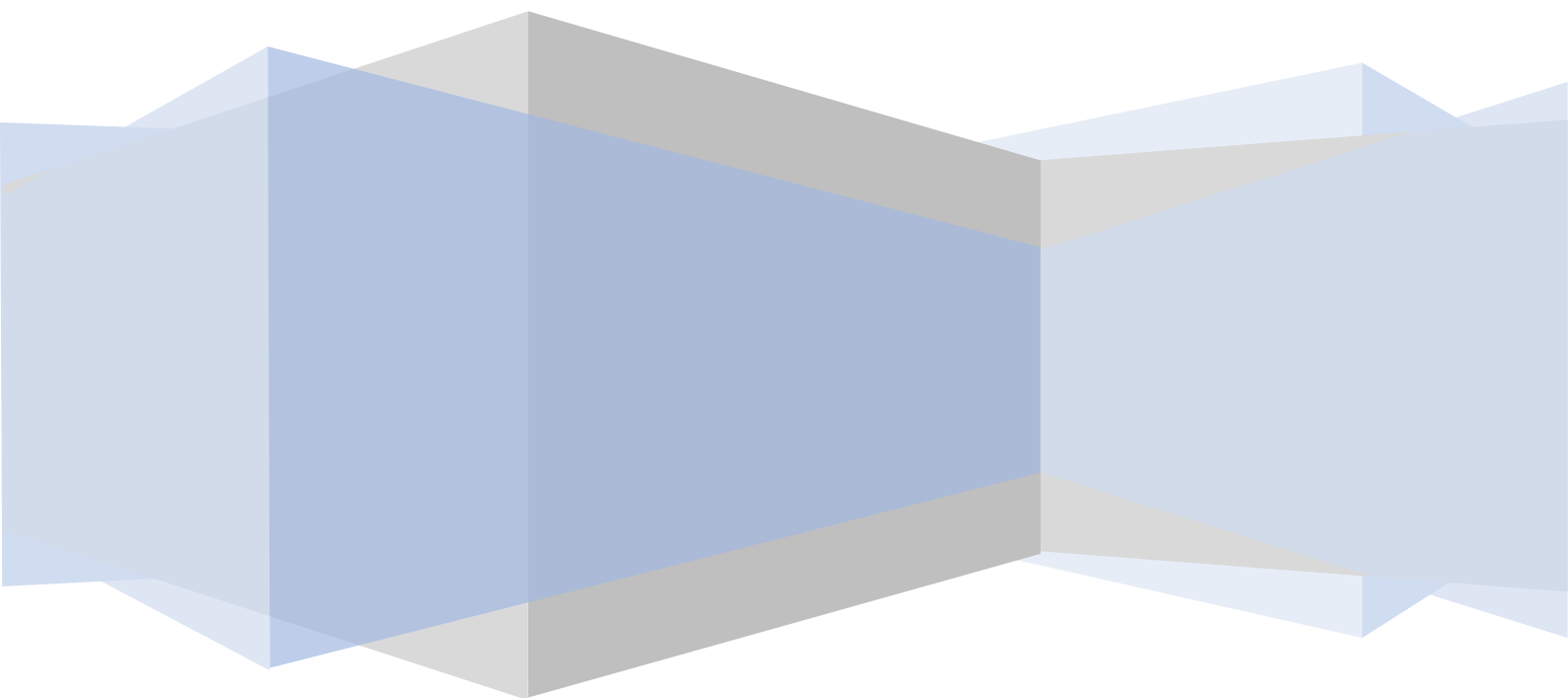# A. ELHAFIDH BOUSSOUF UNIVERSITY CENTER
SCIENCES &TECHNOLOGIE INSTITUTE
## PROCESS ENGINEERING DEPARTEMENT

Mineral Chemistry

CHAPTER V: THE MAJOR MINERAL SYNTHESIS

V.1. SULFURIC ACID:

sulfuric acid is a chemical compound, colorless, odorless, extremely oily liquid and highly corrosive strong mineral acid with the molecular formula H_2SO_4 and molecular weight 98.079 g/mol. which is soluble in water at all concentrations and sometimes called oil of vitriol.
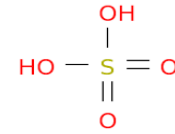
V.1.1. METHODS OF SYNTHESIS :

There are two major processes (available commercially) for production of sulfuric acid:

V.1.1.1. THE LEAD CHAMBERS PROCESS:

The process of sulfur burning produces a relatively dilute acid (62%-78% H_2SO_4) used in fertilizers. It involves sulfur entering a furnace with air and producing sulfur dioxide (SO_2). The hot sulfur dioxide is purified and mixed with nitrogen oxides in a tower called the Glover Tower. The mixture is then transferred to lead-lined chambers, where sulfur dioxide oxidizes to sulfur trioxide (SO_3). The gases are colorless in the first room, but brown due to higher nitrogen oxides. The gases then pass through the chambers in succession, forming the fertilizer acid, which contains 62% to 68% H_2SO_4. The gases are then passed into a reactor called the Gay-Lussac Tower, where they are washed with cooled dilute sulfuric acid. The nitrogen oxides and unreacted sulfur dioxide dissolve in the acid, forming the nitrous vitriol used in the Glover tower. The process is an older method of sulfur burning, but it is still used for fertilizer production.
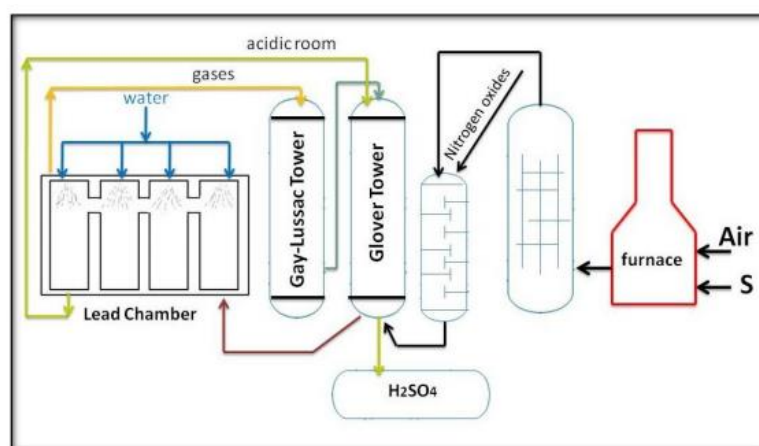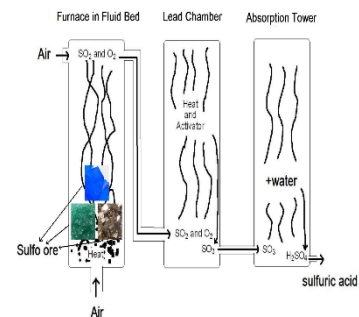
V.1.1.2. CONTACT PROCESS

The contact process, discovered in 1831 by Englishman Phillips, is a modern method for producing sulfur dioxide (SO_2) and sulfur trioxide (SO_3). This process is efficient due to the need for oleum and high concentration acid for slfonation and dye manufacturing. The process begins with burning sulfur with air to produce SO_2, which is oxidized to SO_3 in both contact and lead chambers processes. The sulfur dioxide is obtained from burning pyrites (iron sulfides) or hydrogen sulfide gas. In the contact process, SO_2 is converted to SO_3 using vanadium oxide (V_2O_5) as a catalyst. In the final stage, sulfur trioxide is converted to sulfuric acid, which is absorbed into concentrated sulfuric acid, producing a thick fuming liquid called oleum. The sulfuric trioxide reacts with water to form sulfuric acid with a 98% concentration.

$$SO_{3\,(g)} + H_2O_{\,(L)} \longrightarrow H_2SO_{4\,(L)}$$

The contact process is the preferred commercial method for sulfuric acid production due to its safety, low cost, and availability of available equipment. This newer method produces sulfuric acid in high concentrations, making it crucial for manufacturing, as it reduces costs and time consumption.

V.1.2. USES OF SULFURIC ACID:

 The important uses of sulfuric acid are:

1. Production Fertilizer.
2. Paints and dyes.
3. Uses in water treatment.
4. Making Detergents.
5. A Dehydrating agent.
6. Metal treatment and anodizing.
7. A Catalyst.
8. The acid in a car battery.
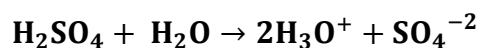
V.1.3. PHYSICAL PROPERTIES OF SULFURIC ACID:

- It is colorless, heavy and only liquid.
- It has specific gravity of 1.84.
- It is odorless dilute solution it has sour taste.
- It is extremely corrosive to skin and all body tissues hence causes severe burns.
- Its boiling point is 348 °C.
- Its M.P is 10-15 °C.

- It is soluble in water in all preparations with the evolution of a large amount of heat.

- Pure H₂SO₄ is non-conductor of electricity as it is not dissociated.

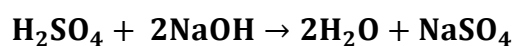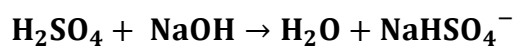- With addition of water, it becomes good conductor.

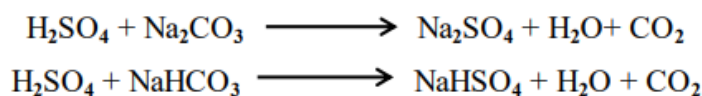## V.1.4. CHEMICAL PROPERTIES OF H₂SO₄:
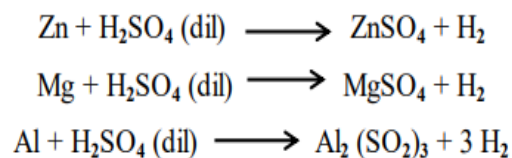
The sulfuric acid can react with:

- H₂O:

$$H_2SO_4 + H_2O \rightarrow 2H_3O^+ + SO_4^{-2}$$

- Alkalines:

$$H_2SO_4 + NaOH \rightarrow H_2O + NaHSO_4^-$$

$$H_2SO_4 + 2NaOH \rightarrow 2H_2O + NaSO_4$$

- Carbonates and bicarbonates:

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
$$H_2SO_4 + NaHCO_3 \longrightarrow NaHSO_4 + H_2O + CO_2$$

- Metal

$$Zn + H_2SO_4 \text{ (dil)} \longrightarrow ZnSO_4 + H_2$$
$$Mg + H_2SO_4 \text{ (dil)} \longrightarrow MgSO_4 + H_2$$
$$Al + H_2SO_4 \text{ (dil)} \longrightarrow Al_2(SO_2)_3 + 3H_2$$

- Metal with hot concentrated acid

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + H_2O + SO_2$$

$$Pb + H_2SO_4 \longrightarrow PbSO_4 + H_2O + SO_2$$
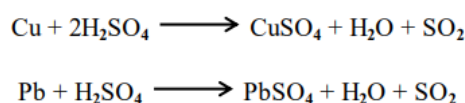
- Dissociation in boiling

$$H_2SO_4 \rightarrow H_2O + SO_3$$

- As oxidant

$$C + H_2SO_4 \longrightarrow CO_2 + SO_2 + H_2O$$
$$S + 2H_2SO_4 \longrightarrow 2SO_2 + H_2O$$

$$HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$
$$HBr + H_2So_4 \longrightarrow Br_2 + SO_2 + H_2O$$

$$H_2S + H_2SO_4 \longrightarrow S + SO_2 + H_2O$$
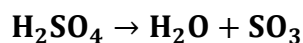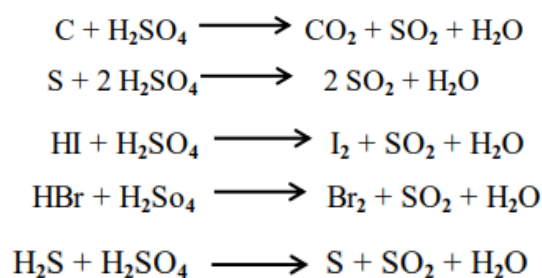
- As Drying and Dehydration Agent

$$CuSO_4 . 5H_2O \longrightarrow CuSO_4 + 5H_2O$$

$$C_{12}H_{22}O_{11} \longrightarrow C + 11\ H_2O$$

$$HCOOH \longrightarrow CO + H_2O$$
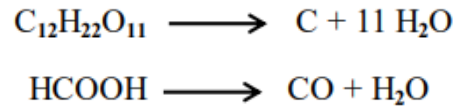
V.2. PHOSPHORIC ACID

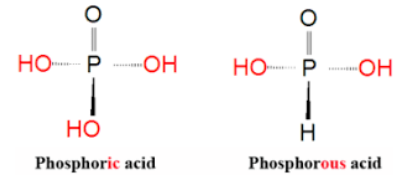Phosphoric acid, or orthophosphoric acid, is a phosphorus-based oxoacid with the chemical formula H_3PO_4. It is a triacid and holds the distinction of being the second-largest globally produced acid after sulfuric acid. This compound plays a crucial role in various industrial applications, including the production of fertilizers (approximately 85%), surface treatment of metals, pharmaceutical and fermentation industries, wastewater treatment, cleaning products, refractory binders, mineral chemistry, and the food industry.

Users often express the concentration of phosphoric acid in terms of P_2O_5. The conversion formula is as follow :

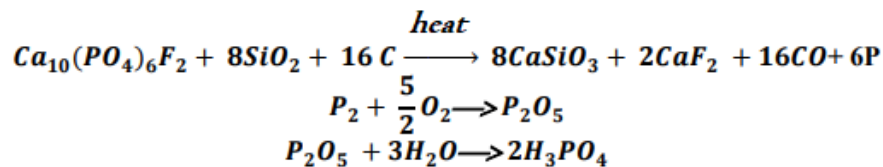$$[H_3PO_4] = [P_2O_5] \times 196\ /142$$

Hence, an acid stated to be 54% in P_2O_5 is equivalent to a concentrated acid at 74.5%.

V.2.1. METHODS OF SYNTHESIS:

The synthesis of phosphoric acid can be carried out through two different pathways:

V.2.2.1. THERMAL PATHWAY (ABANDONED DUE TO ITS HIGH ENERGY CONSUMPTION):

The phosphorus prepared in an electric furnace at a temperature between 1200 and 1500 is oxidized with coke and silica to produce phosphate anhydride, which is then hydrated into phosphoric acid according to the following reactions:

$$Ca_{10}(PO_4)_6F_2 + 8SiO_2 + 16\ C \xrightarrow{\ heat\ } 8CaSiO_3 + 2CaF_2 + 16CO + 6P$$

$$P_2 + \frac{5}{2}O_2 \longrightarrow P_2O_5$$

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

V.2.2.2. WET PROCESS:

Industrial wet processes are based on the leaching of natural ores containing phosphorus with concentrated sulfuric acid (75-98%). Typically, the ores are of the natural calcium phosphate type:

- $Ca_{10}(PO_4)_6F_2$:fluorapatite
- $Ca_3(PO_4)_2.CaCl_2$: chlorapatite
- $Ca_3(PO_4)_2.Ca(OH)_2$: hydroxylapatite

The wet process is subdivided into five stages:

1. **Storage, handling, and grinding of the ore**: This operation simply involves grinding the phosphate ore from extraction mines. The grain size is less than 500μm. The grinding of the raw phosphate aims to increase the ore's surface area for sulfuric acid attack.

2. **Leaching of the ore:** The leaching is carried out in a leaching tank with a volume of $914m^3$. The ground phosphate is attacked by concentrated sulfuric acid at 98.5% and medium-phosphoric acid (18 to 22% P_2O_5) in aqueous media. Insoluble products are formed and precipitate in the reaction medium (slurry). The reaction medium consists of:

Liquids: H_3PO_4, H_2SO_4, and H_2SiF_6 in solution.

Solids: $CaSO_4$, $2H_2O$ or $1/2H_2O$, and sodium and potassium fluosilicate.

The residence time depends on the reactivity of the phosphates and is greater than 2 hours. The reactions are exothermic, so cooling is required to maintain the temperature between 75°C and 80°C.

The attack of phosphate ore with acid (sulfuric acid), which can be subdivided into 2 categories of processes:
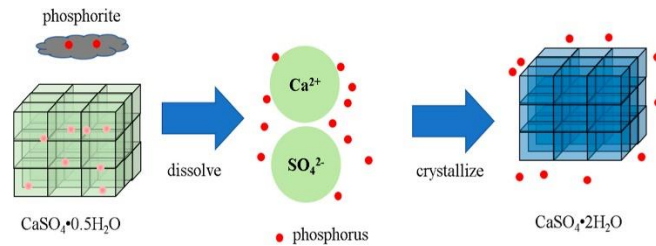
- Single-attack process → producing dihydrate gypsum.

- Two-step attack process → producing hemihydrate or semihydrate gypsum.

Different processes for crystallizing calcium sulfate during sulfuric attack vary based on attack conditions and filtration stages. The quality of phosphate significantly influences technological choice, with differences in specific consumption, energy, sulfuric acid, process water, and loss of P_2O_5 observed between processes, as well as the resulting acid concentration and quality.

(A) DIHYDRATE DH PROCESS

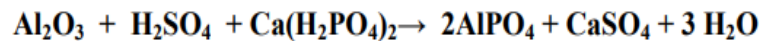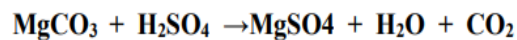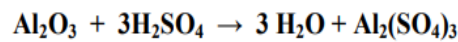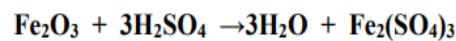The manufacturing process of phosphoric acid with precipitation of dihydrate sulfate is the most well-known among all processes. Phosphate and sulfuric acid are introduced into the reactor where the reaction takes place among sulfuric acid, phosphate, and recycled phosphoric acid

from the filtration juice. The resulting slurry is filtered, resulting in dihydrate gypsum and phosphoric acid with 28 to 32% P_2O_5.

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \text{---------} > 10CaSO_4.2H_2O + 6H_3PO_4 + 2HF$$

The reaction is accompanied by several secondary reactions such as:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow 3H_2O + Fe_2(SO_4)_3$$

$$Al_2O_3 + 3H_2SO_4 \rightarrow 3H_2O + Al_2(SO_4)_3$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO4 + H_2O + CO_2$$

$$Al_2O_3 + H_2SO_4 + Ca(H_2PO_4)_2 \rightarrow 2AlPO_4 + CaSO_4 + 3H_2O$$

$$Fe_2O_3 + H_2SO_4 + Ca(H_2PO_4)_2 \rightarrow 2FePO_4 + CaSO_4 + 3H_2O$$
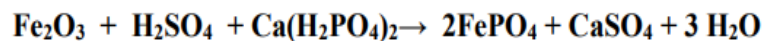
The precipitation of these phosphates, which will then be separated along with dihydrate gypsum, constitutes a significant loss of P_2O_5.
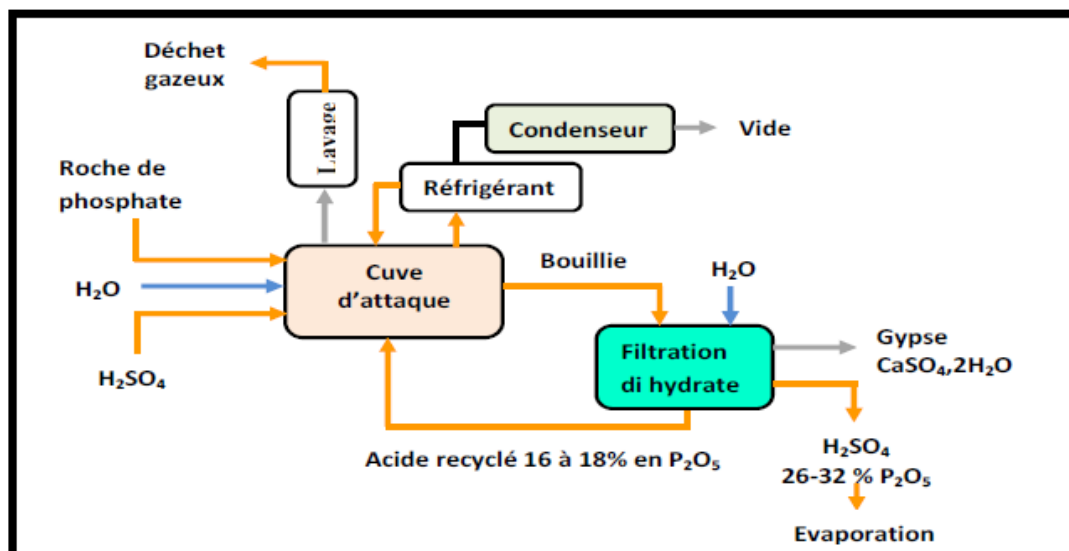
The optimum operating conditions for dihydrate precipitation are 26-32% P_2O_5 and 70-80°C. The slurry temperature is controlled by using a flash cooler. This also degasses the slurry, making pumping easier. The temperature can be controlled, for example, by using a circulated air cooler.

Advantages of dihydrate systems include:

- There is no restriction on the quality of the phosphate rock.

- The operational uptime is high.

- Operating temperatures are kept at a low level.

- Initiating and stopping processes are straightforward.

- Wet phosphate rock can be utilized, leading to savings in drying expenses.

  However, there are drawbacks:

- The acid content is relatively low, ranging from 26-32% P_2O_5.

- The gypsum produced is impure.

- The acid contains elevated levels of fluorine and aluminum.

- Approximately 5-6 tons of raw materials are required to produce 1 ton of phosphoric acid.

- Despite an annual production of around 1 million tons of phosphoric acid, a significant challenge is the substantial by-product generated: phosphogypsum, known for its acidity and containing soluble heavy metals.

- For every ton of phosphoric acid produced, approximately 5 tons of gypsum and compounds containing fluorine are generated, attributed to the fluorine content in the original ore.

(B) HEMIHYDRATE PROCESSHH

The operating conditions of the process are set to allow calcium sulfate to precipitate as hemihydrate (temperature between 90 and 100°C). In this way, it is possible to directly produce concentrated acid (40 to 48% P_2O_5), enabling significant energy savings.
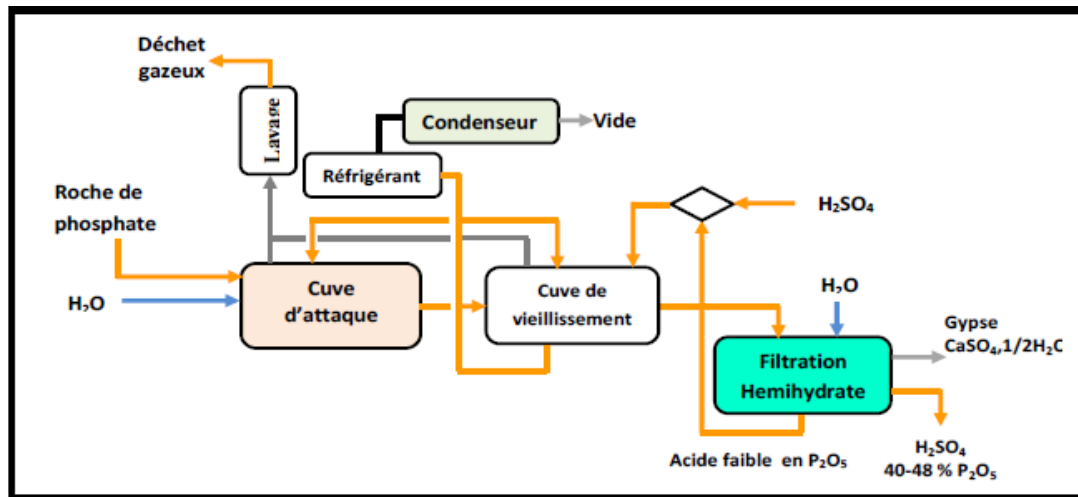
Advantages of hemihydrate systems include:

- Production of acid with a high P_2O_5 content (40-48%).

- Ability to utilize unground rocks due to the more stringent reaction conditions in the hemihydrate process.

- The acid obtained from the hemihydrate process tends to have significantly lower levels of free sulfate, suspended solids, aluminum, and fluoride.

- Operational simplicity.

    Disadvantages of hemihydrate systems include:

- Limited range of treated rocks.

- The filter cake obtained after filtration (hemihydrate) is more acidic compared to the gypsum filter cake (dihydrate) due to additional P_2O_5 losses. It also contains higher levels of fluoride and calcium.

- Lower P_2O_5 yield of 94-96% (attributed to crystallization blockage of hemihydrate into gypsum in the pipelines). To address this issue, a single two-stage tank is replaced.

3. **extraction of phosphoric acid through filtration**:

    The slurry is filtered by separating 29% P_2O_5 phosphoric acid from phosphogypsum using a rotary filter. The product is stored in settling tanks and filtered on flat vacuum filters. 15 tons of slurry are needed for 1 ton of P_2O_5, resulting in 4-5 tons of gypsum.

4. **Concentration and storage of phosphoric acid:** The industrial acid from the previous sections contains 26 to 45% P2O5, while the marketed product is standardized to 50% and above. The acid is brought to its boiling temperature between 120°C and 150°C,

under a pressure ranging from 80 to 150mbar and air with CO_2 and traces of fluorine are introduced. The by-products include:

- Gypsum (calcium sulfate) for plaster and cement additive.
- Fluosilicic acid (H_2SiF_6) for the production of fluosilicates, fluorides, and cryolites.

5. **Neutralization**: formation of the final product, and by-product generation.

V.2.2. USES OF PHOSPHORIC ACID

Phosphoric acid and its molecular form P_2O_5 are among the significant substances in the chemical industry, often ranking as the second most widely used acid after H_2SO_4. Annual production is around 65 million tons, compared to 40 million tons in the late 1970s. Aqueous phosphoric acid finds essential applications in various industries:

- Manufacture of superphosphate fertilizers.

- Synthesis of detergents and various phosphate forms.

- Pickling and rust treatment of metal surfaces.

- Cleaning metal and other hard surfaces such as tiles and porcelain.

- Cleaning equipment in the food industry.

- Binders for refractory materials and ceramics.

- Food industry, as an acidifying agent, especially in cola.

- Wastewater treatment.

- Coagulation of rubber latex.

- Acid catalysis in petrochemistry.

- Synthesis of pharmaceutical products.

- Acid regulator, antioxidant.

- dyeing in the textile industry.

- Manufacturing fertilizers.

V.2.2. PHYSICAL PROPERTIES:

1. **Physical State:** At room temperature, phosphoric acid is a colorless, odorless liquid.

2. **Density:** The density of phosphoric acid is higher than that of water, and it is a relatively dense liquid.

3. **Melting Point:** Phosphoric acid does not have a distinct melting point because it decomposes before reaching a specific temperature.

4. **Boiling Point:** Phosphoric acid decomposes before reaching a boiling point under normal atmospheric pressure.

5. **Solubility:** Phosphoric acid is highly soluble in water, forming a clear solution.

6. **Viscosity:** The viscosity of phosphoric acid increases with concentration. More concentrated solutions are more viscous.

7. **Hygroscopic Nature:** Phosphoric acid is hygroscopic, meaning it readily absorbs moisture from the air.

8. **Corrosiveness:** Phosphoric acid is corrosive and can react with metals, causing corrosion.

9. **Odor:** Phosphoric acid is generally odorless in its pure form.

V.2.4. CHEMICAL PROPERTIES:

1. **Acidic Nature:** Phosphoric acid is a tri-acid, meaning it has three replaceable hydrogen ions (protons) per molecule. It can undergo successive ionizations in water.

   - $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ (First ionization)

   - $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ (Second ionization)

   - $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ (Third ionization)

2. **Reactivity with Metals:** Phosphoric acid reacts with certain metals, producing hydrogen gas and forming metal phosphates. However, this reactivity is generally slower compared to other mineral acids.

3. **Dehydration Reactions:** Phosphoric acid can undergo dehydration reactions, losing water molecules to form polyphosphoric acids:

$$H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

4. **Formation of Phosphates:** Phosphoric acid reacts with bases to form phosphates. For example, reacting with sodium hydroxide:

$$NaOH + H_3PO_4 \rightarrow Na_2HPO_4 + 2H_2O$$
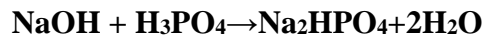
5. **Corrosive Nature:** Phosphoric acid is corrosive and can react with metals, causing corrosion.

6. **Reaction with Carbonates:** Phosphoric acid reacts with metal carbonates, producing carbon dioxide, water, and the corresponding metal phosphate.

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2 + H_2O$$

7. **Buffering Capacity:** Due to its multiple ionization steps, phosphoric acid has a buffering capacity, allowing it to resist drastic changes in pH.

V.3. AMMONIA:

Ammonia is produced from water, air, and energy, typically hydrocarbons, coal, or electricity. Steam reforming of light hydrocarbons is the most efficient route, with 77% of world ammonia capacity based on natural gas.
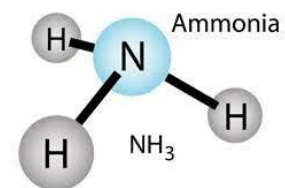
V.3.1. SYNTHESIS OF AMMONIA:

There are two main types of production processes for ammonia synthesis gas:

1. Steam reforming of natural gas or other light hydrocarbons (Natural Gas Liquids, Liquefied Petroleum Gas, Naphtha).

2. Partial oxidation of heavy fuel oil or vacuum residue.

Natural gas reforming with steam and air is the most efficient method for ammonia synthesis gas production, with approximate consumption figures based on modern technological standards.

	Natural gas	Heavy oil	Coal
Energy consumption	1.0	1.3	1.7
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7

The production processes currently and in the future primarily involve steam/air reforming based on natural gas and light hydrocarbons. These processes can be categorized into conventional steam reforming, mild steam reforming, and heat exchange autothermal reforming. Conventional steam reforming uses a fired primary reformer and stoichiometric air secondary reforming, while mild steam reforming uses a fired primary reformer and excess air secondary reforming.

V.3.1.1. CONVENTIONAL STEAM REFORMING (HIBER-BOSCH PROCESS)

The Haber-Bosch process

Generating of the nitrogen-hydrogen mixture   Synthesis of ammonia
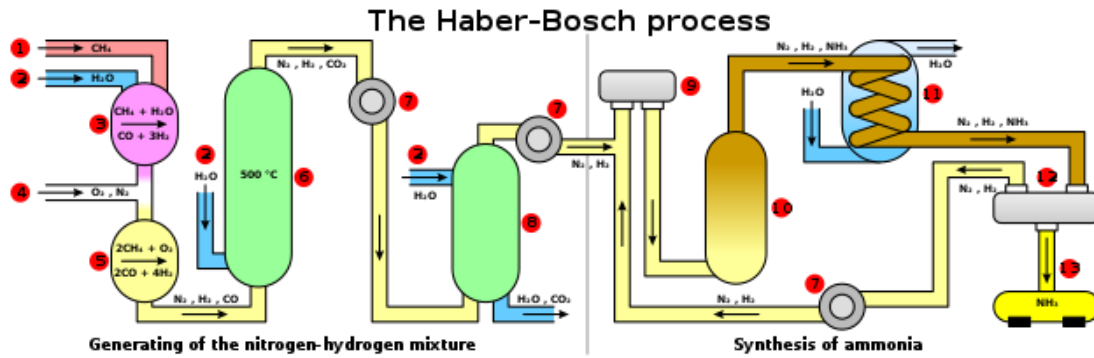
(A) OVERALL CONVERSION

The theoretical process conversions, based on methane feedstock, are given in the following approximate formulae:

$$0.88CH_4 + 1.26Air + 1.24H_2O \longrightarrow 0.88CO_2 + N_2 + 3H_2$$
$$N_2 + 3H_2 \longrightarrow 2NH_3$$
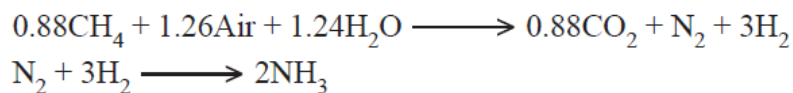
Synthesis gas production and purification typically occur at 25-35bar pressure, while ammonia synthesis pressure typically falls between 100-250bar.

(B) FEEDSTOCK DESULPHURISATION

The process involves preheating feed-gas to 350-400°C, treating it in a desulphurisation vessel, and hydrogenating sulphur compounds to H_2S using a cobalt molybdenum catalyst. The sulphur compounds are then adsorbed on pelletised zinc oxide.

$$R\text{-}SH + H_2 \longrightarrow H_2S + RH$$
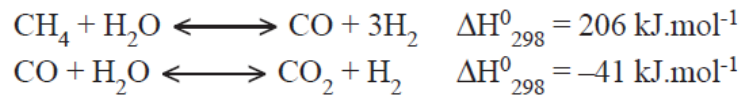$$H_2S + ZnO \longrightarrow ZnS + H_2O$$
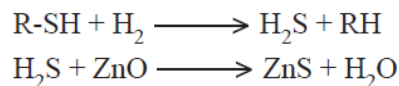
The sulphur is reduced to less than 0.1ppm in the gas feed, while zinc sulphide remains in the adsorption bed, and hydrogen is recycled from the synthesis section.

(C) PRIMARY REFORMING

The process of reforming involves mixing gas from a desulfuriser with process steam from an extraction turbine, heating it to 500-600°C in the convection section before entering the primary reformer. In some plants, the mixture is reheated in an adiabatic pre-reformer or feed-gas saturation. The process steam to carbon molar ratio (S/Cratio) determines the amount of process steam, with the optimum ratio varying based on factors like feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and plant steam balance. The primary reformer consists of high-nickel chromium alloy tubes filled with a nickel-containing catalyst.

The composition of the gas leaving the primary reformer can be determined by examining the chemical equilibria following:

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206 \text{ kJ.mol}^{-1}$$
$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ.mol}^{-1}$$

The primary reforming process uses natural gas or other gaseous fuel to supply heat. The flue-gas, which has temperatures over 900°C, is used in the process, with only 50-60% of the fuel's heat value directly used. Flue-gas emissions include CO_2, NOx, SO_2, and CO.

(D) SECONDARY REFORMING

The process involves compressing process air to reforming pressure and heating it to 600°C in the primary reformer. The process gas is mixed with air and passed over a nickel-containing secondary reformer catalyst, converting up to 99% of hydrocarbon feed. The process gas is then cooled to 350-400°C in a waste heat steam boiler or superheater downstream.

(E) SHIFT CONVERSION

The process gas from the secondary reformer contains 12-15% CO (dry gas base) and most of the CO is converted in the shift section according to the reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ.mol}^{-1}$$
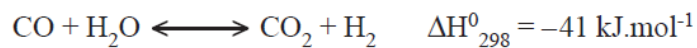
The High Temperature Shift (HTS) conversion involves passing gas through an iron oxide/chromium oxide catalyst at 400°C, reducing CO content to 3%. Copper-containing catalysts are used for increased conversion. The gas is then cooled and passed through a Low Temperature Shift (LTS) converter at 200-220°C, with a residual CO content of 0.2-0.4%, crucial for process efficiency.

(F) CO₂ REMOVAL :

CO_2 is removed through chemical or physical absorption processes, with solvents mainly aqueous amine solutions (MEA), Activated Methyl DiEthanolamine (aMDEA), or hot potassium carbonate solutions. Physical solvents include glycol dimethylethers (Selexol) and propylene carbonate. Chemical absorption processes have a typical heat consumption range of 30-60MJ.kmol-1 CO_2, while physical absorption processes may be designed for zero heat consumption. Residual CO_2 contents range from 100-1,000ppmv, depending on the removal unit type and design. Contents down to about 50ppmv are achievable.

(G) METHANATION :

The ammonia synthesis catalyst requires the removal of small amounts of CO and CO_2, which are poisonous, through conversion to CH_4 in the methanator.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$
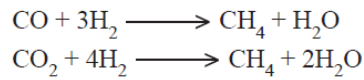
The synthesis reaction occurs at 300°C in a nickel-containing reactor, removing water from methane through cooling, condensation, and condensation/absorption in the product ammonia, ensuring water is removed before entering the converter.

(H) SYNTHESIS GAS COMPRESSION AND AMMONIA SYNTHESIS:

Ammonia synthesis occurs on an iron catalyst at pressures of 100-250bar and temperatures of 350-550°C.

$$N_2 + 3H_2 \longleftrightarrow 2NH_3 \quad \Delta H^0{}_{298} = -46 \text{ kJ.mol}^{-1} \text{ NH}_3$$

The converter only reacts 20-30% per pass due to unfavorable equilibrium conditions. The ammonia is separated from the recycle gas by cooling/condensation, and the reacted gas is replaced by fresh synthesis gas. Extensive heat exchange is required due to the exothermic reaction and large temperature range. A new ammonia synthesis catalyst with ruthenium on graphite supports can increase conversion and lower operating pressures. Ammonia condensation is not complete with water or air cooling, and is usually unsatisfactory. Vaporising ammonia is used as a refrigerant in most plants to achieve low ammonia concentrations in recycled gas, which are liquified in a refrigeration compressor.
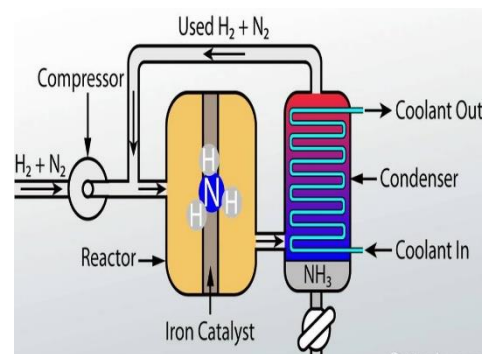
V.3.1.2. STEAM REFORMING WITH EXCESS AIR SECONDARY REFORMING (PROCESS FLOWSHEET):

Some processes are designed for reduced primary reforming by moving some of the duty to the secondary reformer because of the marginal low efficiency of the primary reformer:

(a) *Decreased firing in the primary reformer*: Lower heat supply in the primary reformer lowers process outlet temperature, increases firing efficiency, and reduces size and cost. These milder operating conditions prolong catalyst service lives and reduce reforming extent.

(b) *Increased process air flow to the secondary reforming*: The primary reformer requires increased internal firing due to decreased heat supply, resulting in a higher methane slip and lower secondary reformer outlet temperature. The process air requirement is 50% higher than conventional methods, requiring increased compression capacity and energy.

(c)*Cryogenic final purification after methanation*: The cryogenic purifier removes methane, excess nitrogen, and argon from synthesis gas, producing cooling through depressurisation. This process eliminates impurities, except for a small amount of argon. The cryogenic unit also receives purge from the synthesis section and delivers fuel off-gas.

(d) *Lower inert level of the make-up syngas*: The make-up synthesis gas undergoes significant improvement in efficiency compared to conventional purification methods due to higher conversion per pass and reduced purge flow.

V.3.1.3 HEAT EXCHANGE AUTOTHERMAL REFORMING:

The high-level heat from secondary reformer outlet gas and primary reformer flue-gas is wasted when used to raise steam. Recent developments recycle this heat by using the heat content of the secondary reformed gas in a newly-developed primary reformer, eliminating the fired furnace. Surplus or oxygen-enriched air is required in the secondary reformer to meet the heat balance. This autothermal concept significantly reduces emissions to the atmosphere and NOx emissions, with two processes currently in operation and others at the pilot stage.

V.3.1.4. BAT REFORMING PROCESSES FOR NEW PLANTS:

The modern versions of the conventional steam reforming and excess air reforming processes will still be used for new plants for many years to come. Developments are expected to go in the following directions:

– Lowering the steam to carbon ratio

– Shifting duty from primary to secondary reformer

– Improved final purification

– Improved synthesis loop efficiency

– Improved power energy system

– Low NOx burners

– Non-iron-based ammonia synthesis catalyst

The new autothermal concepts are expected to be developed further, and will continue the developments outlined above.

V.3.1.5. PARTIAL OXIDATION OF HEAVY OILS:

The partial oxidation process is a non-catalytic method used for gasifying heavy feedstocks like residual oils, coal, and viscous hydrocarbons and plastic wastes. It requires an air separation unit for oxygen production and nitrogen in the liquid nitrogen wash to remove impurities. The process occurs at high pressure and temperatures around 1,400°C, with steam added for temperature moderation.

$$CH_n - + 0.5O_2 \longrightarrow CO + n/2H_2$$

The ammonia synthesis process involves the formation of carbon dioxide, methane, and some soot, as well as the conversion of sulphur compounds into hydrogen sulphide and mineral compounds into specific ashes. The process gas is freed from solids through water scrubbing and the soot is recycled. Heavy metals like V, Ni, and Fe are recovered, and hydrogen sulphide is separated and reprocessed to elementary sulphur in a Claus unit. The shift conversion process uses two high-temperature shift catalyst beds with intermediate cooling, and CO_2 is removed using an absorption agent. Residual traces are removed before final purification by a liquid nitrogen wash, which removes impurities and adds nitrogen to achieve a stoichiometric hydrogen to nitrogen ratio. This process is simpler and more efficient than steam reforming plants.

Compressors driven by steam require auxiliary boilers, primarily due to SO_2, NO_x, and CO_2 emissions. Imported electric power drives compressors with low site emissions.

V.3.2. AMMONIA USES:

- The major use of ammonia is as a fertilizer. It is usually applied directly to the soil from tanks containing the liquefied gas

- Ammonia is also used in the manufacture of commercial explosives (trinitrotoluene [TNT], nitro-glycerine, and nitrocellulose).

- In the textile industry, ammonia is used in the manufacture of synthetic fibres, such as nylon and rayon. In addition, it is employed in the dyeing and scouring of cotton, wool, and silk

- Ammonia serves as a catalyst in the production of some synthetic resins.

- It neutralizes acidic by-products of petroleum refining.

- In the rubber industry it prevents the coagulation of raw latex during transportation from plantation to factory.

- Ammonia is utilized in the ammonia-soda process, also known as the Solvay process, a widely used method for producing soda ash.

- The Ostwald process is a method used to convert ammonia into nitric acid.

- Ammonia is utilized in metallurgical processes like alloy sheet nitriding, and as a portable source of atomic hydrogen for welding due to its easy decomposition.

- Ammonia, with a capacity to absorb 327 calories of heat, is a valuable coolant in refrigeration and air-conditioning equipment due to its significant heat absorption capacity.

- Ammonia has minor applications, such as its inclusion in certain household cleansing agents.

V.3.3. PHYSICAL PROPERTIES OF AMMONIA

- **State at Room Temperature:** Ammonia is a gas at room temperature and atmospheric pressure.

- **Odor:** It has a sharp and pungent odor.

- **Color:** It is a colorless gas.

- **Boiling Point:** The boiling point of ammonia is -33.35 °C (-28.03 °F).

- **Freezing Point:** The freezing point of ammonia is -77.7 °C (-107.8 °F).

- **Density:** The density of gaseous ammonia is about 0.73 kg/m³ at standard temperature and pressure.

- **Solubility:** Ammonia is highly soluble in water, forming ammonium hydroxide.

- **Heat of Vaporization:** Ammonia has a high heat of vaporization (23.3 kilojoules per mole at its boiling point).

- **Molecular Structure:** The ammonia molecule has a trigonal pyramidal shape with three hydrogen atoms and an unshared pair of electrons attached to the nitrogen atom.

- **Polarity:** Ammonia is a polar molecule, and it exhibits strong intermolecular hydrogen bonding.

- **Dielectric Constant:** The dielectric constant of ammonia is lower than that of water but still allows it to act as a moderately good ionizing solvent.

- **Self-Ionization:** Ammonia undergoes self-ionization, although to a lesser extent than water.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
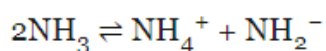
V.3.4. CHEMICAL PROPERTIES OF AMMONIA

1. **Combustion Reaction:**

Combustion of ammonia under certain conditions produces nitrogen gas (N_2) and water (H_2O).

$$4NH_3 + 3O_2 + heat \rightarrow 2N_2 + 6H_2O$$
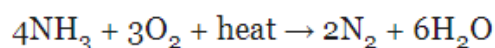
2. **Catalyzed Reaction for Nitric Oxide Production:**

Ammonia reacts with oxygen, catalyzed under specific temperature conditions, forming nitric oxide (NO), which is further oxidized to nitrogen dioxide (NO_2) (used in the synthesis of nitric acid)
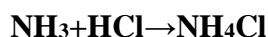
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H2O$$
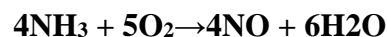
3. **Basicity:**

Ammonia is a weak base, and it readily accepts protons (H^+) to form ammonium ions (NH_4^+) in aqueous solutions.

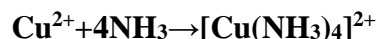$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

4. **Acid-Base Reactions:**

Ammonia reacts with acids to form ammonium salts.

$$NH_3 + HCl \rightarrow NH_4Cl$$

5. **Complex Formation:**

Ammonia can form complexes with various metal ions.

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$$

6. **Redox Reactions:**

Ammonia can act as a reducing agent in some reactions.

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H2O$$
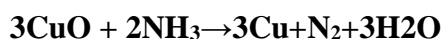
7. **Formation of Nitrides:**

Ammonia reacts with certain metals to form nitrides.

$$3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$$
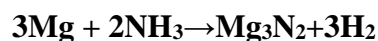
8. **Complexation with Transition Metals:**

Ammonia forms coordination complexes with transition metal ions.

$$Co^{3+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{3+}$$
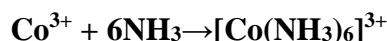
9. **Ligand Properties:**

Ammonia acts as a ligand in coordination complexes, contributing lone pair electrons.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

V.4. NITRIC ACID:

It was named aqua fortis (meaning strong water) by alchemists. Glauber obtained it by the action of sulphuric acid on nitre. Nitric acid is crucial for explosives, fertilizers, dyes, and drugs. Before World War I, distilling nitre with concentrated sulphuric acid was the only method. Today, Birkeland and Eyde process or Arc process and Ostwald's process are used for nitric acid production.
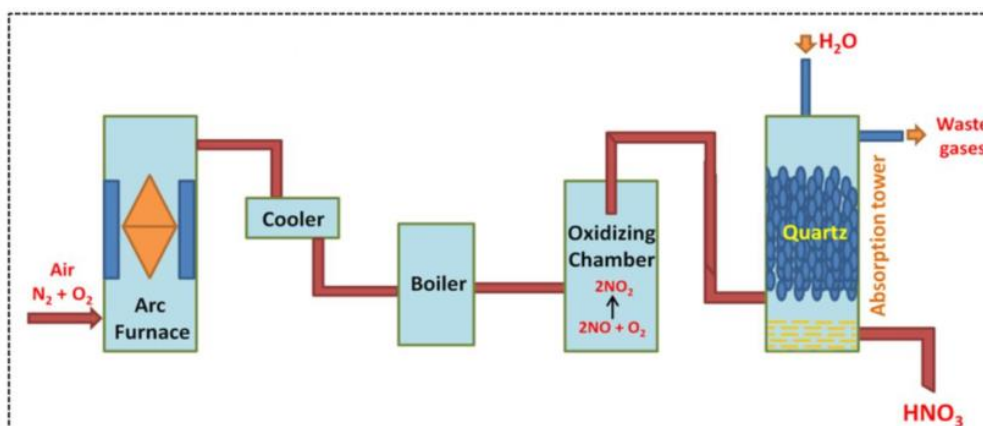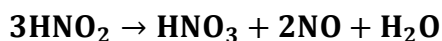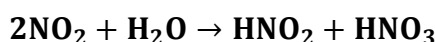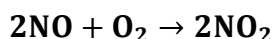
V.4.1. SYNTHESIS OF NITIRIC ACID:

Nitric acid is one of the most important inorganic chemicals. Quantity wise it is one of the top ten industrial chemicals.
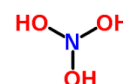
V.4.1.1. BIRKELAND AND EYDE PROCESS PRINCIPLE:

The reaction between nitrogen and oxygen is reversible and endothermic, favoring the formation of nitric oxide. To prevent decomposition, the temperature is maintained at 3000°C using an electric arc. Nitric oxide then combines with oxygen to form nitrogen dioxide. The vapours are then passed through water when nitric acid is produced.

$$N_2 + O_2 <=> 2NO \quad \Delta H= -43,2 \text{ calories}$$

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

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

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$
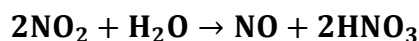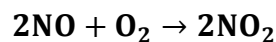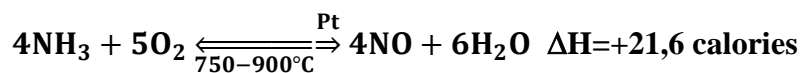

- **Process Overview:**

Air is blown into an electric arc established between water-cooled copper electrodes, and a strong magnetic field applied at right angles helps spread the arc into a disc.

- **Temperature Generation:** The electric arc produces an intense temperature of approximately 3000°C.

- **Nitric Oxide Formation:** Nitrogen and oxygen combine in the high-temperature environment, resulting in the formation of nitric oxide.

- **Gas Composition:** The gases emerging from the furnace contain 1.25 to 2% nitric oxide.

- **Cooling Stages:** Quick cooling reduces the temperature of the gases to 1000°C. Further cooling to 150°C is achieved by passing the gases through boiler pipes.

- **Oxidation Chamber:** Gases enter the oxidation chamber, and Nitric oxide reacts with oxygen, oxidizing into nitrogen dioxide.

- **Absorption Tower:** Nitrogen dioxide produced is absorbed in water within an absorption tower. The tower, measuring 70 ft in height and 20 ft in diameter, is packed with quartz.

- **Nitric Acid Strength:** The nitric acid in the first tower reaches a strength of 30 to 40%, but Successive towers yield nitric acid with strengths of about 20%, 10%, and 5%.

The method's utility has declined due to poor yield and high electrical power consumption, and it considered outdated in contemporary practices.

V.4.1.2. OSTWALD'S PROCESS (MODERN PROCESS)

The ammonia-air mixture is oxidized to nitric oxide (NO) (exothermic reaction) using a platinum gauze catalyst at 750-900°C, maintaining the catalyst's temperature. The nitric oxide is then converted to nitrogen dioxide (NO_2), which is cooled to 50°C and absorbed in water, allowing volatilization and recycling.

$$4NH_3 + 5O_2 \underset{750-900°C}{\overset{Pt}{\rightleftharpoons}} 4NO + 6H_2O \quad \Delta H = +21{,}6 \text{ calories}$$

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

$$2NO_2 + H_2O \rightarrow NO + 2HNO_3$$

Overview process :

- **Mixture Composition:** Dry ammonia and purified air are combined in a ratio of 1:10 (by volume).

- **Catalyst Chamber**: The mixture is directed through the catalyst chamber.

- **Catalyst Type**: Platinum gauze is utilized as the catalyst.

- **Initial Heating:** The platinum gauze is electrically heated to approximately 800 ℃.

- **Temperature Maintenance:** Subsequently, the temperature is sustained by the heat generated during the reaction.

- **Oxidation Reaction:** Ammonia undergoes rapid oxidation, resulting in the formation of nitric oxide.

- **Yield Percentage:** The yield of nitric oxide ranges between 90-95%.

- **Cooling:** Gases from the converter are cooled and introduced into an oxidation chamber.

- **Oxidation of nitric oxide:** Nitric oxide (NO) present in the gases undergoes oxidation to form nitrogen dioxide (NO_2).

- **Absorption by water:** The nitrogen dioxide is absorbed in water within an absorption tower packed with broken quartz.

- **Second oxidation:** In the absorption tower, nitric oxide is oxidized again by oxygen, and nitrogen dioxide is further absorbed by water.

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3.$$
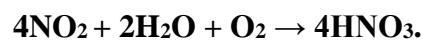
- **The final yield:** The concentration of the produced acid is approximately 50-60%.
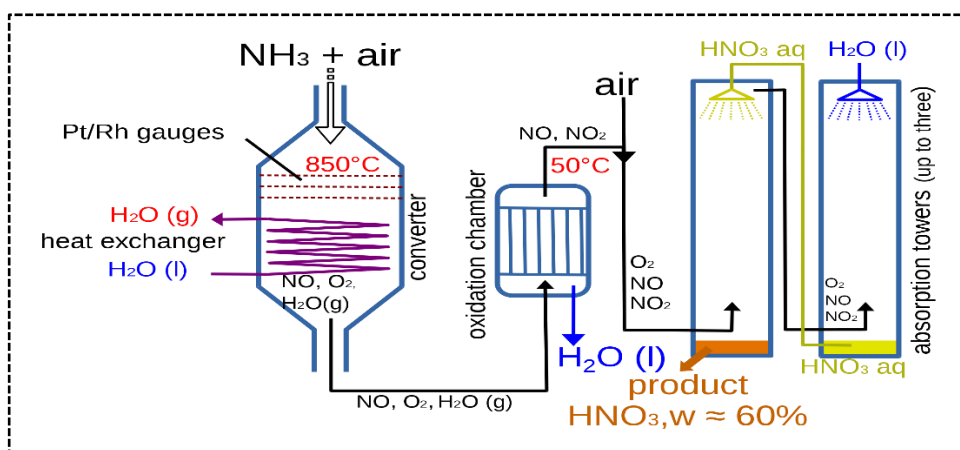
CONCENTRATION OF NITRIC ACID: Dilute nitric acid (50-60%) obtained in the above process is concentrated by distillation till a constant boiling mixture (121 °C) is formed. This is ordinary concentrated nitric acid and its strength is 68%. More concentrated HNO_3 is produced by distilling the ordinary concentrated nitric acid with concentrated sulphuric acid. The distillate is 98% HNO_3. The cent percent HNO_3 is obtained by cooling 98% HNO_3 in a freezing mixture. The colourless crystals (m.pt. -42 °C) are melted to get 100% HNO_3.

V.4.2. USES OF NITRIC ACID:

❖ In the manufacture of explosives like T.N.T. (trinitrotoluene), picric acid, nitroglycerine, dynamite, etc.

❖ In the manufacture of fertilizers like ammonium nitrate, basic calcium nitrate, etc.

❖ In the manufacture of artificial silk, dyes, drugs, perfumes, etc.

❖ In the purification of silver and gold.

❖ As a laboratory reagent.

❖ As a solvent for metals, for etching designs on wares of brass, bronze, etc.

❖ In the preparation of aqua-regia.

❖ In the manufacture of sulphuric acid.

❖ For nitration of organic compounds.

❖ For the manufacture of nitrates such as silver nitrate, sodium nitrate, potassium nitrate, etc

PHYSICAL PROPERTIES:

1. **Physical State:** Nitric acid is a liquid at room temperature, appearing as a colorless to a pale yellow liquid.

2. **Odor:** Nitric acid has a pungent and suffocating odor.

3. **Melting Point:** The pure compound freezes at -42°C (-43.6°F), forming white crystals. However, commercially available nitric acid is often a solution and may have a lower freezing point.

4. **Boiling Point:** Nitric acid boils at 83°C (181.4°F) under normal atmospheric pressure.

5. **Density:** The density of nitric acid varies with concentration. For instance, 68% concentrated nitric acid has a density of approximately 1.4 g/cm³.

6. **Solubility:** Nitric acid is highly soluble in water. It forms a solution with water in all proportions.

7. **Corrosiveness:** Nitric acid is a strong oxidizing agent and is extremely corrosive to most metals and tissues.

8. **Hygroscopicity:** It is hygroscopic, meaning it readily absorbs moisture from the air.

9. **Miscibility:** Nitric acid is miscible with many organic solvents.

10. **Electrical Conductivity:** Dilute solutions of nitric acid conduct electricity due to the presence of ions.

V.4.4. CHEMICAL PROPERTIES:

1. **Acidic Nature:** Nitric acid is a strong acid, capable of donating a proton (H^+) in aqueous solutions.

2. **Dissociation:** In water, nitric acid undergoes dissociation to produce hydronium ions (H_3O^+) and nitrate ions (NO_3^-).

$$HNO3 \rightarrow H^+ + NO3^-$$
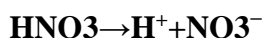
3. **Oxidizing Agent:** Nitric acid is a potent oxidizing agent, readily donating oxygen and accepting electrons in redox reactions.

$$6HNO_3 + 2Al \rightarrow 2Al(NO_3)_3 + 3H_2O + 3NO_2$$

4. **Reaction with Metals:** Nitric acid reacts with many metals, often producing nitrogen dioxide gas and metal nitrates.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

5. **Formation of Nitrogen Oxides:** Nitric acid can decompose to form nitrogen oxides, such as nitrogen dioxide (NO_2) and nitrogen trioxide (NO_3).

$$4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$$

6. **Reaction with Bases:** Nitric acid reacts with bases to form salts and water in neutralization reactions:

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

7. **Dehydrating Agent:** Nitric acid can act as a dehydrating agent, removing water molecules from substances:

$$HNO_3 + H_2SO_4 \rightarrow NO_2+ + H_3O^+ + HSO_4^-$$

8. **Reaction with Organic Compounds:** Nitric acid reacts with organic compounds, leading to nitration reactions, where nitro groups are introduced into the molecules.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$
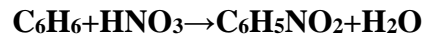
9. **Decomposition at Elevated Temperatures:** Nitric acid decomposes at high temperatures to produce nitrogen dioxide, oxygen, and water.

$$4HNO_3 \xrightarrow{\text{Heat} > 150°C} 2H_2O + 4NO_2 + O_2$$