

Lecture 1

Syllabus

1. Treatment of industrial water
2. Industrial carbon
3. Gases (CO₂, NH₃, ...)
4. Sulfur and its compounds
5. Sulfur and Sulfuric acid production

References

1. Kirk, R. E., and D. F. Othmer, "Encyclopedia of Chemical Technology,"
2. R. NORRIS SHREVE "THE CHEMICAL PROCESS INDUSTRIES".

THE CHEMICAL PROCESS INDUSTRIES

These processes may usually be resolved into a coordinated series of unit physical operations and unit chemical processes.

These unit operations (or physical changes) and these unit processes (or chemical changes) may be accepted as the units or blocks into which we can break down the manufacturing processes of the various chemical industries.

The objectives sought are to present a cross section of the manufacturing procedures employed by modern chemical industries, largely, separated into their unit chemical processes and unit physical operations through the help of flow diagram.

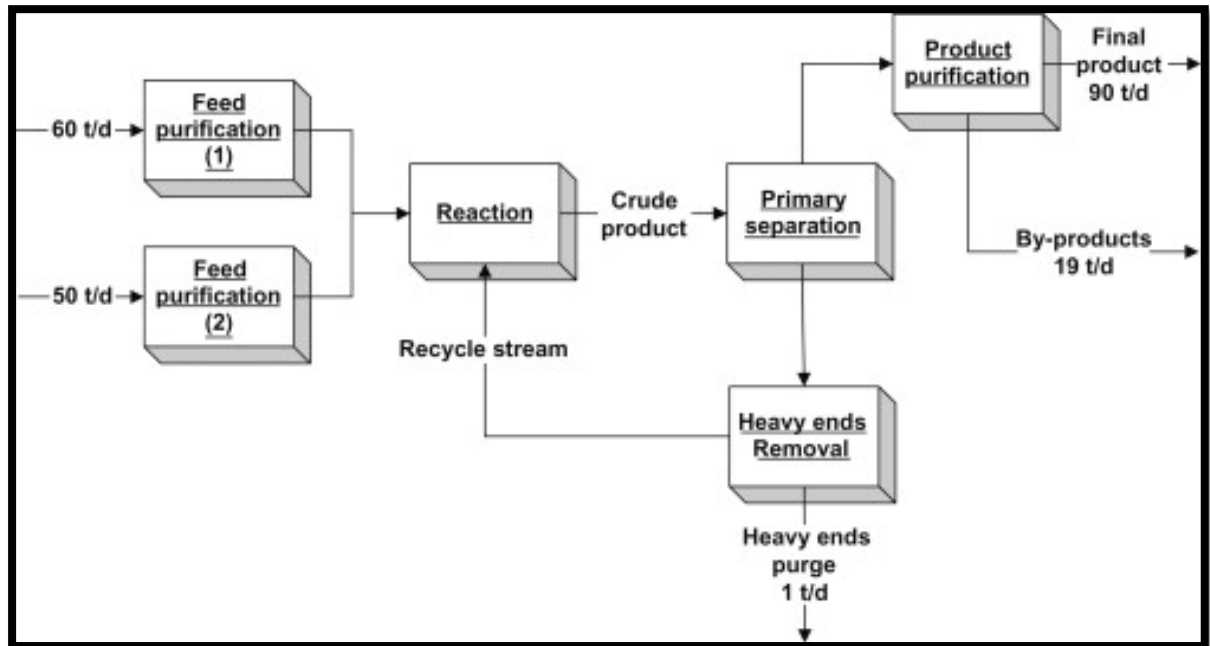


Figure. Example of Block flow diagram

UNIT PROCESSES AND UNIT OPERATIONS

We may define chemical engineering in its modern sense by the following equation:

$$\text{Chemical engineering} = \text{unit processes} + \text{unit operations}$$

(chemical changes) (physical changes)

Indeed, the development of chemical manufacturing procedures is largely through *flow sheets* which are definitely constructed from a coordinated sequence of unit processes and operations that fabricate the raw materials into the finished product and by-products.

Unit process	Unit operation
Combustion	Gas absorption
Oxidation	Solvent extraction
Neutralization	Humidification
Causticization	Evaporation

Unit operation	Equipment	Unit process	Equipment
Fluid flow	Pumps	Combustion	Boilers
Heat transfer	Heat exchanger	Oxidation	Converters

Water Conditioning And Waste-Water Treatment

As is well known, the purity and the quantity of available water are very important in the location of a chemical plant. Two types of water are considered:

1. The surface water
2. The ground water

Hard waters, are those containing objectionable amounts of dissolved salts of calcium and magnesium. These are present as bicarbonates, chlorides, or sulfates. These salts give insoluble precipitates with soap and form clogging scales with low thermal conductivities when used in boilers.

Hardness is usually expressed in terms of the dissolved calcium and magnesium salts calculated as calcium carbonate equivalent, CaCO_3 .

Water hardness may be divided into two classes:

1. Carbonate (temporary) hardness
2. Non-carbonate (permanent) hardness.

Temporary hardness can usually be greatly reduced by boiling; permanent hardness requires the use of chemical agents.

In addition to hardness, there may also be present varying amounts of sodium salts, silica, alumina, iron, or manganese.

Other water impurities that may be present are suspended insoluble matter (classed usually as turbidity), organic matter, color, and dissolved gases. Such gases are carbon dioxide (largely as bicarbonate), oxygen, nitrogen, and, in sulfur waters, hydrogen sulfide.

Water Conditioning

Water conditioning must be adapted to the particular use for which the water is designed.

laundries require zero hardness to prevent precipitation of calcium and magnesium soap on the clothes. Likewise calcium and magnesium salts cause undesirable precipitates with dyes in the textile industries or with the dyes in paper manufacture.

Methods Of Conditioning Water

Softening is the term applied to those processes which remove or reduce the hardness of the water. While purification usually refers to the removal of organic matter and microorganisms from the water.

1. Ion exchange

This is The most important method for softening water.

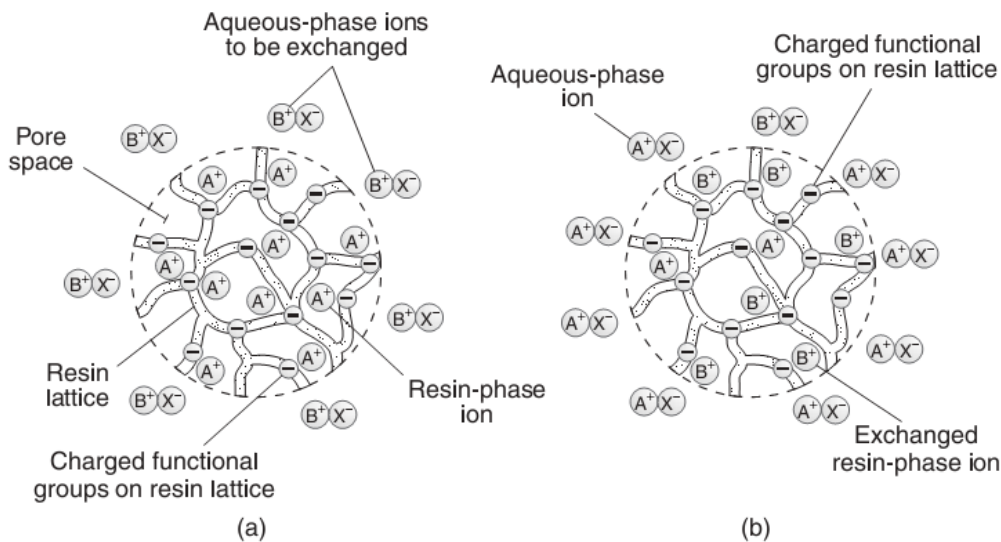
Facilities

The ion exchange process requires the following basic components:

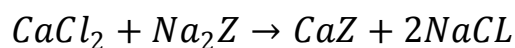
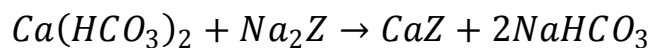
- Ion exchange materials (resins or zeolite),
- Ion exchange units, and
- Salt storage tanks.

1. Zeolite Exchange (or cation-exchange system): Early ion exchangers were natural silica compounds called zeolites. the "inorganic" zeolites are composed principally of hydrated alkali alumina-silicates ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$) that contain easily exchangeable ions such as sodium or potassium.

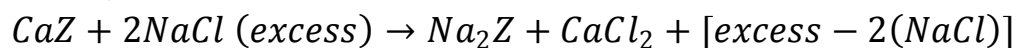
During the softening process, the Ca and Mg ions are exchanged from the hard water by the zeolite for the Na ions. When the zeolite becomes almost all changed to calcium and magnesium compounds, it is regenerated to restore the sodium zeolite. This is usually done with salt solution and in the pH range between 6 and 8.

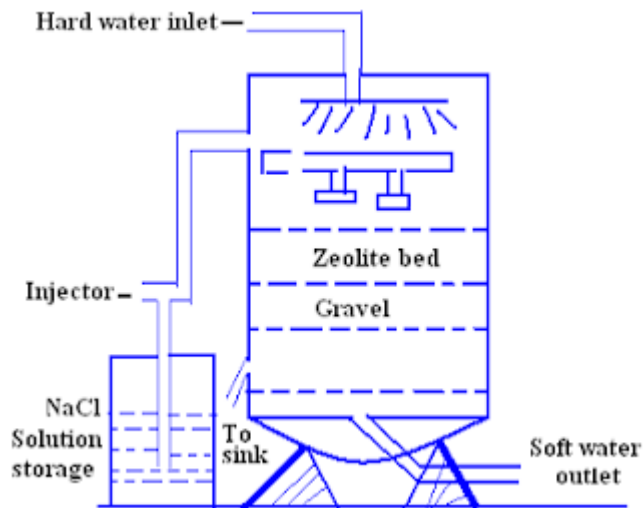


Reactions: Using water containing calcium bicarbonate, for example, a typical equation for zeolite softeners follows, where Z represents the complex cation exchanger radical:



For regeneration:





The equipment for the process, shown in Fig., is a large closed cylindrical tank in which the zeolite is supported on graded gravel. The water to be softened may flow down through the tank. Auxiliary apparatus includes both brine- and salt-storage tanks.

advantage

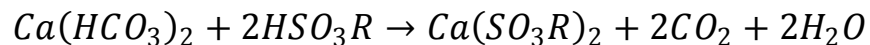
The great advantage of the zeolite softeners is their convenience and the fact that they furnish a water of zero hardness.

2. Organic Ion Exchange:

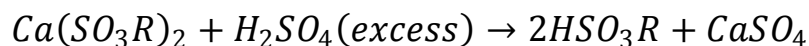
1. Cation organic exchangers: may be classified as:

1. Synthetic organic resins such as sulfonated styrene resins (most widely used), sulfonated phenolic resins.
2. Processed natural organic materials such as sulfonated coal, coke.

These contain an exchangeable hydrogen ion and can be employed to remove all cations according to the following reactions:



The regeneration is usually effected by sulfuric acid as follows:

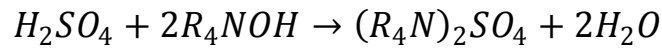


2. Anion exchanger

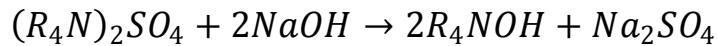
They are of two types- highly basic type and weakly basic type. Both types will remove strongly ionized acids such as sulfuric,

hydrochloric or nitric, but only the highly basic anion exchangers will remove weakly ionized acids such as silicic and carbonic as well as the strongly ionized acids.

For the anion exchange of a strongly ionized acid:



Regeneration:



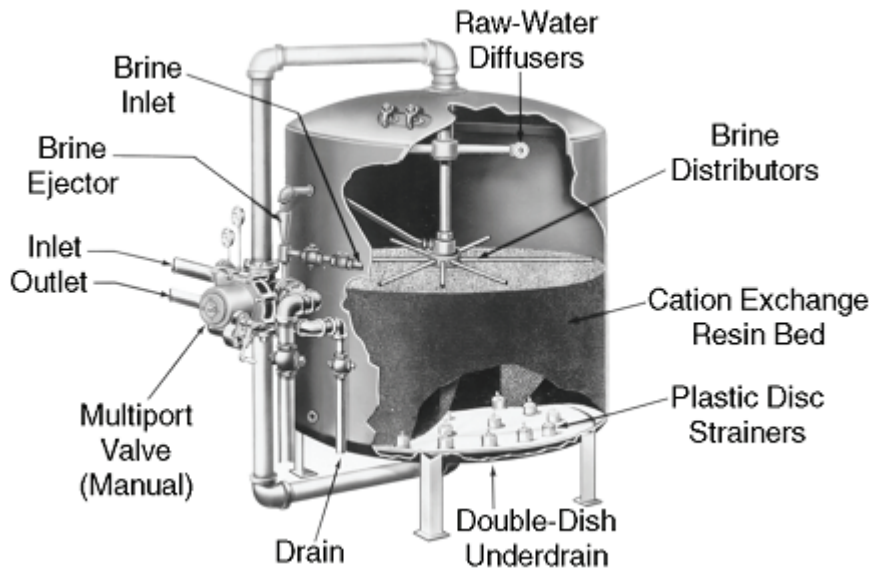
3. Ion Exchange Units

The vessels used in ion exchange systems resemble those used in pressure filters. Vertical-downflow ion exchange unit designed with the following components:

- Hard-water inlet
- Soft-water outlet
- Wash-water inlet and collector
- Brine inlet and distribution system
- Brine and rinse-water outlet
- Rate-of-flow controllers
- Sampling taps
- Underdrain system, which also serves to distribute backwash water
- Graded gravel to support the ion exchange resins

The size of the ion exchange unit and the volume of resin required are determined by the concentration of ions to be removed, e.g., the hardness of the raw water and the desired length of time between regenerations. The minimum recommended depth is 24 in. (0.6 m).

The resin is supported either by an underdrain system or by 15–18 in. (0.40–0.45 m) of graded gravel.



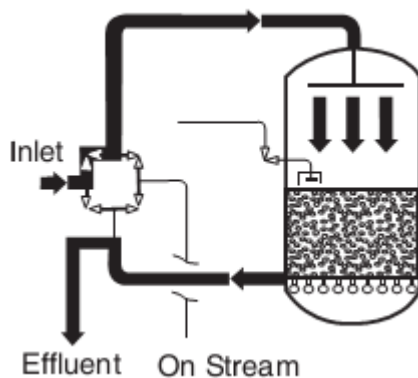
Regenerant Storage Tanks

Sodium chloride or potassium chloride are the most common salts used in the water softening process to form brine, which is used to regenerate the resin. The amount of salt used in creating the brine ranges from 0.25 to 0.45 lb (0.11 to 0.20 kg) for every 1,000 grains of hardness removed (7,000 grains = 1 lb, 1 grain/gal = 17.1 mg/L).

Operation Of Ion Exchange Processes

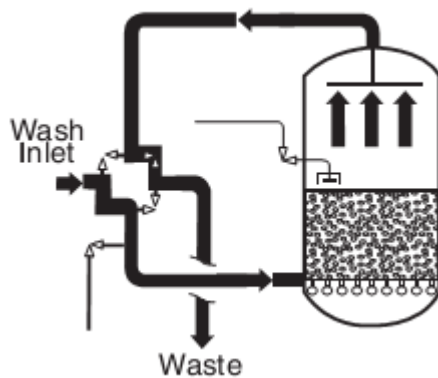
There are four basic cycles in the ion exchange water softening process. As shown in Figure , these are:

1. Softening: Influent water passes downward through the bed of ion exchange material to the effluent.

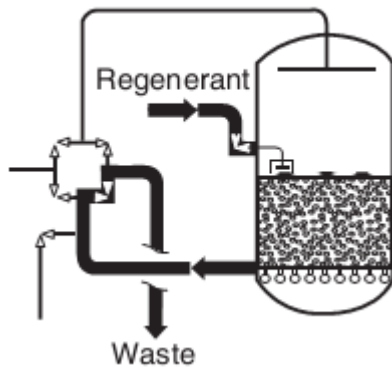


2. Backwash

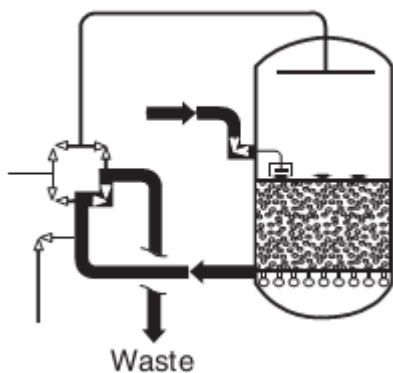
The function of the backwash cycle is to loosen the resin that has compacted during the service cycle, randomly mix the resin, and remove any silt, dirt, precipitated iron, or other accumulated insoluble matter.



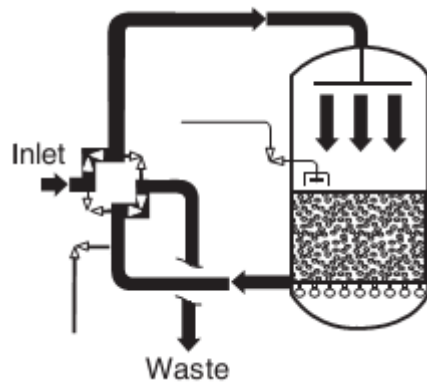
3. Regeneration: Regenerant solution is passed through to waste at a controlled concentration and flow.



4. Slow rinse : Water is passed through the bed to displace the regenerant solution to waste.



5. Fast rinse: Influent water is passed through the bed to waste to remove the last traces of regenerant chemicals.



Lecture 2

Lime-soda ash softening Process

Both lime and soda ash are necessary when there is a nominal amount of magnesium hardness in the water.

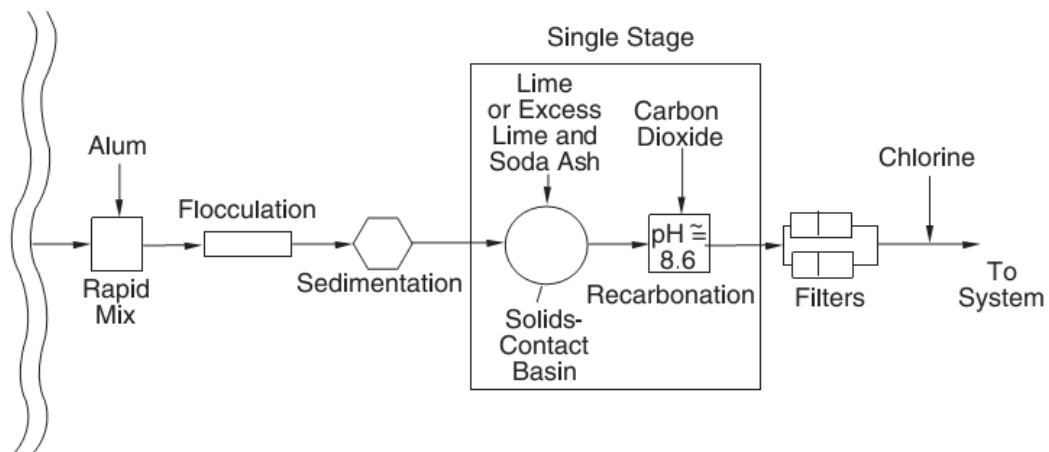
When the lime and soda ash are added, the minerals form nearly insoluble precipitates, which are then removed by:

1. Flocculation,
2. Sedimentation,
3. Filtration.

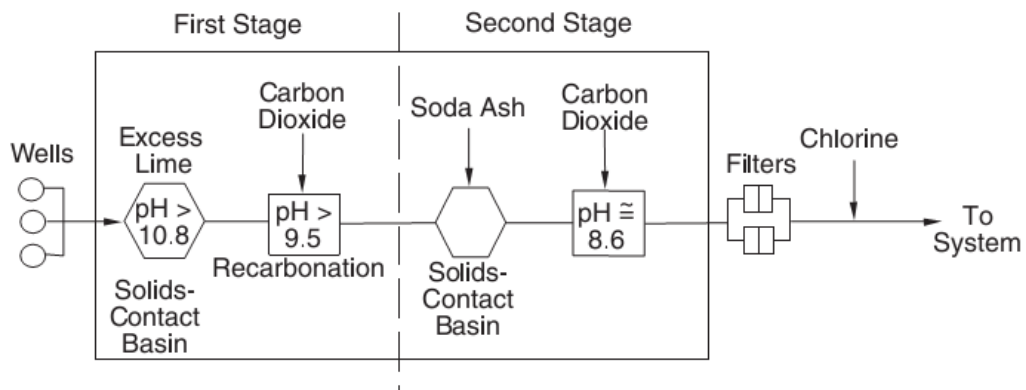
The modern application has been divided into:

1. The cold lime process : this process is employed chiefly for partial softening (It reduces the calcium hardness to 35 p.p.m). its application are:
 - conditioning of cooling water
 - paper-mill waters
2. The hot lime-soda process. This process is employed almost entirely for conditioning boiler feed water. Since it is operated near the boiling point of the water:
 - the reactions proceed faster,
 - the coagulation and the precipitation are facilitated,
 - much of the dissolved gases such as carbon dioxide and air is driven out.

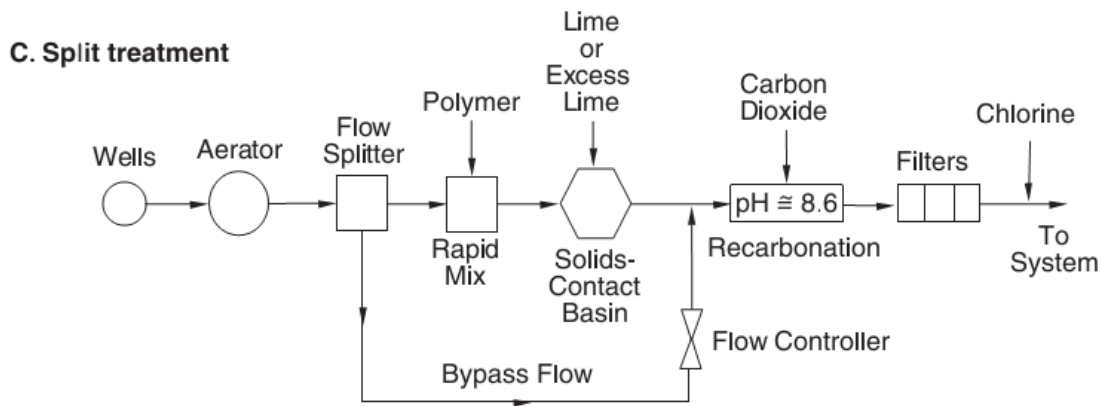
Treatment is typically performed through the single-stage process shown in Figure.

A. Single-stage process**Excess-lime treatment**

It is usually desirable to reduce the magnesium hardness of water when it exceeds about 40 mg/L. The extra lime will raise the pH above 10.6 so that magnesium hydroxide will precipitate out of the water.

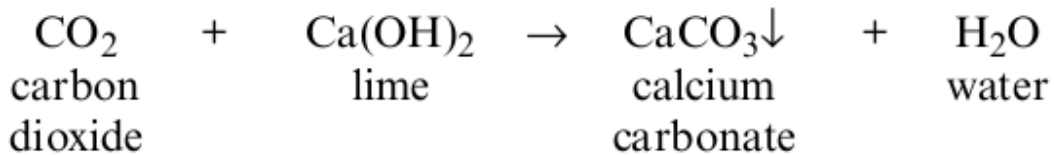
B. Double-stage process**Split treatment**

Split treatment is a modification of the excess-lime process and is used to reduce the amount of chemicals required.

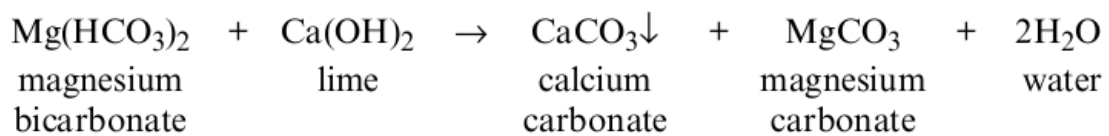
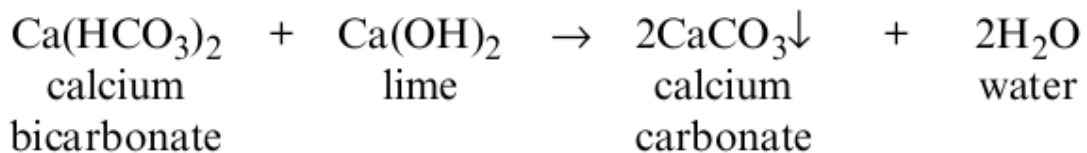


Chemical Reactions

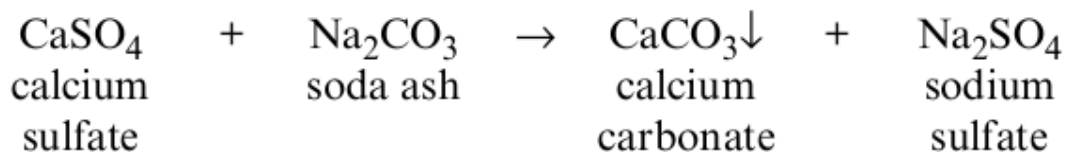
First, although carbon dioxide does not cause hardness, it reacts with and consumes the lime added to remove hardness.

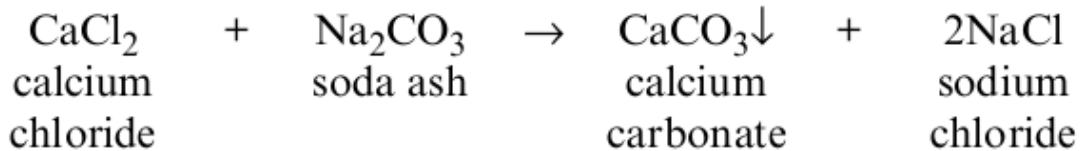


For carbonate hardness:

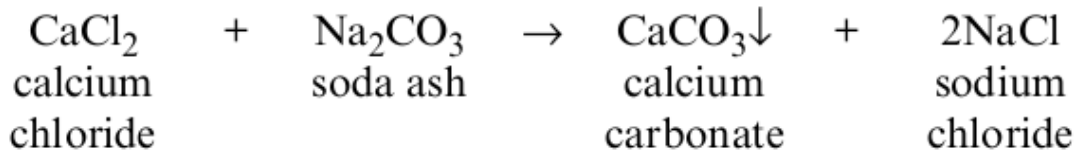
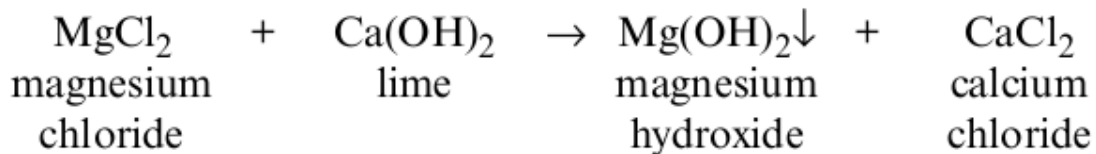


The minerals that cause noncarbonate calcium hardness are precipitated out of the water by the addition of soda ash:





The minerals that cause noncarbonate magnesium hardness are precipitated out of the water by the addition of lime:



Softening Facilities

The lime–soda ash softening process involves the following components:

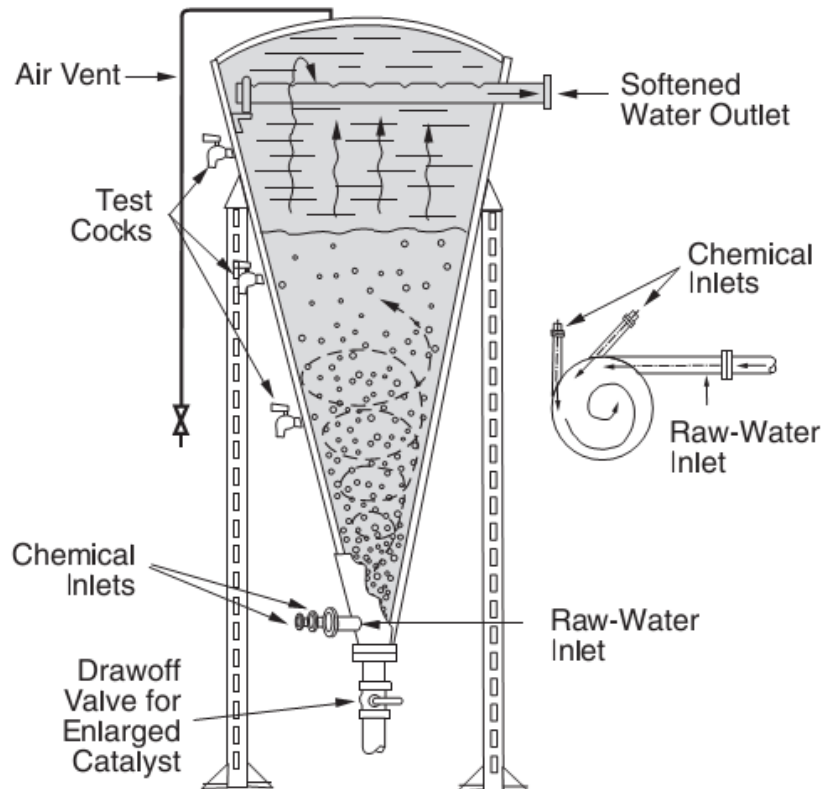
1. Chemical storage facilities
2. Chemical feed facilities
3. Rapid-mix basins
4. Flocculation basins
5. Sedimentation basins and related equipment
6. Solids-contact basins (often used in place of the rapid-mix, flocculation, and sedimentation basins)
7. Pellet reactors (may be used in place of rapid-mix, flocculation, and sedimentation basins)
8. Sludge recirculation, dewatering, and disposal equipment
9. Recarbonation facilities
10. Filtration facilities

Pellet Reactors

A pellet reactor is a conical tank in which the softening reactions take place quite rapidly as the water passes upward through the unit.

In operation:

- the tank is half-filled with fine granules of calcium carbonate.
- Raw water enters the bottom through a nozzle placed at an angle so that an upward swirling action is produced.
- At the same time, a dose of lime or lime and soda ash is introduced through another opening.



Lecture 3

Industrial carbon

Carbon is chemically inert and is infusible at atmospheric pressure.

The element carbon exists in three allotropic modifications; these three varieties, namely,

- Amorphous carbon,
- Graphite,
- Diamond

Graphite and diamond resist oxidation even at fairly high temperatures. Some of the industrial applications depend upon the chemical inertness of carbon.

On the other hand, the amorphous carbon can be activated, in which case it has a great capacity for selective adsorption from either the gaseous or the liquid state.

Applications

- Black pigment of the ink
- Carbon paper, pencils
- Black color in many paints
- In the construction of electrical equipment
- Structural materials in chemical and metallurgical industries (e.g., electrodes made of carbon and graphite)

Non-fabricated industrial carbon is represented by:

- Lampblack, (Amorphous)
- Carbon black, (Amorphous)
- Activated carbon, (Amorphous)
- Graphite,
- Industrial diamonds.

Lampblack

Lampblack or soot is an old product, made for many years by the restricted combustion of resins, oils, or other hydrocarbons.

in the manufacture of carbon brushes for electrical equipment and lighting carbons, lampblack is still a very important constituent. Its color is a bluish-gray black, rather than the deep black of carbon black; this steely black is desired for some metal polishes and pencils.

CARBON BLACK

Carbon black is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon.

The carbon black was produced by cooling a burning gas flame against soapstone slabs and scraping off the carbon produced.

Uses and Economics

- About 95 per cent of the domestic carbon black consumption is in rubber products, especially tires, and mechanical goods,
- Carbon black is also the basis for most printing inks

Manufacture

The two major processes for making carbon black are:

- The channel process
- The furnace process

Raw materials are:

- Natural gas (most important)
- Liquefied petroleum gases,
- Natural gasoline,
- Gas oils,
- Fuel oils,
- Residuum

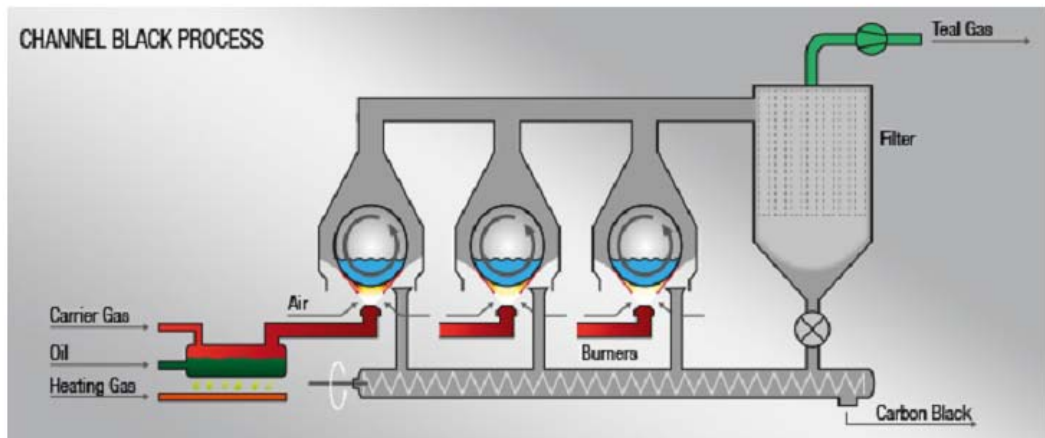
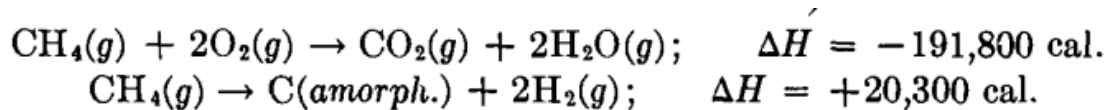
Channel Process

The name channel came from the steel channel iron used to collect carbon black deposited by small natural gas flames impinging on their surface iron channels.

The unit changes' involved are:

- Natural gas is "dried" of its gasoline, usually by adsorption (Op.).
- Natural gas is cracked or pyrolyzed by contact with moving and cooled channel iron (Pr.). where the gas is burned with an insufficient supply of air.
- here the temperature of the products of combustion of 1000°C. is reduced to 500°C.
- Carbon black is scraped off the channel, conveyed to packing house, sifted, and packaged (Op.).

Reactions:



Furnace Process

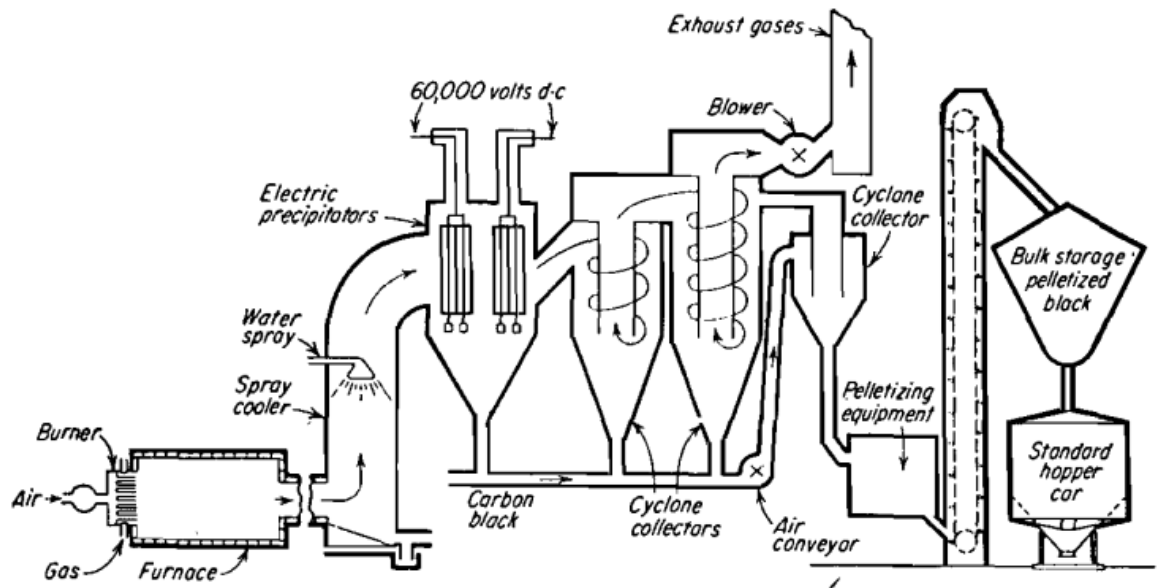
In the furnace process, the unit changes are:

- Combustion chamber (furnace)
- Feed pre-heater
- spray cooling tower (quench tower)
- electrostatic precipitator
- centrifugal "cyclones."
- Pelletizer

The basic process consists of:

- Atomizing the preheated feedstock into the combustion zone of the furnace
- Partial Combustion of natural gas and air(50% of that required for complete combustion) create high temperature of 1200-1900 °C

- Instantly feedstock vaporizes and decomposes to carbon black and hydrogen
- The reaction product are rapidly quenched (spray cooling tower) with water spray to prevent loss of carbon black product
- Carbon particles are collected by electrostatic precipitator and final separation by cyclones
- The carbon particles are pelletized using wet or dry methods



Activated carbon

Activated carbon is an amorphous solid that has an extraordinary large internal surface and pore volume. These unique characteristics are responsible for its adsorptive properties, which are exploited in many different liquid – and gas-phase applications.

Activated carbon produced in the forms:

- Powders
- Granules
- Shaped products

Most applications are:

- Purification of potable water
- Control of gasoline emissions from motor vehicles.

Manufacturing processes

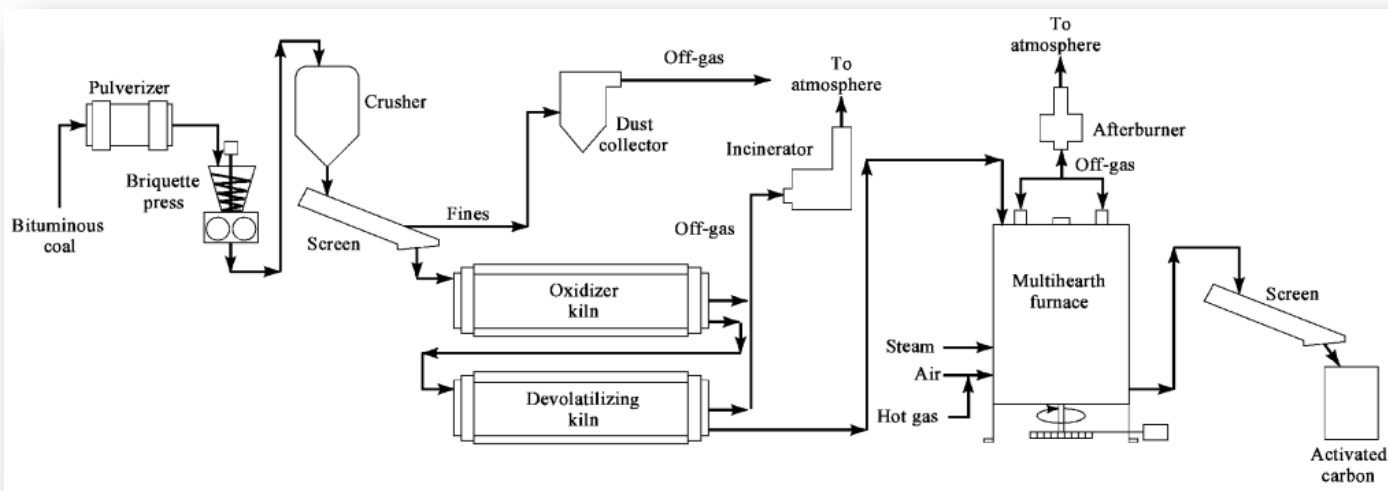
There are main two categories;

- **Thermal activation** : the effective porosity is the result of gasification of the carbon at relatively high temperature
- **Chemical activation**: the porosity is created by chemical dehydration reactions occurring at significantly lower temperatures.

Thermal activation process

Thermal activation occurs in two stages:

1. Thermal decomposition or carbonization of the precursor :
Elements such as hydrogen and oxygen are eliminated from the precursor to produce a carbon skeleton possessing a latent pore structure.
2. Controlled gasification or activation of the crud char:
The char is exposed to an oxidizing atmosphere that increases the pore volume and surface area of the product through elimination of volatile pyrolysis products and from carbon burn-off. Typical yield of activated carbon is 30-35% based on raw coal.



- Bituminous coal is pulverized and passed to briquette press
- Briquette coal is the crashed and passed through a screen
- On-sized material passed to an oxidizing kiln where the coking properties of the coal are destroyed
- The oxidized coal is devolatilized in a second rotary kiln
- The devolatilized coal particles are transport to a direct-fired multihearth furnace where they are activated by holding the temperature of furnace at about 1000°C.

Chemical activation processes

In contrast to thermal activation of coal, chemical activation is carried out in a single kiln.

The precursor, usually wood, is impregnated with phosphoric acid and the blend is heated to a temperature of 450-700 °C. Carbon yields as high as 50% by weight of the wood precursor.

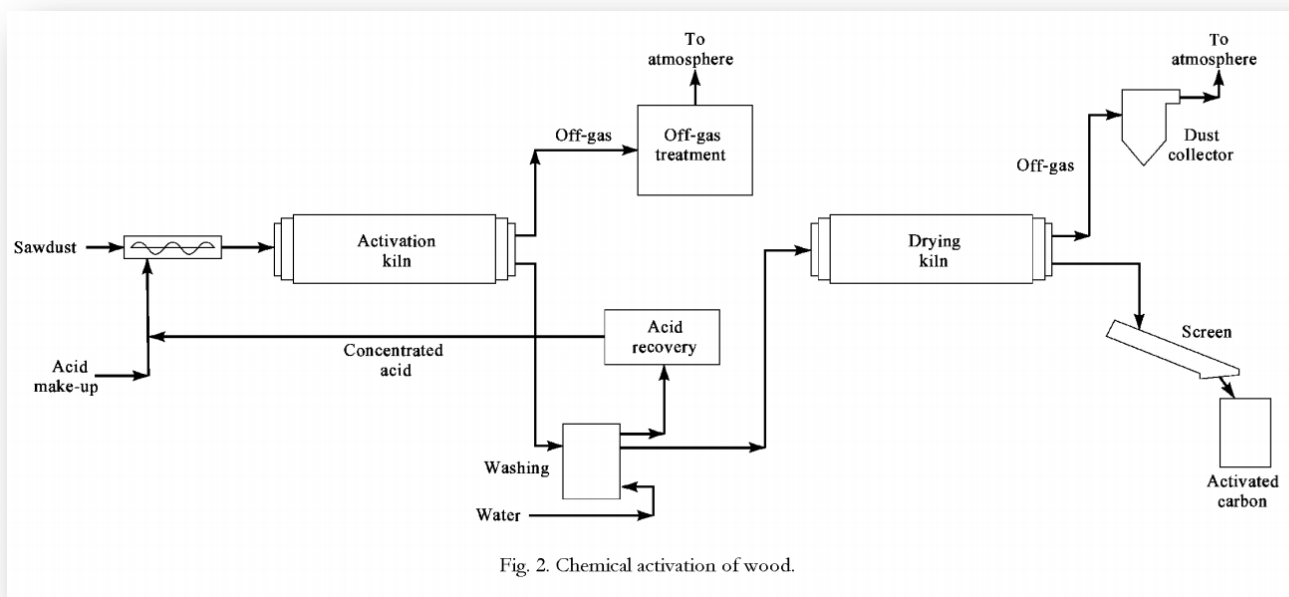


Fig. 2. Chemical activation of wood.

- Sawdust is impregnated with concentrated phosphoric acid and fed to rotary kiln, where it is dried, carbonized, and activated at a moderate temperature.
- The char is washed with water to remove acid from water
- Carbon is separated from the slurry
- The pH of the activated carbon is adjusted, and the product is dried
- The dry product is screened and classified into the size range

Lecture 4

Industrial gases**Carbon dioxide**

Carbon dioxide in liquid and solid forms has been known for a century.

Uses

1. Refrigerating ice cream, meat (solid form)
2. carbonated beverages (solid and liquid form)
3. fire-extinguishing material (liquid form)
4. making of salicylic acid (gaseous form)
5. Raw material for soda ash (gaseous form)

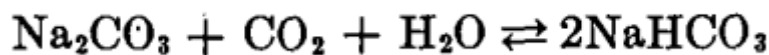
Manufacturing process

there are many sources of CO₂:

1. Flue gases: result from burning carbonaceous materials and contain about 10-18% CO₂
2. By-product from the fermentation industries through dextrose breakdown into alcohol and carbon dioxide, the gas containing about 99 per cent carbon dioxide.
3. By-product of limekiln operation where carbonates are calcined to the oxides; the gases analyze from 10 to 40 per cent CO₂.

An absorption system is used for concentrating the CO₂ gas obtained in (1) and (3) to over 99 per cent.

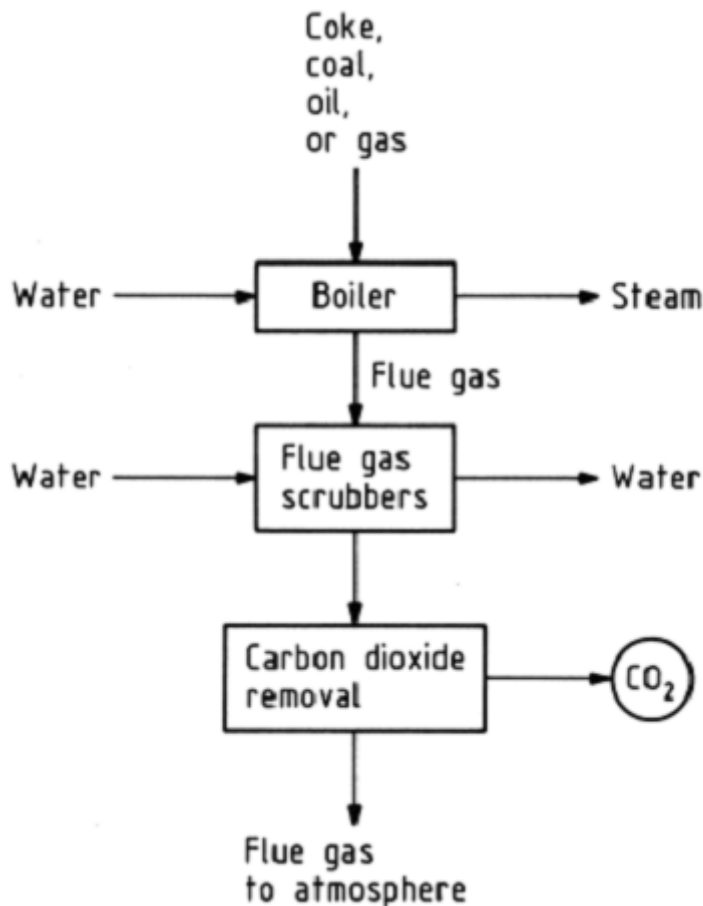
One of the reactions for the concentration of the carbon dioxide is:



This reaction is forced to the right by increasing the partial pressure of the CO₂ and by reducing the temperature. It is forced to the left by heating up the sodium bicarbonate solution.

1. CO₂ from flue gases

Carbon dioxide is a component of all flue gases produced by the complete combustion of carbonaceous fuels. The product obtained from flue gases is generally contaminated with small amounts of sulfur compounds.

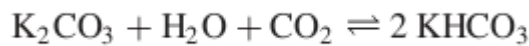


- Coke or other carbonaceous fuel burned, giving heat for steam, and furnishing 18 per cent CO₂ (Pr. and Op.).
- The flue gases are cooled and cleaned by passing through a water scrubber(OP.)
- Then gases passed through an alkaline carbonate solution or an amine solution that absorbs carbon dioxide(Pr.)
- Concentrated (99.9 per cent) CO₂ boiled out of NaHCO₃ solution (Pr. and Op.).
- CO₂ purified and dried (Pr.).
- CO₂ compressed, cooled, and liquefied (Op.).

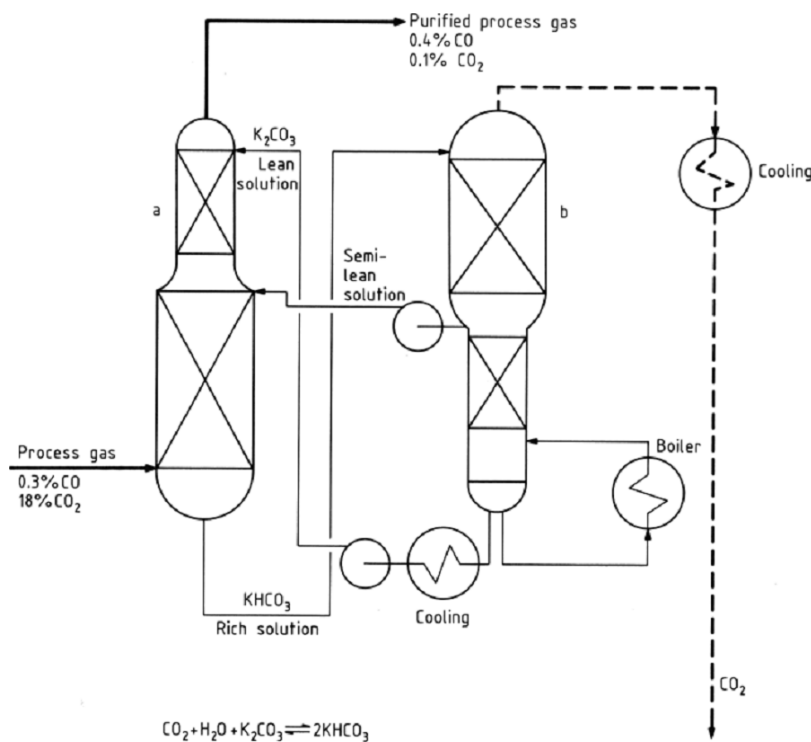
2. Carbon Dioxide from Ammonia and Hydrogen Plants (Process Gas CO₂)

catalytic steam reforming of the hydrocarbon to give a gaseous mixture of hydrogen, carbon dioxide, and carbon monoxide.

- Because only hydrogen and nitrogen are required to make ammonia, carbon oxide is removed from the gas stream.
- Several methods are available; all are based on the absorption of carbon dioxide into a solution, under pressure, which flows countercurrent to the process-gas Stream(main stream).
- The absorbed gas is liberated in a separate vessel by raising the temperature and lowering the pressure above the solution.
- Potassium Carbonate is added to water to increase solubility of CO₂.



- Figure below shows the usual arrangement of absorber(a) and regenerator(b).



Lecture 5

Hydrogen production

Hydrogen is an important and diverse raw material for the chemical industry.

Uses

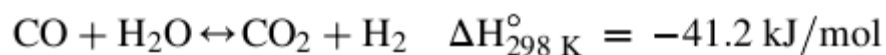
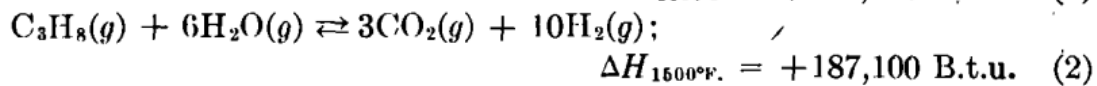
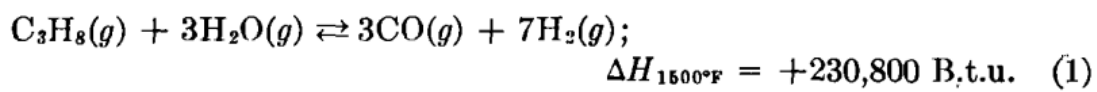
1. Raw material for ammonia production
2. hydrogenation processes especially in the chemical, petroleum, and food industries
3. welding and other heating processes

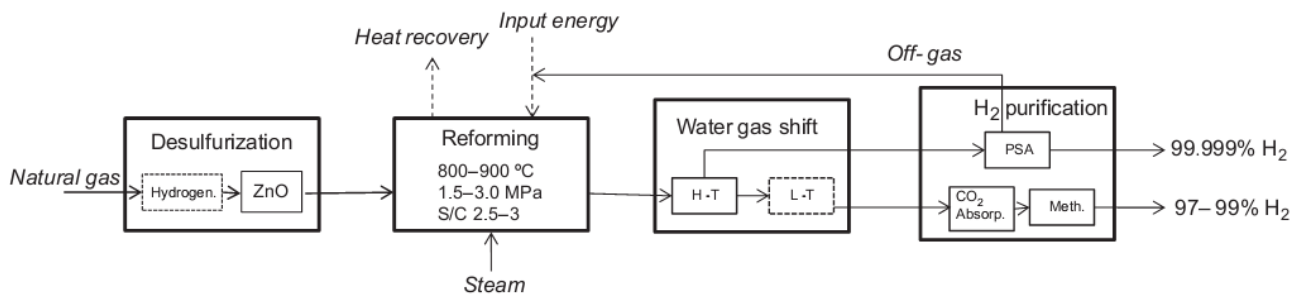
Hydrogen Manufacture

1. Steam-hydrocarbon process.
2. Water-gas catalytic process.
3. Steam-iron process.
4. Electrolysis of water.
5. Thermal dissociation of hydrocarbons such as natural gas.
6. Partial oxidation of hydrocarbons followed by "shift reaction."

Steam-hydrocarbon process

The reaction between hydrocarbons, especially methane and propane, and steam to produce carbon oxides and hydrogen is highly endothermic:

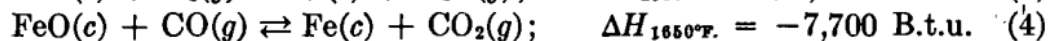
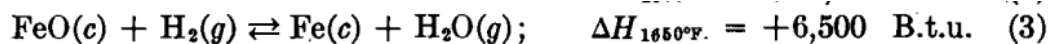
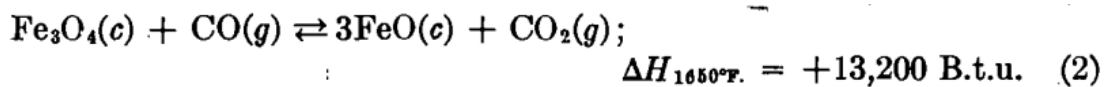
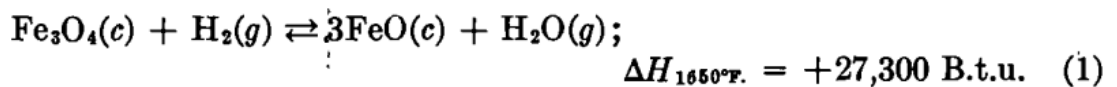




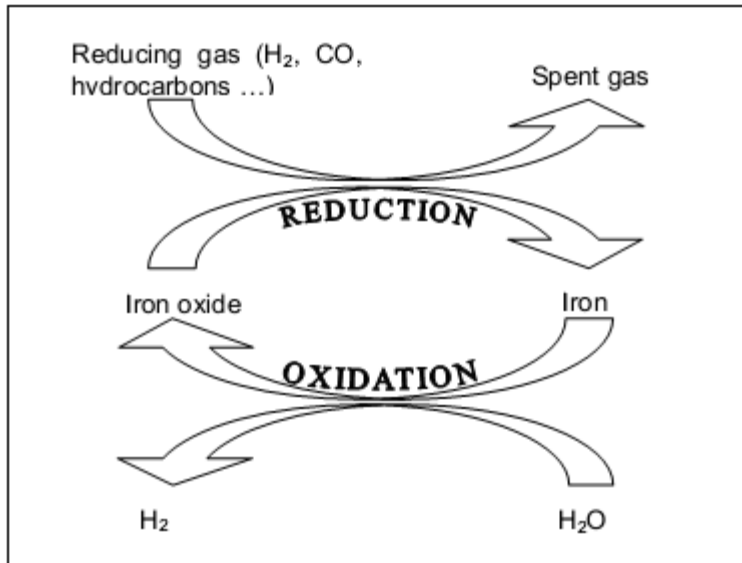
- Desulfurized propane is mixed with steam and passes through the hydrogen furnace where reaction takes place at about 1500°F
- At the furnace outlet, more steam is added to cool the gas to about 750°F. and to increase the partial pressure of the H₂O
- The mixture is passed into an iron oxide shift converter where most of the CO is oxidized to CO₂
- The gas is conducted through a heat exchanger and into the first CO₂ absorber where a stream of monoethanolamine solution removes the CO₂
- The final product (hydrogen) is more than 99.9 percent pure, with less than 0.01 per cent of CO or CO₂, and less than 0.1 per cent residual hydrocarbons.

Steam-iron Method

- Pure hydrogen is produced by passing excess steam over spongy iron at temperatures of 1400 to 1900°F
- the following reversible reactions occur:



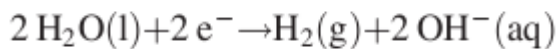
- After the reducing period of 5 to 7 min., steam is passed through the reduced oxides for an equal amount of time, reversing reactions (1) and (3) producing hydrogen and the original oxides.
- The cycle is then repeated.



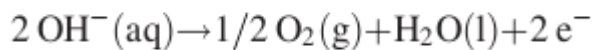
Electrolytic Method

If a potential is applied to the electrodes of an electrolysis cell filled with a suitable electrolyte, the following reaction occurs at the electrodes:

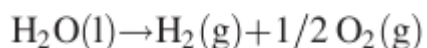
1. Cathode



2. Anode



3. Cell reaction



the theoretical minimum decomposition potential at standard conditions is 1.48 V. Owing to overvoltage of hydrogen on the electrodes and also to cell resistance itself, voltages of 2.0 to 2.25 volts are usually required. And operate at 60-70 °C.

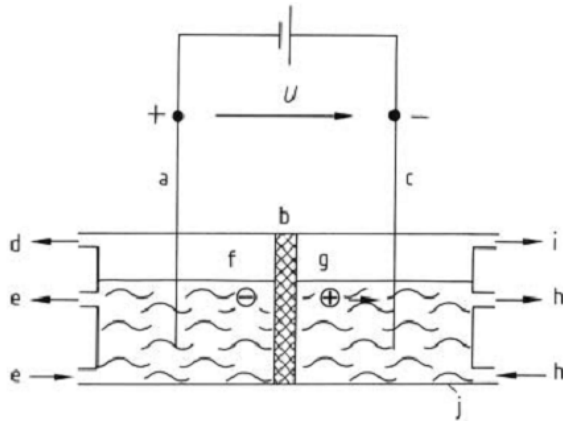


Figure 18. Schematic of a water electrolysis cell
 a) Anode; b) Diaphragm; c) Cathode; d) Oxygen outlet;
 e) Anodic electrolyte cycle; f) Anion; g) Cation; h) Cathodic electrolyte cycle; i) Hydrogen outlet; j) Cell wall

A typical commercial cell consist of

1. iron cathode
2. nickel-plated iron anode
3. NaOH solution
4. asbestos diaphragm

Most types of cells produce about 7.0 cu. ft. (9.408 cu. ft. theoretically) of hydrogen and half as much oxygen per kilowatt-hour. The gas is around 99.7 per cent pure.

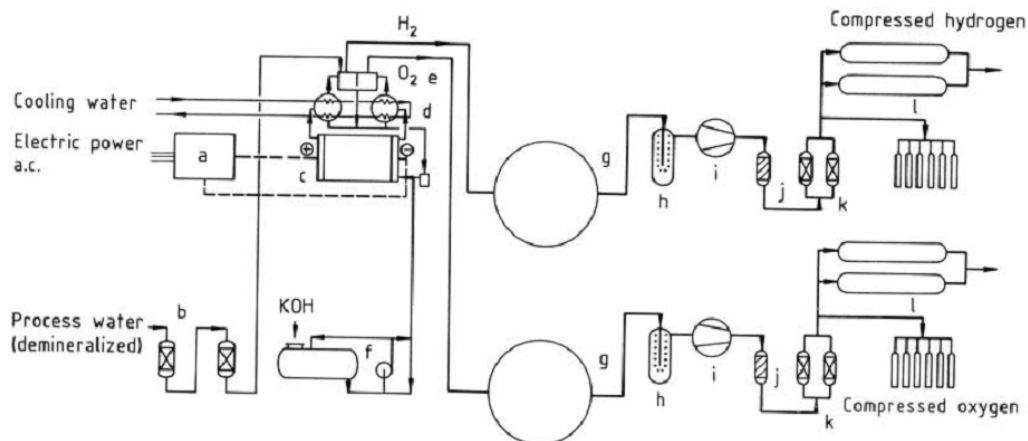


Figure 25. Process diagram of an electrolysis unit with the most important components
 a) Rectifier unit; b) Process water demineralizer ion exchange unit; c) Electrolytic cell's water electrolyzer; d) Gas separator and cooler; e) Gas scrubber; f) Electrolyte tank and transfer pump; g) Gas holder; h) Filter; i) Compressor; j) Gas purifier; k) Drying; l) High-pressure storage tank and cylinder filling station

Lecture 6

Oxygen and Nitrogen

Uses and Economics

- The biggest use is in steel operations such as welding, cutting, and scarfing, (O₂)
- chemical manufacture and in some open-hearth and blast furnaces as it raises temperatures and accelerates steel production. (O₂)
- ammonia synthesis (N₂)
- as a protective atmosphere in the bright annealing of metals,(N₂)
- shield to prevent oxidation in food products (N₂)
- welding areas (N₂)
- a reagent,(N₂)
- grinding aid for very hard or heat-sensitive materials.(N₂)

Manufacture process

Oxygen is produced by two markedly different methods:

1. The electrolysis of water process
2. The liquefaction and subsequent rectification of liquid air

High-purity oxygen (99.54 per cent) and nitrogen are produced commercially from air by a typical flow sheet as presented in Fig.

TABLE 4. PROPERTIES OF AIR AND CONSTANT CONSTITUENTS^a

Gas	Volume, per cent	Boiling point, °C.	Boiling point, °K.	Critical temperature, °K.	By weight
Air.....	100	-194	79	132.3	
Nitrogen.....	78.03	-195.81	77.19	126.0	
Oxygen.....	20.99	-182.96	90.04	154.2	
Argon.....	0.94	-185.84	87.16	156	
Hydrogen.....	0.01 ^b	-252.44	20.56	33.1	
Neon.....	0.0015	-246.3	26.7	53	1 lb. in 44 tons
Helium.....	0.0005	-268.98	4.02	5.2	1 lb. in 173 tons
Krypton.....	0.00011	-152.9	120.1	210	1 lb. in 725 tons
Xenon.....	0.000009	-107.1	165.9	258	1 lb. in 1,208 tons
Carbon dioxide ^c	0.03-0.07	- 79.0	194.0 ^d	304.1	
Water ^e	0.01-0.02	+100.0	373.0	647	

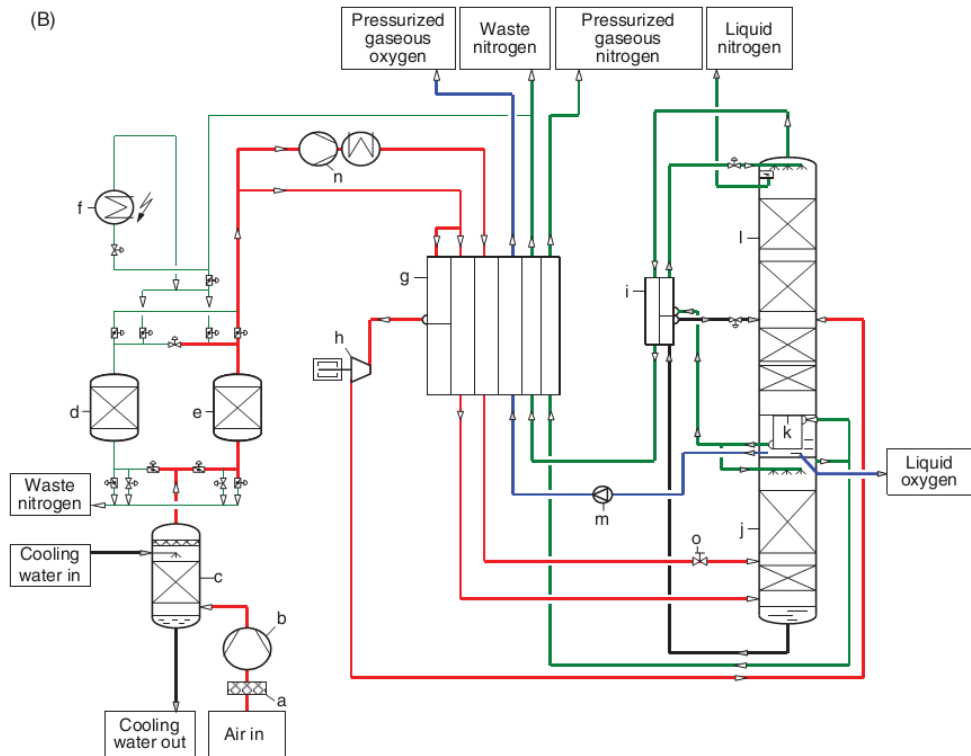


Figure 2. Simplified process flow diagram for cryogenic oxygen plant

A) Pressureless oxygen production; B) Pressurized oxygen based on internal compression

a) Air filter; b) Air compressor, c) Water wash cooler, d, e) Adsorber beds for drying and purification, f) Heater for regeneration of adsorber beds, g) Heat exchanger, h) Expander (turbine), i) Sub-cooler, j) High pressure column, k) Condenser–evaporator, l) Low pressure column, m) Liquid oxygen pump, n) Booster air compressor, o) Throttle valve

1. **Purification** of the incoming air to remove particles, carbon dioxide, and water:

- The air is first compressed,
- The CO₂ and any dust present are removed by scrubbing with KOH solution.
- The air is further compressed to 200 atm. in four stages, with water cooling between each stage

2. **Refrigeration**

- The gas coming from the fourth compression stage is at 170°C.; it is water-cooled to 10 to 30°C. and usually then further cooled to -30°C. by ammonia refrigeration.

3. **Separation by rectification**

- The air, at 200 atm. and -30°C., goes to a combined liquefier and separator
- Here the purified, compressed, and cooled air is liquefied and separated into its constituents according to the following fundamental principles:

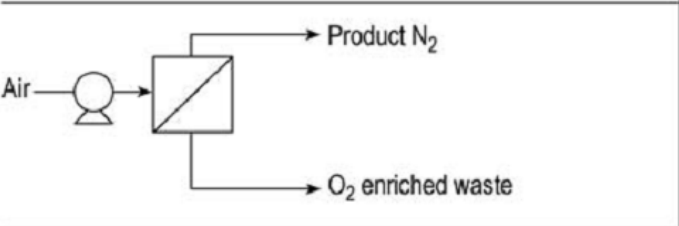
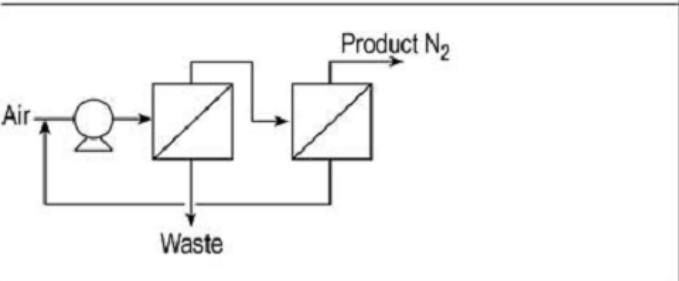
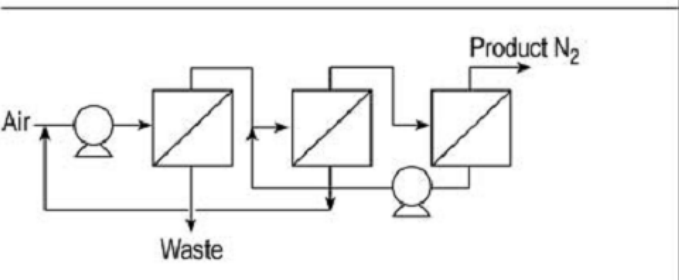
- The interchange of heat in heat exchangers such as double pipe coils
- The adiabatic expansion of the compressed air to cool by the Joule-Thomson effect
- The cooling of the compressed gases by allowing them to perform work (Claude modification)
- The cooling of the liquids by evaporation.
- The separation of liquid oxygen from the more volatile nitrogen in a bubble-cap column.
- Nitrogen boils at -195.8°C . and oxygen at -183°C . The difference of 12.8° in boiling point permits a fractional separation of the two liquids.

3. Nitrogen Production by Membrane Separation

Membranes can also be used for the separation of oxygen and nitrogen. Gases permeate through dense nonporous membranes by solution diffusion.

Virtually all membranes are more permeable to oxygen than they are to nitrogen. Hence, the nitrogen product from a membrane separation stage is the retentate on the high-pressure feed side.

Early membrane systems used single-stage processes for N_2 production, which are best suited for low-purity nitrogen. More sophisticated, multistage processes are better suited for higher purities and larger capacities.

Process schematic	Description
	<p>1 - stage Low purity</p>
	<p>2 - stage Medium purity</p>
	<p>3 - stage High purity</p>

The main components of a membrane system include:

- the compressor,
- the feed-conditioning package,
- the membrane modules
- the system controls

. A schematic of a typical arrangement of these components is shown in

Figure.

Air is compressed to 6 – 15 bar, and conditioned to remove contaminants and to provide temperatures and humidity levels for optimal membrane performance. The separation unit typically comprises one or more separation stages, each consisting of one or more membrane modules in parallel.

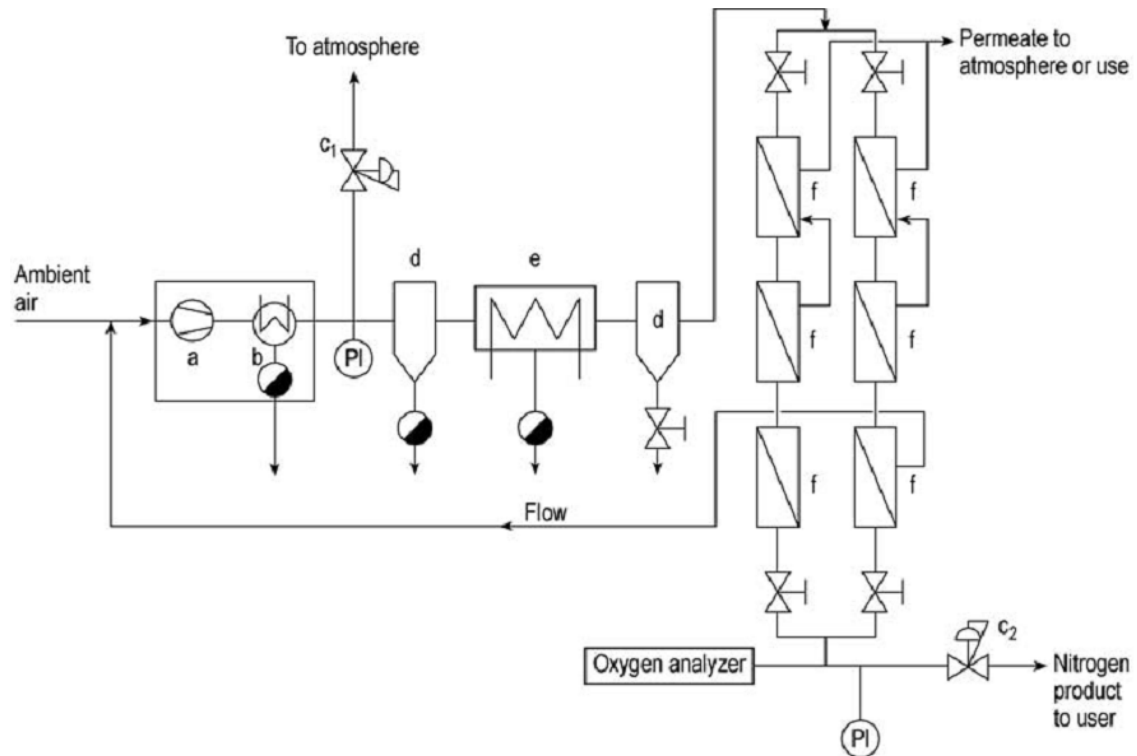


Figure 12. Schematic of a membrane nitrogen generator a) Compressor; b) Cooler with condensate drain; c_1), c_2) Pressure control valves; d) Filter with condensate drain or valve; e) Refrigerant cooler with condensate drain; f) Membrane modules

Lecture 7

Ammonia production

Ammonia, NH_3 , a colorless alkaline gas, is lighter than air and possesses a unique, penetrating odor.

Ammonia is comparatively stable at ordinary temperatures, but decomposes into hydrogen and nitrogen at elevated temperatures.

Table 1. Physical Properties of Anhydrous Ammonia

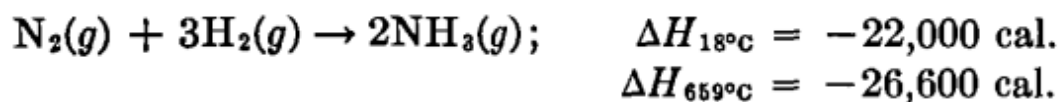
Property	Value
molecular weight	17.03
boiling point, °C	-33.35
freezing point, °C	-77.7
critical temp, °C	133.0
critical pressure, kPa ^a	11,425

Uses

- The vast majority of ammonia is used for nitrogen fertilizers such as, ammonium nitrate, NH_4NO_3 , ammonia sulfate, $(\text{NH}_4)\text{SO}_4$, and ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$
- The catalytic oxidation of ammonia in the presence of methane is commercially used for the production of hydrogen cyanide.
- Acrylonitrile, $\text{CH}_2=\text{CHCN}$, is produced in commercial quantities almost exclusively by the ammoxidation of propylene.
- Urea, formed from the reaction of ammonia with carbon dioxide, as most common nitrogen fertilizer
- Caprolactam is made from ammonia and cyclohexanone, where Caprolactam is the monomer for nylon 6.
- Ammonia is also used in the production of pyridines, amines and amides

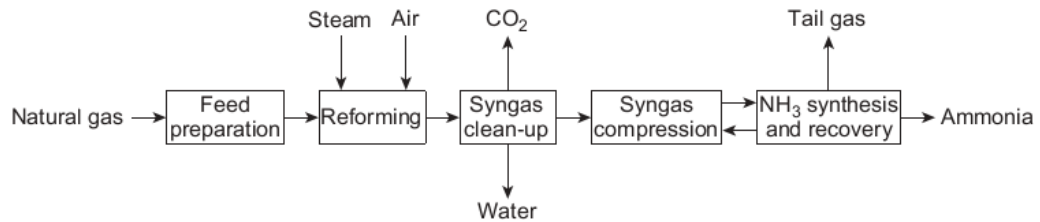
Manufacture

The ammonia synthesis reaction is deceptively simple: nitrogen is combined with hydrogen in a 1:3 stoichiometric ratio to give ammonia with no by-products.



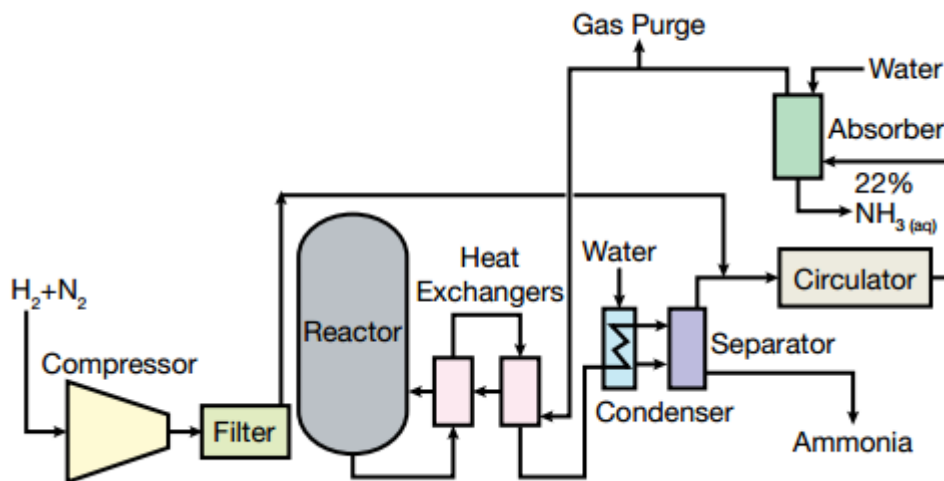
1. Steam Reforming With Conventional Gas Purification

Today's prevailing plant design is the single-train plant in which all of the large equipment and machinery are single units.



The main steps are

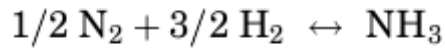
- (1) feed preparation: where the natural gas is compressed to reforming pressures and desulfurized to protect downstream catalysts,
- (2) reforming: where the natural gas is mixed with steam and air to produce a crude syngas mixture,
- (3) Syngas clean-up: where a purified stream of nitrogen and hydrogen is produced in the correct stoichiometric ratio,
- (4) Syngas compression followed by
- (5) ammonia synthesis and recovery.



The reformer effluent gas contains the desired hydrogen and nitrogen plus bulk impurities such as carbon monoxide, carbon dioxide, water, residual methane and trace impurities such as argon and helium.

The bulk impurities have to be removed prior to ammonia synthesis.

The stoichiometry and thermo-dynamics of the ammonia synthesis reaction are at 25°C,



The ammonia synthesis reaction is a reversible equilibrium type reaction and the reaction is exothermic.

Ammonia synthesis typically occurs in the range of 350–550°C. A quench converter is a common reactor configuration. A quench converter contains a series of adiabatic beds which are used to produce ammonia from syngas.

Cold feed is injected between the beds to cool the reaction products,

Typical per pass conversions are only ca 25–35%.

A wide range of pressures have been used in commercial processes, ranging from 8 to 40 MPa with most recent plants operating in the range of 15–25 MPa.

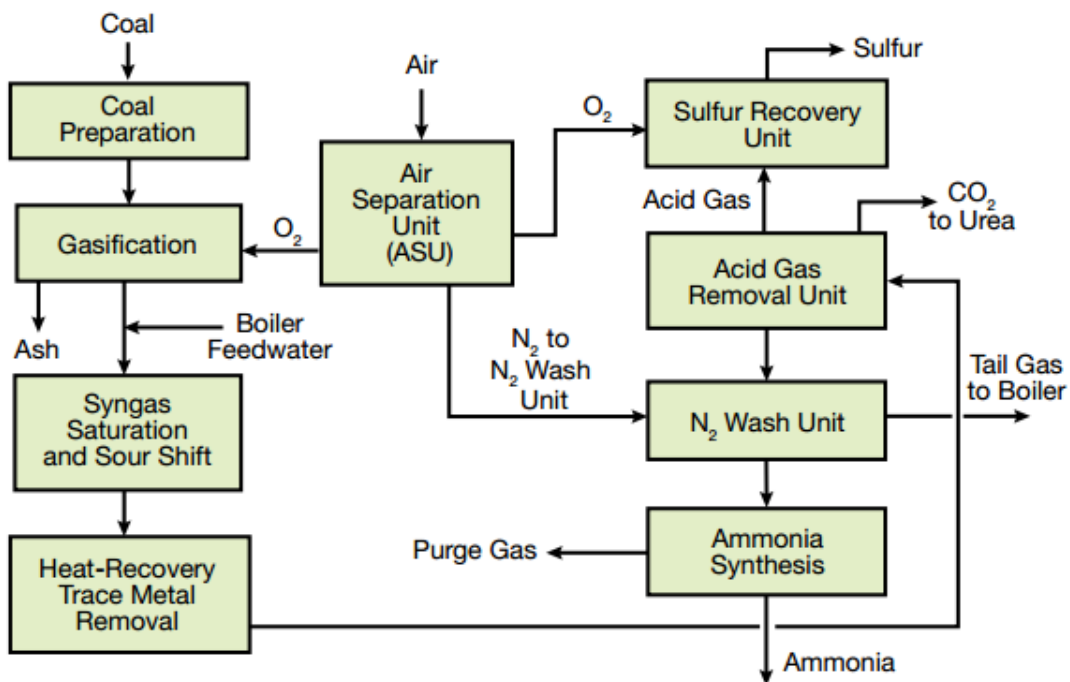
2. Ammonia from coal

The basic processing units in a coal-based ammonia plant are:

- ASU for the separation of O₂ and N₂ from air
- The gasifier
- The sour gas shift unit (SGS)
- The acid gas removal unit (AGRU)
- The ammonia synthesis unit

Basic steps to produce ammonia are:

- Oxygen is fed to the gasifier to convert coal into synthesis gas (H₂, CO₂, CO) and CH₄.
- Steam added to the SGS unit to reduce CO concentration in synthesis gas to less than 1 vol%.
- The synthesis gas is fed to an AGRU, where CO₂ and sulfur are removed.
- Syngas is fed to synthesis loop



Lecture 8

Helium production

Helium is the lightest of the noble gases. It is colorless, odorless, tasteless and non-toxic. It does not normally react with other elements. Liquid helium has the lowest viscosity of all liquids. The boiling and freezing points of helium are lower than those of any other known substance.

helium behaves more like an ideal gas than any other commonly known fluid. Helium can be liquefied at normal pressure but it does not solidify even at absolute zero.

Helium Uses

- Liquid helium is used in medical diagnostic equipment (as a cooler) such as MRI(Magnetic Resonance Imaging)
- Helium-neon lasers for eye surgery.
- Breathing gas for divers (a mixture of 20% oxygen and 80% helium).
- Optical fiber manufacturing.
- Leak detection in pipelines.
- Cooling medium for High Temperature Nuclear Reactors.

Helium Removal Processes from Natural Gas

Helium is difficult to remove from natural gas unless nitrogen rejection is used. Typical processing steps include:

- CO₂ removal
- Molecular sieve dehydration
- Higher hydrocarbons removal
- Mercury removal
- Nitrogen rejection
- Crude helium pre-treatment, purification and liquefaction

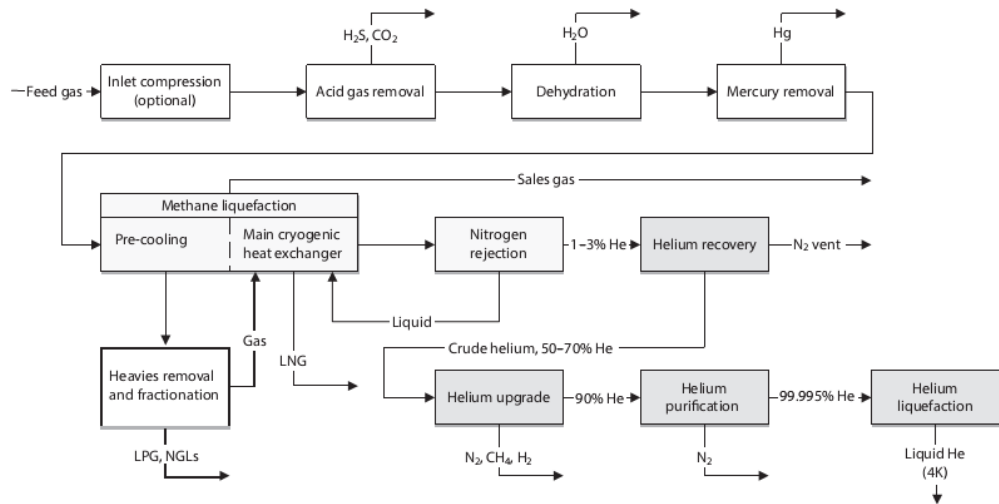


Figure 9 Natural gas processing to produce liquid helium.

Helium can be produced using:

1. Cryogenic processes
2. Pressure swing adsorption
3. Membranes
4. Non-cryogenic absorption
5. Hybrid processes

Cryogenic Processes

- Natural gas is cooled in stages until practically all the components, with the exception of helium, have condensed.
- The residual gas phase is the crude helium product.
- Purification the helium to >99.995% for Grade-A Helium.
- Gaseous purified helium can then be liquefied.

Hybrid processes

The most economically attractive process is a hybrid system that combines cryogenic, membrane and PSA units to produce 99.99% helium from dilute natural gas.

- The feed is natural gas containing 2.1% helium
- The feed is first cooled to $-60\text{ }^{\circ}\text{F}$ ($-51\text{ }^{\circ}\text{C}$) to condense the heavier hydrocarbons.
- Then the gas is cooled to $-240\text{ }^{\circ}\text{F}$ ($-151\text{ }^{\circ}\text{C}$) to condense most of the methane and some nitrogen
- At this point the gas contains 30–35% helium.

- The crude helium is then fed to a two-stage membrane unit that produces a 95% helium stream.
- PSA is used to upgrade this stream to Grade-A purity.

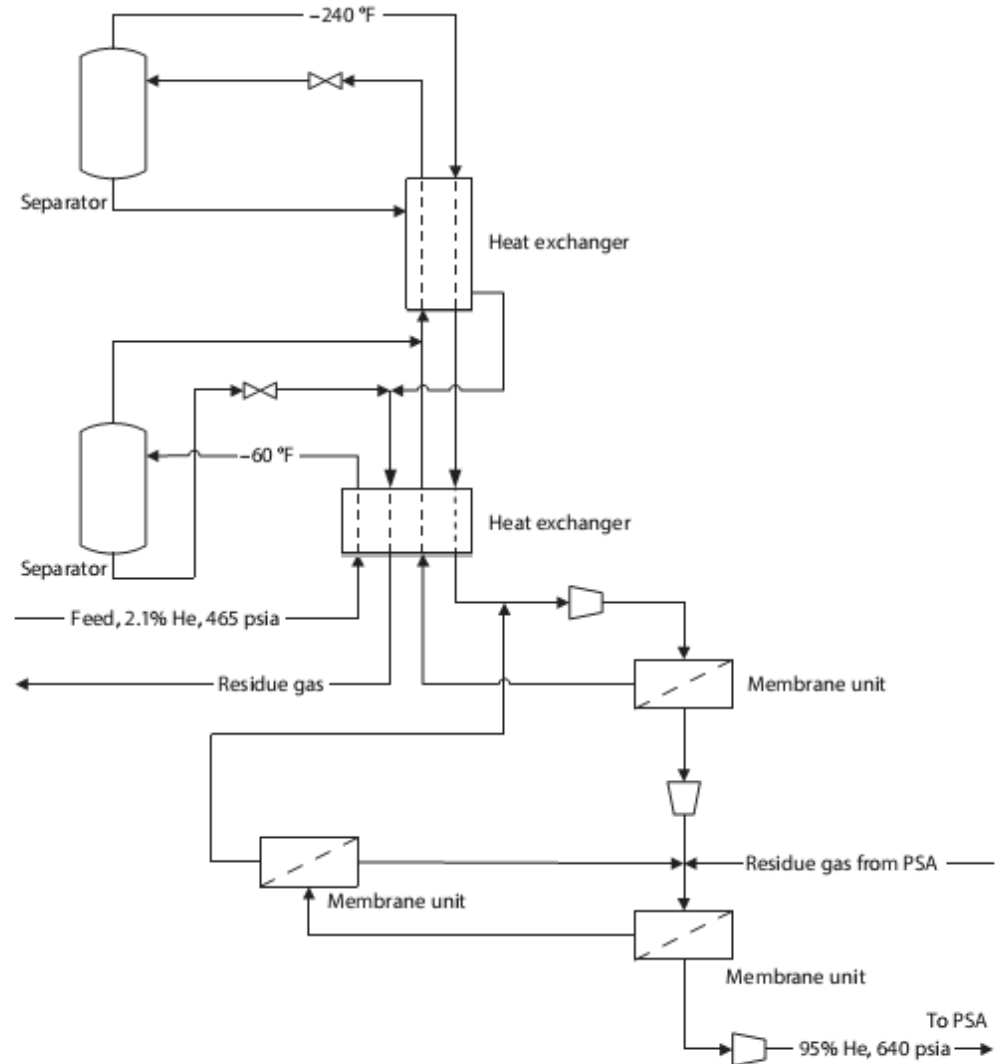


Figure 10 Cryogenic/Membrane/PSA hybrid process for removing helium from natural gas.

Helium Liquefaction

Helium liquefaction is the last step in the series of processes for helium recovery and purification.

liquid helium is needed in a host of applications, including MRI superconducting components and it is more economical to ship liquid helium around the world.

- The process of liquefying helium involves compression followed by cooling in countercurrent heat exchangers.

- The extra cold needed to cool the helium is provided by turbo expanders
- Crude helium, ~70% He, contains nitrogen, argon, neon and hydrogen.
- It undergoes final purification at pressures up to 18.7 MPa.
- The stream is chilled to 77 K in liquid nitrogen-cooled coils of a heat exchanger.
- most of the remaining nitrogen and argon liquefies, and the remaining gaseous helium contains last traces of nitrogen, neon, and hydrogen.
- Activated charcoal operating at liquid nitrogen temperatures, or below, adsorbs all non-helium gases, yielding helium of 99.9999% or more purity.

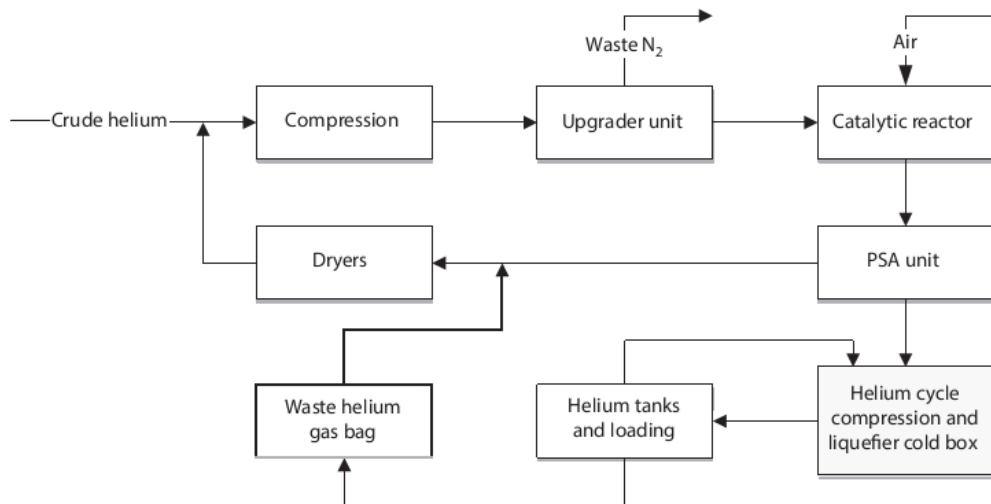


Figure 13 Block scheme of pure liquid helium recovery from the crude - example: Qatar.

Lecture 9

Sulfur and sulfuric acid

A yellow solid at normal temperatures, sulfur becomes progressively lighter in color at lower temperatures and is almost white at the temperature of liquid air.

It melts at 114 to 119°C.

The recovery of sulfur values from sour fuels for environmental reasons is the largest source of sulfur today.

Sulfur Production Processes

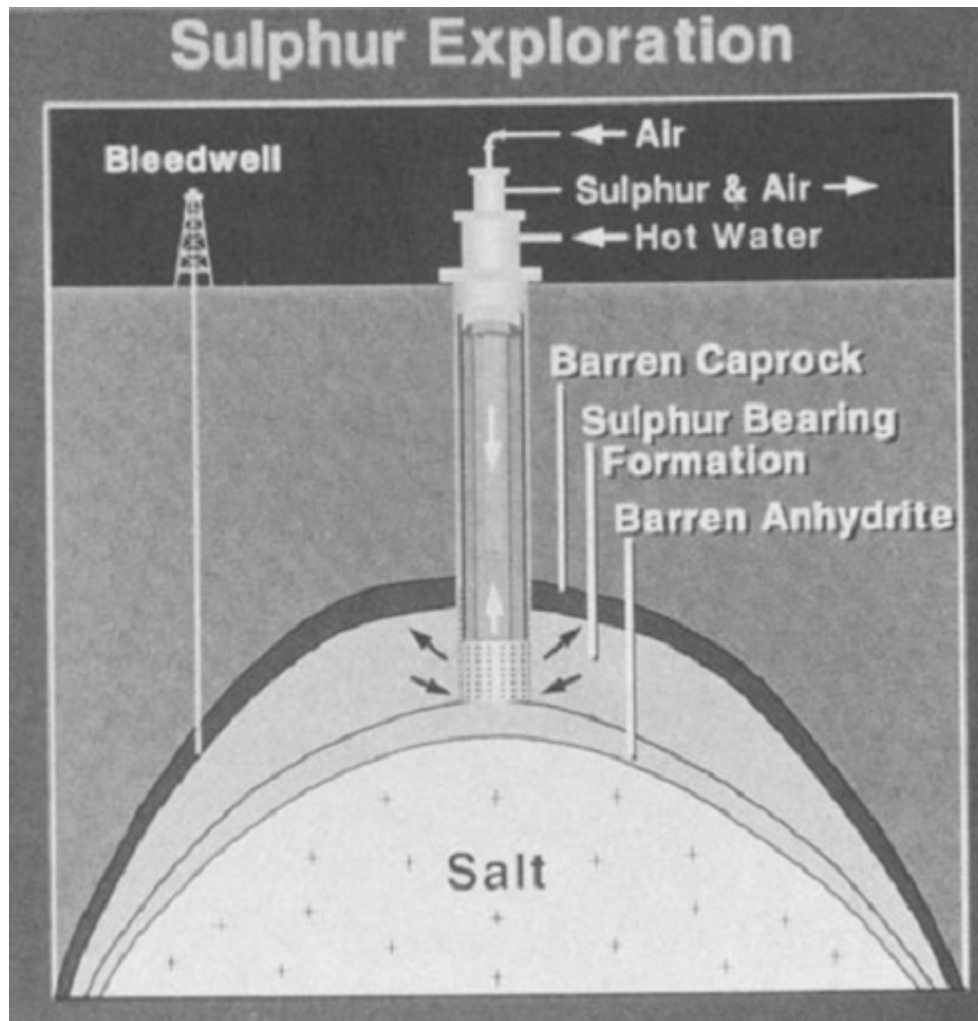
the Frasch process is the most economical method for extracting sulfur from native deposits.

Figure 14.1 shows the structure needed for Frasch mining from salt domes.

A sulfur well consists of a casing and three concentric pipes reaching into the sulfur-bearing strata.

- The outer 8-to 10-inch pipe carries 165°C water pumped into the formation to melt the sulfur.
- An inner cement-lined 3-to 6-inch pipe is used to transport the sulfur to the surface.
- Compressed air is passed through the 1-inch tube in the center to air-lift the sulfur.
- Without the air lift the molten sulfur would rise only partway in the middle pipe.

The compressed air produces a low-density sulfur froth that rises to the surface.

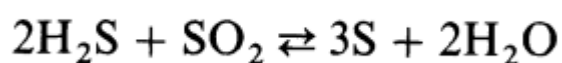


Recovered Sulfur

Hydrogen sulfide is recovered from natural gas or refinery gases by absorption in a solvent or by regenerative chemical absorption.

In either case a concentrated hydrogen sulfide stream is produced that is treated further by the **Claus process**.

The Claus process is based on the reaction of hydrogen sulfide with sulfur dioxide according to the highly exothermic reaction:



In practice the sulfur dioxide is produced in situ by partial oxidation of the hydrogen sulfide with air or oxygen in a furnace.

A flow diagram for a typical Claus process is shown in Fig. 14.3.

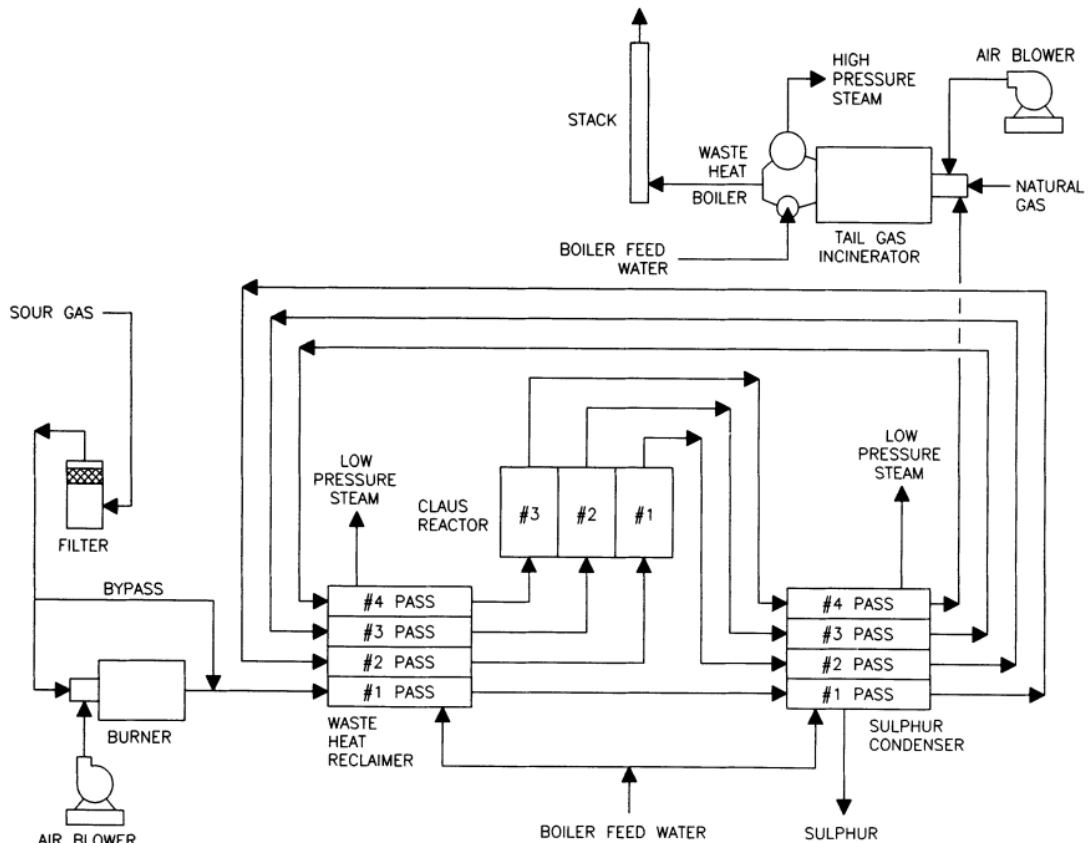


Fig. 14.3. Claus process flow diagram.

- The hydrogen sulfide is burned in a fuel-fired furnace (950-1250°C) with air to produce sulfur and a gas stream containing H₂S and SO₂
- Process controls maintain the H₂S:SO₂ ratio near 2 in accordance with the stoichiometry.
- Heat is removed from the gas stream in a waste heat boiler to control the process gas temperature.
- The process gas is passed through one or more catalyst beds to convert the H₂S and SO₂ to sulfur, which is removed in condensers between each bed.
- High temperature shifts the equilibria toward the reactants,
- whereas low temperature causes sulfur condensation on the catalyst bed, leading to decreased catalyst activity.

The tail gas from the Claus reactors may be further processed to remove any remaining sulfur compounds. This done by:

1. low-temperature Claus-type solid bed processes
2. wet-Claus absorption/ oxidation processes

- or hydrogenation of the off-gas to form H₂S for recycle
- Residual sulfur compounds in the processed tail gas then are incinerated to SO₂.
- The residual SO₂ in the oxidized tail gas may be scrubbed by any of several processes before being vented to the environment.

Sulfuric acid

Pure sulfuric acid is an oily, water-white, slightly viscous liquid with a melting point of 10.4°C and a boiling point of 279.6°C.

It is infinitely miscible with water, forming sulfuric acid solutions characterized by their weight percent H₂SO₄.

Oleum may be formed by dissolving SO₃ in sulfuric acid to attain fuming sulfuric acid, with concentrations nominally greater than 100 percent H₂SO₄.

Uses of Sulfuric Acid

- The primary industrial uses of sulfuric acid are in phosphate fertilizer manufacture,
- petroleum refining, copper ore leaching,
- synthetic rubber and plastics,
- and pulp and paper mills.

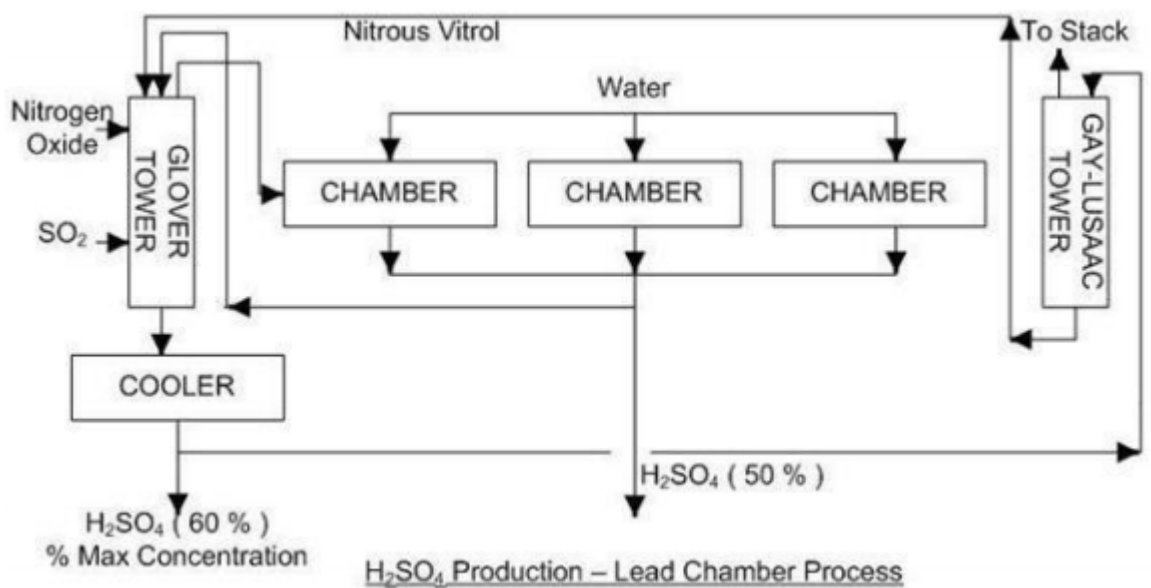
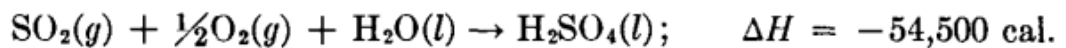
There have long been two main procedures for the making of sulfuric acid: the chamber process and the contact process.

Manufacture BY THE CHAMBER PROCESS

A typical flow sheet for the chamber process is presented in Fig. 3.

- The process starts when either the sulfur or pyrite (FeS₂) is burned
- and the hot gases are conducted through a combustion chamber which also may collect some dust.
- Sufficient oxides of nitrogen; NO and NO₂, are introduced into the hot mixture of air and sulfur dioxide from the burner
- The hot gaseous mixture passes up the Glover tower where it is met by the downward flow of the diluted Gay-Lussac acid or the nitrous vitriol.

- In the Glover tower about 10 per cent of the sulfuric acid is produced
- after the gas has been cooled by its passage up the Glover tower.
- The cooled gases are blown to the chambers where most of the acid is made and condensed.
- Finally, the unreacted gases pass to the Gay-Lussac tower for the absorption of the oxides of nitrogen in the strong Glover acid, producing the Gay-Lussac acid or the nitrous vitriol.



Unit processes and unit operations

- Transportation of sulfur or sulfides to plant (Op.).
- Melting of sulfur (Op.).
- Burning of sulfur or sulfide (Pr.).
- Recovery of heat from hot sulfur dioxide gas (Op.).
- Purification of sulfur dioxide gas (Op.).
- Mixing of sulfur dioxide gas with the nitrogen oxides catalyst in Glover tower (Pr. and Op.).

- Oxidation of sulfur dioxide to sulfur trioxide (see Reactions) (Pr.).
- Hydration of sulfur trioxide to sulfuric acid in Glover tower and chambers (Pr.).
- Settling of sulfuric acid mist and dissipation of heat of reactions (Op.).
- Absorption of nitrogen oxides from residual gas, forming nitrous-vitriol in Gay-Lussac tower (Pr.).
- Pumping of acids over towers and through coolers (Op.).
- Blowing of gases through system (Op.).
- Oxidizing of ammonia to nitrogen oxide, NO, for catalyst make-up (Pr.).

Lecture 10

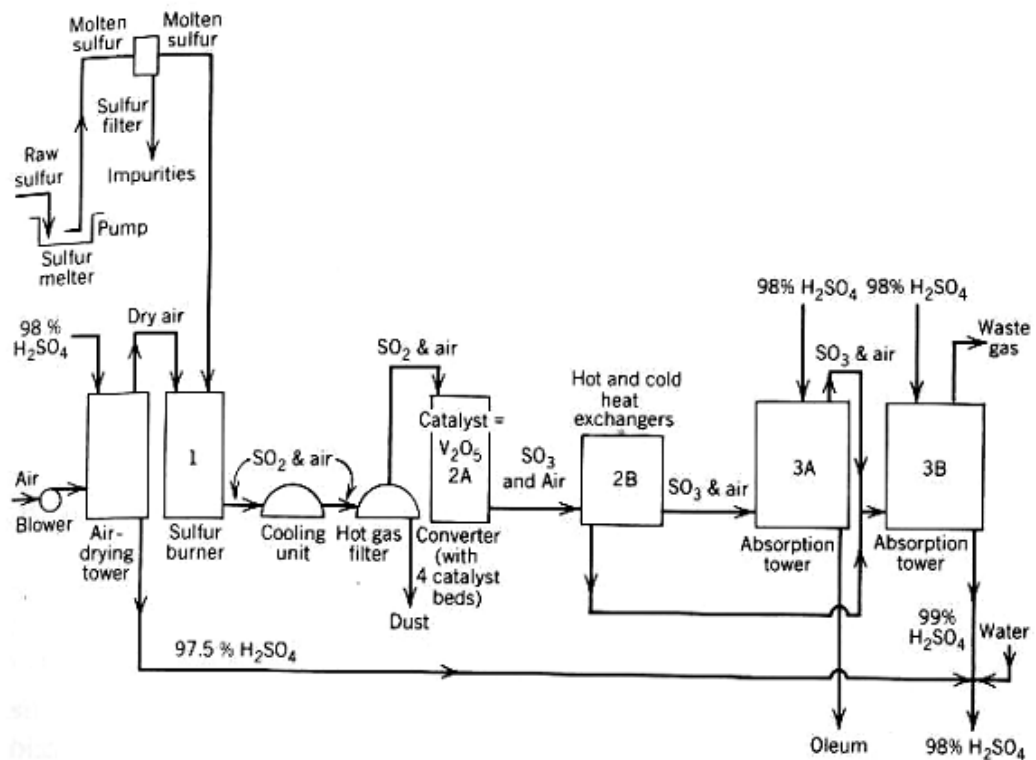
Contact process

Contact plants are classified according to the raw materials charged to them:

- elemental sulfur burning,
- spent sulfuric acid and hydrogen sulfide burning,
- metal sulfide ores and smelter gas burning.

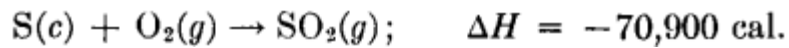
The basic steps in the contact process are:

- production of sulfur dioxide
- cooling and cleaning of the process gas;
- conversion of the sulfur dioxide to sulfur trioxide
- cooling of the sulfur trioxide gas
- absorption of the sulfur trioxide in sulfuric acid.



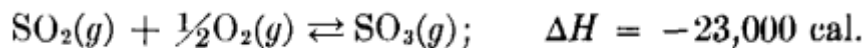
1. production of sulfur dioxide

sulfur is converted to sulfur dioxide by burning molten sulfur with dried air in a sulfur burner to yield a 1000 to 1100°C gas stream containing 10 to 11 percent SO₂.



2. Conversion of SO₂ to SO₃

Oxidation of SO₂ to SO₃ is accomplished in multi-stage fixed-bed catalytic converters equipped with interstage boilers or heat exchangers to remove the heat of reaction.



3. Absorption of SO₃

Sulfur trioxide from the converter is absorbed in 98 percent H₂SO₄ recirculated counter-currently through a packed tower maintained at 60 to 80 °C by indirect cooling.

A portion of the SO₃ stream to the absorber is diverted to the oleum tower where it is absorbed in 98 percent acid.

