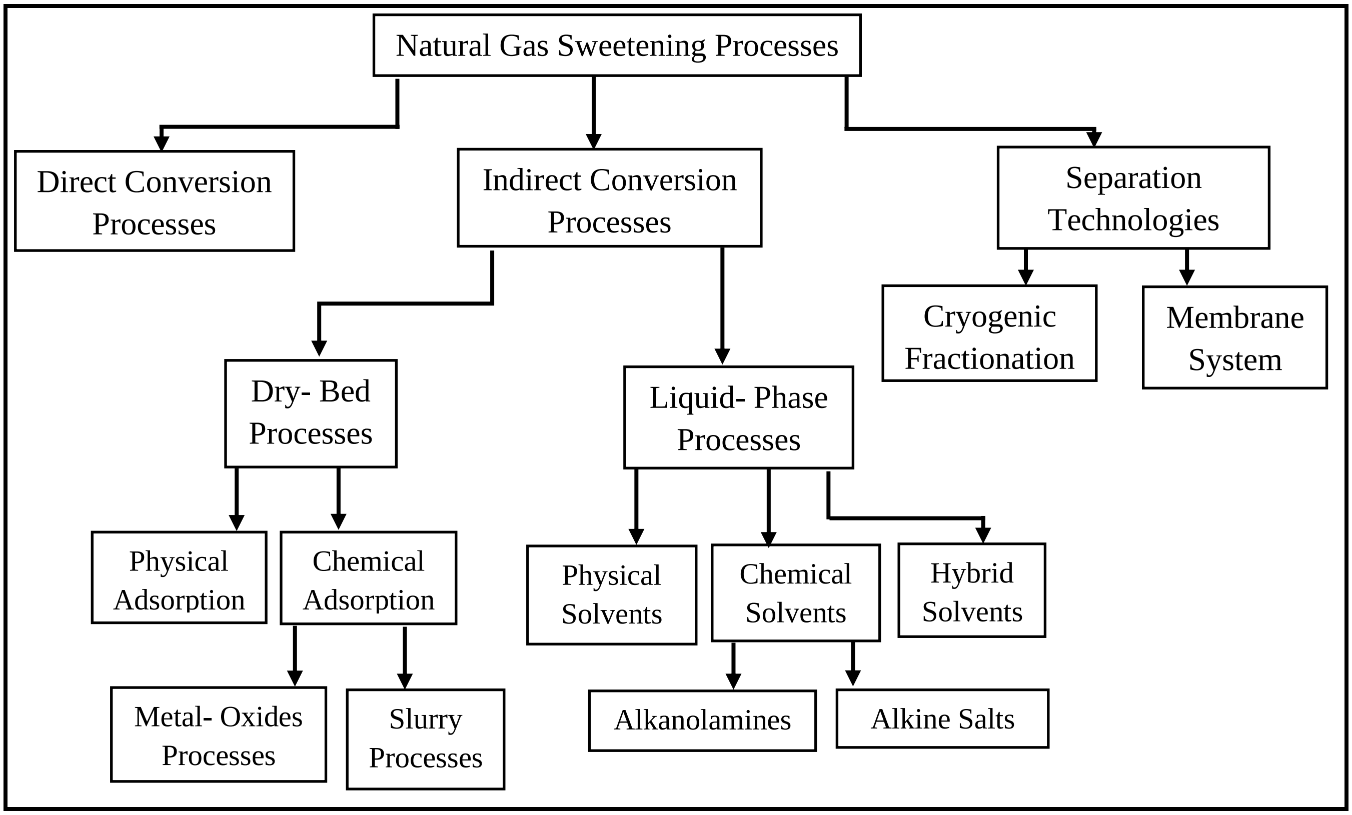
8. Natural Gas Treating

- Natural gas contains acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) and other sulfur contaminants such as mercaptans (R-SH) and carbonyl sulfide (COS) and carbon disulfide (CS_2).
- Sour gas can cause corrosion to natural gas processing equipment and pipelines.
- Combustion of sulfur compounds produces sulfur oxide air pollutants that must be limited to protect the environment and to prevent health-related problems.
- Carbon dioxide is an inert gas that does not have any heating value, but it is also the main source of greenhouse gas responsible for climate changes.
- The natural gas treating processes can be grouped in several categories as shown in Fig. below.



Alternatives for natural gas treating.

- If the sulfur content is relatively low, direct conversion processes are an option. These processes use an alkaline solution for absorption of H_2S and then a chelate agent and oxidation with air to form elemental sulfur.
- There are two types of indirect acid gas removal: **adsorption** and **absorption**.
- **Adsorption** is a physical-chemical phenomenon, in which impurities of the gas is trapped and removed physically or chemically by the surface of a selective solid.
- **Absorption** is the removal of acid gases by physical absorption by physical solvent toward acid gases or by chemical reaction with the acid gases using a chemical solvent.
- The dry-bed processes, which use a fixed bed of solid materials to remove acid gases either through ionic bonding or chemical reactions.

8.1. Chemical Solvent Processes

- In chemical solvent processes, absorption of the acid gases is achieved mainly by use of **alkanolamines** or **alkaline salts** of various weak acids such as sodium and potassium salts of carbonate (e.g. Potassium carbonate solution).
- Chemical absorption processes chemically absorb the H_2S, CO_2, and to some extent COS.
- Chemical solvents are specifically suitable when contaminants at relatively **low partial pressure** have to be removed to very low concentrations.
- Chemical solvents will not remove mercaptans down to low levels due to the low solubility of these components.

8.1.1. Alkanolamine Solvents

- Amines are compounds formed from ammonia (NH_3) by replacing one or more of the hydrogen atoms with another hydrocarbon group.
- Amines are categorized as **primary**, **secondary**, and **tertiary**, depending upon the degree of substitution of the hydrogen atoms by organic groups.

- Replacement of a single hydrogen atom produces a **primary amine** such as monoethanolamine (MEA) and diglycolamine (DGA).
- Replacement of two hydrogen atoms produces a **secondary amine** such as diethanolamine (DEA) and diisopropanolamine.
- Replacement of all three hydrogen atoms produces a **tertiary amine** such as methyldiethanolamine (MDEA).
- The chemical solvent processes are characterized by a relatively high heat of acid gas absorption. A substantial amount of heat is required for solvent regeneration.
- Amines are thermally stable, but are sensitive to degradation from oxidation and high temperatures, and may have various side reactions with CO_2, COS, and CS_2.
- Acid gas loading of amines is not very sensitive to changes in acid gas partial pressure as compared with physical solvents. While acid gas loading of a physical solvent increases with partial pressure of the acid gases.
- H2S reacts rapidly with primary, secondary, or tertiary amines via a direct proton transfer reaction, as shown in Equation below to form the amine hydrosulfide:

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+HS^-$$

- The reaction between the amine and the CO_2 is more complex because CO_2 reacts via two different mechanisms. When dissolved in water, CO_2 hydrolyzes to form carbonic acid, which in turn slowly dissociates to bicarbonate. The bicarbonate then undergoes an acid– base reaction with the amine.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \left(\text{carbonic acid}\right)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \left(\text{bicarbonate}\right)$$

$$H^+ + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+$$

$$CO_2 + H_2O + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+HCO_3^- \left(\text{overall reaction}\right)$$

- Some of the specific details for the amine processes are discussed in the following points:

1. Monoethanolamine (MEA)

Advantages:

- MEA is a primary amine
- MEA is the lowest cost solvent.
- MEA can remove both H_2S and CO_2 from gas streams.

Disadvantages:

- MEA solvent is very corrosive at high acid gas loadings and high solution concentrations.
- It reacts irreversibly with carbonyl sulfide (COS) and carbon disulfide (CS_2), which can degrade the solvent and form heat-stable salts.
- MEA has a higher vapor pressure than other amines.

2. Diglycolamine (DGA)

Advantages:

- The advantage of DGA is that it can operate with air cooling in hot climate locations.
- DGA is similar in many respects to MEA except that it exhibits lower vapor pressure, lower solution corrosion tendency and improved solution properties
- can operate at higher concentrations than MEA. (up to 60 wt%) which results in significantly lower circulation rates and energy consumption.

Disadvantages:

- DGA can remove COS, CS_2, and (partially) mercaptans but also forms degradation products which are not reversible at normal amine regenerator temperature.
- To maintain the amine activity, thermal reclaiming of a slipstream of the circulating amine is required.

3. Diethanolamine

Advantages:

- DEA is a secondary amine.
- The amine reactivity and corrosivity are lower than primary amines.

- Vapor pressure and heat of reaction are also lower.
- DEA is common amine used for H_2S and CO_2 removal in refineries due to its stabilities with contaminants in the refinery gas streams.
- DEA can partially remove COS and CS_2.
- The solution strength of DEA solvent is typically 25 to 30 wt%. When used for high pressure acid gas removal.

Disadvantages:

- The reaction rate of DEA with COS and CS_2 is lower than with MEA.

4. Diisopropanolamine (DIPA)

Advantages:

- DIPA is a secondary amine.
- Its reactivity with acid gases is similar to DEA.
- It can be used either selectively to remove H_2S (at low pressures) or to remove both CO_2 and H_2S (at higher pressures).
- DIPA can be used to partially remove COS and CS_2.
- The solution strength of DIPA solvent is typically 20 to 40 wt%.

5. Methyldiethanolamine (MEDA)

Advantages:

- MDEA is a tertiary amine.
- Unlike primary and secondary amines, MDEA cannot react with CO_2 by the carbamate reaction. It can only absorb CO_2 by the slow bicarbonate formation. This property allows MDEA to selectively remove H_2S when treating a gas stream containing both H_2S and CO_2.
- The slippage of CO_2 opens up more capacities in gas treating units. By reducing CO_2 absorption, more solvent is available for H_2S removal.
- Low vapor pressure and solution losses, low energy for solvent regeneration, low corrosiveness, and resistance to degradation.

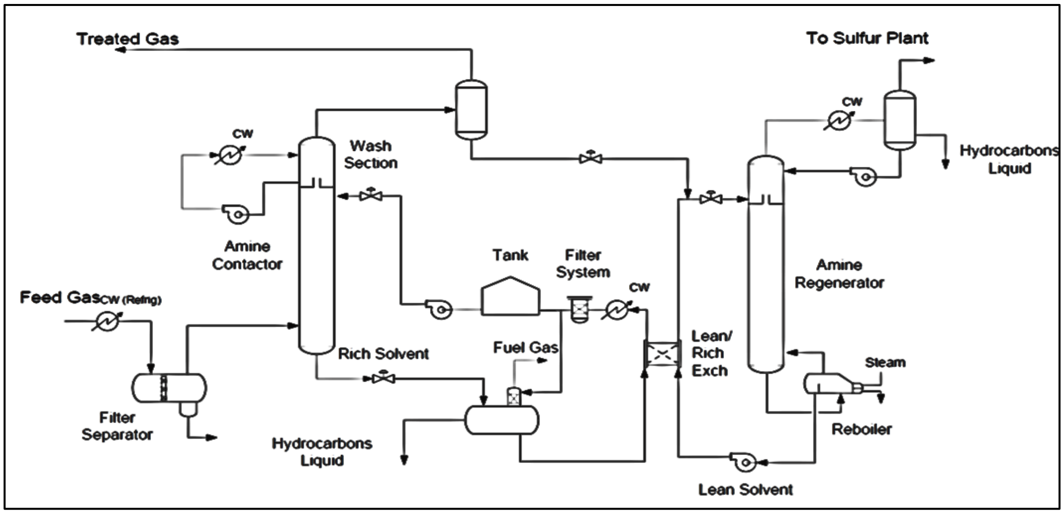
- The solution strength of MDEA solvents is 35-50 wt%.

Disadvantages:

- MDEA process would require low absorption temperature to improve the amine-H_2S equilibrium for absorption to meet low H_2S specification.
- Generic MDEA has minimal COS and CS_2 removal capability.

8.1.2. Amine Processes

- A typical process flow diagram of the amine unit is shown in Fig. below.



Typical flow schematic of an amine treating unit.

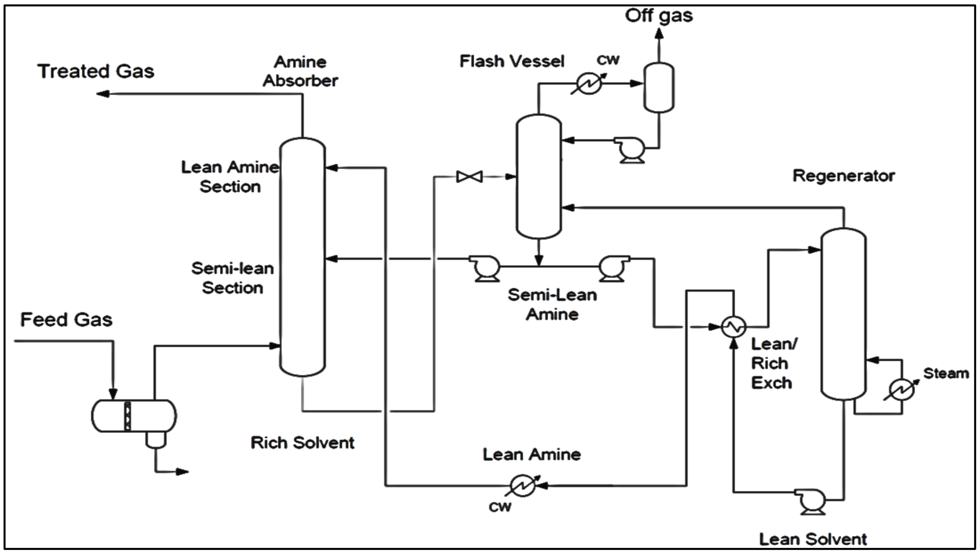
- Typically, sour feed gas is filtered and cleaned of entrained liquids and pipe scales using an inlet filter separator.
- The separator gas is fed to the amine absorber where the acid gas content is removed by an aqueous amine solution, producing a rich amine at the bottom and a H_2S-depleted gas from the top.
- Depending on the applications, some CO_2 as much as 2 mol% can be left in the treated gas if the gas is used as pipeline gas. If the gas is sent to an NGL recovery unit or an LNG production plant, deeper CO_2 removal is required.

- The rich amine is letdown in pressure to the rich amine flash drum. The rich amine flash drum is a three-phase separator designed for hydrocarbon liquids and amine separation.
- Hydrocarbon liquids are removed from the flash drum using a skimming device to avoid buildup that would cause foaming. The flashed gas containing some H_2S is treated using a small packed section and recovered as fuel gas.
- The flashed amine is preheated in the lean/rich exchanger to about 200-215 °F, before entering the regenerator.
- Amine unit requires steam for solvent regeneration and is a major steam consumer in a gas plant.
- The regenerator typically operates at about 10-15 psig producing an acid gas to the sulfur recovery unit.
- The rich amine is heated in the regenerator and stripped with steam, producing a lean amine.
- The lean amine is cooled in the lean/rich exchanger, lean amine cooler, and filtered prior to returning to the absorber. The filter system typically includes a particulate filter for removal of corrosion materials and a carbon filter for removal of heavy hydrocarbons.
- The filtration system is typically installed on the lean amine side which is easier for maintenance as the system is free of H_2S.
- Alternatively, it can also be installed on the rich amine side which has the advantage of protecting the amine regenerator from fouling. In this design, proper operating procedure must be exercised because of the H_2S content in the rich amine.
- The amine storage tank acts as a surge for the amine system which dampens out flow fluctuation, maintaining a constant circulation.
- The amine tank content should be periodically checked for active amine and purity, and should be adjusted by makeup as necessary.

- The complexity depends on the **solvent used**, **the acid gas concentration**, **operating pressure** and **temperature**, and the product gas specifications.

8.1.3. Two-Stage Absorption Process

- The two-stage amine absorption process is applicable to MDEA solvent, which can be partially regenerated by pressure letdown, reducing the overall steam consumption.
- The two-stage MDEA process has been used in treating high CO_2 content synthesis gas in ammonia plants.
- Synthesis gas mainly consists of hydrogen, CO and CO_2, and H_2S and does not contain any hydrocarbons. For this reason, there is typically no foaming problem in synthesis gas plants.
- On the other hand, there are problems with a two-stage MDEA process in natural gas plants. This is typically due to the adequate solvent regeneration which results in buildup of hydrocarbons in the amine circuit, resulting in foaming and failure to meet specifications. For this reason, two-stage amine unit is seldom used in natural gas processing plants.
- A typical process configuration of a two-stage process is shown in Fig. below.

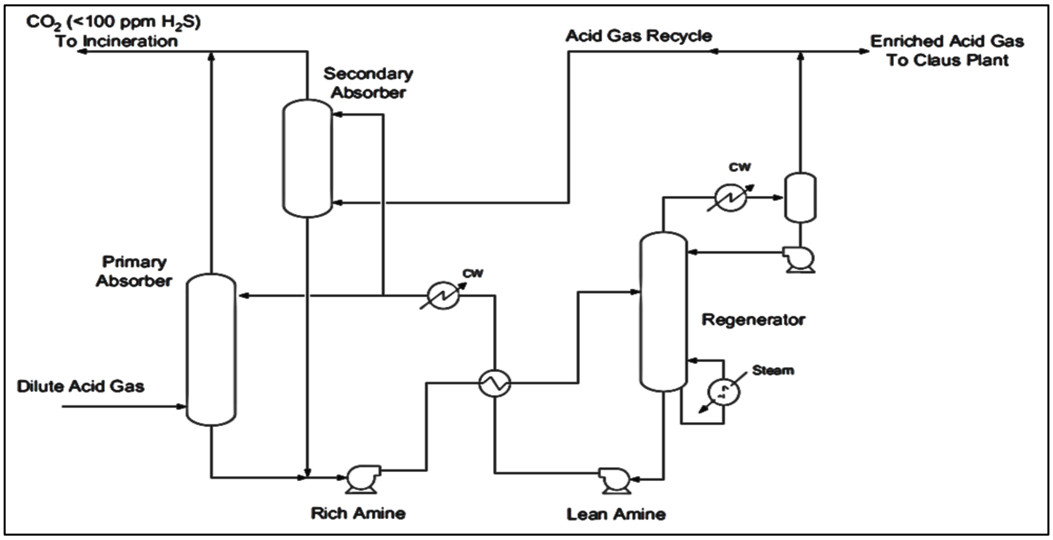


Flow schematic of two-stage methyldiethanolamine process.

- The amine absorber consists of two absorption sections: a top lean amine section and a lower semi-lean solvent section. The lean amine is produced by steam stripping and the semi-lean solvent is produced by flash regeneration.
- The main purpose of the two-stage pressure is to reduce steam consumption using the semi-lean amine.
- The ratio of lean and semi-lean solvent flow is an important parameter in designing a two-stage MDEA system.
- Increasing the lean to semi-lean ratio will increase the steam consumption but would enhance stripping of hydrocarbons and can produce a lean amine to meet a more stringent CO_2 specification.

8.1.4. Double Absorption Process

- The double absorption process is used for enriching the H_2S content in the feed gas to operate a straight-through Claus sulfur recovery unit.
- When the gas plant is used to treat a high CO_2 content feed gas, the H_2S content in the acid gas from the amine unit frequently falls below 10%, which makes operating a conventional Claus sulfur recovery unit difficult.
  - The process uses a selective solvent, such as MDEA, to process a dilute acid gas to produce two gas streams via selective absorption of H_2S.
- The acid gas can be processed an innovative method using a patented double absorption process as shown in Fig. below.



Flow schematic of double amine absorption process

8.1.5. Special Design Considerations

Followings are the design options that are normally not covered in typical amine unit design.

1. Water Wash Trays: When the absorber operates at high ambient temperature, the vaporization loss of amine can be significant. To minimize amine losses, a water wash section can be installed on the upper section of the amine absorber.

2. Feed Gas and Amine Temperatures: To avoid hydrocarbon condensation, lean amine must be controlled at 10-15 °F above the feed temperature. In the hot climate applications, it may be more cost-effective to cool the feed gas first to reduce the inlet temperature.

3. Lean Amine Feed Locations: Multiple lean amine feed points can be installed in the absorber to provide the flexibility for selective CO_2 removal. When producing a pipeline gas, the feed location can be lowered to minimize CO_2 absorption. This is particularly useful in tail gas treating unit operation which requires maximum slippage of CO_2, and moving the feed location to a lower location will help to concentrate H_2S content in the acid gas.

4. Absorber Side Cooler: When amine is used to treat high partial pressure acid gases, especially CO_2, the heat of reaction would be significant, which would raise the temperature of the absorber. The amount of acid gas that can be absorbed by the amine is determined by the rich amine acid gas loading at the bottom, which is a function of operating temperature.

5. Design Guidelines: The operating parameters of an amine process vary with the type of the amine as well as the feed gas conditions.

8.1.6. Amine Unit Operating Problems

- Absorber and regenerator typically experience foaming problems, resulting in carryover of amine to downstream units. Foaming is caused by hydrocarbon entrainment in the feed gas.
- Hydrocarbon contamination can be mitigated by maintaining a temperature approach between the lean amine and the feed gas, skimming of hydrocarbons from the rich amine flash drum and reflux drum, and frequent change-out of particulate filters and carbon filters.
- Foaming can also be caused by heat-stable salts, which are formed from amine degradation.
- There are different methods that can be used to control the levels of heat-stable salts, including purging, caustic addition, and reclamation.
- Continuous amine reclaiming is considered more effective in solving the heat-stable salt (HSS) problems.
- Formation of heat-stable salts depends on the feed gas compositions, particularly sulfur contaminants and the H_2S to CO_2 ratio. Most amine units can operate without reclaiming for some time, especially with low H_2S content gases. Most amine suppliers are knowledgeable of the heat stable salt problems and can provide the reclaiming equipment to maintain the amine purity.

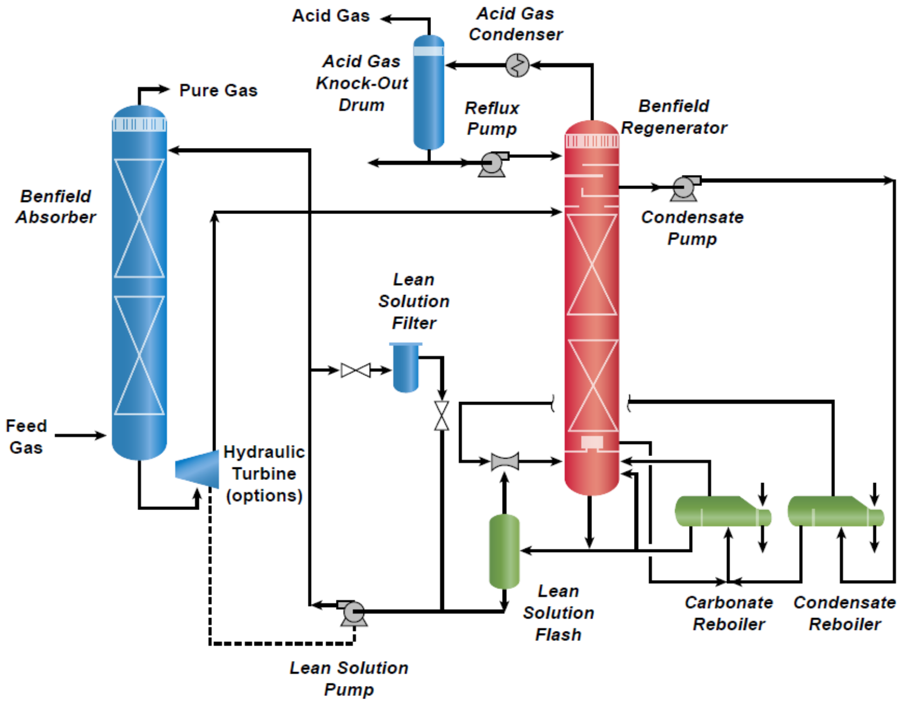
8.2. The Potassium Carbonate Solution (K_2CO_3)

- In the potassium carbonate process, which is referred to as the "hot pot" process, the process system operates at high temperature (in the range of 230-240°F) and was very popular in CO_2 removal in ammonia plant.
- The reaction of K_2CO_3 with CO_2 and H2S can be represented as:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3$$

- Potassium carbonate is known to cause equipment failure from excessive corrosion.
- Potassium carbonate solvent absorbs CO_2 at a relatively slow rate. The reaction rates are increased through the use of catalytic promoters, such as DEA.
- There are three potassium carbonate processes using different additive: Catacarb, Vetrocoke, and Benfield.
- The Catacarb process uses amine borates additive and vanadium-based inhibitors to mitigate the corrosion, which are toxic materials.
- The Vetrocoke process utilizes organic and inorganic additives to activate the solution. One of the common corrosion inhibitors is arsenic trioxide, which, however, is also a toxic material.
- The Benfield process, licensed by UOP, uses the less toxic DEA as an activator.
- A typical flow scheme for the UOP Benfield process is shown in Fig. below.



Flow scheme for the UOP Benfield process

8.3. Physical Solvent Processes

- Physical solvent processes can remove acid gases and organic sulfur based on physical absorption, and no chemical reaction occurs.
- The physical solvent's acid gas holding capacity increases with the partial pressure of acid gas (Henry's Law). Thus, they are more economical over chemical solvents in treating high pressure high CO_2 content gas.
- Unlike chemical solvents, physical solvents operate at ambient to sub ambient temperatures.
- They are noncorrosive and do not require stainless steel material to combat corrosion.
- Physical solvents can be regenerated by reduction in solvent pressure.
- Compared with chemical solvents, physical solvents absorb more hydrocarbons and have high hydrocarbon losses. For this reason, physical solvents are more common in treating synthesis gas which has no hydrocarbons.

- Some of the more common physical solvents used in gas treating include the following:

- Propylene carbonate $C_4H_6O_3$ (PC) (The Fluor Solvent process)

- Dimethyl ether of polyethylene glycol (DEPG) (the Selexol solvent)

- Methanol (MeOH) (Rectisol process)

- N-methyl-2-pyrrolidone (NMP) (Purisol process)

- These solvents are used to remove CO_2 from high-pressure sour gases. During the absorption processes, they also coabsorb other components.
- To minimize hydrocarbon losses, the solvent that has the lowest solubility with methane and ethane is preferred.
- PC and DEPG solvents have been used for both natural gas and syngas treating units.
- Among all the physical solvents, PC exhibits the lowest hydrocarbon solubility, which means a lower hydrocarbon loss in the CO_2 stream; hence PC is more suitable for treating natural gas streams than other physical solvents.
- Methanol and NMP solvents are common in syngas treating units. They are seldom used in natural gas treating units mainly due to their high solubility of hydrocarbons.
- Unlike amine processes, physical solvent process configurations are much more complex. Physical solvent processes require proven design and engineering skill, unit operating data, coupled with accurate thermodynamic data and heat and mass transfer model that are only available from licensors.
- The process configurations must be customized for specific feed gas compositions, operating temperatures and pressures, and product specifications.

8.4. Mixed Physical and Chemical Solvent Process

- Some chemical manufacturers have developed processes that take advantage of the benefits of physical and chemical solvents.
- These mixed solvents or “hybrid solvents” have different formulation of the solvent mixtures and are trademarked by the solvent manufacturers.
- These solvents take advantage of physical solvent properties, such as high acid gas solubility at high pressure, high solubility of mercaptans and organic sulfur. It also has the acid gas reactivity of a chemical solvent to meet tight specifications.
- The use of hybrid solvents is more beneficial at high acid gas partial pressures. By using various amine combinations with the physical solvents, the hybrid solvents can be formulated to allow for complete CO_2 removal, bulk CO_2 removal, or CO_2 slip, while achieving H_2S removal comparable with alkanolamines.
- In hybrid systems, mercaptans and organic sulfur can be removed by the physical solvent portion.
- However, the hybrid solvent system also inherits some of the drawbacks of a physical solvent system, such as more absorber stages, high hydrocarbon losses, and ineffective treating at low pressures.
- Examples of hybrid solvents include Sulfinol from Shell and UCARSOL from Dow Chemical (Ucarsol LE-701, 702, and 703).
- Three different solvents are available for the Sulfinol process: Sulfinol-X consists of sulfolane, MDEA, piperazine, and water. Sulfinol-M consists of sulfolane, MDEA, and water. Sulfinol-D consists of sulfolane, DIPA, and water.

8.5. Solid Bed Adsorption Process (H_2S Scavenger Processes)

The solid fixed bed adsorption processes remove a small quantity of H_2S from gas stream to meet a tight sulfur specification. The absorption processes rely on reaction of a metal oxide with H_2S to form a metal sulfide compound. The metal oxides can be regenerated with oxygen or air, producing the sulfur waste product. The metal oxides used for the absorption processes are typically iron oxide and zinc oxide.

1. Iron Sponge Process

Iron sponge is very selective for H_2S removal. In this process, the inlet gas is fed at the top of the fixed-bed reactor filled with hydrated ferric oxide (Fe_2O_3). The basic reaction is:

$$2Fe_2O_3 + 6H_2S \qquad 2Fe_2S_3 + 6H_2O$$

The reaction requires the presence of slightly alkaline water and a temperature below 110°F. A pH level, in the order of 8-10, should be maintained through the injection of caustic soda with the water. The bed is regenerated by controlled oxidation as:

$$2Fe_2S_3 + 3O_2 \qquad 2Fe_2O_3 + 6S$$

For the conversion process, oxygen should be introduced slowly to react with the iron sulfide. If oxygen is introduced quickly, there is a danger of intensive heat of reaction that may ignite the bed.

$$S_2 + 2O_2 \qquad 2SO_2$$

Generally, the iron oxide process is suitable for small to moderate quantities of hydrogen sulfide (300 ppm) operating at low to moderate pressures (50-500 psig).

2. Zinc Oxide Process

The zinc oxide process can also be used for H_2S removal from various gas streams. It uses a solid bed of granular zinc oxide to react with hydrogen sulfide:

$$ZnO + H_2S \qquad ZnS + H_2O$$

The zinc oxide process can produce a treated gas with H_2S concentration as low as 1 ppm but would require operating temperature as high as 550°F. The use of this process has been decreasing in recent years due to the problems on disposing the zinc sulfide waste product, which is considered a hazardous material.

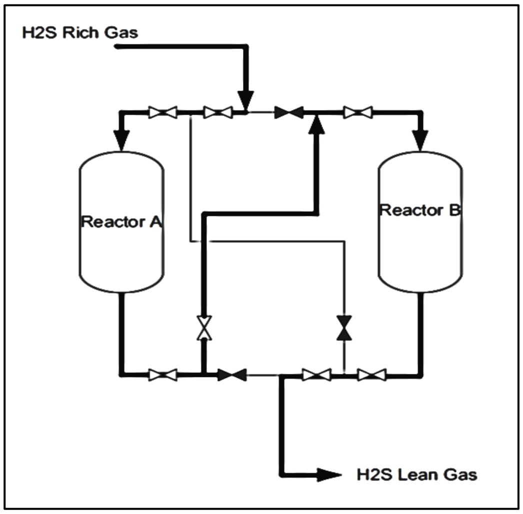
3. PURASPEC

PURASPEC technology was originally developed by Johnson Matthey based on their catalytic absorbents for the refining industries. It can be used for natural gas processing plants to remove impurities, such as H_2S, COS, mercury, and chlorides, from liquid and gaseous hydrocarbon streams to extremely low levels. H_2S and COS are removed by irreversible reactions with metal oxides (MO).

$$MO + H_2S \qquad MS + H_2O$$

$$MO + COS \qquad MS + CO_2$$

The PURASPEC catalysts are proprietary formulation oxides which have higher capacities and selectivity than generic metal oxides. The absorption beds are typically designed in a lead-lag reactor configuration as shown in Fig. below, which would facilitate the catalyst bed change-out.



Typical lead-lag absorption reactors

4. Slurry Process

Slurries of iron oxide have been used to selectively absorb H_2S. Two different slurry processes are described below.

a) Chemsweet Process

The Chemsweet process (developed by NATCO) is a zinc oxide-based process for the removal of H_2S from natural gas. The Chemsweet white powder, which is an aqueous mixture of **zinc oxide and zinc acetate**, is also a dispersant that keeps the zinc oxide particles in suspension. The following reactions are performed in this process:

Absorption: $ZnAc_2 + H_2S \longleftrightarrow ZnS + 2HAc$

Regeneration: $ZnO + 2HAc \longleftrightarrow 4ZnAc_2 + H_2O$

Overall: $ZnO + H_2S \longleftrightarrow ZnS + H_2O$

The Chemsweet process can treat gas streams with high H_2S concentration between pressures of 90 and 1400 psia. The presence of mercaptans in gas streams can be a problem. Some of the mercaptans will react with the zinc oxide forming a sludge composed of zinc mercaptides, Zn(OH)RH, which potentially can cause foaming problems.

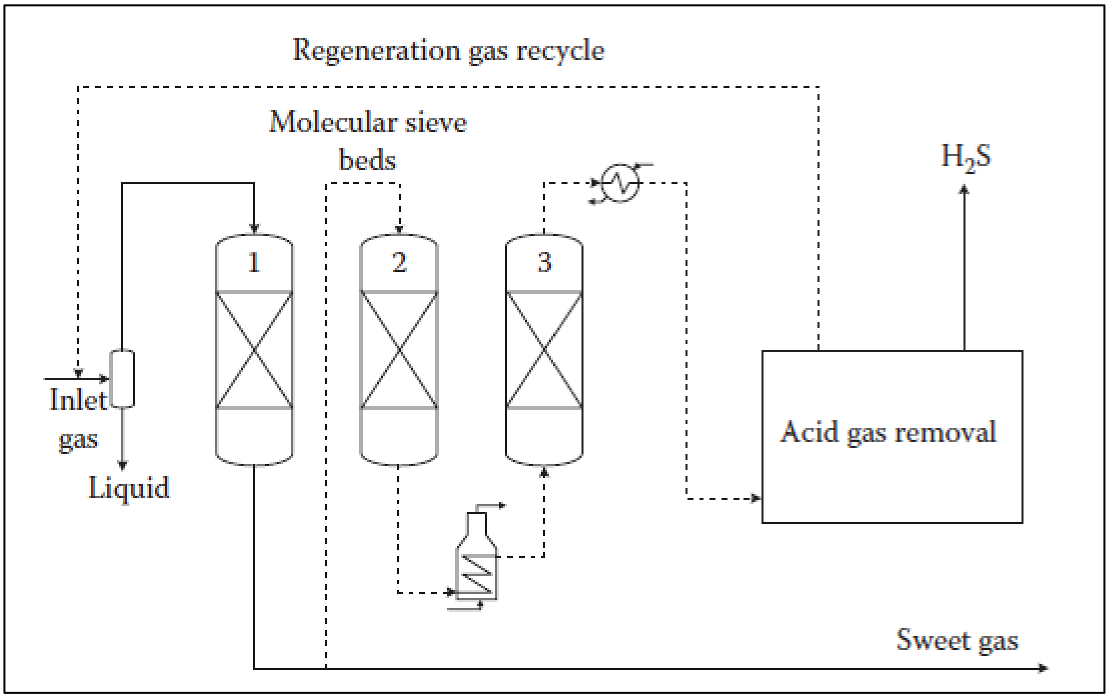
b) Sulfa-Check Process: The Sulfa-Check process selectively removes H_2S from natural gas, in the presence of CO_2. This process is accomplished using an aqueous solution of sodium nitrite ($NaNO_2$) which is buffered to stabilize the pH of the solution to above 8. This process is generally operated at ambient temperature and produces a slurry of sulfur and sodium salts.

$NaNO_2 + 3H_2S \longleftrightarrow 4NaOH + NH_3 + 3S + H_2O$

CO_2 also reacts with the sodium hydroxide to form sodium carbonate and sodium bicarbonate. Sodium nitrite and sodium hydroxide are consumed in the processes. When the chemicals are completely reacted, the system must be shut down to remove and replenish the chemicals.

8.6 Solid Bed Adsorption Process

- For physical adsorption, the holding forces of the adsorbate on the adsorbent are weaker than chemical bonding, and the adsorbate can be desorbed by raising the temperature or reducing the partial pressure.
- When an adsorbed component reacts chemically with the adsorbent, the process is termed chemisorption and desorption by pressure reduction is generally not possible.
- The main advantage of physical adsorption over chemical is lower energy consumption in regeneration, which can be achieved using a **pressure swing or temperature swing cycle.**
- The most common adsorbents in the natural gas treating industries are molecular sieves, activated alumina, and silica gels.
- **Molecular sieve** adsorbents are zeolite-based compounds which are commonly used for removal of CO_2 and H_2S, mercaptans, and other sulfur compounds.
- A molecular sieve works by adsorbing gas or liquid molecules that are smaller than the effective diameter of its pores, while excluding those molecules that are larger than the openings.
- This technology is used for treating low concentrations of sulfur components in natural gas stream where deep removal is required.
- The typical molecular sieve unit consists of two or more fixed-bed adsorbers and a regeneration system. With two molecular sieve beds, one bed is treating the feed gas while the other bed is being regenerated.
- Switching between the beds is automated using programmed timer and switching valves.
- During regeneration, the molecular sieve bed is heated up by a slipstream of the product gas, which desorbs the sour components from the molecular sieves.
- The hot regeneration gas is cooled and treated by an amine or physical solvent (depending on the mercaptans level), which is later regenerated and sent to the sulfur recovery unit.



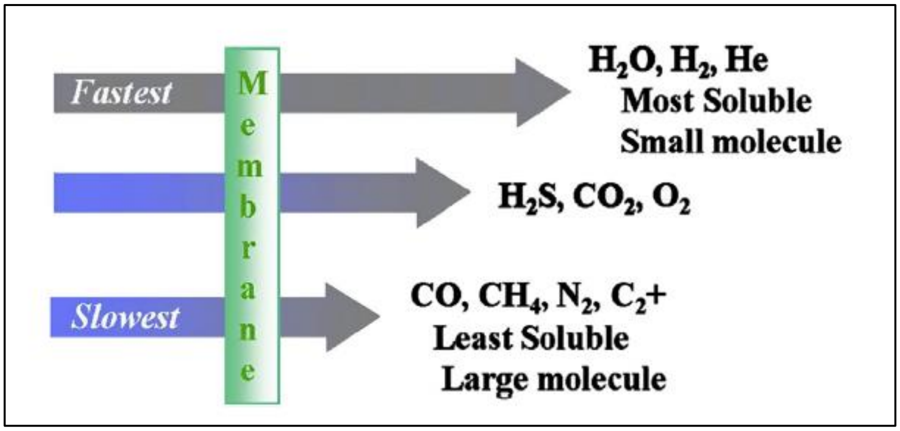
Schematic of natural gas adsorption (Dashed line denotes regeneration gas stream).

8.7. Membrane

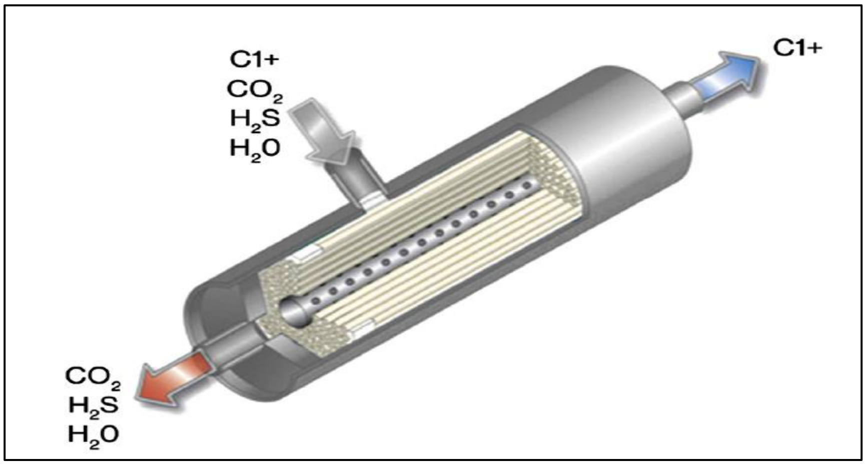
- Membrane systems, which consist of semipermeable elements (polymeric membranes), separate gases by selective permeation of the gas constituents.
- The gases dissolve in the membrane materials and move across the membrane barrier under a partial pressure gradient, which is established by maintaining a high feed pressure on one side of the membrane while maintaining the low pressure on the permeate side.
- Many different types of membranes have been developed for gas separations. For natural gas separation, most common membranes are of the “glassy” type of which the industry’s common standard is cellulose acetate.
- These membranes are of the solution-diffusion type, which consists of a thin layer of cellulose acetate built on top of a thicker layer of a porous support material.

- The membranes are thin to maximize mass transfer, which requires a supporting layer for mechanical strength.
- Other membrane in natural gas service includes polyimides and more recent a class of membrane using “rubbery” polymers.
- The solution–diffusion mechanism has been successfully employed to describe the transport of gas in dense membranes. It is assumed that no permanent pores exist in the membrane and there are no specific interactions between gas and membranes. Generally, the gases transport through the membrane by three steps. Firstly, gases are absorbed in the membrane surface at the upstream side. Secondly, gases diffuse through the membrane. Finally, gases are desorbed at the downstream side
- The smaller and more soluble components such as H_2O, H_2, He, CO_2, H_2S permeate quicker, leaving behind the less soluble components such as CO, methane, and nitrogen.
- Membranes are characterized by two properties; permeability and selectivity. Permeability is the gas permeation flux across unit area of membrane under unit pressure difference over unit membrane thickness, while selectivity is the ratio of permeabilities for different gases through the same membrane
- The driving force is the partial pressure differential of the permeate components. The preferable operating conditions are (1) high feed gas pressure (because it offers a higher acid gas partial pressure for a given component concentration) and (2) low permeate pressure (lower acid gas partial pressure).
- In most cases, the feed gas pressure is set by available well pressures or by required pipeline pressures. If the feed gas is available at a lower pressure than the pipeline requirement, compression would typically take place prior to membrane separation to take advantage of the higher pressure.

- In addition to the component partial pressures, the performance of membrane depends on the permeability and selectivity of the membrane elements for the different compounds.



Relative permeation rates in membrane



A sketch of single acid gas hollow fiber module

8.7.1 Membrane Advantages

Membrane process offers several advantages over solvent-treating processes such as:

1. Membranes are skid-mounted units. They can be installed in modules, relatively inexpensive to install.
2. The membrane module is compact, requiring small plot space for installation, suitable for offshore applications.

3. Membranes have no moving parts, requiring minimal operator attention and low operating and maintenance cost.
4. Membranes are self-supporting and do not require utilities such as water and instrument air.

8.7.2 Membrane Disadvantages

The decision to go with membrane for separation must consider the following shortcomings:

1. Losses of hydrocarbon products with the permeate. If the permeate is vented to atmosphere, this may create greenhouse gas impacts. In most applications, it is desirable to minimize hydrocarbon losses as it represents a revenue loss.
2. Prone to fouling from contaminants. The elements are prone to degradation from heavy hydrocarbons and aromatics.
3. An upstream pretreatment unit is required to prevent damage to the membranes, and depending on the feed stream, the pretreatment can be limited such as a filter, heater, and carbon bed or elaborate such as regenerable adsorbent beds.
4. Limited membrane manufacturer suppliers, making the membrane less competitive.
5. There is no economy of scale compared with the solvent treating process. Additional membrane modules must be added to handle higher flow. The number of membrane modules is directly proportional to the feed gas flow rate. Solvent process can accommodate the higher feed gas flow by increasing the solvent circulation.

8.8. Cryogenic separation

- ❖ Cryogenic separation involves cooling the acid gases to a very low temperature so that the CO_2 can be liquefied and separated.
- ❖ This technology requires substantial power to operate the refrigeration unit.
- ❖ It also needs pretreatment and dehydration of the feed gas to remove components that would result in hydrate formation and CO_2 freezing in cold section of the fractionation equipment.

- The advantages of cryogenic are recovery of pure CO_2 in liquid form and avoidance of chemical solvents and absence of secondary pollution.
- In other hand, cryogenic separation is less popular because it is too expensive, energy intensive, a restricted range of potential applications and a high operating cost associated with cold production.

8.9. Selecting The Gas Treating Process

The gas treating process selection should be based on the feed gas compositions, acid gas contents and sulfur compound levels, as well as the treated gas product specifications. A number of variables must be considered and evaluated in the selection process such as:

1. Variation in sour gas flow rate and composition, pressure, and temperature.
2. Unit capacity, site location, ambient temperatures, and onshore or offshore units.
3. Treated gas, acid gas, and liquid products specifications.
4. Unit turn-up and turn-down requirements.
5. Environmental requirements on air emissions, liquid effluent, and solid waste discharges.
6. Capital and operating costs.
7. Desired selectivity for acid gas removal.