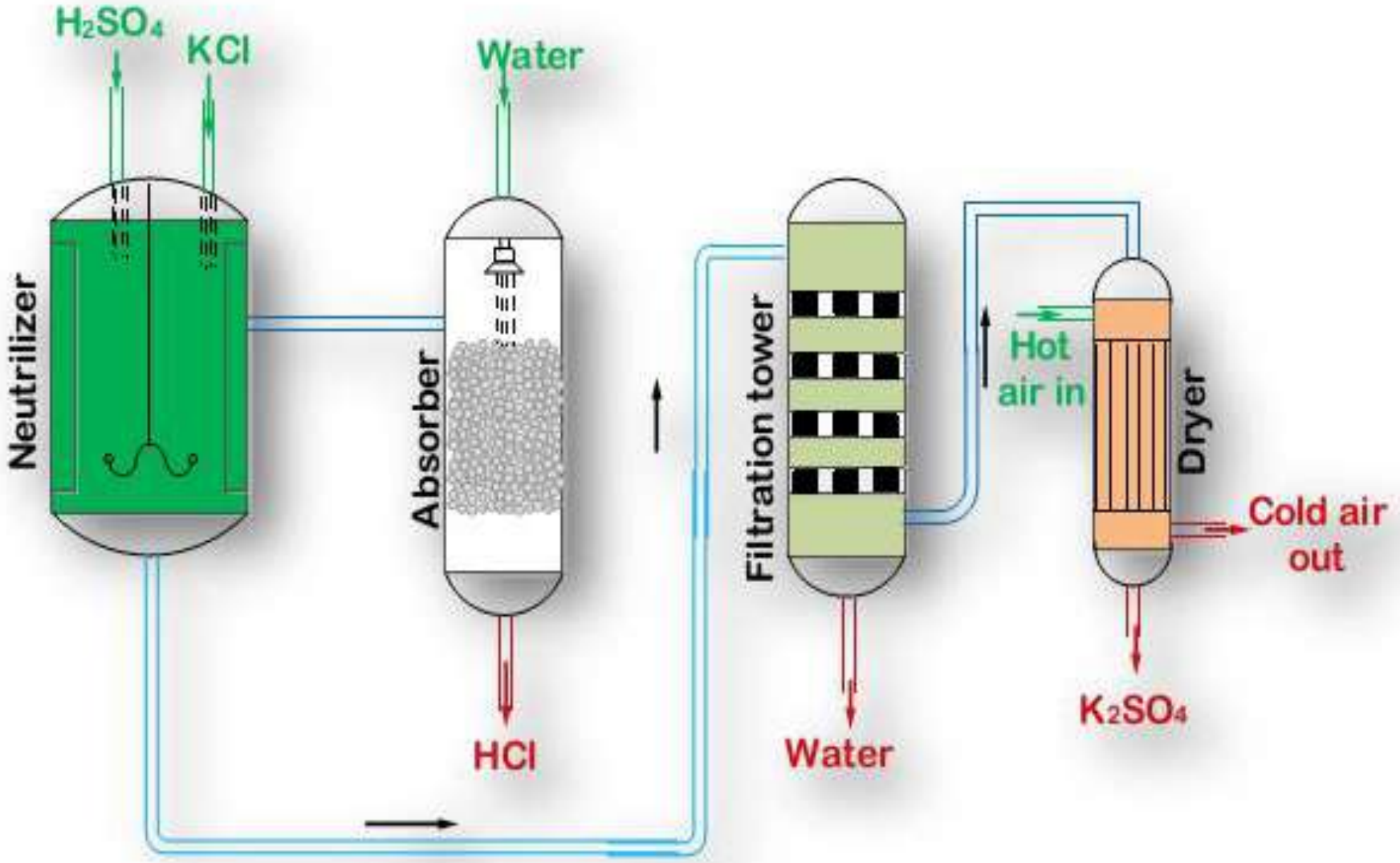


Figure: Manufacturing of Pottasium Sulfate

- **By-product:** Hydrochloric acid is cooled and absorbed into water to produce 33% hydrochloric acid.
- **Final product**: Precipitated potassium sulfate fertilizer is cooled, filtered and the lumps are crushed and granulated.
- **Cost:** Potassium sulfate is twice as costly as potassium chloride. Granulation adds further to its cost.
- **Composition:** Potassium sulfate contains over 50% potassium (as K_2O) and less than 1 % chlorine.

Handling and storage

- The crystalline potassium sulfate is free flowing so it is easy in handling and storage.
- It is imported as bulk cargo and transported to NPK fertilizer mixing plants and dealers in bulk or in bags. It is stored in bulk in closed storage yards.

POTASSIUM CHLORIDE

Molecular formula	KCl
Solubility, g/100g	Soluble in glycerol & water, slightly soluble in alcohol, insoluble in ether
Boiling point	1420^0C
Melting point, ^{o}C	770^0C
Viscosity	147cP (100%)
Molecular weight	74.55gm/mole
Sp.gravity,20/4 ^{o}C	1.769
Bulk density, gm/ml	1.984 gm/ml

- Potassium chloride crystals are face centered cubic (FCC).
- **Other name**: "**Muriate of potash**" containing 60% plant food as K_2O.
- Potash varies in colour from **pink or red to white** depending on the mining and recovery process used.
- **White potash** or soluble potash is usually higher in analysis and is used primarily for making liquid starter fertilizers.
- **Occurrence:** The mineral sylvite and in combination with sodium chloride as sylvinite.

USES

- As a fertilizer
- Used as thickeners, stabilizer, mineral salts and acidity regulator in food
- Used as a salt replacer in foods, for recovery of potassium in the human body.
- As a salt substitute in brewing, gelling agent.
- Used in various pharmaceutical preparations to correct potassium deficiency.
- As a substitute for table salt in the diet of people with cardiovascular disorders.
- As a constituent of Ringer's solution.

Raw Materials

Basis: 1000 kg of Potassium chloride (Muriate)

Sylvinite = 2510 kg Steam = 1250 kg Water =170-200 m^3 Electricity = 180 MJ

Direct labour= 4-5 work-hr

Potash mineral or Potash mineral or sylvinite contain potassium chloride and sodium chloride

Manufacturing Methods :

1. Leaching process
2. Flotation process

Flotation process

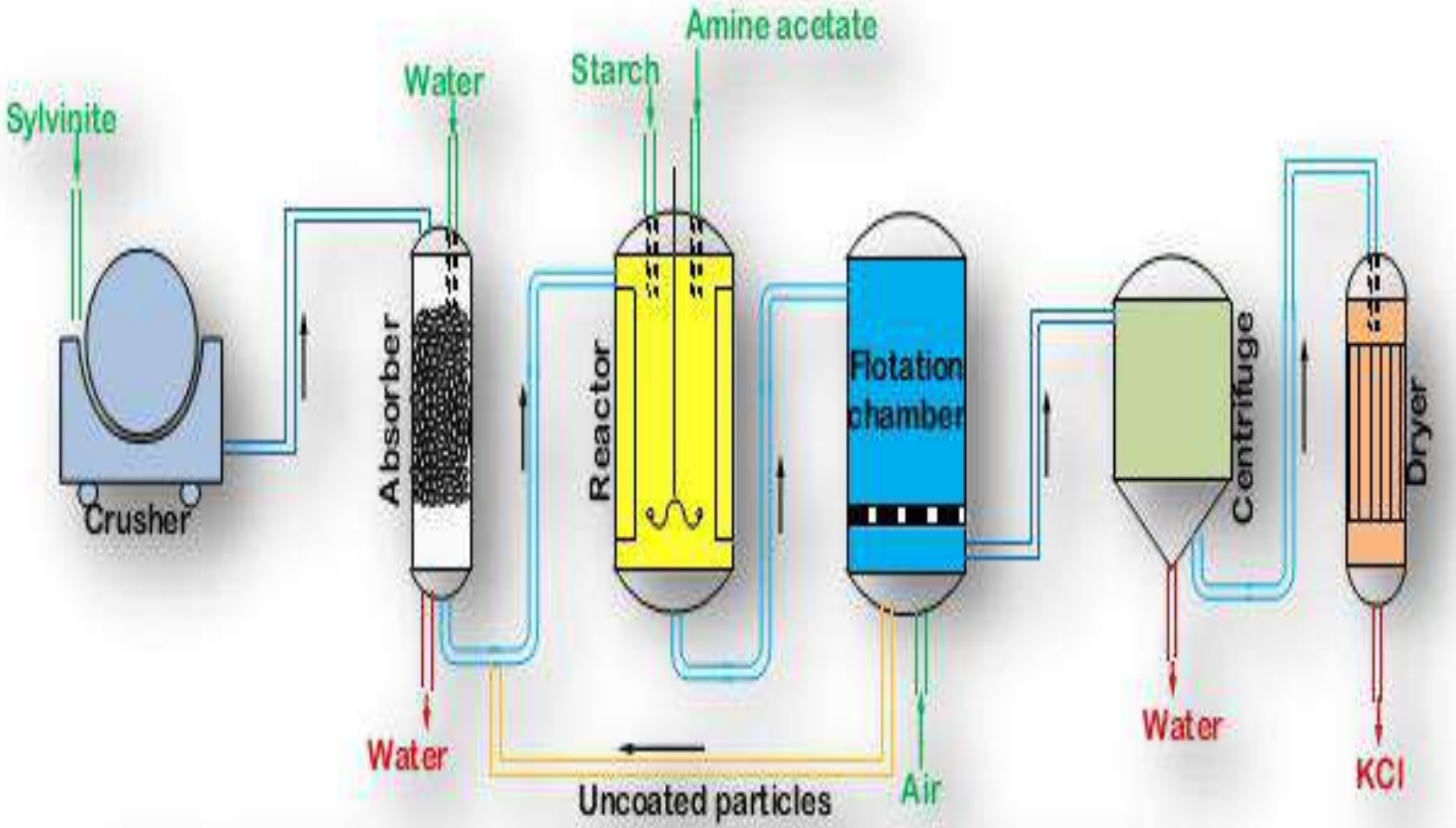


Figure: Manufacturing of Pottasium Chloride by Flotation Process

Leaching Process

- Solubility characteristics are used to extract potassium chloride from sylvinite. Solubility of KCl and NaCl increases with increases of temperature.

With increase in T	NaCl	KCl
Solubility	Increases	Increases
Concentration	Decreases	Increases

- Crushed ore is mixed with sufficient quantity of recycle brine which is already saturated with NaCl and heated almost to hilling to dissolve KCl.
- The KCl rich brine on clarification and then cooling by vacuum evaporation produces KCl crystals which are centrifuged, washed, dried and packed.
- The filtrate (brine) is recycled for leaching more ore.

Floatation process

- Potassium chloride is much cheaper than in leaching process.
- Ore is crushed to +10 mesh size then washed to remove clay slimes.
- To render it inert to amines, washed crushed ore
    1. Is treated first with starch or mannogalactan gums
    2. With an amine acetate which selectively coats KCl particles.
- Air is then bubbled through the slurry in order to float the coated particles to surface while the uncoated particles sink.
- The floated KCl is centrifuged, dried and packed.

SUPERPHOSPHATE

Molecular formula	KCl
Solubility, g/100g	Soluble in glycerol & water, slightly soluble in alcohol, insoluble in ether
Boiling point	1420^0C
Melting point, ^{o}C	770^0C
Viscosity	147cP (100%)
Molecular weight	74.55gm/mole
Sp.gravity,20/4 ^{o}C	1.769
Bulk density, gm/ml	1.984 gm/ml

USES

- It is the principal carrier of phosphate, the form of phosphorus usable by plants, and is one of the world's most important fertilizers.
- It is low cost source of phosphorous in a wide range of pasture and cropping situations
- Generally mixed with sulfate of ammonia and muriate of potash, but can be blended with other fertilizers

MANUFACTURE

Raw Materials

Basis: 1000 kg Superphosphate (den process)

Calcium phosphate = 625 kg Sulfuric acid = 320 kg Water = 90 kg Electricity = 0.2 kWH

Reactions

- $Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O$ ----------$CaH_4(PO_4)_2 + 2(CaSO_4.2H_2O)$
- $CaF_2 + H_2SO_4 + 2H_2O$ ---------- $CaSO_4.2H_2O + 2HF$
- $4HF + SiO_2$ ---------- $SiF_4 + 2H_2O$
- $3SiF_4 + 2H_2O$ ---------- $SiO_2 + 2H_2SiF_6$

Overall reaction

$CaF_2.3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O$ ---$3CaH_4(PO_4)_2.H_2O + 2HF + 7CaSO_4$

Phosphate rock or fluorapatite

Superphosphate manufacturing involves following steps :

1.Preparation of phosphate rock

2.Mixing with acid

3.Curing and drying of the original slurry by completion of the reactions

4.Excavation, milling, and bagging of the finished product

5.Granulation

1. Batch 2. Continious

a) Preparation of phosphate rock :

- Quality of the product is depends on grade of phosphate rock. Fine grinding is demanded due to low reactivity of the rock.
- Phosphate rock is finely ground up to the size of less than 100 meshes. Grinding of phosphate rock to fine powder has following advantages :

1. Increase the rate of reaction
2. Less sulfuric acid is needed
3. A higher grade of product in better condition is obtained.

- It is difficult to make SSP from igneous apatite. The presence of aluminum and iron compounds reduces the solubility of phosphorus in water.
- The increase in the ratio of $CaO:P_2O_5$ raises the consumption of sulfuric acid per unit of P_2O_5 and decreases the grade.
- Silica has no adverse effect and higher chloride content in the phosphate rock is acceptable.

b) Mixing with acid : Phosphate rock is mixed with sulfuric acid(68 to 75)%in a cone mixer.

c) Curing and drying of the original slurry by completion of the reactions :

- In den the fluid material is solidifies owing to a continued reaction and crystallization of monocalcium phosphate.
- The superphosphate is removed from the den after 0.5 to 4 hours.
- It is still at temperature of about 100°C and plastic in nature.

d) Excavation, milling, and bagging of the finished product :

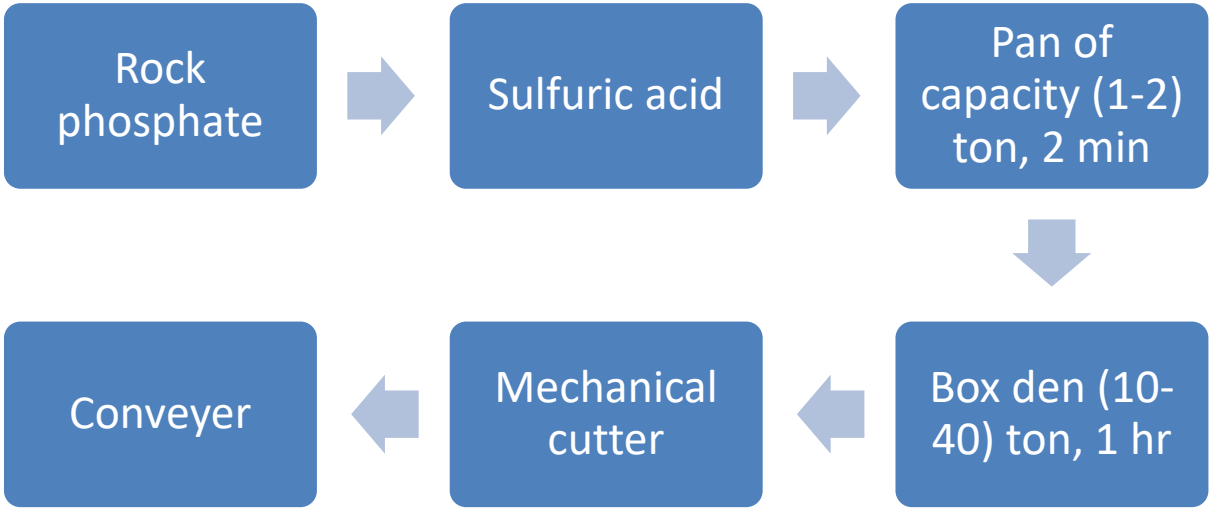
- The product from the den is sent to storage piles for final curing of 2 to 6 weeks.
- During curing, the free acid, moisture and the unreacted rock content decreases, whereas the available water-soluble phosphorus content increases.
- As the reaction approaches completion during curing, the material hardens and cools.
- The cured product is crushed in a hammer mill or cage mill to a size of about 6 mesh.

e) Granulation :

- When granular superphosphate is required, the product is granulated before or after curing.
- Granulation before curing is advantageous as it requires less steam or water.
- After granulation, the product is dried in a direct contact drier and screened. Super phosphate is manufactured by

1. Batch process
2. Continuous process

Batch - den process :



- This set up gives a production rate of 40 tons per hour.

Advantages

- Igneous rock is available, batch mixing are preferred due to precise control of mixing conditions available and den can be made tight enough to contain the very fluid slurry.
- For a small phosphate source, batch process can be built.
- All plants first pulverize the rock with modern pulverizing and air-separation equipment, most rock is ground so that 70 to 80% of particles are passed through 200 mesh screen.

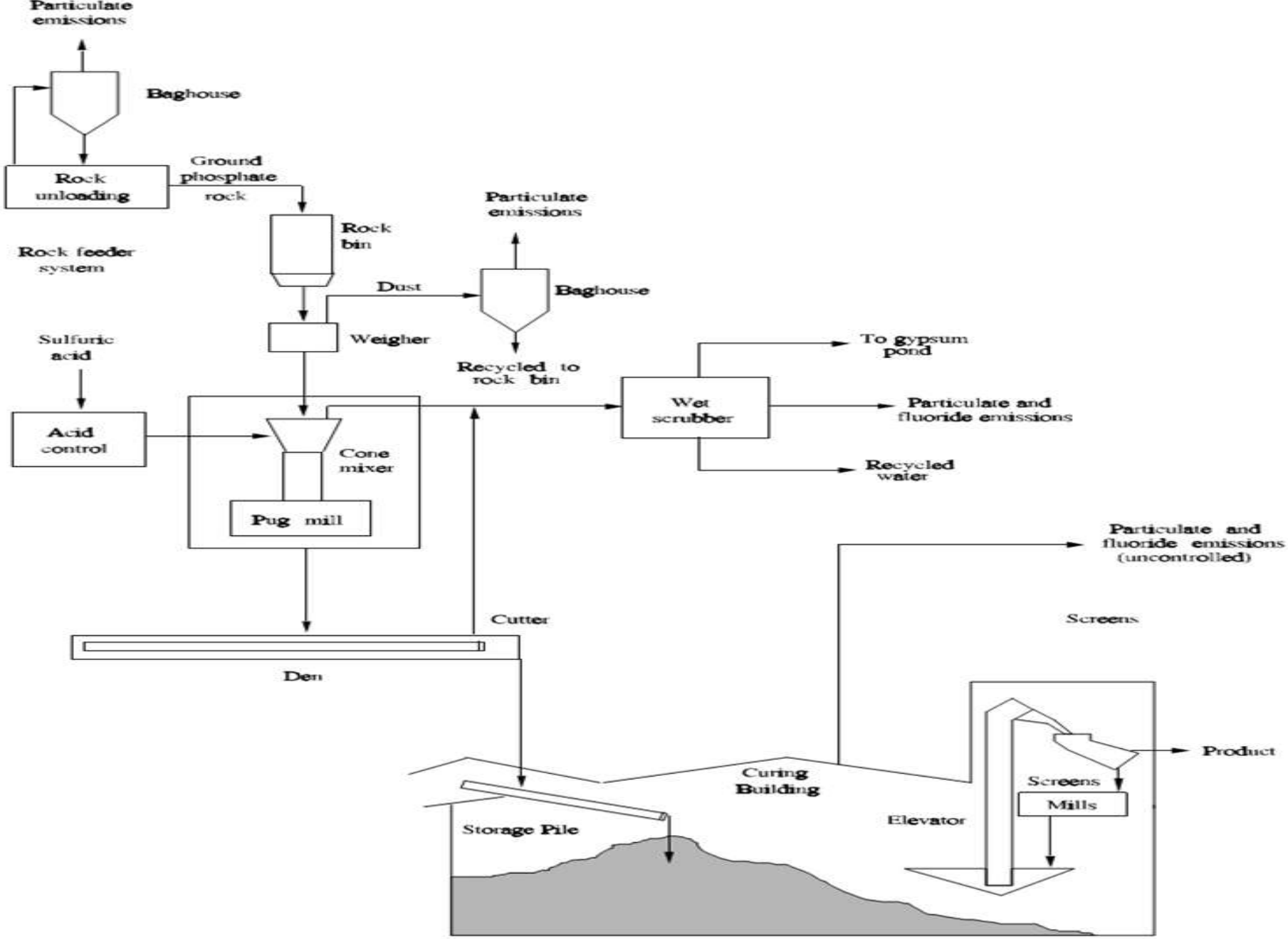
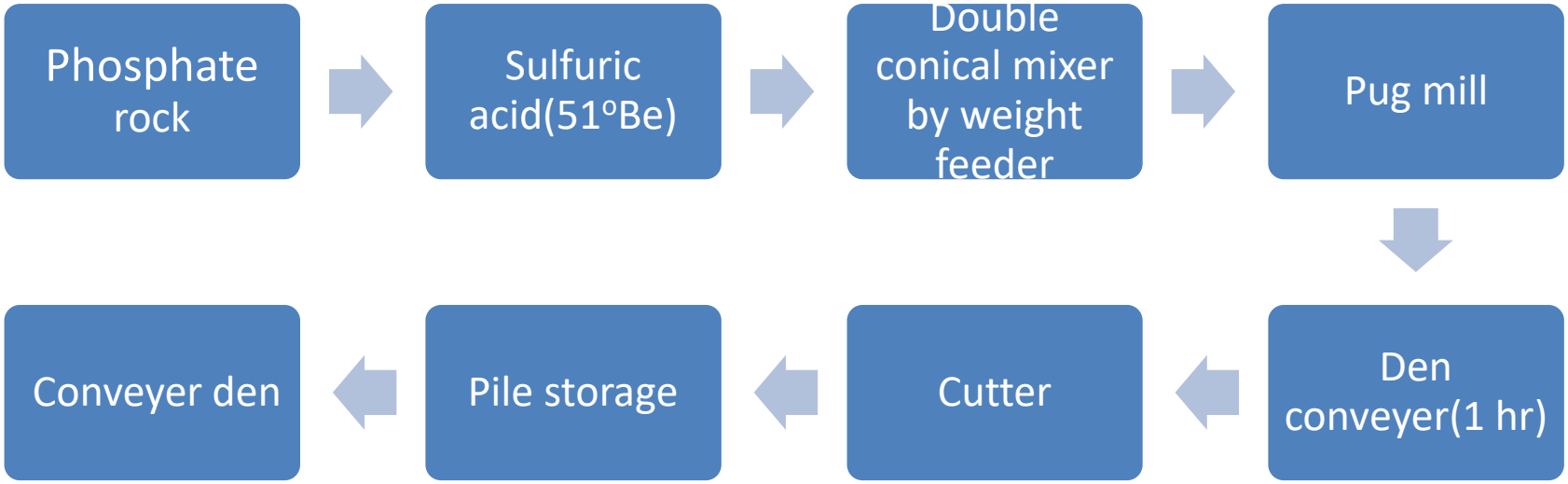


Figure 8.5.1-1. Normal superphosphate process flow diagram.[1]

Continuous-den process



- The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock.
- The heat of dilution of the sulfuric acid serves to maintain proper reaction temperature, and excess heat is dissipated by evaporation of extra water added.
- "Currying" or completion of the chemical reaction, which takes 10-20 day to reach P_2O_5 availability acceptable for plant food in pile storage.
- The conveyers den is enclosed so that fumes do not escape into the working area.
- These fumes are scrubbed will water sprays to remove acid and fluoride before being exhausted to the atmosphere.
- Scrubber water is neutralized by passing through the limestone bed.

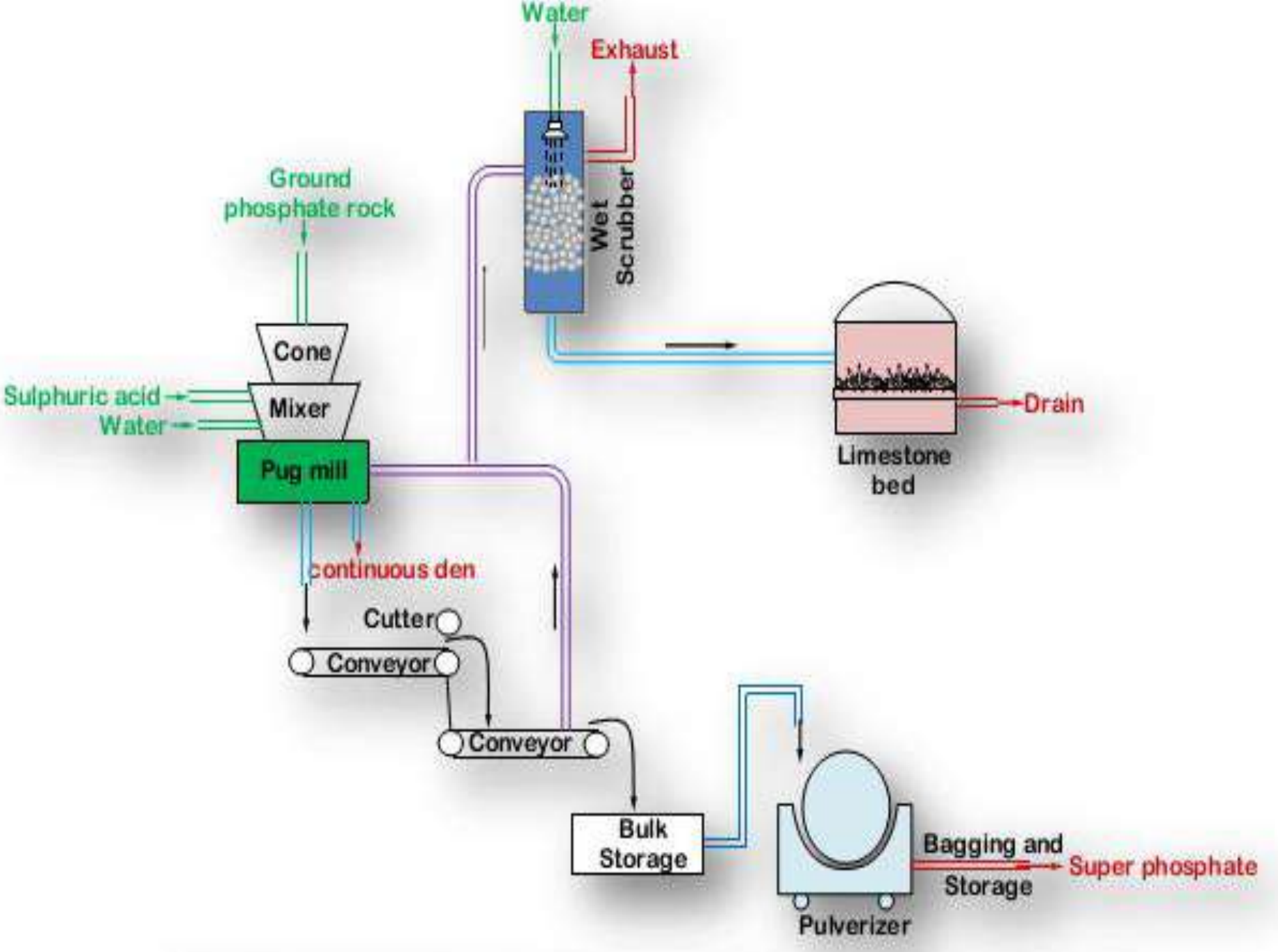


Figure: Manufacturing of Superphosphate by Continuous-den process

Granulation

- Both granulation and drying of the SSP are carried out in the same piece of equipment.
- The powdered superphosphate enters to rotary drum granulator, where it is mixed and granulated with recycled fines (recycle ratio: > 0.6).
- Granulation is controlled by adjusting the water content and temperature of the product in the 1st part of the rotary drum.
- Drying is achieved near the exit from the granulator and involves adding more sulfuric acid and ground limestone (about 60 kg/ton SSP).
- The heat produced by the reaction dries the product and the calcium sulfate formed encapsulates the product in such a way that caking is avoided during final curing and storage of the product.
- No P_2O_5 reversion is noticed. Product is sized using a conventional system of screens and crushers such that 90% of the product is between 1 and 4 mm in size.
- Final curing of the product occurs during storage for less than two weeks.

TRIPLE SUPERPHOSPHATE

Solubility, g/100g	Water soluble
Appearance	White and grey granules
pH	2.5-3
P_2O_5 (water soluble)	42.5% minimum
Molecular weight	252.07gm/mole
Sp.gravity,20/4 °C	1.089
Bulk density, gm/ml	800-881kg/m^3

- Triple superphosphate (TSP) is the more concentrated fertilizer than ordinary superphosphate, containing from 44 to 51% of available P_2O_5 or nearly three times the amount in the regular superphosphate and 17 to 20% lime. Owing to the high concentration of phosphorus, TSP is used widely in the production of high analysis compound fertilizers.
- Its concentrated form is cheaper to transport, store and apply when compared with the dilute form.
- TSP is manufactured by adding phosphoric acid to rock phosphate, producing mainly water-soluble monocalcium phosphate with no calcium sulfate.
- In most processes, a large percentage of fluorine remains in the product, probably as fluorosilicate or calcium fluoride.
- When triple superphosphate is used as a fertilizer, the yield from short season crops like cereals, potato and some vegetables is markedly higher.
- This fertilizer lets a weak root system establish itself firmly and supports the crop to stand during the growing period.

USES

- TSP can be used in wastewater treatment to reduce lead levels
- As a low cost source of phosphorus, TSP is the main substitute for single superphosphate in cropping blends.
- It is used mainly in blends with DAP and MAP
- Source of phosphorus in situations where no nitrogen is required e.g. good fallow after clover dominant pasture.
- In horticultural blends where the phosphorus content needs boosting

Advantages

- It is a highly concentrated straight phosphate fertilizer.
- It has a low-cost source.
- Its manufacture requires small capital investment and low-skilled manpower.

Disadvantages

- Its total nutrient content is lower than that of ammonium phosphate.
- Its acidic character deteriorates storage bags.
- It is not suitable for blending with urea as it causes the latter to deteriorate

Manufacturing Process involves following steps

a) Reaction
b) Denning or Den process step
c) Storage and curing
d) Granulation

MANUFACTURE

Raw Materials

- Basis: 1000 kg Triple superphosphate

Phosphate rock = 386 kg Phosphoric acid = 540 kg Power= 40 kWH Steam = 20 kg Labour = 0.3 man-hr Fuel = 140000 Btu

Reaction

- $CaF_2.3Ca_3(PO_4)_2 + 14H_3PO_4$ ---------- $10Ca(H_2PO_4)_2 + 2HF$

Manufacturing Steps :

- Finely ground phosphate rock and 62% H_3PO_4 are charged continuously to the granulator, where reaction and granulation take place.
- Fines from the product screen are recycled to the granulator, and the moisture and temperature required for proper granulation are maintained by addition of water and/or steam.
- The granulator is a cylindrical vessel rotating about a horizontal axis and has in overflow dam at the discharge end.
- The phosphoric acid is fed uniformly under the bed of material through a perforated pipe. When wet-process phosphoric acid is used, it is also necessary to provide an acid pre-heater.
- The granules overflow the dam into the rotary cooler, where they are cooled and dried slightly by counter current flow of air.

Manufacture

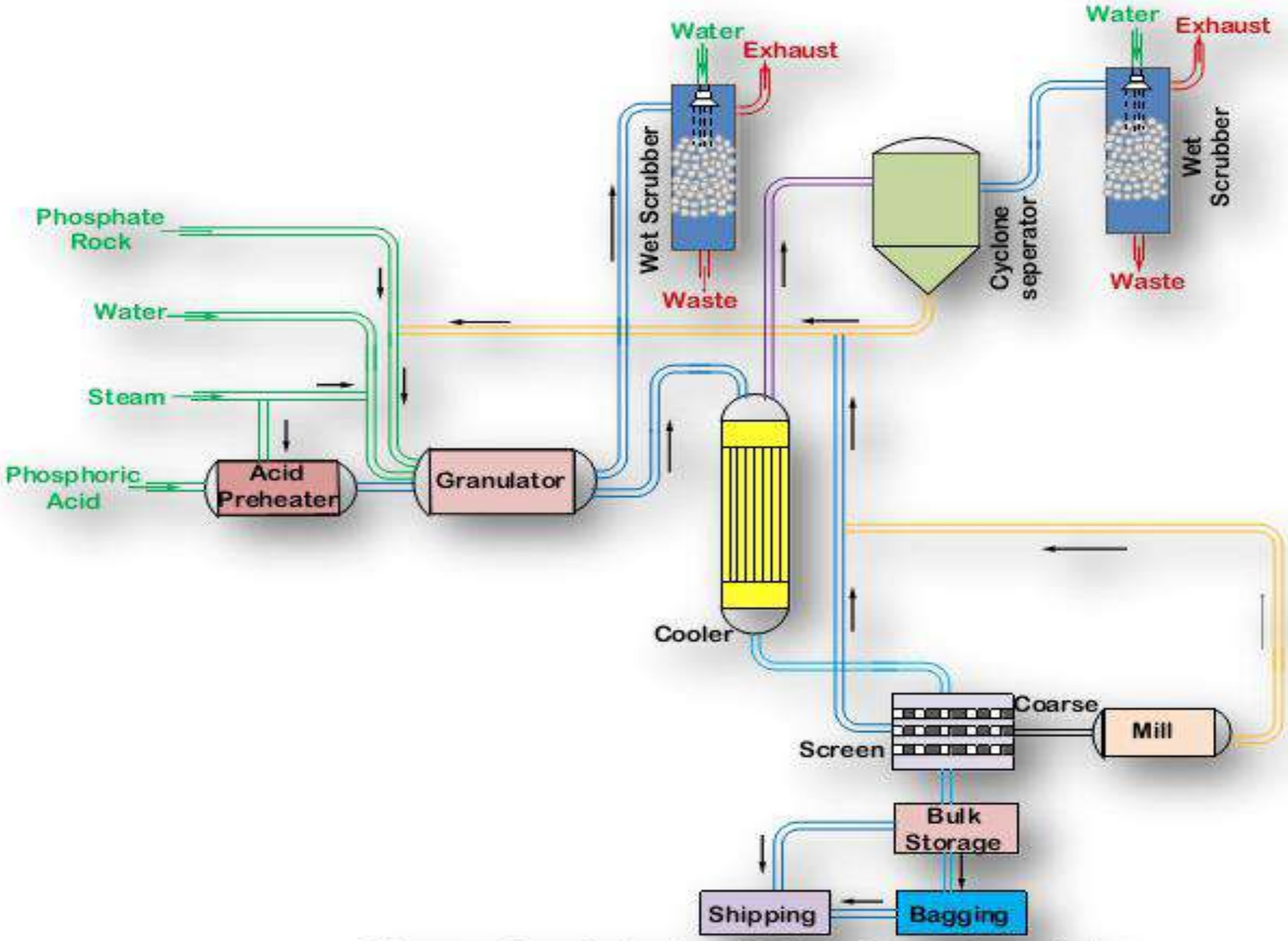


Figure: Manufacturing of Triple Superphosphate

- The exhaust gases from the cooler pass through the cyclone, where dust is collected and returned to the granulator as recycle, the cooled product is screened, the coarse material being milled and returned, along with the fines, to the granulator.
- The product is then conveyed to bulk storage, where the material is cured for 1 to 2 weeks, during which a further reaction of acid and rock occurs, which, increases the availability of P_2O_5 as plant food, the exhaust gases from the granulator and cooler are scrubbed with water to remove silicofluorides.
- The cost per unit of P_2O_5 is higher as compared to ordinary superphosphate, because of more capital investment and additional labour and processing.
- However, this is balance to the great extent by the ability to use the lower-grade, cheaper phosphate rock to make the phosphoric acid.
- There are also substantial savings on handling, bagging, shipping, and distributing.

Advantages of the direct slurry granulation process

- Product is available at a lower cost
- Generate denser and stronger granules
- Use of conventional granulation equipment

Disadvantages

- Uses phosphate rocks which have a short reaction time, resulting in a greater loss of soluble phosphorus (as P_2O_5) due to an incomplete reaction or higher ratio of phosphoric acid Granular triple superphosphate is produced directly rather than from the powder fertilizer.

Urea

Solubility, g/100g	Solubility in water, ethanol, glycerol
Appearance	White granules
pH	2.5-3
Molecular weight	60.06 gm/mole
Density	1.32 gm/ml
Bulk density, gm/ml	673-721 kg/m^3
Melting point	132-135^{0}C

- It is highly soluble in water and practically non-toxic (LD_{50} is 15 gm/kg for rat).
- Dissolved in water, it is neither acidic nor alkaline.
- As soon as urea dissolves in the soil, it forms around it a zoning layer of high pH and ammonia concentration turning the soil to be acidic and toxic at the same level.
- Urea is high moisture absorbent therefore it should be stored in sealed and well enclosed bags.

USES

- As a fertilizer
- As a protein food supplements for ruminant
- As an ingredient in the manufacture of resins, plastics, adhesive,
- Coatings textiles anti-shrink agents and ion exchange resins.
- It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid (H_3NSO_3)