"GAS SWEETENING PROCESSES"

APPENDIX

Excerpt from PRODEM

1.   GENERAL

Natural Gas (from a natural reservoir or associated to a crude production) can contain acid gas (H_2S and/or CO_2).
The Gas Sweetening Process aims to remove part or all of the acid gas that the natural gas contains for different reasons as follows:

- For safety reason, to remove the H_2S content of the natural gas stream.
- To satisfy a Sales Gas specification : H_2S content of the Sales Gas must be below 4 ppm V (about 5.7 mg of H_2S/Sm3 of gas or 0.25 grains of H_2S/100 SCF of gas).

CO_2 content must be adjusted to allow the Sales Gas to fit with the required range of gross calorific value (GCV).

- To allow a downstream process to work properly. This is the case for a cryogenic process (the CO_2 can freeze at temperatures around -70 deg.C).
- To decrease the H_2S content of a gas used in a crude cold stripping.
- For Enhance Oil Recovery (EOR) by CO_2 injection (CO_2 is removed from the gas and injected the oil reservoir).

2.   GAS SWEETENING PROCESSES

The different Gas Sweetening Processes to be applied depend on the quality and quantity of acid gas contaminants to be removed:

- CO_2 when this is the sole contaminant of the gas
- H_2S when this is the sole contaminant of the gas
- CO_2 and H_2S simultaneously
- Selective removal of H_2S when both CO_2 and H_2S are present in the gas

The existing processes are as follows:

- **Chemical Absorption**
- **Physical Absorption**
- **Physico-chemical Absorption**
- **Physical Adsorption**
- **Cryogenic Fractionation**
- **Permeation (membrane)**
- **Direct conversion to sulfur**

2.1.   chemical absorption

Several chemical solvents are available for gas sweetening processes, almost all of them being based on alkanolamine products. **They are all used under form of aqueous solutions.**

The main alkanolamine products used in the gas sweetening industry are as follows :

- **Mononethanolamine or MEA**
- **Diglycolamine (â) or DGA**
- **Diethanolamine or DEA**
- **Diisopropanolamine or DIPA**
- **Methyldiethanolamine or MDEA**

As an alternative to alkanolamine products, an alkaline salt is also used :

- **Hot Potassium Carbonate or HPC or Hot Pot**

Chemical formulas of alkanolamines are shown in figure XI-B.1. Main properties of these products are shown in table XI-B.1a).

Chemical absorption process is based on a contact between the gas to be treated (feed gas) and an aqueous solution containing one of the above solvents. Acid gas in the feed gas is a weak acid which reacts with the alkanolamine (alkaline product) or alkaline salt (in the case of potassium carbonate) to give bisulfide (with H2S) and bicarbonate (with CO2).

The chemical reaction (chemical absorption) takes place in a fractionation column (absorber or contactor) which is equipped with trays or packing. The gas enters the column at the bottom tray (or at the bottom part of the packing). The aqueous solution enters the column at the top tray (or at the top section of the packing).

There is a heat of reaction between the solvent and the acid gas during this absorption, which is exothermic. The treated gas exits the unit at a higher temperature than the feed gas. This implies that the treated gas water content will be higher than the feed gas water content. As a consequence should a dehydration of the gas be also required, this unit will be always installed downstream of the sweetening unit.

The alkanolamine salt is then re-transformed into alkaline solution in a regeneration section and the cycle is repeated again.

2.1.1. Description of an Amine process

This process flow scheme varies little, regardless of the aqueous amine solution used as the sweetening agent. Slight modifications can appear linked to the type of amine which is selected and to the optimization of the scheme for specific purposes.

The general process flow for an amine sweetening plant is shown in figure XI-B.2.

The feed gas (sour gas) containing H2S and/or CO2 always must enter the plant through an **Inlet Separator** (or feed gas knock-out drum) to remove free liquids and/or entrained solids.

Excerpt from PRODEM

Inlet Separator

Objective
Catch liquid entrainments (water and hydrocarbon condensate and mist) to prevent entries of contaminants in the amine system

Characteristics
Generally vertical drum equipped with Demister pad to prevent liquid droplets carry-over

Alternatives
Cartridge filter-separator

The gas from this separator enters the bottom of the **Absorber** and flows upward trough the column in intimate counter-current contact with the aqueous amine solution (lean solution). In the column the **chemical reaction** between the amine and the feed gas acid gas occurs and the amine solution absorbs the acid gas. The chemical reaction (due to the heat of reaction between the amine and the acid gas) is **exothermic**. It will raise the temperature of the gas.
Treated gas (lean gas or sweet gas) leaves the top of the column and the amine solution loaded with acid gas (rich solution) leaves the bottom of the column.

Absorber

Objective
Acid gas removal from feed

Characteristics
- Fractionation column equipped with trays (generally around 20) or packing beds (generally 2 or 3 beds).
- The column must be equipped with pressure differential instrument to monitor the differential pressure across the trays (or beds)
  . sharp ΔP increase indicated foaming
  . slow ΔP indicated tray (or bed) fouling
- The column generally is fitted with three (3) level glasses at bottom to detect the real level in the bottom where there is foaming or oil layer
- Lean solution inlet temperature = at least feed gas temperature + 5 deg.C to avoid hydrocarbon condensation. Higher lean solution inlet temperatures will result in lower acid gas pickup up by the solution and higher water losses (treated gas higher temperatures).

The absorber column operates at the feed gas pressure. A minimum pressure of 4/5 b.a is required to make the process feasible and operable. There is no limitation on high pressure as far as the process is concerned. The only limitation relates to the thickness of the still plates to form the body of the column (anticipated construction problems for thickness above 150 mm).
Feed gas temperature must be positive (high freezing point of the amine solutions). However high temperatures will affect the performances of the unit. *Should the feed gas be at high temperature,*

Excerpt from PRODEM

an inlet cooler (using air or water) or a gas/gas exchanger (using the hot treated gas as heating medium) will be provided. This equipment will be installed upstream of the inlet separator.

The top of the absorber can be equipped with additional trays (2 to 4) to accommodate a water wash section. The injected water will remove the amine carried over with the treated gas. It is injected at the top tray and completely withdrawn at last tray of the water wash section.

The treated gas is then handled by a separator (or **Treated Gas KO Drum**) to collect entrained liquid before being routed to the downstream facilities.

Treated Gas KO Drum

Objective
Dry the treated gas by removing entrained amine

Characteristics
Vertical drum equipped with Demister pad

Alternative
Cartridge filter-separator

The rich solution from the Absorber is then let down and generally routed to the **Amine Flash Drum**. This drum (which operating pressure is between 7 and 15 b.a) allows to remove a portion of acid gas which evolves from the solution by the pressure let-down effect. The acid gas stream from the Amine Flash Drum is routed either to the fuel gas pool of the facilities or to the acid gas disposal system.

Amine Flash Drum

Objective
Removal of dissolved gas and entrained liquid hydrocarbons upstream the amine/amine heat exchanger and the regenerator

Characteristics
- Generally horizontal three-phase drum (liquid hydrocarbons skimming system is required
- Should be operated at minimum pressure (for a better degassing of the solution)
- Liquid retention of 10 to 20 minutes have been used

The rich solution from the Amine Flash Drum then passes through an **Amine/Amine Heat Exchanger**. This heat exchanger serves as a heat conservation device and lowers the total heat requirements for the process. The rich solution is heated by the regenerated solution (lean solution) coming from the regenerator.

Amine/Amine Heat Exchanger

Objective
Preheat the rich solution to the regenerator

Characteristics
- Shell and tube exchanger with rich solution tube side/lean solution shell side
- Minimum vaporization should take place in the exchanger (tube side) to prevent erosion/corrosion due to mixed flow
- Velocity must be limited to 1 m/s
- Should several exchanger be required, they will be stacked vertically with the rich solution entering at the lower part of the bottom exchanger so any liberated gas will be removed in the upward flow of amine solution
- Lean solution inlet temperature between 110 to 130 deg.C
- Rich solution outlet temperature between 90 and 110 deg.C

Alternative
Plate frame exchanger. This type of exchanger offers larger surface areas and higher heat transfer rates in a small volume. It is however more susceptible to fouling

Then the rich solution is let down to the operating pressure of the **Regenerator** (generally between 1.2 and 2 b.a) also called stripper is a fractionation column (with trays or packing) with a condenser (using water or air as cooling medium) and a reboiler.

Regenerator

Objective
Regenerate the rich amine by stripping of the acid gas

Characteristics
- Fractionation column equipped with trays (generally around 20) or packing beds (generally 2 or 3 beds).
- The column must be equipped with pressure differential instrument to monitor the differential pressure across the trays (or beds)
    . sharp ΔP increase indicated foaming
    . slow ΔP indicated tray (or bed) fouling/plugging
- Demister pad can be installed at the top to reduce amine loss caused by physical entrainments

The Regenerator trapout product feeds the **Reboiler** which is a shell and tube exchanger (using hot oil or steam as heating medium).

Excerpt from PRODEM

Reboiler

Objective

Heat up the rich solution to produce the energy to reverse the chemical reaction to free acid gas from the amine solution and to generate steam to strip acid gas from solution. The stripping efficiency is controlled by the overhead reflux ratio.

Characteristics
- Generally kettle type reboiler. Square tube pitch pattern is recommended
- Regenerated solution outlet temperature is only function of operating pressure and amine strength
- Reboiler duty controlled by heating medium rate (steam or hot oil)
- Tube skin temperature <145 deg.C to avoid amine degradation
- Space to be provided below the bundle to have a good natural circulation and leave room for sludge deposit
- Liquid layer above the bundle high enough to prevent localized drying and overheating (150 to 200 mm height)
- Sufficient vapor volume above the liquid level to have no solution entrainments

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This Reboiler can be a direct fired heater. In this case precaution must be taken to avoid local overheating of the solution (this would lead to formation of corrosion by-products and amine excessive vaporization).

The regenerated solution from the Reboiler (at its bubble point at the operating pressure of the Regenerator) at temperatures generally between 110 and 130 deg.C, is then routed back to the Amine/Amine Exchanger.

The top product of the Regenerator is a water vapor/acid gas mixture. This stream is handled by the **Condenser** where the water vapor is condensed to generate reflux to the Regenerator. It uses ambient available cooling medium (water or air). Classical shell and tube exchanger (water cooling) or air cooler (air cooling) are used for this purpose.

A **Reflux Drum** (or Regenerator Overhead Drum) is provided to collect the condensed water and acid gas from the condenser. The acid gas stream from the Reflux Drum is routed to the acid gas disposal system. Water from the Reflux Drum is handled by **Reflux Pumps** (generally two reflux pumps: one in operation and one stand-by) and routed back to the top of the Regenerator.

Reflux ratios between 0.9/1 to 3/1 mole of water per mole of acid gas are generally used to make the process to work properly.

Reflux drum

Objective
- Recover as stripper reflux the water condensed in the condenser
- Catch possible condensed hydrocarbons

Characteristics
- Vertical or horizontal drum equipped with Demister pad
- Temperature as low as possible to minimize amine concentration and water entrainments to downstream facilities (for example Sulfur recovery unit)
- Oil skimming facilities to be provided

Excerpt from PRODEM

The temperature of the lean solution leaving the Amine/Amine Exchanger is generally still far above the feed gas inlet temperature. Lean solution high temperatures will result in lower acid gas pickup up by the solution and higher water losses (treated gas higher temperatures). A final **Lean Solution Cooler** is then provided (using water or air as cooling medium) to cool the solution.

Circulation Pumps (generally 2 x 100 % or 3 x 50 %) are provided to send the cooled lean solution back to the Absorber.

In large units, the amine pumping system can include first a set of Booster Pumps and then the set of Circulation Pumps. The objective of the booster pumps is to feed the main pumps without NPSH problems.

Pumps can be driven by electric motors or turbines (gas or steam turbines). *Rich solution let down from the Absorber pressure to the Amine Flash Drum pressure can be done through hydraulic turbine (instead of J-T valve). Power recovered on the shaft of the hydraulic turbine can be used to drive a Circulation Pump.*

Solid impurities such as iron sulfide, iron oxide, sand, pipeline dust must be removed from the solution in order to prevent erosion and foaming. Filtration of the solution is then mandatory.

The **Mechanical Filter** (main filter) is normally located on the lean solution stream to the Absorber after the Amine/Amine Exchanger.

Mechanical Filter (main filter)

Objective
- Removal of the solids from amine solution (lean amine solid content < 100 ppm Wt).

Characteristics
- Generally leaf-type precoat filter (Filtration mesh : 10 µ maximum)
- Inlet flow rate : 10 to 20 (for large units) % of the solution circulation rate
- Pressure drop : 1 b maximum

An **Activated Carbon Filter** can be added downstream of the main filter to remove products not stopped by the main filter (hydrocarbon, water soluble compounds, unknown foam contributors). The flow rate to the Activated Carbon Filter can be less than the flow to the main filter.

Activated Carbon Filter

Characteristics
- Liquid velocity through the activated carbon bed would be less than 1cm/s.
- Height of the bed would be above 1.5 m
- Diameter of carbon particles would be 1/8″ to 1/4″ (4x10 mesh)
- Density of about 300 kg/m3
- Pressure drop : 1 b maximum
- The life of the activated carbon bed is at least 1 year.

Should a Carbon Filter be provided, a downstream additional filter (**Polishing Filter**) must be installed to remove particles of carbon.

Excerpt from PRODEM

An amine **Storage Tank** (surge tank) is provided. Pumping facilities are provided to route the stored solution to the unit.

Surge Tank

Objective
Spare capacity equivalent to amine solution hold-up (inventory of the unit) for emergency or maintenance unloading

Characteristics
- Atmospheric classical storage tank (fixed roof or cone roof)
- Blanketing with nitrogen or treated gas to avoid amine degradation with oxygen (*always avoid amine contact with air*)
- Oil recovery : skimming facilities
- Operating temperature above the freezing point of the solution

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A solution preparation sump is also provided to replenish losses of amine from the unit. Equipment drains should be connected to the amine sump such as :

- filter casings
- pump seals
- amine sampling points
- purge systems

A pump is provided to route the solution from the sump to the unit and/or to the surge tank.

Solution flow velocities in any piping must not exceed 2 m/s.

A certain quantity of water is continuously lost from the solution during the absorption and regeneration stages (due to the exothermic chemical reaction between the solution and the acid gas and due to the fact that acid gas from the regenerator is saturated with water at low pressure). To replenish losses of water from the solution, a continuous water make-up (**demineralized water**) is required.

2.1.2. Monoethanolamine

MEA is a primary amine. It is the oldest solvent used in modern Gas Sweetening plants.
Gas sweetening process using MEA is in the public domain. Figure XI-B.3 is a process flow diagram of a MEA unit.

- ***Concentration***

MEA is used in aqueous solutions with concentrations between 10 and 20 Wt. % MEA. By far the most common concentration is 15 Wt. % MEA. A 15 Wt. % MEA solution freezes at -4 deg.C.

The molar composition of a 15 Wt. % MEA solution is as follows:

Aqueous Solution	Wt. %	Mole %
MEA	15	4.95
H2O	85	95.05
total	*100*	*100.00*

- ● *Utilization*

The MEA solution is used for deep removal of CO_2 (when the feed gas is free from H_2S), H_2S (when the feed gas is free from CO_2) or both H_2S and CO_2 when both components are present in the feed gas. This is therefore not a suitable process for a selective removal of H_2S when both H_2S and CO_2 are present in the gas.

MEA will easily reduce the H_2S concentrations to less than 4 ppm V in the treated gas. However, this amine reacts with derivative sulfur products like carbonyl sulfide (COS) and carbon disufide (CS2) ; therefore a special equipment (reclaimer) is required to clean the solution.

Should mercaptans be present in the feed gas, the MEA solution will remove only a portion of these contaminants with a priority given to light mercaptans (methyl-mercaptan).

- ● *Chemical reactions*

H_2S reacts faster than CO_2.
- - H_2S

Reaction with H_2S proceeds to form bisulfide of the ethanolamine.

$RNH_2 + H_2S \leftrightarrow RNH_3HS$
- - CO_2
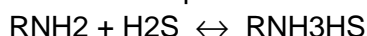
The chemical absorption of CO_2 is more complex. Carbon dioxide reacts with MEA to form carbamate salt (difficult or regenerate and which can promote corrosion problems) :

$$2RNH_2 + CO_2 \leftrightarrow RNHCOORNH_3$$
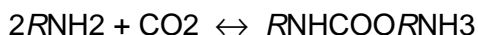
In water solution, organic acid (CO_2+H_2O) reacts with MEA to form bicarbonate salt (easier to regenerate) :

$$RNH_2 + H_2O + CO_2 \leftrightarrow RNH_3HCO_3$$

where $R = C_2H_4OH$

The above reactions are reversible. The left to the right direction of the reactions represents the absorption phase (better at low temperature and high pressure). This is an exothermic reaction.

The right to the left direction of the reactions represents the regeneration phase (better at high temperature and low pressure). This is an endothermic reaction.

Excerpt from PRODEM

- ### *MEA Solution Loading*

The gross acid gas quantity picked up by the solution (the concentration of acid gas in the rich solution leaving the absorber) is around 0.35 moles per mole of pure MEA. Above this loading, severe corrosion can occur. However, the regenerated solution (the lean solution which enters the absorber) still contains acid gas. Table 2.1.2.1 shows the residual acid gas content in the lean solution for different H_2S/CO_2 ratio in the feed gas.

Table 2.1.2.1: Acid Gas content in the MEA regenerated solution

(H_2S/CO_2) in Feed		0.1	1	10
H_2S in Lean solution	mole/mole pure MEA	0.002	0.006	0.03
CO_2 in lean solution	mole/mole pure MEA	0.134	0.129	0.05

As a result the net quantity of acid gas picked up by the lean solution (net acid gas pick up) is around 0.25 mole per mole of pure MEA. This corresponds to approximately 10 kg of pure MEA per Sm3 of acid gas to be removed.

- ### *Regenerator*

Degradation of MEA solutions increases rapidly when subjected to excessive temperatures. The pressure is generally between 1.2/2 b.a in order to keep the bottom temperature (bubble point of the solution) in the range 107/122 deg.C. Reflux ratios vary between 2.5 and 3 (mole water/mole Acid Gas).

- ### *MEA Degradation*

Many products such as oxygen, CO_2, COS (carbonyl sulfide), CS2 (carbon disulphide), may cause degradation of the MEA solution. Degradation products can cause severe corrosion of the equipment.

Oxygen

As other ethanolamines, MEA is subject to oxidation and subsequent degradation. Degradation products (dithiocarbamates for instance) may form. These products cannot be reconverted to free amine by application of heat.

- CO_2

MEA carbamate reacts slowly to produce a stronger base than MEA and it is more difficult to regenerate. Its carbonate salts are believed to be corrosive agents acting as chelating agents.

Excerpt from PRODEM

- COS

COS either present in the feed gas (as for example the feed gas to ADGAS LNG plant of DAS Island) or formed by inter reaction between H2S and CO2 reacts with MEA to form heat stable salts.

- CS2

CS2 also reacts with MEA to contribute to the presence of heat stable salts in the solution.

- ***MEA Reclaiming***

The reclaimer plays an important part in reducing corrosion, foaming and fouling. It restores the amine usefulness by removing high boiling and non volatile impurities (heat stable salts, volatile acids, solids, iron products). The amine solution is normally reclaimed by means of a semi-continuous batch distillation in a heated vessel (kettle). The vessel normally has a liquid capacity of approximately 100 times the feed rate expressed as m3/minute.

A side stream (usually 1 to 3 % of the circulating solution) is diverted to the reclaimer. This side stream is withdrawn from the bottom product of the Regenerator (see figure XI-B.4). The reclaimer is then filled until the heating tubes are fully immersed. Then, the feed is shut off and the kettle is brought to its operating temperature. The vapor phase evolving from the reclaimer is routed back to the regenerator. As the liquid begins to distill in the reclaimer, the overhead vapor is mainly steam. As the distillation continues, the liquid phase becomes more concentrated in MEA. Increments of fresh feed are added to maintain the liquid level in the kettle. The MEA concentration will increase until the vapor composition approximates the composition of the circulating solution. From figure XI-B.5, for a Regenerator operating at 0.7 b.g, the dew point of a 15 Wt. % MEA solution is 131 deg.C. The 15 Wt % MEA vapor phase is in equilibrium with a 64 Wt. % MEA liquid phase.

When equilibrium is reached, the predetermined flow to the reclaimer is turned in. Should the solution be not contaminated, the temperature will stay constant. With a contaminated solution, the boiling point of the solution will rise and the contaminants will concentrate in the liquid residual phase. When the temperature of the reclaimer is about 150/160 deg.C (higher temperature could possibly lead to promote the degradation of the MEA), the feed to the reclaimer is halted. The reclaiming cycle is over when essentially all the amine has been removed from the residue. The remaining bottoms, a thick sludge, is discarded by flushing with water and another cycle is begun.

Soda ash or caustic soda is added during the initial filling of the reclaimer to neutralize the heat stable salts and volatile acids (generally 0.03 Wt % is added but excess will raise the boiling temperature of the liquid).

- ***MEA Foaming***

Foaming has a direct effect on the treatment capacity of the unit (loss of proper vapor/liquid contact, solution hold-up and poor solution distribution).
Foaming of MEA solution can be attributed to :

- Suspended solids
- Liquid hydrocarbons
- Organic acids to form soap like materials with MEA
- Surface acting agents containing inhibitors, machinery lube oil

Excerpt from PRODEM

- MEA decomposition and degradation by-products
- Pre-commissioning operation poorly carried out

- **MEA losses**

Losses of MEA are due to vaporization, chemical losses and mechanical losses. According to information from the literature, the MEA losses are reported to be 16 kg of MEA/(MSm3/d of feed gas x Mole % of acid gas) when the feed gas is COS free. When COS is present in the feed gas, the losses increase.

2.1.3. Diglycolamine (â)

This is not the proper chemical name for this product: The actual name is 2-2 Aminoethoxyethanol. This is a primary amine which then shows a high reactivity with acid gases.

The registered mark comes from the manufacturer JEFFERSON Chemical Company in the late sixty's, a predecessor to TEXACO Chemical that has been recently bought by HUNTSMAN Specialty Chemicals Corporation. FLUOR was the licenser who developed a patented process based on the use of this solvent (*Improved Econamine Process)*. However FLUOR is no longer involved in patented processes and this DGA® process in now in the public domain.
The process is close to the MEA process.

- **Concentration**

DGA is used in aqueous solutions with concentrations between 50 and 65 Wt.%. A reason is that bubble points of a 60 Wt. % DGA solution are 16 to 21 deg.C lower than those of a 15 Wt. % MEA solution. Higher concentrations lead to lower circulation rates than those based on MEA.
The low freezing point of the solution (a 50 Wt. % DGA has a freezing point of -35 deg.C) offers an advantage over the other amine solutions especially in cold weather areas
The Improved Econamine process works with a DGA concentration of 65 Wt. % in the lean aqueous solution.
The molar composition of a 65 Wt. % DGA solution is as follows:

Aqueous Solution	Wt. %	Mole %
DGA	65	24.14
H2O	35	75.86
total	*100*	*100.00*

- **Utilization**

Inlet feed gas composition should include a minimum of 1.5 to 2 mole % acid gas for optimum use of the DGA Gas Sweetening process. This solution is used to remove CO2 (when the feed gas is free from H2S), H2S (when the feed gas is free from CO2) or both H2S and CO2. This is therefore

not a suitable process for a selective removal of H2S when both H2S and CO2 are present in the gas.

(CO2/H2S) ratio can vary from 100/1 to 0.1/1. Acid gas content can be in excess of 30 mole % in the feed gas. DGA will easily reduce the H2S concentrations to less than 4 ppm V in the treated gas.

DGA is similar in many respects to MEA. DGA also reacts with derivative sulfur products (COS and CS2) and therefore a reclaimer is provided to clean the solution (it works like that of MEA).

Should mercaptans be present in the feed gas, the DGA solution will remove only a small portion of these contaminants. Bulk of these contaminants will remain in the treated gas.

- ### *Chemical reactions*

Due to the nature of this product, it behaves like MEA.
In the case of DGA, *R* = C2H4OH-C2H4O

- ### *DGA Solution Loading*

For a 65 Wt. % DGA solution, the gross acid gas picked up by the solution is between 0.35 and 0.4 moles per mole of pure DGA. However, the regenerated solution still contains between 0.05 and 0.1 mole of acid gas (mainly CO2 when CO2 is one of the acid contaminants to be removed) per mole of pure DGA. As a result, the net quantity of acid gas picked up by the lean solution is between 0.25 and 0.35 mole per mole of DGA.

- ### *Absorber*

The high concentration of the solution leads to high chemical absorption temperatures (the bottom temperature of the Absorber is around 85 deg.C).
In order to increase the efficiency of absorption, a side cooler (using water or air as cooling medium) of the solution is provided at the bottom section of the column as shown in figure XI-B.6. The use of the side cooler will keep the circulation rate down, thereby lowering the required reboiler duty as well as loads in the amine/amine exchanger and lean amine cooler.

- ### *Regenerator*

The solution is regenerated at temperatures between 127/138 deg.C (reboiler temperature).

- ### *DGA Degradation/Foaming*

Sources of degradation and consequences are identical to those pertaining to MEA. Problems related to foamiing are identical to those met in a MEA unit.
The process of purification of the solution by a reclaimer is basically identical to MEA.

Excerpt from PRODEM

- ***DGA losses***

From available data and published information, losses of DGA (based on a gas having less than 50 ppm V of COS) are as follows:

mole % acid gas	DGA losses (kg/MSm3 of feed gas)
5	45 to 75
10	70 to 100
1 5	95 to 125

2.1.4. 2.1.4. Diethanolamine

This amine is a secondary amine.
The processing scheme of DEA is similar to MEA processing scheme with the exception of *the reclaimer which is not required*.

- ***Concentration***

DEA is used in aqueous solution with concentrations between 25 and 35 Wt.%. A 25 Wt. % DEA solution freezes at -6 deg.C.
Basically this process is in the public domain. Non licensed processes are generally based on 25 Wt. % DEA solutions.
The molar composition of a 25 Wt. % DEA solution is as follows:

Aqueous Solution	Wt. %	Mole %
DEA	25	5.4
H_2O	75	94.6
total	*100*	*100.0*

- ***Utilization***

DEA is non selective and will remove both H_2S and CO_2. Both contaminants can be removed at any low level required regardless of the initial content in the feed gas. This is therefore not a suitable process for a selective removal of H_2S when both H_2S and CO_2 are present in the gas.
Due to the absence (or weak) of reaction of DEA with COS and CS2, DEA has been widely used in the treatment of natural gas. The reclaimer is not required in a DEA unit. This is one of its main advantage over the primary amines.

COS and CS2 are removed by DEA (through a believed hydrolysis reaction).

In order to achieve a very low H2S concentration in the treated gas (4 ppm V or even less) when treating high H2S feed gas, a high solution rate will be required with a 25 Wt. % solution. In such a case, higher DEA concentrations are desirable. However, high concentrations (35 Wt. %) solutions are based on licenser's design such as EE(P).

Should mercaptans be present in the feed gas, the DEA solution will remove from 10 to 60 % according to their boiling points.

- **Chemical reactions**

H2S reacts faster than CO2.

- H_2S

Reaction with H2S proceeds to form bisulfide of the ethanolamine.

R2NH + H2S $\leftrightarrow$ R2NH2HS

- CO2
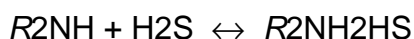
The chemical absorption of CO2 is more complex.

Carbon dioxide reacts with DEA to form carbamate salt of DEA

2R2NH + CO2 $\leftrightarrow$ R2NCOOR2NH2
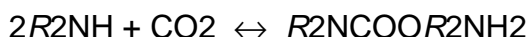
In water solution, organic acid (CO2+H2O) reacts with DEA to form bicarbonate salt (easier to regenerate).

R2NH + H2O + CO2 $\leftrightarrow$ R2NH2HC03

where R= C2H4OH

The above reactions are reversible. They are exothermic from left to right (absorption) and endothermic from right to left (regeneration).

- **DEA Solution Loading**

Gross acid gas pick-up (solution loading) by the DEA solution generally does not exceed 0.4 mole of acid gas/mole of pure DEA. Residual acid gas content of the regenerated solution generally is not above 0.07 mole/mole of pure DEA. The net acid gas quantity picked up by a 25 Wt. % solution is around 0.3 moles per mole of pure DEA.

- **Regenerator**

Degradation of DEA solutions increases rapidly when subjected to excessive temperatures. For a 25 Wt. % DEA solution, a regeneration pressure of 2.5 b.a will lead to a regeneration temperature (reboiler exit) of 130 deg.C. Reflux ratios vary between 2 and 2.5 mole water/mole Acid Gas.

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- ***DEA Degradation***

As other ethanolamines, DEA is subject to oxidation and subsequent degradation. Degradation products may form. These products cannot be reconverted to free amine by application of heat. Air ingress would then be prohibiteed in any part of the process.

- ***DEA Foaming***

Foaming has a direct effect on the treatment capacity of the unit (loss of proper vapor/liquid contact, solution hold-up and poor solution distribution).
Foaming of DEA solution can be attributed to:

- Suspended solids
- Liquid hydrocarbons
- Surface acting agents
- Pre-commissioning operation poorly carried out

2.1.5. Diisopropanolamine

DIPA is a secondary amine. Whilst the product is available from manufacturers of chemical products, SHELL is the licenser for two (2) processes using DIPA :

- The ADIP Process which is a chemical absorption process based on the use of DIPA in aqueous solution

- The **SULFINOL-D** process which is a physico-chemical process based on the use of a mixture (DIPA and Sulfolane) in aqueous solution.

The ADIP process was first applied in 1959. At present, well over 150 units are in operation (on gas and liquid services). Figure XI-B.8 shows a typical flowsheet.

- ***Concentration***

Diisopropanolamine is used in aqueous solutions with concentrations between 30 and 40 Wt. %.
The molar composition of a 30 Wt. % DIPA solution is as follows:

Aqueous Solution	Wt. %	Mole %
DIPA	30	5.48
H2O	70	94.52
total	*100*	*100.00*

- **Utilization**

DIPA is classified as a selective amine to remove H_2S when both H_2S and CO_2 are present in the feed gas.

When compared against other amines, the DIPA rate of CO_2 absorption is 2.1 times less than DEA and 5.6 times less than MEA.

DIPA like DEA is not degraded by CO_2, COS and CS_2. Therefore reclaiming the amine solution is not necessary.

Reflux ratios of the Regenerator vary between 0.9 and 1.8 mole water/mole Acid Gas removed.

- **DIPA Solution Loading**

DIPA solution loading depends on the respective concentration of CO_2 and H_2S and on the required H_2S content of the treated gas.

An existing ADIP Plant in the Middle East shows performances as indicated in table below:

Table 2.1.5.1. ADIP process

		Feed Gas		Treated Gas	
Pressure	b.a	24.8		24.5	
Temperature	deg.C	30		43	
Flow Rate	kmole/h	867.1		811.06	
Water content	kmole/h	0		3.17	
Acid Gas		mole %	kmole/h	mole %	kmole/h
CO2		7.17	62.25	1.92	15.56
H2S		1.50	13.03	0.002	0.02
Lean Solution		Wt. %	kmole/h		
DGA		27	142.95		
H2O		73	2855.94		

- CO2 slippage (not absorbed by amine) is 25 % of the inlet CO2 flow
- Net Acid Gas pick-up is 0.42 mole/mole of pure DIPA

2.1.6. Methyldiethanolamine

MDEA is a tertiary amine. It is a newcomer to the group of ethanolamines used for natural gas sweetening and has received a great deal of attention recently because of its capability for selective reaction with H_2S in the presence of CO_2. When MDEA is used as the sole pure solvent in the aqueous solution, it is the main reason of its selection.

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Conversely MDEA is also interesting for the bulk removal of CO_2 due to its low heat of reaction with this compound (energy saving at the level of the regeneration section). Generic MDEA is available on the market of chemical products (HUNTSMAN for instance) but almost all processes based on the use of MDEA are from licensers. Licensers add activated agents to the MDEA to suit the type of acid gas removal requirements.

Main licensers of MDEA-based processes are :

- **BASF** : *Activated MDEA (aMDEA)*. The first industrial plant was built in 1971. Now, there are 80 worldwide references (22 % in Natural gas). The activated agent, *Piperazin*, is added to the MDEA.

- **DOW** CHEMICAL : *Gas-Spec Process* using an activated MDEA derived product (Gas Spec SS Selective Solvent) originally preferably used for the selective removal of H2S with high CO_2 slippage percentages: % slippage = 100 x (Outlet gas CO_2 content/Inlet Gas CO_2 content).
  The formulation of the solvent is such that it can be also used for controlled CO_2 removal (CS-3 MDEA solvent) to adjust the GCV of an export gas.

- **EE(P)** : *Activated MDEA process* (see figure XI-B.9). The activated agent added to the MDEA is adapted to the type of contaminant to be preferably removed. The specific feature of this design is that a small portion of the rich amine solution is regenerated in the conventional regeneration section (with a fractionation column with reboiler and condenser). The rest of the rich solution is regenerated by multi-stage (generally 2 stages) flash separation (semi-lean solution).

- **UOP** : *Amine Guard* process (see figure XI-B.10) using generic MDEA and a collection of so-called Ucarsol **solvents** (fabricated by UOP and designed for selective removal of H2S, deep removal of both H2S and CO_2, removal of CO_2 from H2S free feed gas).

- *Concentration*

Pure MDEA is generally used in aqueous solutions with concentrations between 35 and 50 Wt. %. The molar composition of a 50 Wt. % MDEA solution is as follows:

Aqueous Solution	Wt. %	Mole %
MDEA	50	13.13
H2O	50	86.87
total	*100*	*100.00*

Excerpt from PRODEM

- ***Utilization***

Generic MDEA is used to remove selectively H2S (down to 4 ppm V and even lower) from a feed gas containing both CO2 and H2S (CO2 slippage: 60 to 80 %). Activated MDEA (through licensers) can be used for deep removal of both H2S and CO2 (to satisfy a LNG specification for instance).
When CO2 is the sole gas contaminant, bulk removal can be realized with generic MDEA but this would require higher circulation rates than with primary and secondary amines (*thermal energy, however would be lower*). For deep removal of CO2, activated MDEA from licensers will be required.

- ***Chemical reaction***

  - H_2S

H2S reacts immediately with MDEA.

R2NCH3 + H2S $\leftrightarrow$ R2NHCH3HS
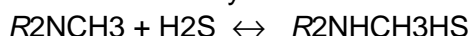
  - CO2

MDEA being a tertiary amine, the molecule does not have an hydrogen atom attached directly to the nitrogen atom. This has an important impact on the chemistry of CO2/MDEA reaction. The carbamate formation which is important for primary and secondary amines is inhibited and the bicarbonate formation (easy to remove from the rich solution to reconstitute a poorly CO2 loaded lean solution) becomes the only important reaction.

R2NCH3 + CO2 + H2O $\leftrightarrow$ R2NHCH3HCO3
where R= C2H4OH
The above reactions are reversible.

- ***MDEA Solution Loading***

For generic MDEA solutions free from licenser's processes, the gross acid gas pick-up must remain below 0.45 mole/mole of pure MDEA to avoid corrosion.
The lean solution CO2 loading is around 0.01 mole CO2/mole pure solvent.

Other sound amine process : Hindered Amine
EXXON is a licenser for processes (*Flexorb processes*) using formulated amines (*hindered amines*). The solvent (based on alkanolamine) is formulated according to the acid gas pick-up requirements. The different type of processes are as follows :

- *Flexorb SE* (commercially available since 1983) for the selective removal of H2S
- *Flexorb PS* (available since 1984) for both removal of H2S and CO2 (and COS). In this case, the formation of stable carbamate with CO2 and classical primary and secondary amines (which limit the acid gas pick-up to 0.45/0.5 mole of CO2/mole of pure amine) is reduced. According to EXXON tests, Flexorb agent also offers a capacity advantage over MDEA.

- *Flexorb HP* for removal of CO2 when the feed gas is free from H2S.

Remark: When dealing with a licenser, for any kind of gas sweetening study (feasibility study, pre-project, basic engineering), a secrecy agreement has to be signed between the Company and the licenser and then the licenser will start the requested work and disclose the features of its design (process flow diagram, material balance, utility balance, preliminary sizing of the major equipment, cost of solvent, inventory, chemical consumption's).

A licensing fee is then requested by the licenser when a firm contract is signed between the Company and the licenser.

2.1.7. Potassium Carbonate

Potassium carbonate (K2CO3) is an alkaline salt which is used for the removal of acid gas. At ambient condition, Potassium carbonate is under solid form. *It is used in aqueous solution.* In order to keep the carbonate dissolved in the water, the solution must be kept under temperature (more than 60 deg.C for a 30 Wt. % carbonate solution).

Unlike amine solutions, Potassium carbonate solution is not susceptible to oxygen contamination.

The product is available on the market but processes based on its use are developed by licensers. The major licenser is UOP with the **Benfield** processes which have the largest number of industrial references in natural gas sweetening.

CATACARB process is also based on Potassium carbonate but with less industrial reference.

- ● *Concentration*

Potassium carbonate is used in aqueous solutions with concentrations around 30 Wt. % (molecular weight of Potassium carbonate is 138.2).

The molar composition of a 30 Wt. % HPC solution is as follows:

Aqueous Solution	Wt. %	Mole %
Potassium Carbonate	30	5.29
H2O	70	94.71
total	*100*	*100.00*

- ● *Chemical reaction*
  - H2S

The chemical reaction with H2S is as follows :

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3$$
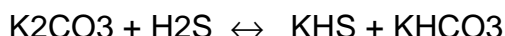
The absorption reaction is exothermic : Heat of reaction of K2CO3 with H2S is 22 BTU/SCF (819 kJ/Sm3 of H2S).

The Potassium bisulfide (KHS) is very difficult to regenerate so the Hot Pot process is not suitable for sweetening gas mixtures containing little or no CO2.

Excerpt from PRODEM

- CO2

Chemical reaction with CO2 is as follows :

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

The absorption reaction is exothermic : Heat of reaction of K_2CO_3 with CO_2 is 32 BTU/SCF of CO_2 (1191 kJ/Sm3 of CO2).

The carbonate is transformed into bicarbonate during the absorption cycle. During the regeneration cycle, the bicarbonate is again transformed into carbonate once the CO2 is removed (in fact, all the bicarbonate is not converted into carbonate).

- ● *Utilization*

Potassium carbonate is suitable for the bulk removal of CO2 from a free from H2S feed gas or from a feed gas with high CO2/H2S ratio.
When H2S is present with CO2 in the feed gas, sulfur salt resulting from the chemical reaction with H2S are difficult to regenerate and thus loads unnecessarily the solution which then looses its efficiency. Therefore this process is not suitable for selective removal of CO2 when H2S is present in non negligible molar quantities in the feed gas.

To enhance the absorption of acid gas, an additive (amine) can be added to the potassium carbonate.
COS and CS2 as well are removed by Hot Pot process. Hydrolysis of these products lead to formation of CO2 and H2S.
Mercaptans can be to certain degree (depending of their molecular weight) removed by the Potassium carbonate solution.

- ● *UOP Benfield Process*

BENFIELD process originally developed by BENSON and FIELD is now owned by UOP. The original design has been improved by UOP and its last development is the **LoHeat process**.
The net CO2 picked-up can vary among 2 and 4 SCF by Gallon of solution (8.5 Sm3 and 17.5 Sm3 per liter of solution).
The process basically comprises two columns : the absorber and the regenerator. Both columns operates at close temperatures (the process is more or less isothermal, the circulating solution being kept at temperatures between 102/116 deg.C).
Lo-Heat process requires a regenerator reboiler thermal energy between 13875 and 19425 kcal/kmole of CO2 extracted.
This process (see figure XI-B.12) uses steam (which can be generated in the regeneration section of the unit) to reduce the amount of residual CO2 that remains in the lean solution (a lower residual quantity of CO2 in the lean solution decreases the required circulation rate).

*Remark : Based on the Benfield design, a morte complicated process (**Hi-Pure process**) has been developped (also a UOP property). It is based on a combination of potassium carbonate and amine (generally DEA) for a deep removal of both CO2 and H2S when both contaminants are present in the feed gas. It implies the use of potassium carbonate in an upstream process to remove the bulk*

of the CO2 followed by an amine process (generally DEA but it could as well be MDEA) to remove the rest of CO2 and the H2S.

The Hi-Pure process can achieve LNG specifications (4 ppm V H2S and 50 to 100 ppm V CO2 in the sweet gas). It was installed in the two original LNG trains of ADGAS (DAS island in ABU DHABI). It is also provided in the new third train of this LNG plant. This process is also installed in the LNG trains of P.T ARUN in INDONESIA (SUMATRA).

2.1.8. Advantages and disadvantages of different amines

Figure XI-B.16 shows the advantages and disadvantages of different amines.

2.2. Physical Absorption

The various amine and potassium carbonate processes rely on chemical reaction to remove acid gas from sour gas streams. Removal of acid gas by physical absorption is also possible and there are a number of commercially competitive processes based on this principle.

Physical absorption results from a physical contact between the gas to be treated and a solvent. The solvent is used as a pure product. As a result, there is no need for water make up in a physical absorption process.

The physical absorption is highly dependent upon the feed gas pressure or the partial pressure of acid gas present in the feed gas.

The solvents used for gas sweetening have generally a strong affinity with water therefore the solvent will simultaneously sweeten and dry the gas. However, the solvent water build-up will require a stripper to remove absorbed water from the solvent.

Main characteristics that are desirable in a solvent for physical absorption are shown in table 2.2.1.

Table 2.2.1. Ideal characteristics of a physical solvent

. Low vapor pressure at operating temperature to minimize solvent losses
. Low solubility of hydrocarbon gas components in the solvent
. No degradation under normal operating conditions
. No chemical reaction between solvent and any component in the Feed Gas stream
. No corrosion to common metals

The efficiency of a physical absorption increases when the operating pressure increases and/or the operating temperature decreases. Therefore, the physical absorption process for Gas Sweetening is generally carried out at low temperatures; sometimes, an external mechanical refrigeration cycle (propane cycle for instance) is required.

Solvent regeneration (stripping) is usually accomplished by flashing at lower pressure than absorption with moderate heat input (the efficiency of the stripping operation increases when operating pressure decreases and/or operating temperature increases).

The lower heat requirement for solvent regeneration is due to the relatively low heat of absorption. As a result, physical solvents can be competitive when compared against chemical solvents (however, should an external mechanical refrigeration cycle be provided, the energy required for this equipment can offset this advantage).

In addition, the *physical absorption phenomenon also induces an absorption of hydrocarbons by the solvent (mainly C3+ components)*. This is a significant disadvantage since the hydrocarbons are stripped with acid gas during solvent regeneration. Should a sulfur recovery plant (Claus type design) be installed downstream of the Gas Sweetening unit, the sulfur product will be off specification (presence of carbon spots).

All the processes based on physical absorption (except water which could be considered as a physical solvent for H2S and CO2 bulk removal but with severe corrosion in the corresponding installation) *are from licensers*.

The purpose of this chapter is not to list and detail the process system of all the licensers. Research of new physical solvents is still going on (**Morphysorb â solvent** from KRUPP UHDE for exemple) and several companies/organizations have pilots and/or developments on this subject.

Here are presented some processes which have industrial references in natural gas sweetening, or which are still proposed, or which have potential for future.

- *FLUOR SOLVENT* (Polypropylene Carbonate) from FLUOR
- *SELEXOL* (Dimethyl Ether of Polyethylene Glycol) from UOP
- *PURISOL* (N-Methyl-Pyrrolidone) from LURGI
- *RECTISOL* (Methanol) from LURGI

Flow diagram and required equipment of a dedicated process from a licenser can vary according to the acid gas recovery level and operating conditions. In many cases, the regeneration of the solvent is not only carried out through flash separation but also with a classical regenerator with reboiler and condenser.

2.2.1. Fluor Solvent

This process uses Polypropylene Carbonate. It is primarily intended for the removal of CO2 from high pressure gas streams. According to LEWIS « Fluor Solvent CO2 Removal Process improves Synthesis gas Plant reliability/American Chemical Society/April 1974 », FLUOR SOLVENT usually becomes competitive when the CO2 partial pressure in the Feed Gas is at least 75 PSI (5.2 bar).
A certain number of large FLUOR SOLVENT units have been installed since the 70's (capacity ranging from 10 to 270 MMSCFD) with Absorber pressures between 27 and 137 bar g and CO2 feed concentrations from 17 to 53 mole %.

2.2.2. Selexol

This process uses Dimethyl Ether of Polyethylene Glycol. It was first developed by NORTON and is now owned by UOP.

Basically, it is used for the removal of H2S, CO2, COS and mercaptans from Natural Gas. However, the solvent as a strong preference for sulfur-based components. It is said to remove also water.

Its major drawback is the co-absorption of hydrocarbons (it can be used for NGL extraction since external mechanical refrigeration is sometimes needed). Table 2.2.2.2. gives the relative solubilities of various gases in SELEXOL solvent.

Table 2.2.2.2 : relative solubilities of various gases in SELEXOL solvent

Components	relative solubility (Base = Methane)
C1	1
CO2	15.2
H2S	134
C2	6.5
C3	15.4
nC4	36
nC5	83
C6	167
C7	360
CH3SH	340
COS	35
CS2	360
Benzene	3800
H2O	11000

From the above table, it shows a good potential for the removal of mercaptans from natural gas (more efficient than a classical alkanolamine).

When used to absorb primarily H2S, the process will also remove water and the majority of C7+ hydrocarbon components. When used to absorb primarily CO2, the process will also remove water and a significant proportion of C3+ components.

SELEXOL has a fairly good number of large scale industrial references (both off shore and on shore) but no recent realizations.

2.2.3. Purisol/Rectisol

LURGI Gesellschaft fur Warme-und Chemotechnik Mbh has developed two physical solvents for removing acid gas : The *Rectisol* process which uses a refrigerated solution of methanol as a solvent and the *Purisol* process which uses a solution of N-methyl-2 Pyrrolidone (NMP).

The Purisol process has high potential for absorption of H2S and thus there are potential applications in the natural gas field for it. However the number of industrial references for Natural gas sweetening is small to date.

2.3. Physico-Chemical Absorption

The principle of this process aims at combining the high absorption potential of alkanolamine (chemical absorption) and the low regeneration energy requirement of the physical solvent (physical absorption).
The SULFINOL process is the sole process with large industrial references. SHELL is the licenser of the *SULFINOL* process.

2.3.1. SULFINOL Process

The SULFINOL process is based on the use of an **aqueous mixture of alkanolamine** (diisopropanolamine or methyldiethanolamine) and **sulfolane** (tetrahydrothiophene dioxide). The process is called SULFINOL-D when DIPA is used, and SULFINOL-M when MDEA is used. SULFINOL-D generally is a mixture (45 Wt. % DIPA, 40 Wt. % sulfolane and 15 Wt. % water). It combines the chemical absorption effect of the amine and the physical absorption effect of the sulfolane.
Figure XI-B.13 shows the typical process flow diagram of a SULFINOL process. it is very similar to the classical alkanolamine process with an absorption section and a regeneration section working on thermal swing principle. Table 2.3.1 shows a comparison of performances between classical amines, potassium carbonate and SULFINOL. *However, results from this table must not be generalized to any specific Acid Gas removal problem. Comparisons of processes must have to be carried out before the final selection.*

Table 2.3.1 : Comparison of acid-gas treatment solutions

	MEA	DEA	K2CO3	Sulfinol	DGA
Lean Solution Concentration	15 wt .%	25 wt. %	30 wt. %	80 wt. %	50 wt. %
Stripping Stream Rate LB/Gal. Solution *(1)*	1.2	1.2	0.6	0.8	1.35
Sweet Gas specifications *(2)*	yes	yes	no	yes	yes
HC (C3+) absorption	no	no	no	yes	slight *(3)*
Removal of RSH	partial	partial	no	yes	partial *(4)*
Removal of COS	yes	yes	yes	yes	no
Non regen product due to COS	yes	no	no	no	no
Reclaimer required	yes	no	no	Yes *(5)*	yes

(1) Varies with H2S/CO2 ratio
(2) Pipeline specification typical ¼ H2S grain per 100 Ft3 (Standard conditions) of Treated Gas
(3) 0.01 mole %
(4) Reported 100 grains inlet RSH down to 0.2 grains at 120 PSI with 5 % H2S and 6 % CO2
(5) Required for SULFINOL-D and high CO2 feed concentrations.

Like in amine processes, the Feed Gas enters the bottom part of the Absorber and is in counter current contact with the descending solvent feeding the top of the column. The Treated Gas comes from the top of the Absorber whilst the rich solvent solution leaves the bottom and is flashed at a medium pressure.

The flashed solution collects in the flash drum. The gas from the flash drum can be routed to the fuel gas pool of the facilities.

The rich solution leaving the flash drum is preheated in a lean solution/rich solution heat exchanger and is let down to the Regenerator operating pressure.

The Regenerator top product (Acid Gas and water vapor) is condensed (by water or air) and collects in the Reflux drum. The overhead product from the Reflux drum is the wet Acid Gas which can be routed either to an acid gas flare or to a sulfur recovery unit. Condensed water from the Reflux drum is pumped back to the top of the column (Reflux pump) to serve as reflux.

A potential problem can occur when feeding an acid gas stream from a SULFINOL unit to a sulfur recovery unit (CLAUS process for instance) due to the presence of hydrocarbons (problem of sulfur quality and specification).

The SULFINOL solution can solidify at temperatures around - 2 deg.C (special care is needed for storage of solution).

Degradation of the solution due to COS is negligible. However, a *reclaimer could be required* on DIPA-based units treating large quantities of CO_2 (DIPA quality can be degraded with CO_2).

Like amine processes, SULFINOL can be subject to foaming.

Possible causes for foaming in the Absorber of a SULFINOL unit area as follows :

- *Particulates in solvent* : Standard filtration size for SULFINOL units is 10 microns. A level of < 10 ppm Wt. is considered as clean solvent.

- *Solvent degradation components* : Key sources of solvent degradation are high reboiler tube *temperatures*, acids or oxygen in Feed Gas. Acceptable level of heat stable salts must be < 3 %. Above this value foaming can be expected to form.

- *Hydrocarbon condensation in Absorber* : Should Feed Gas enter the column at low temperature, hydrocarbon can condense in the column and foaming can form.

- *Liquid heavy hydrocarbon in the Feed Gas* : Heavy hydrocarbons are known to contribute to foaming in the Absorber of the SULFINOL systems. SULFINOL solution will absorb a portion of these compounds (particularly the aromatics).
  Liquid light hydrocarbons are contributing to foaming in the Regenerator due to vaporization in the solvent regenerator.

- Valve grea*se* : This cause of foaming would be due to inadequate cleaning procedures.

- *Pump lubricant* : It can contribute to foaming if poor seal arrangements allow significant migration of lubricants into the process.

- *Corrosion inhibitors* : Either from upstream pipeline or contained in the make-up water, they have been suspected of contributing to foaming although this is not often proved.
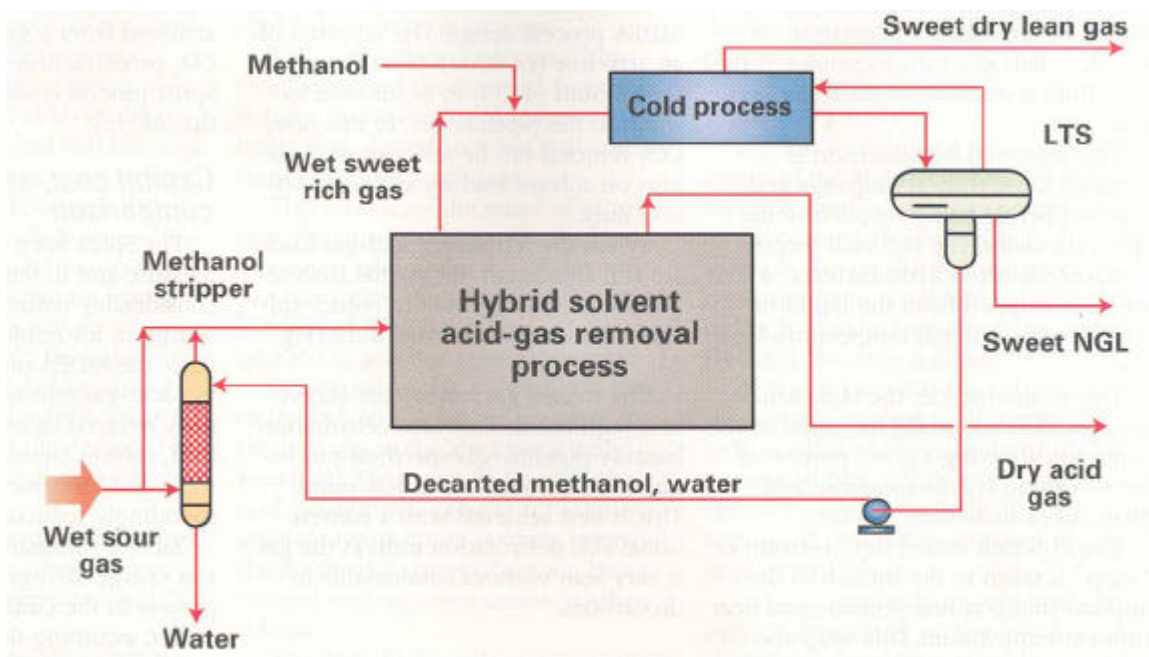
Excerpt from PRODEM

- *Excessive use of anti-foam* : This can in it-self contribute to foaming. This is because anti-foam formulation includes emulsifiers designed to spread the active agent throughout the solution as quickly as possible. Ongoing use of anti-foam can therefore lead to a build up of such emulsifiers which being surface active agents can contribute to foaming.

  This process has a good number of references in the LNG industry (it is the selected gas sweetening process in any LNG plant engineered by SHELL).

- The sweetening unit of each of the LNG trains of BRUNEI (SHELL) is based on the SULFINOL process.

- The sweetening unit of each of the LNG trains of BINTULU in MALAYSIA (SHELL) is based on the SULFINOL process.

- The sweetening unit of each of the three LNG trains of QATARGAS is based on the SULFINOL-D.

2.3.2. Hybrisol process

The Hybrisol process is under development by TFE and IFP, based on IFPEX 1 IFP technology and MDEA TFE knowledge.

The concept, as shown on figure below is to combine an acid gas removal unit based on MDEA in a methanol solution and a cold process for LPG recovery or dewpoint. In the acid gas removal process, the gas is saturated in methanol which helps to hydride inhibition in the cold process and the cold process recovers the methanol by condensation.

In the methanol stripper, the gas is saturated in methanol by stripping of the water methanol mixture issued from the LTS. This process is very similar to that of IFPEX 1.

The acid gas removal is shown on figure below. It operates with a mixture of methanol, water and MDEA and the process scheme is similar to any amine regenerated process except that a cold drum is provided at top of the regeneration column for methanol recovery.
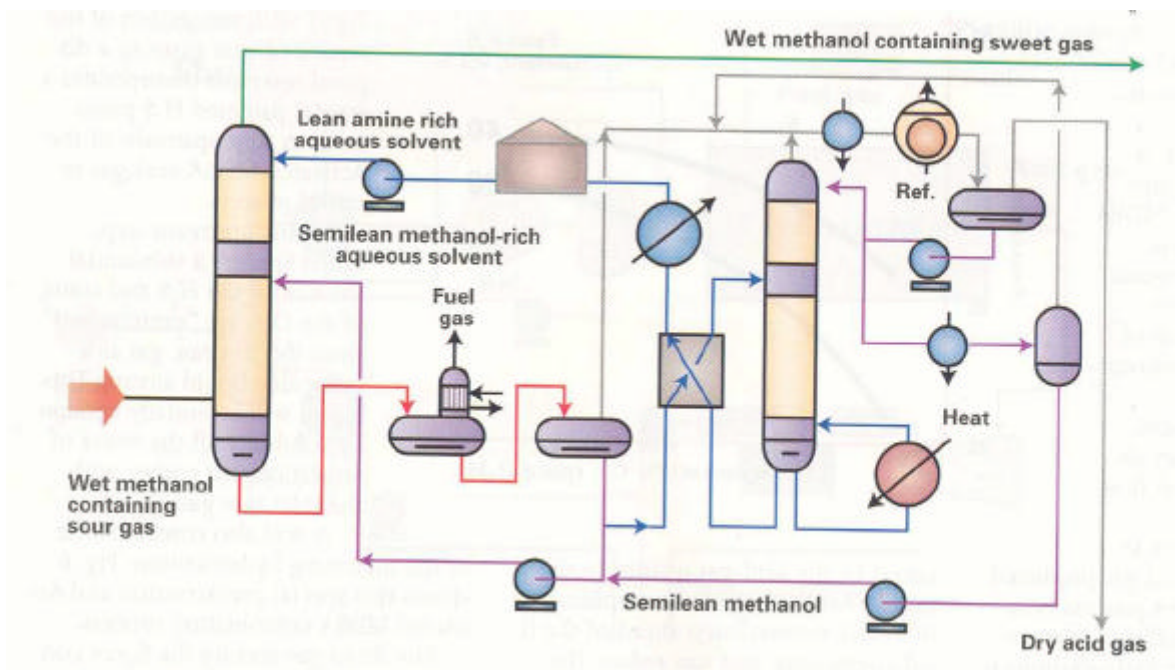
This process is under development by IFP and TFE and a pilot unit has started-up at Lacq research facilities.

This process, which is developed to challenge the Shell Sulfinol process is expected to minimise solvent recirculation for high acid gas content by conbining chemical and physical absorption, this later being significant at high partial pressure. The pilot unit will help to finalise the thermodynamical studies and hopefully confirm the capability to remove the mercaptans.

2.4. Physical Adsorption

Physical adsorption relates to the use of **molecular sieves** for the removal of acid gases. *This process is not suitable for the removal of high quantities of acid gases*. It can be envisaged only to removed traces (*in terms of ppm*) of H2S and/or CO2. It can be also envisaged as a downstream gas polishing treatment to remove sulfur compounds from the feed gas (mercaptans).

The process is identical to the process considered for the gas drying but the type of molecular sieve used is different : the 3A type is suitable for water removal but CO2 and H2S cannot enter the pores of the adsorbent. To remove these components, *4A ,5A or 13 X type will be selected* since it will adsorb the three components : *H2O first, H2S second and CO2 third*.

The process operates under the adsorption/regeneration cycle (generally 8 to 12 hours for both sequences). Regeneration of the beds of sieves generally through the use of a side stream of treated gas. Once the bed has been regerated (Its acid cpompounds having been removed), it is ready for a new adsorption cycle.

When both H2S, CO2 and water vapor are present in the Feed Gas to the molecular sieves, the water can promote the formation of COS (carbonyl sulfide) through inter reaction between CO2 and H2S (this sulfur compound can be a contaminant of the Treated Gas). High pressures, low temperatures, high gas velocities tend to reduce the formation of COS. In this case, *COS depressant molecular sieve type* must be considered .

Another problem relates to the disposal of the regeneration gas (mainly if used as fuel gas). The cyclic nature of an adsorption operation could result in dumping peak CO2 and/or H2S loads in the regeneration gas which would produce bumps as great as 30 to 40 times the initial acid gas concentration.

Figure XI-B.14 shows a physical adsorption process to remove CO2 from a natural gas stream with three molecular sieve vessels (one for the adsorption and the two other for the regeneration of the sieves, one under heating the other under cooling).

2.5. Cryogenic Fractionation

2.5.1. Ryan Holmes

The cryogenic fractionation is a process for the removal of CO2 from Natural Gas. Should H2S be present in the gas and should H2S removal be required, a dedicated process for H2S selective removal would have to be provided upstream of the cryogenic fractionation. *The cryogenic fractionation does not remove H2S from Natural Gas.*

This process originally developed by KOCH Process Systems Inc. was titled "**RYAN/HOLMES Process**" after two employee-inventors and involves the use of a hydrocarbon additive usually present in the Natural Gas to provide a particular benefit to the distillation (*lowering the CO2 freezing point*). The "RYAN/HOLMES Process" uses Natural Gas Liquid (NGL) which is extracted from the feed stream itself.

Figure XI-B.14 shows the principle of the "RYAN/HOLMES Process".
The following two principal distillative separations are involved:

.   *Separation of methane from CO2.* This separation uses the NGL stream to avoid CO2 freezing and takes place in the "RYAN/HOLMES demethanizer".

.   *Separation of CO2 from ethane plus (C2+).* This separation uses the NGL stream to break the CO2/ethane azeotrope.

Since this fractionation require low temperatures, its best utilization is the LNG manufacture. However, none of the existing LNG trains in the word to date uses this process. This process is no longer developped by KOCH and thus falls in the public domain.

Derived cryogenic processes working at temperatures above the CO2 solidification point have been implemented for the bulk removal of CO2 from natural gas.

2.5.2. SPREX

The SPREX is a process under development by TFE and IFP. It is dedicated to very sour gas with typically 40 % H_2S content for bulk removal of this acid gas and re-injection in wells.

It mainly consists in a distillation column the reflux of which is ensured at typically –30°C by a refrigeration unit and supplied with a reboiler. The H_2S / CO_2 mixture is produced at the bottom of the column in a liquid phase. It can be pumped to high pressure for well injection.

The top gas leaves the column with a remaining typical content of 10 % H_2S and can be routed to a classical MDEA process.

A pilot unit is to be erected in the Lacq plant for test and operation demonstration.

2.6. Permeation (Membrane)

Polymeric membrane (which contains no hole or pore) is not a new technology for gas separation. This separation is based on the principle that certain gas compounds dissolve and diffuse through the polymeric material at a faster rate than others. *Carbon dioxide*, hydrogen, helium, hydrogen sulfide and water vapor are highly permeable (« *fast gases* »). Conversely, nitrogen, methane and heavier paraffin compounds are less permeable (« slow gases »). *The best application for membrane separation is to separate gases in the « fast » category (**Permeate**) from gases in the « slow » category (**Residue Gas**)*. For instance, CO2 will pass through a polymer membrane 15 to 40 times faster than methane.

Residue Gas from the membranes is at a pressure close to that of the Feed Gas to the membranes whilst the Permeate is at low pressure (between 1 and 4 atmosphere absolute).

Membrane is then an attractive process to remove CO2 (bulk removal) and traces of H2S from natural gas. H2S removal when present in high concentrations (in terms of mole %) is not applicable due to the detrimental effect of this compound on the membrane.

Theoretically the Permeation process has no rotating equipment and no energy requirement. However this technology cannot allow to satisfy Sales Gas specifications or LNG specifications (H2S lower than 4 ppm V and CO2 less than 90 ppm V). **Its application is for the bulk removal of CO2 from nearly H2S free natural gases.**

The membrane also removes water from the feed gas.

Excerpt from PRODEM

The permeation phenomenon occurs in four (4) steps :

- Adsorption of the CO2 by the active surface of the membrane (at the raw gas pressure)
- Dissolution of the CO2 in the membrane .
- Diffusion of the CO2 through the membrane .
- Desorption of the CO2 from the membrane (at low pressure) .

The adsorption of the CO2 is better at high pressure (high CO2 partial pressures). This process is then not well suited to low pressure operations.

The polymeric material to be selected for membrane construction must be permeable to CO2 but also selective (to avoid permeation of hydrocarbon gas components).

There are two (2) types of membranes :

- **Spiral Wound membrane .**
- **Hollow fiber membrane .**

The main manufacturers of membranes are :

- **CYNARA** (formerly DOW group, thereafter belonging to HELER group and now in the NATCO group) using Hollow Fiber membranes. These membranes are based on the use of a cellulose polymer (cellulose triacetate). This Licenser provided its first plant in 1983 (Sacroc plant in Texas).

  A large off shore plant (PAILIN in THAILAND) operated by UNOCAL equipped with CYNARA membranes is under construction.

  CYNARA membrane can be also used to remove CO2 from light liquid. One plant (Marathon's Burns Point gas plant in St-Mary Parrish in southern Louisiana) uses CYNARA membrane for NGL (natural Gas Liquid stream) sweetening (3000 BPD of NGL with 11.7 mole % CO2 inlet and 5 mole % max. outlet).

  Due to the fact that their current membranes cannot withstand high pressures (less than 100 b), CYNARA is currently testing more robust types of membranes (polyimide and other kind of cellulose acetate).

  The membrane is fitted in a vertical tube. Each tube is vertically installed. This is an advantage for the natural drainage of the condensed liquid which can form due to the displacement of the treated gas hydrocarbon dew curve (reduction of the CO2 content). CYNARA can provide tube with a diameter of 16 inch for a length of 2 m.

- **KVAERNER** (formerly GRACE).

  GRACE originally developed membranes on the Spiral Wound technology (cellulose acetate) from the beginning 1984 to July 1993 date at which they change to polyimide The membrane unit can include several modules (a module is a shell which accommodates the membranes). There are 6 or 7 membranes per module. Each module in horizontally mounted. Hollow Fiber or Spiral Wound membranes can be fitted in the same module.

  From 1990 up to 1993, GRACE has already provided more than 80 acid gas removal (mainly CO2) units (capacity ranging from 0.5 MMSCFD to 20 MMSCFD) based on their old spiral wound technology. After 1993 up to 1996, with the change to hollow

Excerpt from PRODEM

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fiber technology, the KVAERNER reference list includes to date more than 20 membrane plants in operation. In July 1996, a project for 310 MMSCFD membrane plant is launched for Indonesia (ASAMERA with JGC as general engineering).

. **UOP SEPAREX** (formerly HOECHTS-CELANESE Corporation but now owned by UOP) using Spiral Wound membrane (Cellulose acetate membrane).
The membrane unit includes several banks of modules (a module is a cylindrical shell or tube which accommodates the membranes). Each module can accommodate up to 10 membranes (membrane size is 8 inch diameter and 42 inch long).

More than 45 CO2 removal commercial units have been already installed (between 1983 and 1994). There are two on shore plants of large capacity built in 1993 in PAKISTAN using SEPAREX membranes to remove CO2 :

QADIRPUR (265 MMSCFD capacity) where the shareholders are ODGC, PREMIER OIL, BURMA OIL and PAKISTAN PETRO Limited. The CO2 contents in the feed and treated gases are respectively 6.5 mole % and 2 mole % at 845 PSI. This is a two-stage membrane with intermediate compression.

KADANWARI (210 MMSCFD). The CO2 contents in the feed and treated gases are respectively 12 mole % and 3 mole % at 1275 PSI.
A plant in MEXICO (PEMEX) has been recently built based on the UOP SEPAREX technology to treat 120 MMSCFD of high CO2 gas (80 mole %). Sales gas specification is 5 mole % CO2. UOP MemGuard[TM] pretreatment system is provided upstream of the membranes. Rejected CO2 is used for Enhance oil recovery (re-injection).

. **MEDAL** is originally a joint venture between Air-Liquide and Dupont de Nemours. MEDAL (which means Membrane Dupont Air-Liquide) is now a 100 % subsidiary of Air-Liquide and can propose CO_2 removal membranes as well as H_2 up-grading and nitrogen packages.

. **Air Products** bought the former PRISM membrane from Monsanto. Originally developed for H2 up-grading in the chemical, petrochemical and refining industry, the membrane are also proposed for CO_2 removal.

. **Ube** also proposes its own membrane system for CO_2 removal and hydrogen up-grading.
Ube, which is Japanese, is the only non American supplier and may propose the supply of membrane system to countries subject to American embargo.

2.6.1. Spiral Wound membrane

The membrane (see figure XI-B.18) comprises an active layer of cellulosic acetate supported by a porous material to form a leaf or flat sheet. Several leaves (or flat sheets) of this kind are wounded around a central coil drilled with holes. The leaves are separated by spacers, a residue gas spacer and a permeate gas (CO2 rich gas) spacer. An outer epoxy wrap holds everything in place. This

Excerpt from PRODEM

arrangement constitutes one membrane element. The membrane element is then housed in a pressure tube. This tube can include several membrane elements.

Feed gas is introduced to one face of the membrane element. It passes over the membrane leaves of the membrane elements and exits at the other end of the membrane element as a treated gas with essentially no pressure drop. The purity of this gas is determined by the number of membrane elements placed in series. The CO_2 rich gas which permeates through the membrane evolves from the central coil drilled with holes at low pressure.

2.6.2. Hollow Fiber membrane

This technology utilizes small cylindrical fibers (see figure XIB-19) comprising an active layer supported by a porous material. These fibers are hollow in the center to carry the permeate stream. Each fiber generally has an external diameter of 600 micron and a bore less than 300 micron. Due to its construction, the fiber is a porous material and an external coating (silicone) ensures the tightness .

The fibers are arranged in bundles to form a membrane element. In the case of CYNARA, the membrane element is such that the gas to be treated enters a central steel tube drilled with holes. Hollow Fibers are arranged in a bundle around this tube. The fibers are tighten one against the other by an epoxy coating. Each membrane element is then fitted in a pressure tube. The raw gas enters the central tube and leaves the holes of the tube to contact the fibers. CO_2 permeates through the fibers.

Hollow Fiber membrane generally cannot withstand high pressure (which is not the case for Spiral Wound membrane). Moreover the Hollow Fiber membrane has generally a lower permeability than Spiral Wound membrane. However, Hollow Fiber technology allows to provide a better surface area per volume of membrane element (5 to 10 times more than Spiral Wound membrane) and then a better packaging. The result is a significant reduction in number of shells, piping and membrane skids (lower capital cost and plot requirements).

2.6.3. Membrane arrangement

The membrane process can be a single-stage process or a multi-stage (normally two-stage) process.

. One-stage membrane process

Figure XI-B.20 shows a single-stage membrane process.
The set of membranes handles the feed gas and removes the bulk of the CO_2. However **light hydrocarbon losses** (especially methane) cannot be avoided (light hydrocarbons permeate and come with the CO_2 in the permeate stream). *Methane concentration in the permeate stream can exceed 10 mole %.*

Excerpt from PRODEM

. Two stage membrane process

Figure XI-B.21 shows an example of a two-stage membrane process. To mitigate the hydrocarbon losses pertaining to a single-stage system, a two-stage process can be considered.

In a typical two-stage process, the permeate gas from the first stage of membranes (or first set) which still contains hydrocarbons is sent (as a feed gas) to a second stage of membranes (second set) which ensures the separation between CO_2 and hydrocarbons (methane losses can be reduced to less than 2 vol. % of the feed gas methane content). The permeate gas from the first stage being at low pressure, a compression is required to route this gas to the second stage. The methane rich gas evolving from the second stage (second stage Residue Gas) can be either recycled to the plant inlet at the relevant pressure or routed to the fuel gas system of the plant if required .

2.6.4. Membrane Pretreatment

The membranes can be heavily damaged by some free liquids that can be carried over with the feed gas. *Liquid water*, *aromatic and poly-aromatic components* (Naphtalene for instance), *glycol, methanol, amine* are poisons for the membrane. In order to avoid a premature destruction of the membranes due to these contaminants, a feed gas Pre-treatment has to be installed (upstream of the membrane package).

Originally (this was the case for the original GRACE design), the Pre-treatment included a triple filtration (coalescer-filter, guard bed and polishing filter) and a gas heating achieve a membrane feed temperature 10 to 20 deg.C above the dew point (water and hydrocarbon). This simple arrangement is still acceptable when the feed gas does not contain heavy ends. However, it was proved to be not sufficient when the feed gas includes a large number of heavy compounds even in small concentration.

The CYNARA Pre-treatment is far more elaborated. It comprises a certain number (between 2 and 4) of dry desiccant beds to remove water and contaminants (glycol, polyaromatics) and a gas chilling (generally through the use of an external mechanical refrigeration cycle) to obtain a lean gas to feed the membrane unit.

UOP also now comes to propose a proprietary Pretreatment process (**MemGuard ä** system) for a « good » Feed Gas to their membranes. This system comprises generally guard beds (molecular sieves) to remove water and heavy hydrocarbons and can also include a propane refrigeration.

2.6.5. Membrane Life

Even with a high feed gas quality, the **life of the membranes does not exceed 3 to 4 years**. After this period, it will be necessary to replace them with new membranes. Generally the replacement of membranes is done gradually in order to keep the plant on stream.

2.7. Direct conversion to sulfur

These processes are generally used for the removal of small quantities of H2S from gas streams (concentration expressed as ppm) and involve the direct conversion of H2S to sulfur. No significant amount of CO2 is removed.
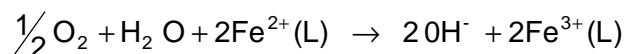
They are based on the direct conversion of H_2S into sulfur by a iron based catalyst.

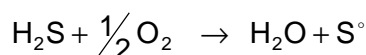The ferric solution is in contact with the gas in the absorber and the H_2S is directly reduced to sulfur:

$$H_2S + 2Fe^{3+}(L) \rightarrow 2H^+ + S^\circ + 2Fe^{2+}(L)$$
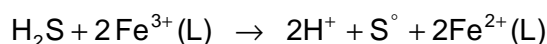
where L is the chelatan.

The solution is regenerated at low pressure by a stream of air according to the reaction:

$$\frac{1}{2}O_2 + H_2O + 2Fe^{2+}(L) \rightarrow 2OH^- + 2Fe^{3+}(L)$$

Considering that $H^+ + OH^- \rightarrow 2H_2O$, the overall reaction is:

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S^\circ$$

The solid sulfur is removed from the regenerator or at high pressure by a solid-liquid separation and the regenerated solution flows back to the absorber.

A few company propose processes based on this chemistry: US Filter with the LO-CAT process, Shell with the SULFEROX and IFP/Le Gaz Intégral with the SULFINT.

These processes apply for low sulphur content (less than 1 000 ppm), for an outlet content of a few ppm. The treated flowrates are low (a few MMSCFD) and, except Sulfint which is proven at 80 bar, they operate at low pressure (a few bars).

2.8. Polishing treatment for H2S Removal

The current accepted worldwide H2S specification of a Sales Gas is around 3 ppm V. In some cases, local regulations can impose a more stringent specification (less than 1 ppm V).

Gases with low H2S content could be treated in a classical gas sweetening amine process but it is unlikely that the solution removes sufficient H2S to achieve 1 ppm V final concentration.

Molecular Sieves could be suitable for such a purpose but the disposal of the regeneration gas can be a problem. In such a situation, installation of a fixed bed absorbent « polishing » unit is probably the most attractive option both technically and economically.

Excerpt from PRODEM

This fixed bed chemical absorption (chemical adsorption expression could perhaps be more appropriate) is a non-regenerative system using a metal oxide like zinc oxide. The bed is accommodated in a vessel. When the bed is saturated with sulfur, the vessel is unloaded and refilled with a fresh load of absorbent. The main drawback of this process is the disposal of the sulfur impregnated absorbent load once removed from the vessel. Processes based on this principle are all patented processes.

Modern fixed bed process is likely to be most attractive if the weight of sulfur to be removed is less than about 200 kg/day. Processes based on this principle are all patented processes.

Among them, one with industrial references is the **PURASPEC䎴** process from ICI Katalco.

For H2S removal, *PURASPEC䎴 process* works on a chemical reaction :

H2S + Metal Oxide $\longrightarrow$ Metal Sulfur + H2O

For COS removal, *PURASPEC䎴 process* works on a chemical reaction :

COS + Metal Oxide $\underrightarrow{\hspace{1cm}}$ Metal Sulfur + CO_2

PURASPEC䎴 first used pure ZnO but in 1995 it was changed to a mixture (Cu/Zn) oxide.
Table 2.8.1 shows a list of existing facilities using this process.

Table 2.8.1. PURASPEC™ units

Company	Location	H2S Content (ppm V)	
		Feed Gas	Treated Gas
AMOCO/North West HUTTON *(1)*	Off Shore	10	3.3
AMERADA HESS/SCOTT *(2)*	Off Shore	11	2
BRITISH GAS/BARROW *(3)*	On Shore	5	2.75

(1) 73000 Nm3/h
(2) 139000 Nm3/h peak
(3) 1.57 MNm3/d peak

Iron sponge is another metal oxyde process used for low flowrate and low H_2S content. It is based on the reduced of iron oxides to form ferric sulfur. Connely GPM inc (California) and Whessoe Varec at Durham (UK) can propose iron sponge processes.

Remark: For 10t/day and above sulfur production, the combination (amine+CLAUS) is generally the selected solution. For less sulfur, the liquid Redox (Sulferox, Lo-Cat) process is the choice. For small quantities of sulfur to be removed (less than 200 kg/day) the process based on fixed bed absorbents is well suited.

2.9. Guideline for the gas sweetening process selection

There is no multipurpose process for gas sweetening, each case is specific and shall be studied accordingly.

Final selection is done on the basis of economical criteria from a short list of processes which seem appropriate to satisfy the treated gas specifications.

Chemical processes are characterised by their ability to react with acid gases, with little influence of the gas pressure. They require a large heat quantity for regeneration.

Physical processes performances are more dependant on gas pressure. At high pressure with high acid gas partial pressure, the absorption is better than for chemical processes.

Selection criteria listed herebelow can be used for preselection of sweetening processes but shall not be considered as definitive.

2.9.1. CO_2 absorption (no H_2S in the gas)

For low CO_2 partial pressure gas (below 15 psia), amine processes will be appropriate (DEA, aMDEA for example). Mainly because its high steam consumption and the corrosion problems, MEA is almost no more used.

For higher partial pressure but still below 100 psia, carbonate potassium, and DGA processes will be considered in addition to amine processes.

For higher pressure, physical processes can become economically attractive.

In an case, if severe acid gas specifications are required, (a few ppm of H_2S and CO_2), hot carbonate and physical solvent shall be avoided.

For bulk CO_2 removal, membranes will be considered if treated gas spec can be achieved in a "one through" process. Membrane process is particularly attractive for offshore treatment because of its simplicity.

Figure XI-B.25 shows the fields of utilisation of the processes related to CO_2 partial pressures in the feed gas and in the treated gas.

2.9.2. Simultaneous absorption of CO_2 and H_2S

This is the most common case. Most of processes can be considered. Generic MDEA may face some difficulties for CO_2 removal and hot carbonate may be polluted by sulphur components. DEA and activated MDEA are most commonly used as well as Sulfinol when low acid gas specifications are required. Note that co-absorption of hydrocarbons in the Sulfinol process leads to operational difficulty if a downstream Claus unit is used.

Excerpt from PRODEM

If no severe specifications are required, physical solvent can be used.

Figure XI-B.26 is of help for preselection.

2.9.3. H_2S Absorption (No CO_2 in the gas)

This is not a frequent situation with natural gases.

2.9.4. H_2S Selective absorption (H_2S and CO_2 in the gas)

Among the chemical processes, only generic, MDEA and DIPA seem to be adapted for this service.

On the other hand physical solvents are particularly well adapted in this case.

In some cases, pipeline specifications requires the removal of all H_2S and part of CO_2. a MDEA and Sulfinol are well adapted to this situation.

Figure XI-B.27 gives the various possibilities of process utilisation.

2.9.5. Sweetening with mercaptan removal

The most adapted process are the physical solvents and, overall, the physical solvent with dissolved amine such as the Sulfinol process. However, the Claus unit is often upset by the co-absorbed hydrocarbons. Amine absorption followed by mercaptan adsorption on molecular sieve are sometimes used. The molecular sieve suffer from low life time in this configuration (about 2 years) and only CECA as molecular sieve supplier (from TFE group) seems to have a valuable experience.

2.9.6. Polishing

Iron sponge, metal reduction (Zno) and charcoal can be used to drop H_2S content from a few tenth of ppm to a few ppm with the drawback of loss solid load.

Direct conversion to sulphur is used for low flowrate of gas. Most of these processes are valid as low pressure, except Sulfint which is experimented at 80 bars.

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