

# Gas Treatment



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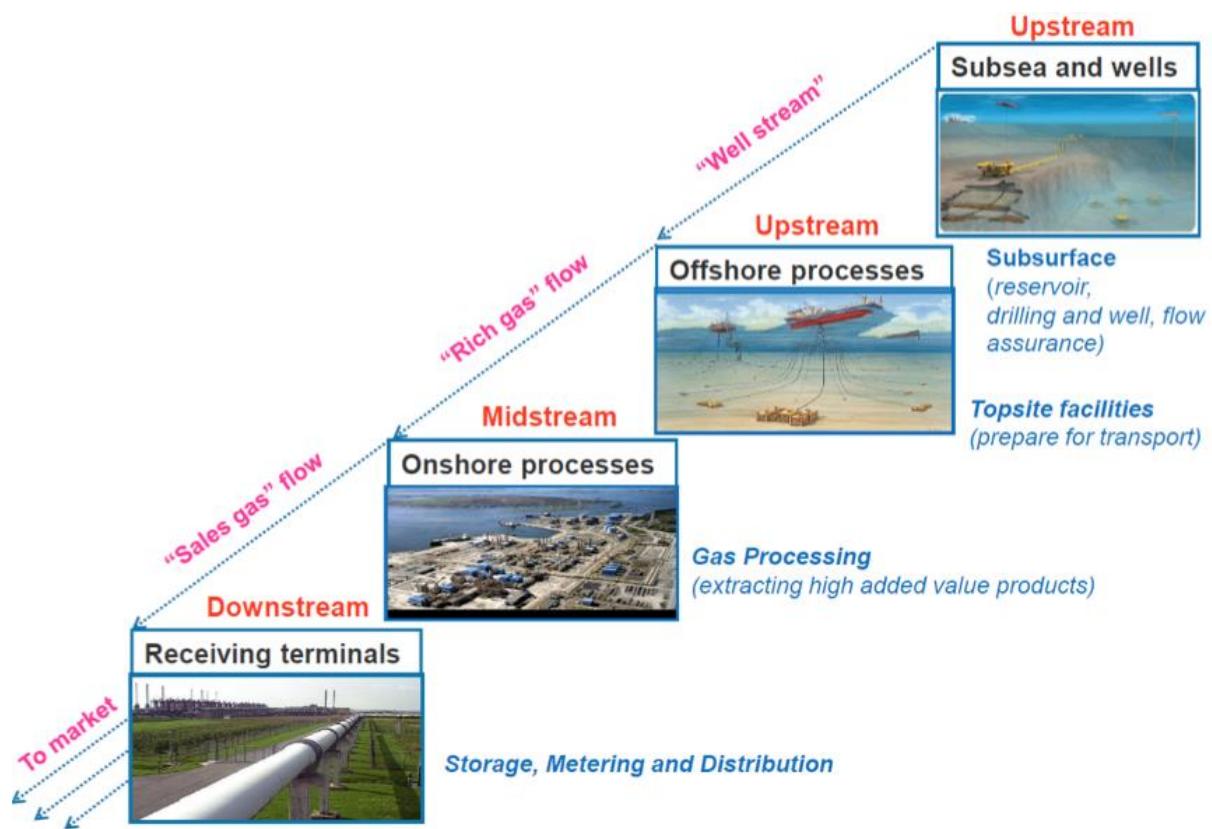
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## 1 Introduction

This module deals with processes for conditioning gas for sales and transport. Gas specifications are reviewed. Water, H<sub>2</sub>S, CO<sub>2</sub>, sulphur and mercury management are presented. Water removal technology using absorption and adsorption is covered together with processes for treating H<sub>2</sub>S and CO<sub>2</sub>. Gas chilling techniques are also covered.

### 1. Gas value Chain

The gas value chain is shown in the following figure. At each stage the gas is conditioned sufficient for movement to the next stage in the value chain. Finally the gas is fully conditioned for industrial or domestic sales.



### 2. Gas Specifications

In order to condition gas for sales distribution a range of quality specifications require to be achieved. These vary from country to country, common features are hydrocarbon and water dewpoint, temperature, pressure and composition e.g. H<sub>2</sub>S, CO<sub>2</sub>, mercury and sulphur compounds.

### 1.1 Water

Water dewpoint limits are required to avoid corrosion and hydrate formation, they depend on surrounding ambient conditions. Water content pipeline specification is less stringent for warm locations. Water content may be stated as a dewpoint (e.g. -10 °C at 69 barg) or as a water content (e.g. 2lb/ mmscf, 30mg/Sm<sup>3</sup>).

Pipeline corrosion and hydrate formation are shown in the following photographs. The presence of water is required for both corrosion and hydrate formation to occur.



### 1.2 Temperature and Pressure

A maximum temperature at the delivery point is often specified, usually around 30-50 °C. This is usually for mechanical reasons – to manage pipe thermal stresses.

The maximum gas pressure will be decided by the design pressure of the system and the allowable back pressure on other system entrants. Nominal gas pressure is the normal entry pressure to the pipeline, typically 70 - 140 bar.

### 1.3 Hydrocarbon Dewpoint

To prevent hydrocarbon condensation, with the consequences of the pipeline flowing two-phase, the pipeline operator often sets a limit on the gas cricondenbar. As stated in previous modules the significance of the cricondenbar is evident from the phase envelope - provided system pressures are higher than the cricondenbar then a single phase will always exist irrespective of temperature. A typical cricondenbar specification is 105-110 bara maximum. An alternative to cricondenbar control is a hydrocarbon dewpoint or a liquid loading maximum value may be given.

## 1.4 Solids

The general requirement is to be free of particulates in amounts detrimental to metering, transmission and equipment operation. Note that solids may be produced from some of the treatment processes.

## 1.5 Calorific Value

The sales gas specification will be subject to a pricing agreement which is likely to include the following:

### 1.5.1 Gross Calorific Value (GCV) or Higher Heating Value (HHV)

The total heat produced by combustion of the fuel

### 1.5.2 Net Calorific Value (NCV) or Lower Heating Value (LHV)

The total heat produced by combustion of the fuel minus the latent heat contained in the water vapour discharged as fuel gas, NCV represents the available heat

### 1.5.3 Wobbe Index (WI)

Wobbe Index is used to compare fuel quality for different gases it characterises flame stability

WI is the ratio of GCV to the square root of the gas s.g. - units are MJ/Sm<sup>3</sup>

$$WI = GCV / (\text{Gas sg})^{0.5}$$

For two fuels with identical Wobbe Indices, the energy output will be the same for a given pressure and combustion valve settings.

## 1.6 Sulphur Content

Sulphur content is controlled for safety reasons, to prevent pipeline corrosion and improve the sales value of the gas. Sulphur compounds affect petrochemical processes by poisoning catalysts. Mercaptans feature here – these are thiols where sulphur substitutes for an oxygen or an OH site. They have unpleasant odours.

If the hydrocarbon is used as fuel, sulphur will result in undesirable oxides of sulphur.

## 1.7 Typical Offshore Gas Pipeline Transportation

A typical pipeline entry specification is shown.

Gas Cricondenbar < 106 bara

As calculated by the Peng Robinson equation of state or such alternative method as may be agreed from time to time.

Pressure 110 to 149.9 bara

Temperature -5°C to 55°C

Water Content < 24 kg/Sm<sup>3</sup>

H<sub>2</sub>S Content < 2.3 ppm (based on present equipment)

Total Sulphur Content < 15 ppm expressed as H<sub>2</sub>S

CO<sub>2</sub> Content < 3.8% mol

O<sub>2</sub> Content < 7.5 ppm

Mercury Maximum mercury content of 0.01 micrograms per m<sup>3</sup>, unless otherwise agreed

Mercaptans < 1.0 ppm v/v

Gas shall be commercially free from objectionable odours and from materials and dust or other solid or fluid matter, waxes, gums and gum forming constituents which might cause injury to, or interference with, the proper operation of the lines, meters, regulators or other appliances or facilities through which it flows.

No chemicals or other substances may be introduced by any means into the Gas, which might be carried over into the transportation system without the prior agreement of the pipeline operator, such agreement not to be unreasonably withheld.

The gas will be redelivered from the Terminal to the National Grid Terminal for entry into the National Transmission System (NTS) in a condition to meet the NTS Specification, with the CO<sub>2</sub> content in accordance with the specification applicable to the Gas Terminal (currently 4% mol).

Note there is no mention above of calorific value or Wobbe index for offshore pipeline transportation. The gas will be further conditioned at the onshore terminal to achieve domestic user specifications hence the gas is only partially processed for transportation between the remote site and the terminal.

The degree of processing will be application specific but is likely to include;

- Water dewpointing
- Hydrocarbon dewpointing
- Acid gas treatment

An alternative to water dewpointing is continuous addition of hydrate suppressant and corrosion inhibitor. This is used in some oil and gas fields and is discussed later.

As a general rule avoid doing anything offshore that can be done onshore.

## 2 Water Content

As stated previously water is a key component which must be managed. Its presence can lead to corrosion and hydrate formation which will affect pipeline operations and system integrity.

Heat and mass balance simulators will saturate the gas at the prevailing conditions of

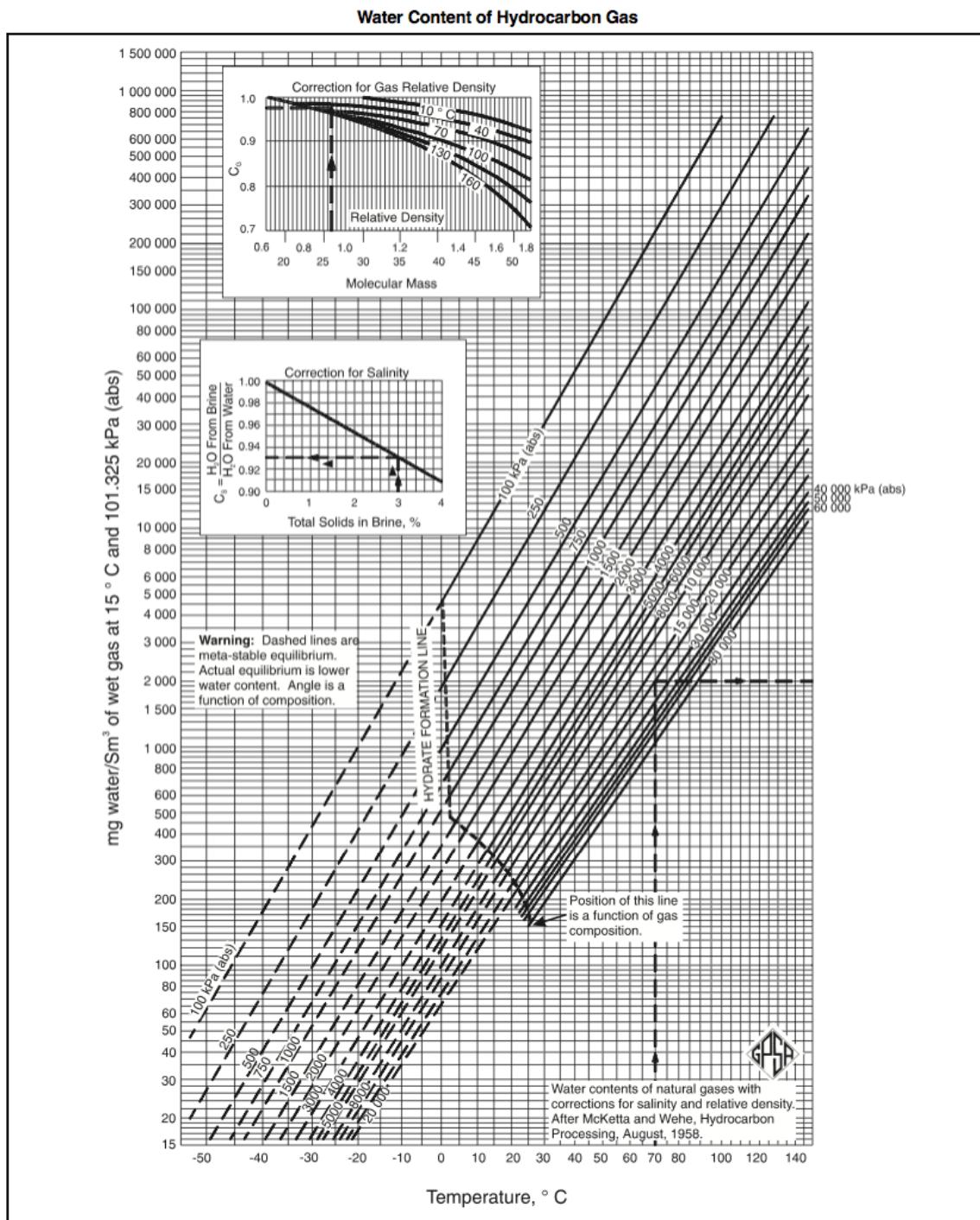
composition, temperature and pressure. Note that the gas water content is a function pressure, temperature and gas composition.

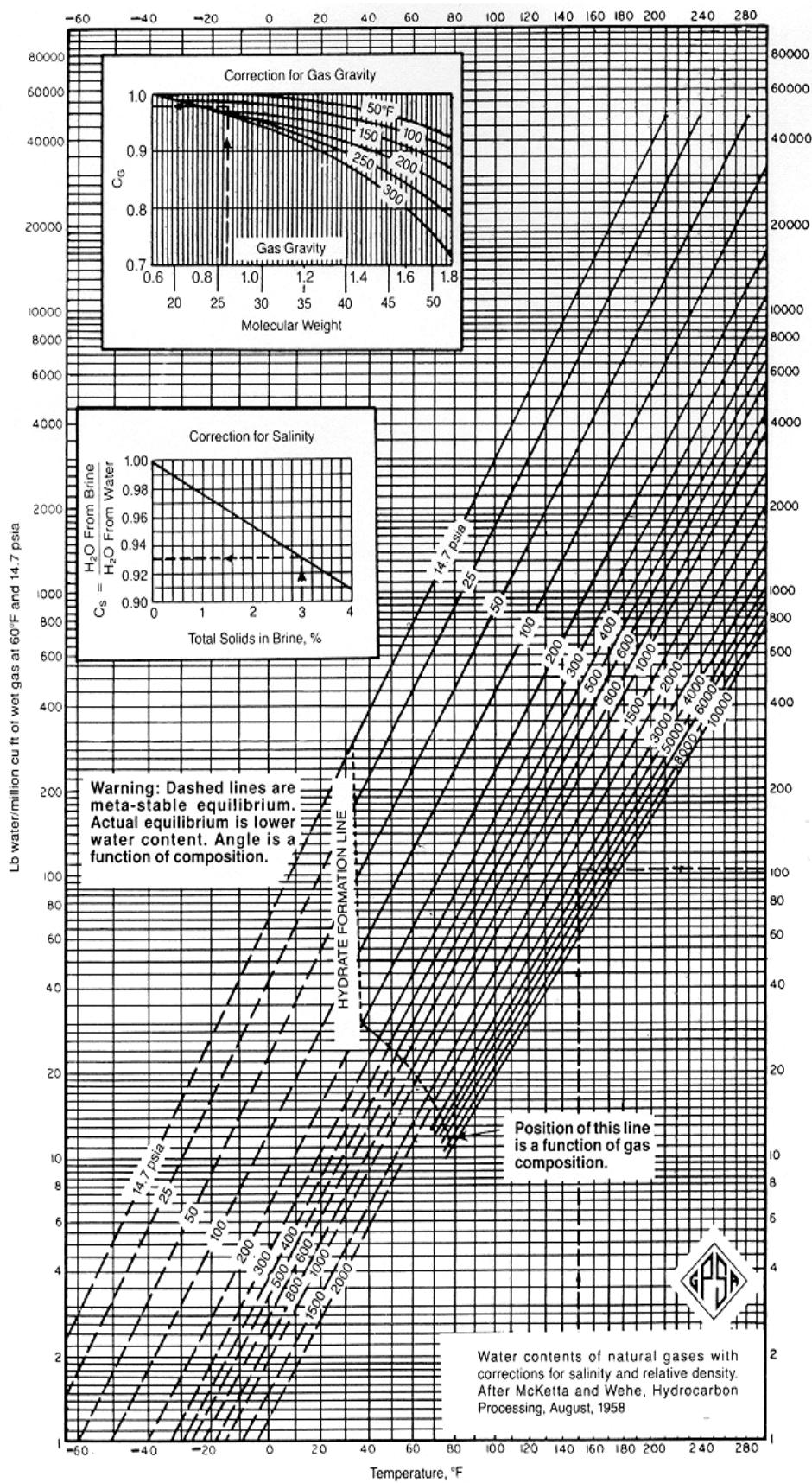
Methods for determining water include;

- Vapour/partial pressure
- Empirical charts
- Equations of State

Hand calculations can be very useful when considering water with the GPSA (Gas Processors of America) water content charts being very useful.

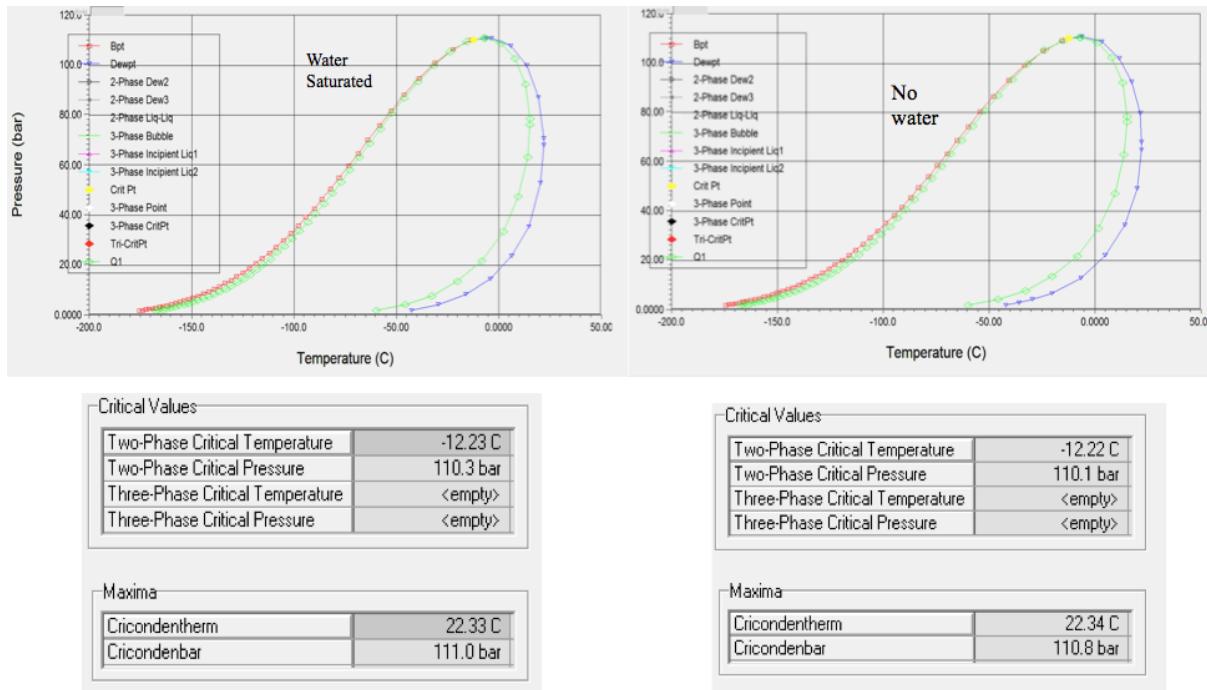
Metric and imperial charts follow.





## 2.1 Effect of Water on Phase Envelope

The following illustrates the effect on the phase envelope of adding water to a typical hydrocarbon gas. As can be seen the effect is minimal.



## 3 Hydrates

Hydrates are ice like crystals which can cause pipeline blockages. It is a clathrate of water and hydrating gases.

Conditions required are;

- presence of free water
- low temperature
- high pressure
- C<sub>1</sub>-C<sub>4</sub>, H<sub>2</sub>S and CO<sub>2</sub>

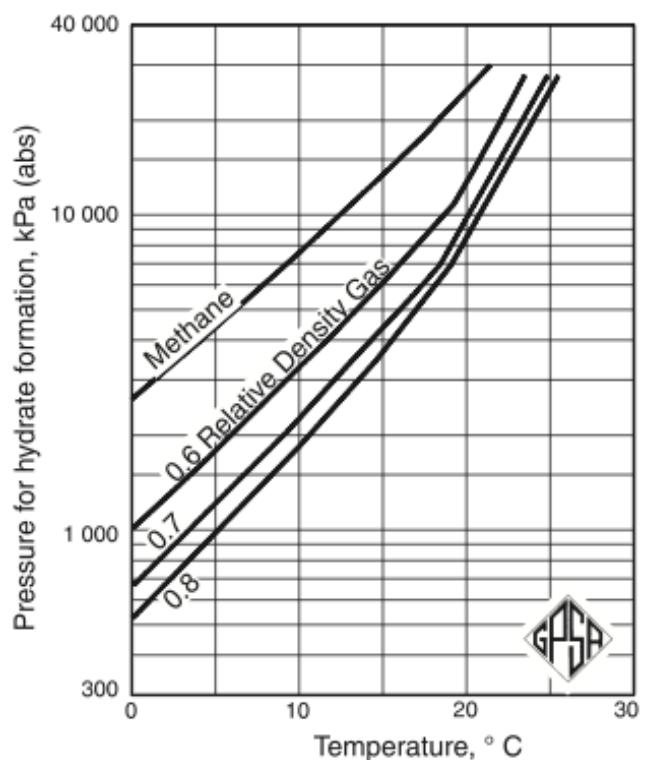
### 3.1 Hydrate Formation Models

Hydrate formation can be estimated by;

Empirical charts (on right).

K (equilibrium) factors using a dewpoint method.

Equations of state – hydrate modules are available within most commercial simulators.



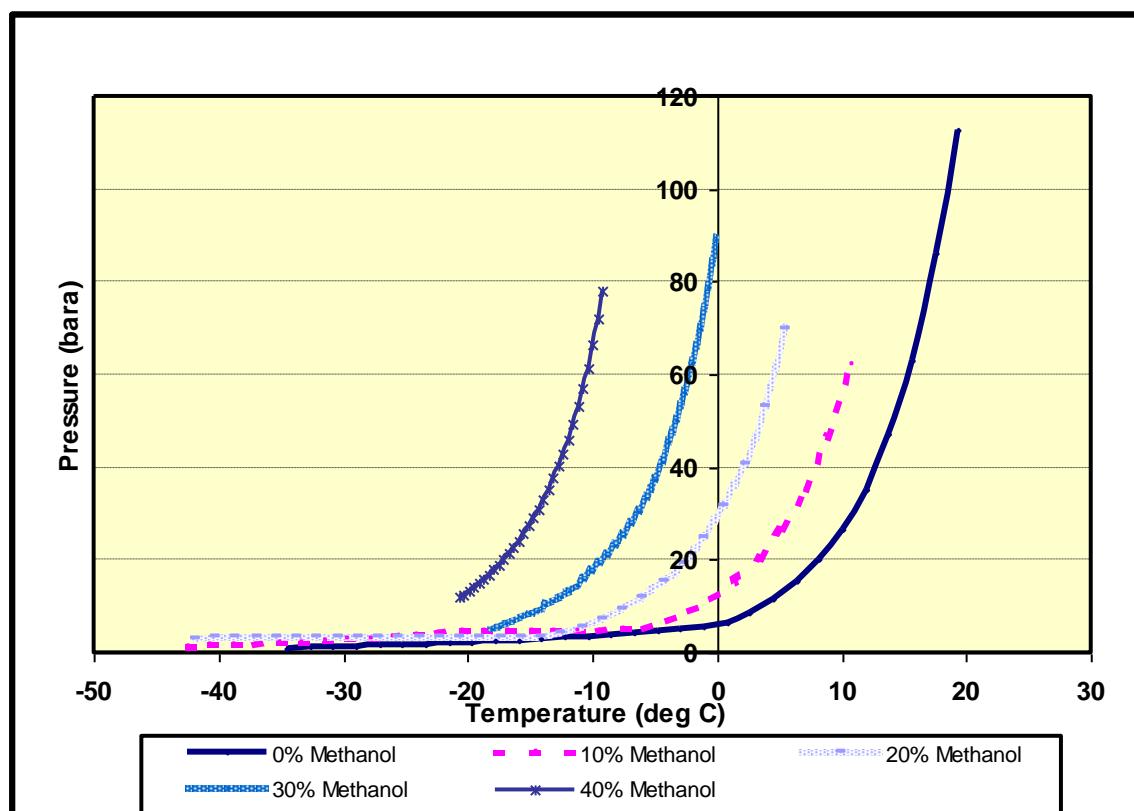
### 3.2 Hydrate Inhibition

A thermodynamic hydrate inhibitor can be injected to suppress hydrate formation, usually methanol, diethylene glycol (DEG) or monoethylene glycol (MEG). The injected alcohol is often recovered and recirculated.

Hydrate prevention with methanol and or glycals can be expensive because of the high effective dosage required (10% to 60% of the water phase). Furthermore, high concentrations of solvents can aggravate potential scale problems by lowering the solubility of scaling salts in water and precipitating scale inhibitors.

The total injection rate of inhibitor required is the amount/concentration of inhibitor in the liquid water phase for the desired hydrate temperature suppression, plus the amount of inhibitor that will distribute in the vapour and liquid hydrocarbon phases. Any inhibitor in the vapour phase or liquid hydrocarbon phase has little effect on hydrate formation conditions. Due to the accuracy limitations of the hydrate depression calculations and flow distribution in the process, a safety factor is often utilised.

The effect of methanol addition is shown. Hydrates will form to the right of each of the graphs.



### 3.3 Hammerschmidt Equation

The Hammerschmidt equation is often used for prediction of the necessary inhibitor concentration to achieve a given amount of hydrate depression:

$$X = 100 \times \frac{d \times M_i}{K_i + d \times M_i}$$

Where;

X      Weight percent of inhibitor in the liquid water phase (wt%)

d      Depression of hydrate point ( $^{\circ}\text{C}$ ) – usually hydrate formation temperature less minimum pipeline temperature.

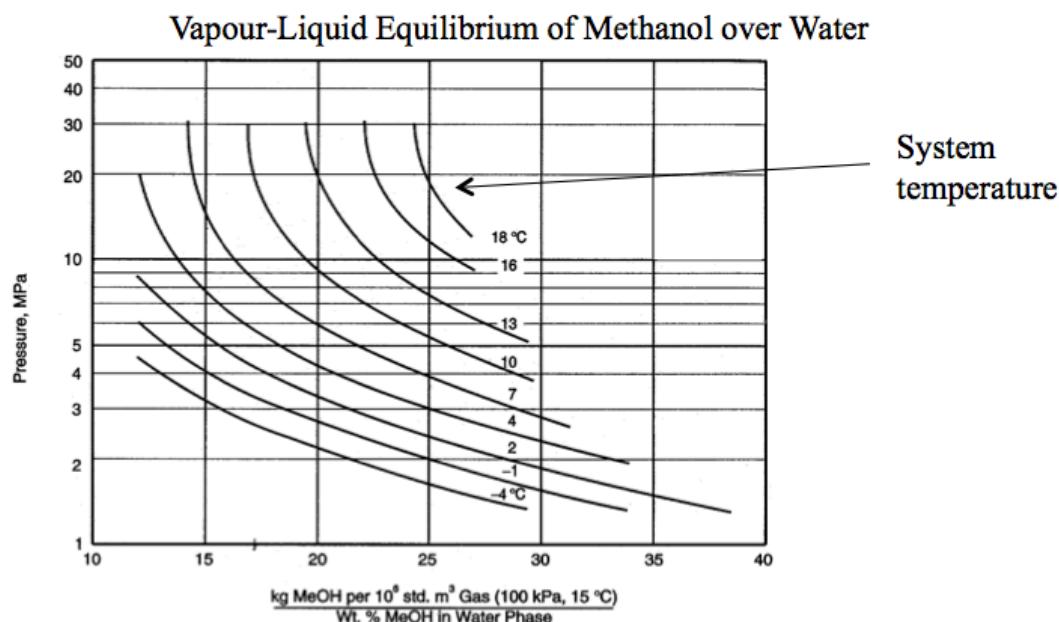
$M_i$     Mol weight of inhibitor (MW methanol = 32)

$K_i$     Constant:

1297 for methanol

2220 for glycols

Note, when methanol or glycol is added for hydrate prevention some of the methanol or glycol will vapourise, much more so with methanol. The amount of hydrate inhibitor which vapourises must be taken into account when estimating inhibitor injection rates. The following chart can be used for estimating methanol losses to the vapour phase.



### 3.4 Inhibitor Worked Example

10 MMscfd ( $2.83 \times 10^5 \text{ stm}^3/\text{d}$ ) of natural gas (specific gravity = 0.65) cools to 4.3°C in a subsea pipeline. The pipeline pressure is 6.2 MPa, outlet is 5.5 MPa. What weight % methanol ( $\rho = 800 \text{ kg/m}^3$ , Molecular Weight = 32) must be added to prevent hydrate formation if the gas enters the line water saturated at 32.2°C and what is the rate of injection?

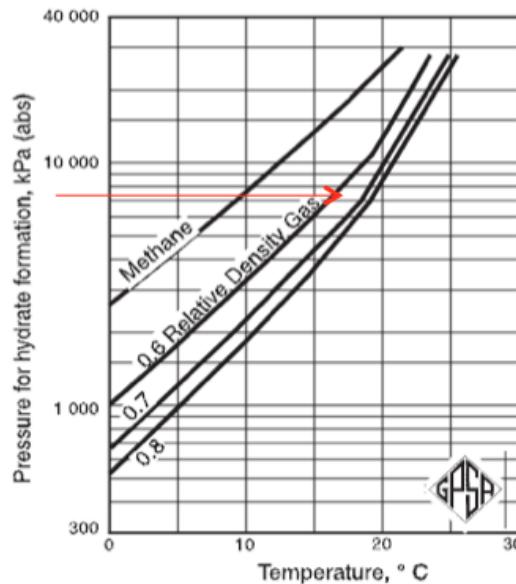
Calculate the hydrate formation point from

GPSA Chart = 21 °C (16 plus 5 °C safety margin)

Calculate required hydrate point depression:

$$d = 21.0 - 4.3 = 16.7^\circ\text{C}$$

Use GPSA chart for water content of lean natural gas and calculate the amount of liquid water formed in pipeline:



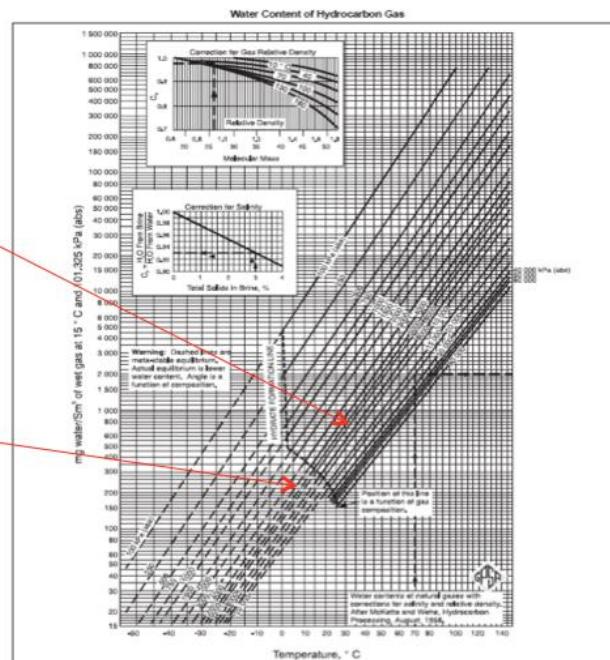
32.2 Deg C and 6.2Mpa

Water Saturation = 800 mg water/ $\text{Sm}^3$  (= kg/million $\text{Sm}^3$ )

( ignore correction)

4.3 Deg C and 5.5Mpa

Water Saturation = 220 mg water/ $\text{Sm}^3$



Water content @ 32.2°C and 6.4 MPa =  $800 \text{ kg}/10^6 \text{ stm}^3$

Water content @ 4.4°C and 5.5 MPa =  $220 \text{ kg}/10^6 \text{ stm}^3$

The difference is the amount of condensed water  $580 \text{ kg}/10^6 \text{ stdm}^3$

$$\text{Total liquid } H_2O = \left| \frac{580 \text{ kg}}{10^6 \text{ stdm}^3} \right| \cdot \left| \frac{0.283 \times 10^6 \text{ stdm}^3}{\text{day}} \right| = 164.1 \text{ kg/day}$$

Use Hammerschmidt equation to calculate methanol concentration:

$$X = 100 \cdot \frac{d \cdot M_i}{K_i + d \cdot M_i}$$

$$X_{MeOH} = 100 \cdot \frac{(16.7)(32)}{1297 + (16.7)(32)} = 29.2 \text{ wt\%}$$

$K_i = 1297$  for methanol

Calculate the required mass of methanol in water:

$$m_{MeOH} = 164.1 \cdot \left[ \frac{29.2}{100 - 29.2} \right] = 67.7 \text{ kg/day}$$

Calculate the methanol loss to the vapour phase using the vapour-liquid equilibrium chart (4.4°C, 5.5 MPa):

$$\text{Vaporisation losses} = 17 \cdot \frac{\text{kg MeOH}/10^6 \text{ stdm}^3}{\text{wt\% MeOH in water phase}}$$

$$m_{MeOH} = \frac{17 \text{ kg MeOH}}{10^6 \text{ stdm}^3} \cdot \frac{0.283 \times 10^6 \text{ stdm}^3}{\text{day}} \cdot 29.2 \text{ wt\% MeOH}$$

$$= 140 \text{ kg/day}$$

Total injection rate =  $67.7 + 140 = 207.7 \text{ kg/day}$

or

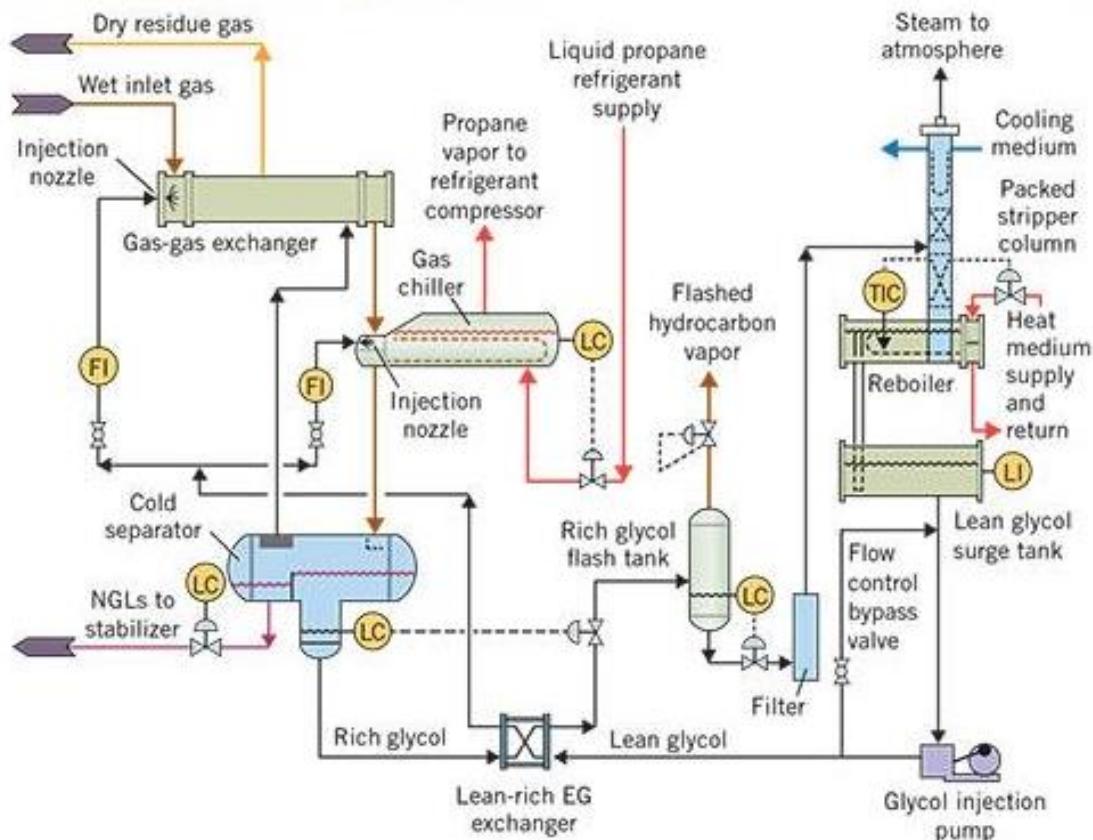
$207.7 / 0.8 = 260$  litres/day of methanol requires to be injected into pipeline

### 3.5 Glycol/Methanol Injection

Glycol injection (usually MEG) or sometimes methanol can be used either to protect against hydrate formation in transmission lines from offshore facilities or upstream of gas refrigeration systems in cold treatment plants. Glycol/methanol injection is possibly the simplest method of dehydrating natural gas, as in its simplest format it consists of an injection pump and injection point(s).

If required, the injected glycol can be recovered in a glycol still where the absorbed water is driven off from the glycol. It is usually almost always economic to recover glycol from a continuous process.

The glycol can be injected into the pipeline or into various sections of the unit upstream of the chilling facilities. Spray nozzles are used to ensure good dispersion into the gas the chilling facilities.



As the gas is cooled and water condenses, the glycol dissolves in the water phase. The gas and liquid phases are separated downstream in one or more separators as the gas is processed further.

The glycol water mixture is drawn off and sent to the glycol regeneration unit. The flow description and facilities are very similar to the glycol regeneration unit described in the conventional glycol absorption system.

#### 4 Gas Dehydration by Glycol Absorption

Glycol absorption is a unit operation in which soluble components of a gas mixture are dissolved in a liquid. The inverse operation, called stripping or desorption, is employed when it is desired to transfer volatile components from a liquid mixture into a gas.

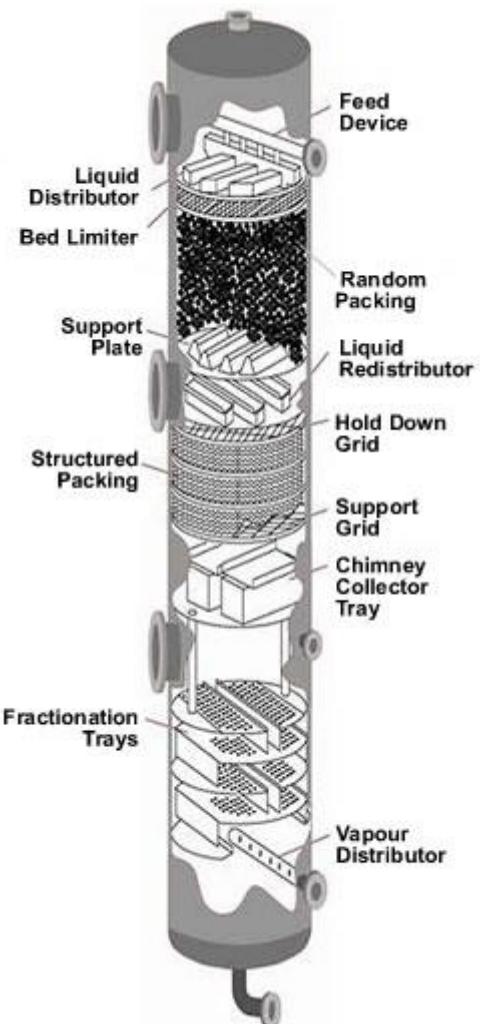
Both absorption and stripping, in common with distillation, make use of mass transfer contacting equipment for bringing gas and liquid phases into intimate contact.

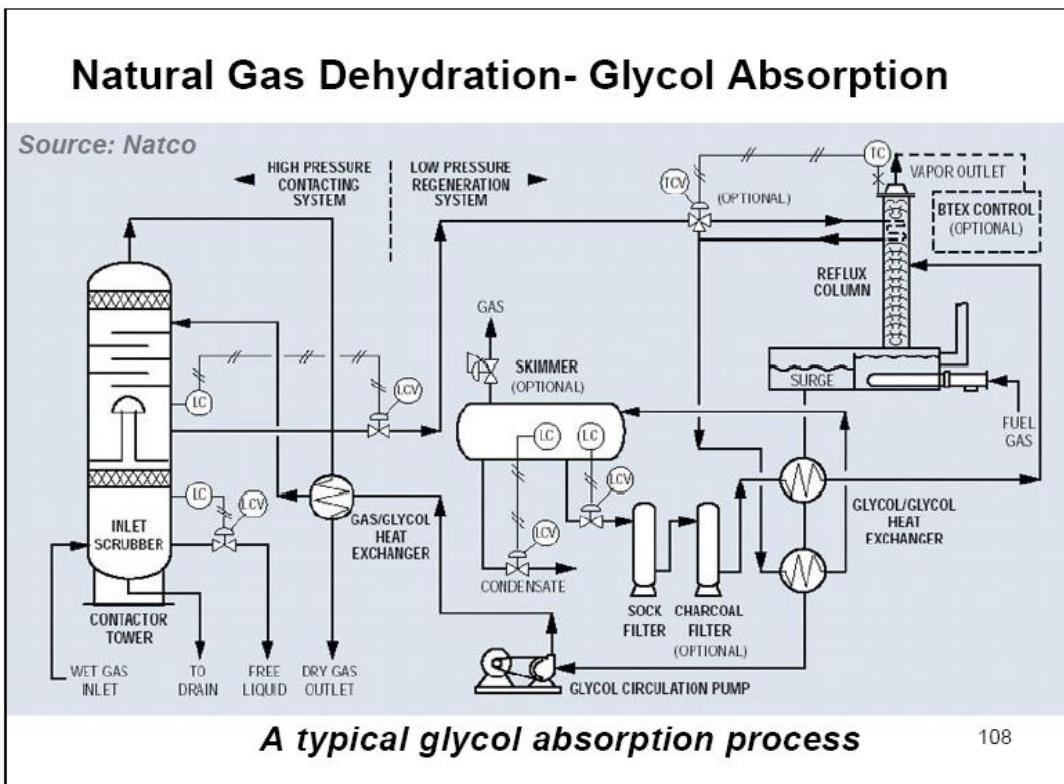
Absorption, stripping, and distillation operations are usually carried out in vertical, cylindrical columns or towers in which devices such as plates or packing elements are placed. The gas

and liquid normally flow countercurrently, and the devices serve to provide the contacting and development of interfacial surface through which mass transfer takes place.

Gas may be dehydrated to pipeline specifications by glycol absorption. In the liquid state, water molecules are highly associated because of hydrogen bonding. The hydroxyl groups in glycols form similar associations with water molecules. This explains why glycols are such good absorbers of water. Almost all glycol contactors use TEG – triethylene glycol.

As shown in the process flow diagram, wet natural gas first flows through an inlet separator or scrubber to remove all liquid and solid impurities. Then the gas flows into and upward through the absorber or contactor where it is contacted countercurrently and dried by glycol. Finally, the dried gas passes through a gas/glycol heat exchanger and then into the sales line. Reconcentrated or lean glycol enters the top of the contactor where it flows downward from tray to tray and absorbs water from the rising gas. The wet or rich glycol leaves the contactor and flows through a coil in the accumulator where it is preheated by hot lean glycol. Rich glycol is also preheated on top of the regeneration tower by hot water vapour. The coil at top of the stripper provides a water reflux at the top of the stripper. This temperature control insures that the water leaving the still does not carry over excess glycol. Heat exchange between the cool, rich glycol and hot lean glycol is improved by using two or more heat exchangers in series. The increased heat recovery reduces fuel consumption in the reboiler and protects the glycol circulation pump from being overheated; it also allows the flash tank and filter to operate at approximately 65°C. After glycol-glycol heat exchange, the rich solution is flashed to remove dissolved hydrocarbons. The latter can be used as fuel and/or as a stripping gas.





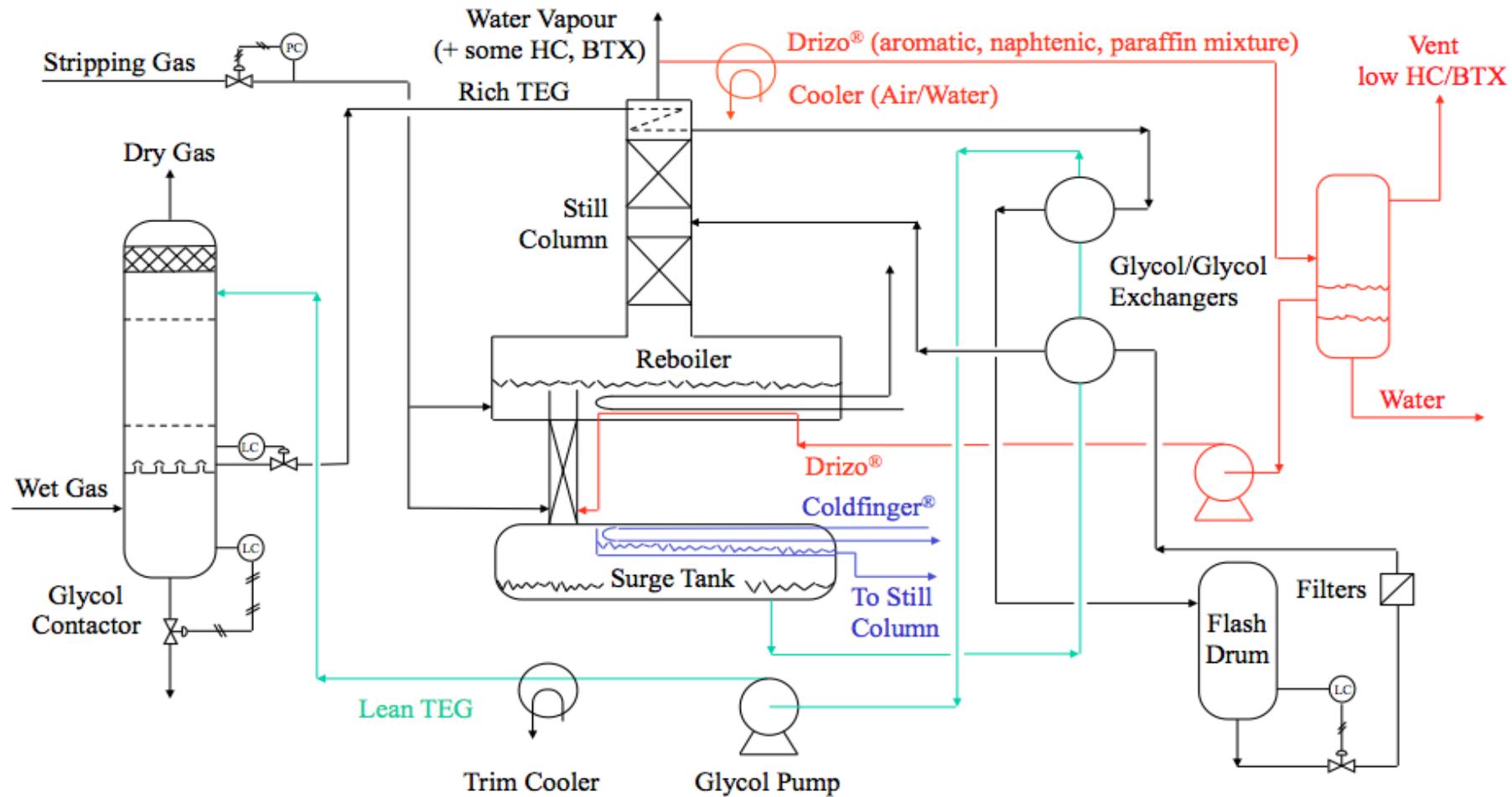
The glycol is filtered before being heated in the regenerator column. This prevents impurities such as solids and heavy hydrocarbons from plugging the trays or packing and fouling the reboiler fire tube. The solution then enters the stripping or regeneration column and flows down the packed section into the reboiler. Steam generated in the reboiler strips water from the liquid glycol as it rises up the packed bed. The water vapour and desorbed natural gas are vented from the top of the stripper. The hot reconcentrated glycol flows out of the reboiler into accumulator where it is cooled by heat exchange with rich glycol. Finally the lean glycol flows through the glycol /gas exchanger and is pumped back into the top of contactor. At the high pressure of the contactor tower, TEG absorbs hydrocarbons most of which are stripped off in the flash tank. Aromatic hydrocarbons have increased solubility in TEG and are not completely flashed off in the flash tank. The water vapour leaving the stripper column from the top contains some aromatic compounds which are known to be carcinogenic. The release of these aromatic compounds, namely benzene, toluene, ethylbenzene and xylenes (ortho, meta and para) known also as BTEX, which have rather close boiling points to that of water, has been restricted by regulating (environmental) organization. Therefore most of the modern glycol regeneration stills are equipped with BTEX removal systems. The BTEX removal systems may work base on effective incineration or condensation of stripper overhead and separation of BTEX in liquid phase. Minor quantities of BTEX may still be present in liquid water, therefore water disposal should be according to water disposal regulations.

## Glycol Regeneration Methods

The purer the lean glycol the lower the outlet gas water content achievable. Hence designers have investigated and incorporated means of achieving high purity lean glycol. Methods utilised are;

- Stripping gas used in reboiler/regenerator column outlet
- DRIZO®-process using an aromatic recycling stripping solvent
- Coldfinger® using a cooling element in the surge tank to condense water, thus reducing the water partial pressure in the vapour space and increasing the lean glycol concentration

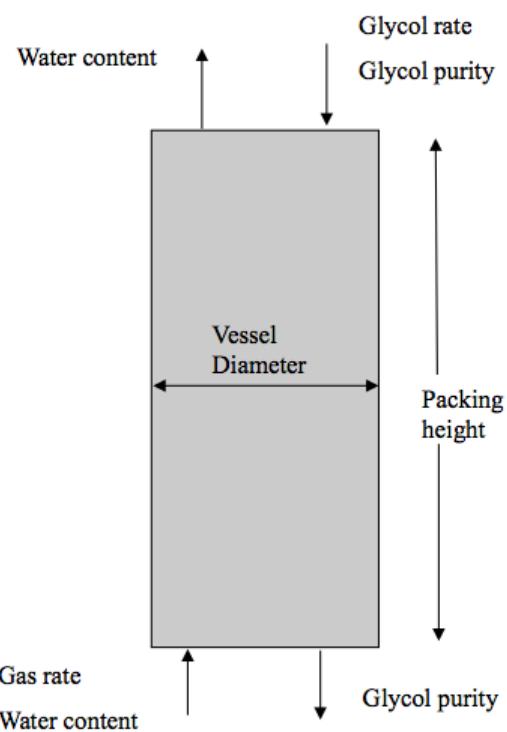
These techniques are illustrated on the following figure. Available stripping gases are usually hydrocarbons. If used as a stripping gas the resultant gas from the stripping action will generally be routed to the LP flare. This is often seen as bad practice on account of the poorer carbon footprint.



#### 4.1 Glycol System Design

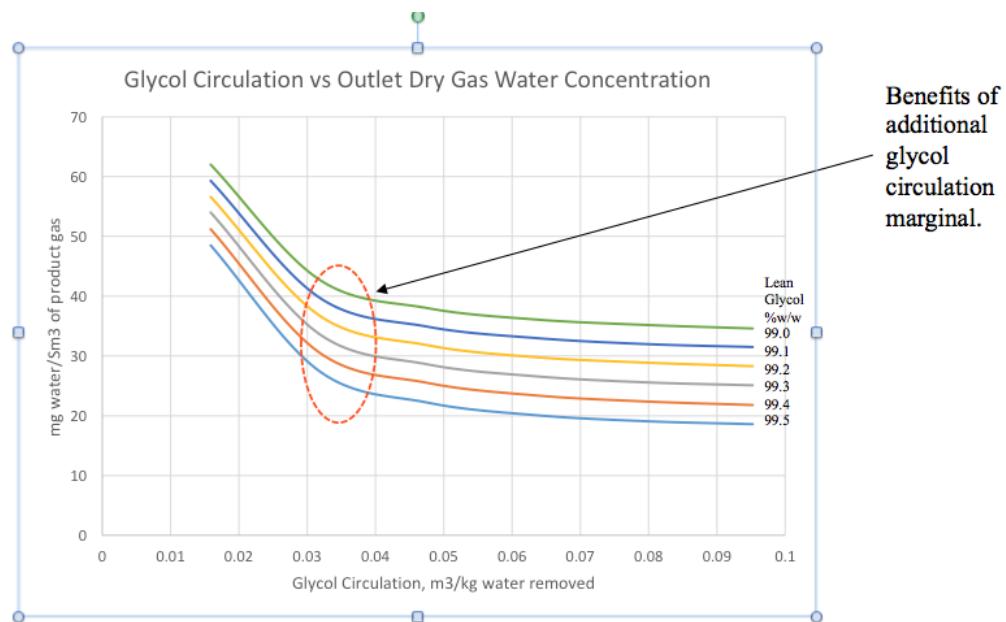
There are numerous variables to be considered for system design. Optimised design of the glycol system requires consideration of;

- Gas rate – design specification
- Inlet and outlet gas water contents – design specification
- Glycol circulation rate
- Contactor diameter
- Number of trays
- Packing height
- Reboiler duty



#### 4.2 Glycol Circulation Rate

The following figure shows the effect on gas outlet water specification with glycol rate at differing purities. As can be seen there is little benefit in increasing rates above 0.03 m<sup>3</sup>/kg of water absorbed. Hence this figure is often the starting point for a design.



#### 4.3 Entrainment

Tower diameter to avoid entrainment can be checked from the Souders-Brown expression.

$$v_{\max} = K_s \cdot \left( \frac{\rho_L - \rho_G}{\rho_G} \right)^{0.5}$$

Where;

$v_{\max}$  Maximum allowable superficial gas velocity (m/s)

$K_s$  Constant (m/s)

0.0488 for trays

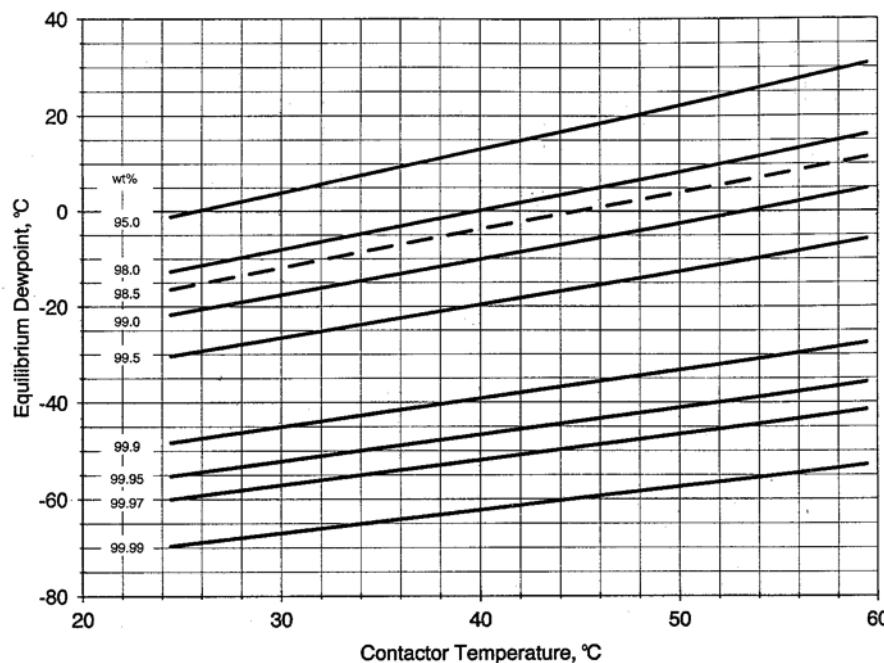
0.1 for structured packing

$\rho_L$  Density of TEG (kg/m<sup>3</sup>)

$\rho_G$  Density of gas (kg/m<sup>3</sup>)

#### 4.4 Contactor Equilibrium Line

Clearly the achievable water dewpoint from the glycol contactor depends on the inlet lean TEG concentration. Equilibrium conditions can be estimated from the following chart.



The equilibrium dewpoint represents the temperature the gas would require to be cooled to for water condensation to take place i.e. the equilibrium temperature. Note this is independent of pressure. Also, it is normal practice to take the desired dewpoint 5-10°C below the equilibrium dewpoint (approach) as equilibrium will not be reached in a contactor.

#### 4.5 Worked Example

Estimate the concentration of a lean TEG solution achieving an equilibrium dewpoint of -15°C in a contactor operating at 30°C.

As a safety margin, an approach of 10°C is subtracted → Equilibrium dewpoint is -25°C

From the chart read the lean TEG concentration at the intersection of the dewpoint line and the contactor temperature line:

Lean TEG concentration = 99.4 wt%

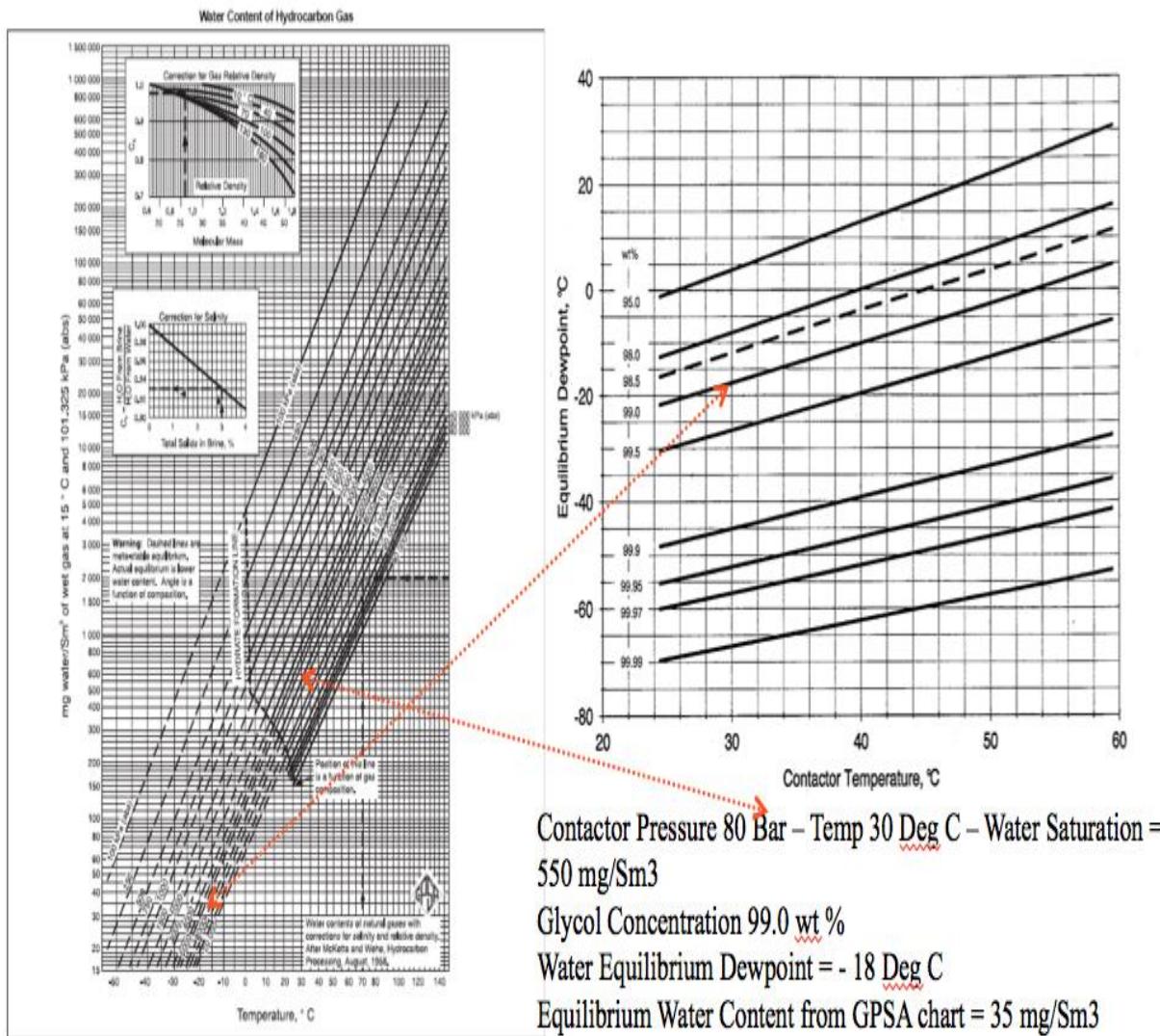
What the above has indicated is the dewpoint temperature which can be achieved. Water specifications are often as mg/sm<sup>3</sup>, hence we need to be able to convert dewpoint temperature into water saturation level and this is where the operating pressure is involved.

The equilibrium chart can be used with the natural gas water saturation chart to predict the equilibrium water vapour content of a gas in contact with TEG.

1. Use the contactor operating temperature to estimate the dewpoint for a known lean TEG concentration.
2. Use the dewpoint temperature at the contactor pressure to estimate the equilibrium water vapour content in mg/sm<sup>3</sup>.

Construction of operating and equilibrium line can now be prepared and the number of ideal and actual stages can be assessed.

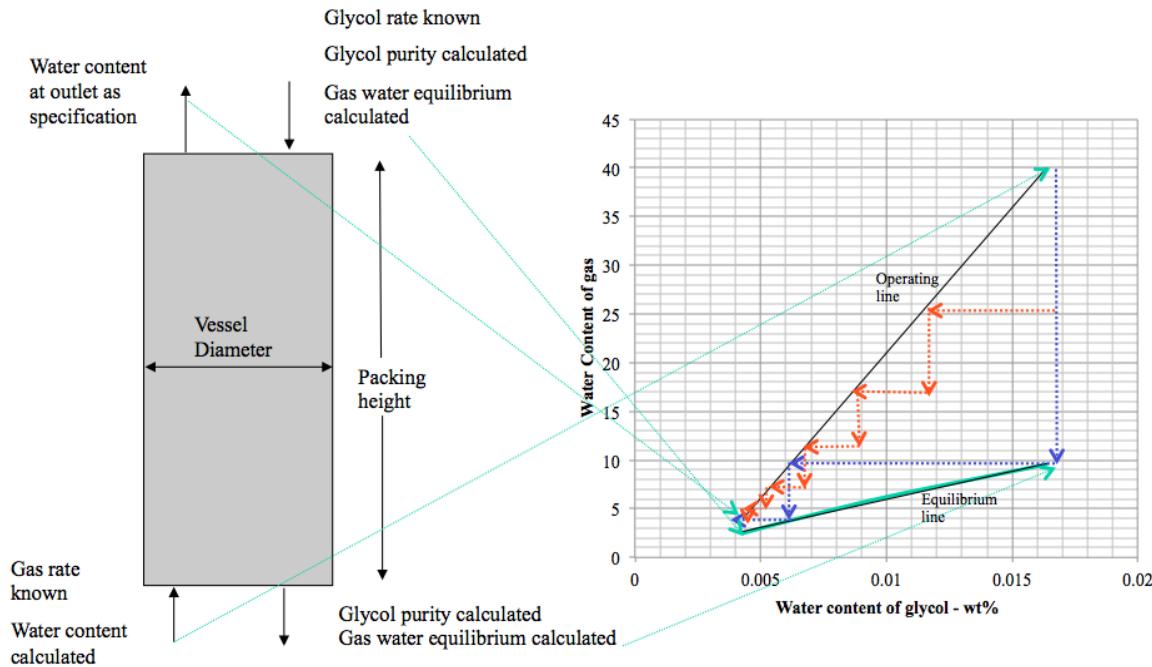
Consider a contactor at 80 bar and 30°C with a lean glycol concentration of 99.0 % wt the following can be calculated.



#### 4.6 Trays and Packing

Modern glycol units offshore tend to be packed towers as a result of the more compact design and reduced sensitivity to motion if located on a floating substructure. Whereas on land, trays, usually sieve, are common.

The number of trays can be calculated from the equilibrium and operating lines as shown;



The above indicates two theoretical stages and 6 actual (50% efficient).

Trays are typically 40 -50% efficient.

#### 4.7 Height Equivalent of Theoretical Plate

GPSA provides 1.5m for the HETP. This can be used for a preliminary design.

#### Diameter and Flooding

The diameter of packed towers is frequently estimated with reference to the flood point.

Typically the design gas velocity is 50-60% of the flooding velocity. The flood point is the condition where the liquid hold-up within the packing increases sharply. At this point the gas velocity is at a value which prevents the liquid from draining through the packing hence the packing floods with liquid.

The work of Sherwood remains the basis for most flooding assessments. This work developed a correlation whereby the flooding velocity could be

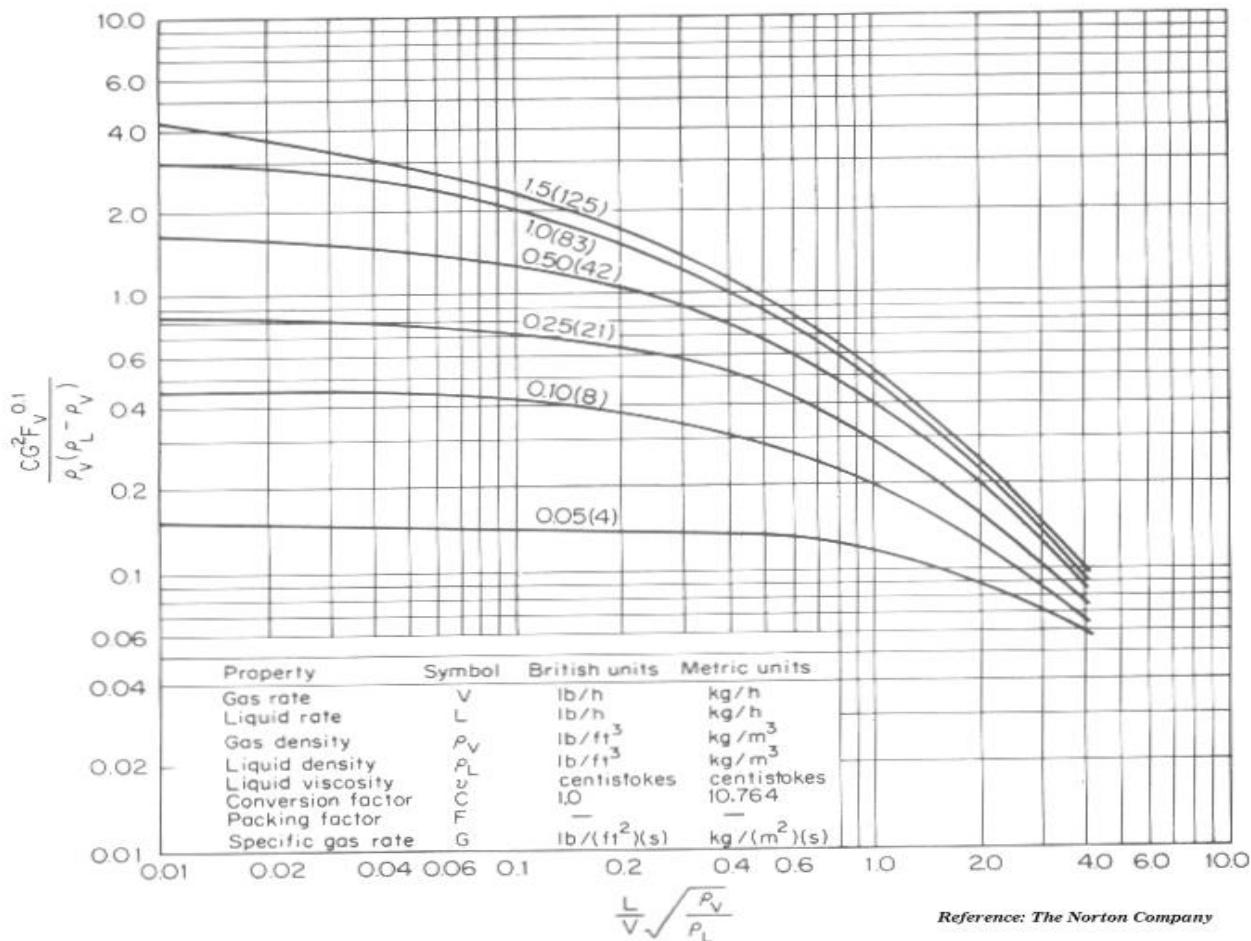
Name	Size or number	Area, m <sup>2</sup> /m <sup>3</sup>	% voids*	Packing factor, m <sup>-1</sup>		Vendor
				Normal F <sub>p</sub> <sup>†</sup>	Dry F <sub>pd</sub> <sup>‡</sup>	
Metals, corrugated sheets						
Mellapak	125Y	125	99	33		Sulzer
	170Y	170	99	39		
	2Y	223	99	46		
	250Y	250	98	66		
	350Y	350	98	75		
	500Y	500	98	112		
	750Y	750	97			
	125X	125	99	16		
	170X	170	99	20		
	2X	223	99	23		
	250X	250	98	26		
	500X	500	98	82		
Mellapak Plus	202Y		99			Sulzer
	252Y	250	98	39		
	352Y		98			
	452Y	350	98	69		
	752Y	500	98	131		
Flexipac	700Y	710	96			Koch-Glitsch
	500Y	495	97			
	1Y	420	98	98	(105)	
	350Y	350	98			
	1.6Y	290	98	59		
	250Y	250	99			
	2Y	220	99	49	(36)	
	2.5Y	150	99			
	3.5Y	80	99	30	(15)	
	4Y	55	99	23	(10.5)	
	1X	420	98	52		
	350X	350	98			
	1.6X	290	98	33		
	250X	250	99			
	2X	220	99	23		
	2.5X	150	99			
	3X	110	99	16		
	3.5X	80	99			
	4X	55	99			
Flexipac High-capacity	700	710	96	223		Koch-Glitsch
	500Z	495	97			
	1Y	420	98	82		
	350Y	350	98			
	1.6Y	290	99	56		
	250Y	250	99			
	2Y	220	99	43		
Intalox	1T	310	98	66		Koch-Glitsch
	1.5T	250	99			
	2T	215	99	56		
	3T	170	99	43		

determined from the fluid physical properties, the characteristics of the packing the liquid and gas loadings of the tower. Flooding was determined as a function of pressure drop.

Flooding is a function of the type of packing. This is presented as a packing factor. Packing factors are supplied by the mass transfer material vendors. It relates packing volume, surface area and void space.

Typical structured packing factors are indicated.

Packing characteristics are determined from the following general chart.



#### 4.8 Flooding Worked Example

Calculate the diameter of a glycol absorber packed with a mass transfer material which has a packing factor of 30.

The density of the gas and glycol are 80 and 1150 kg/m<sup>3</sup> respectively. The gas flowrate is 1.4 x 10<sup>6</sup> std m<sup>3</sup>/day. The glycol rate is 2.5 m<sup>3</sup>/hr, viscosity is 16 centistokes. The gas molecular weight is 18. System pressure is 50 bara, temperature is 30 °C. Z = 0.85.

The acceptable pressure drop for the absorber is 21mm/m packing.

Glycol mass rate, Lm = 2.5 x 1150/3600 = 0.8 kg/s

$$\text{Gas mass rate, } G_m = (1.4 \times 10^6 \times 18)/(23.96 \times 24 \times 3600) \quad (1\text{kgmol} = 23.96 \text{ s m}^3)$$

$$= 12.2 \text{ kg/s}$$

$$X = (L/G) \cdot (\rho_G/\rho_L)^{0.5} = (0.8/12.2) \times (80/1150)^{0.5} = 0.017$$

$$Y = C \cdot G^2 \cdot F \cdot u_L^{0.1} / (\rho_G \cdot (\rho_L - \rho_G)) = 0.85$$

$$G^2 = 0.85 \times 80 \times (1150 - 80)/$$

$$(10.764 \times 30 \times 16^{0.1})$$

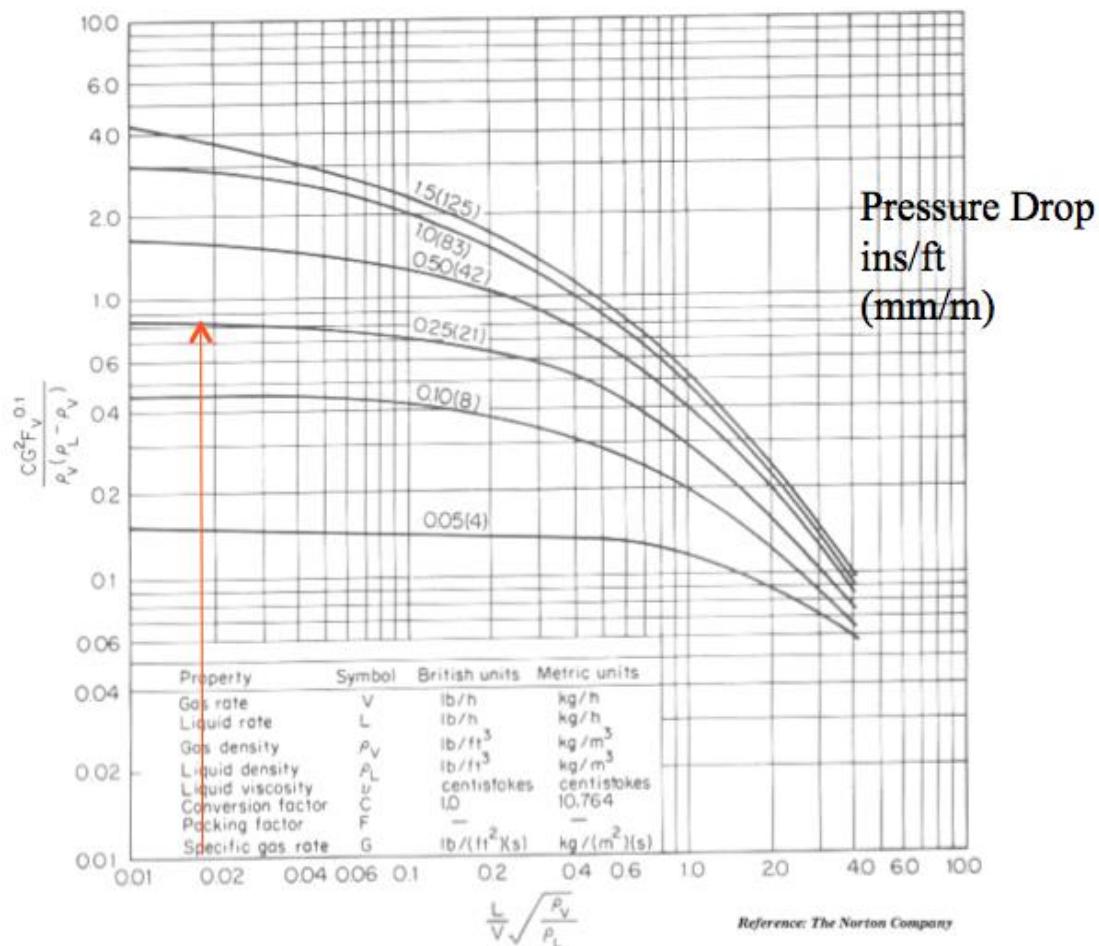
$$= 170$$

$$G = 13 \text{ kg/m}^2 \cdot \text{s}$$

$$G = G_m / \text{Tower CSA}$$

$$= G_m / (3.14 \times D^2 / 4)$$

Solving for D = 1.16m



### Entrainment check

Check for maximum entrainment velocity;

$$v_{\max} = K_s \cdot \left( \frac{r_L - r_G}{r_G} \right)^{0.5}$$

$v_{\max}$  Maximum allowable superficial gas velocity (m/s)

$K_s$  Constant (m/s)

0.0488 for 24" tray spacing and 2" seal  
over bubble cap slots

0.1 for structured packing

$\rho_L$  Density of TEG (kg/m<sup>3</sup>)

$\rho_G$  Density of gas (kg/m<sup>3</sup>)

Calculate gas volume flow;

Volume flow,  $V_g = 1.4 \times 10^6 \text{ Sm}^3/\text{day}$

Actual volume flow =  $1.4 \times 10^6 \cdot Z \cdot 1/P \cdot T/288$

$$= 0.025 \times 10^6 \text{ m}^3/\text{day}$$

$$= 0.29 \text{ m}^3/\text{s}$$

Gas velocity,  $= 0.29/\text{CSA} = 0.29/1.06 = 0.27 \text{ m/s}$

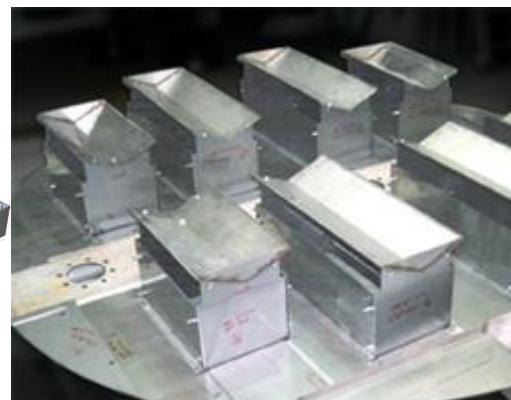
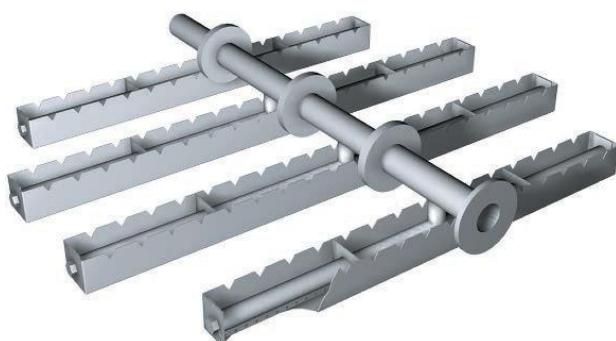
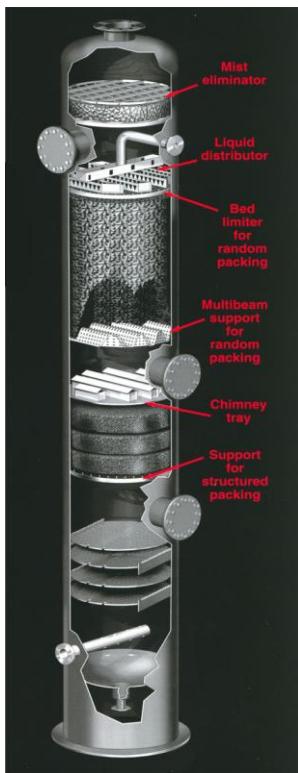
Compare with  $v_{\max}$

$$V_{\max} = 0.1 \times ((1150 - 80)/80)^{0.5} = 0.36 \text{ m/s}$$

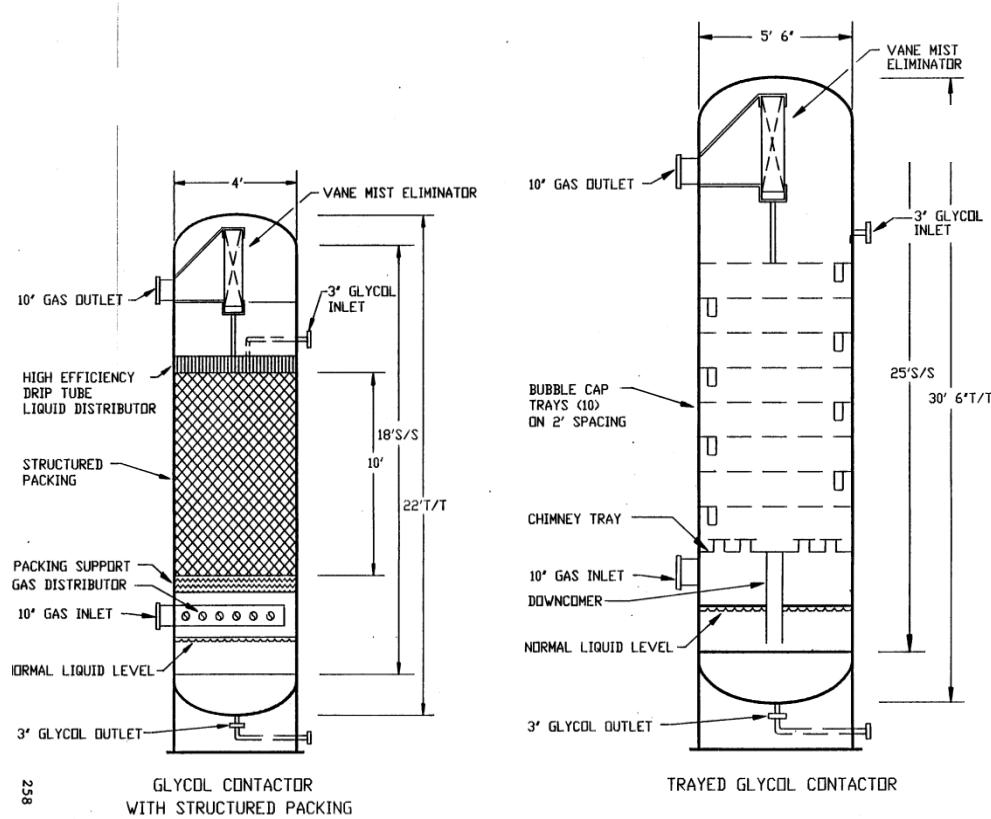
Hence, tower acceptable from entrainment criteria.

#### 4.9 Contactor Internals

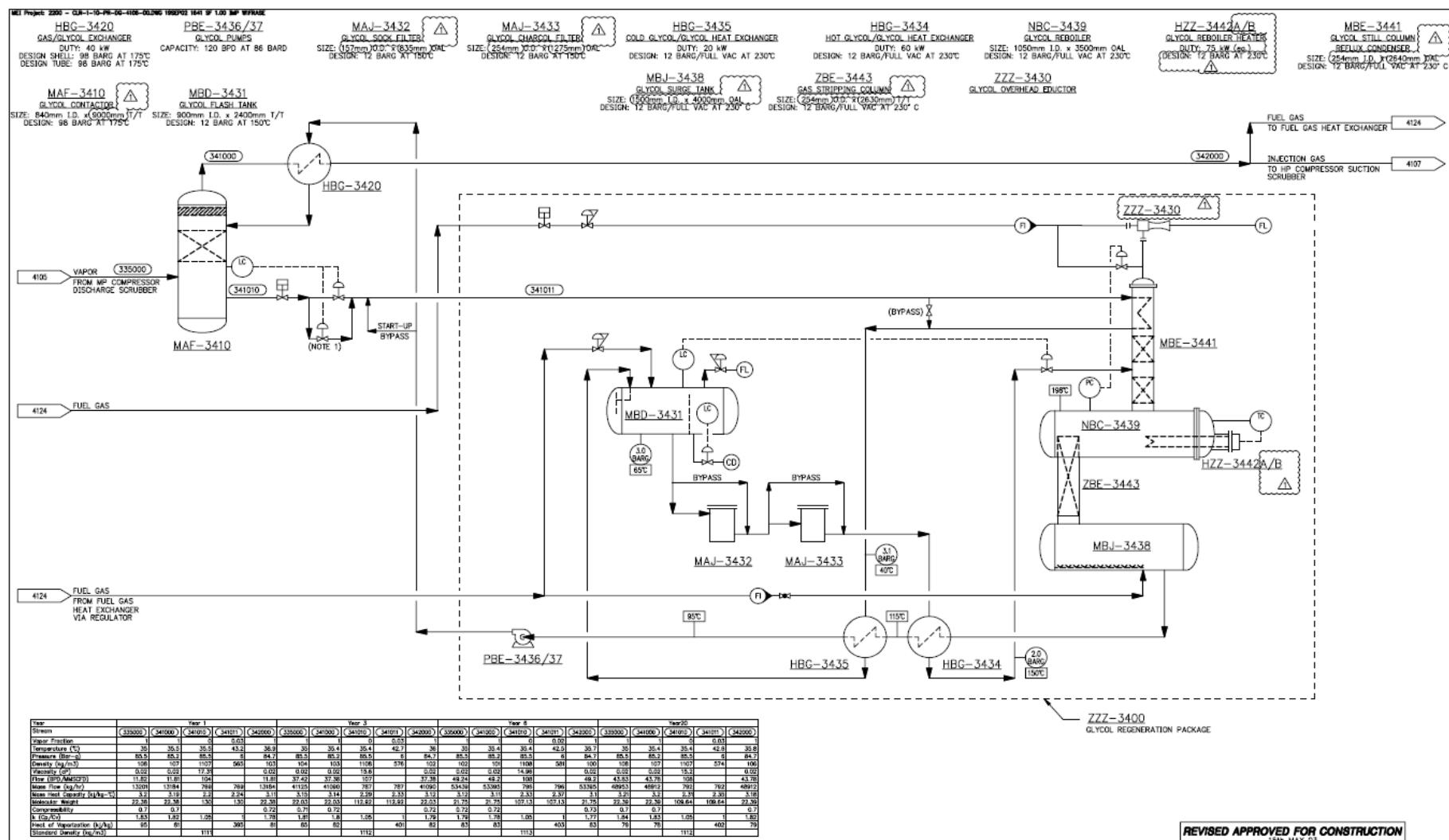
Column internal are required to uniformly distribute the fluids and efficiently collect liquid from the packing/trays.



Typical size savings from packing versus trays are shown.



## Typical Glycol System PFD



#### 4.10 Glycol System Operating Problems

Some common operational problems are listed.

Hydrocarbon liquid carryover from upstream units - If hydrocarbons are present, the unit may be subject to foaming and the formation of gummy or tarry deposits in the reboiler, heat exchangers, and absorber.

Corrosion - A glycol pH of less than 6 indicates a potentially serious corrosion problem with the system.

Foaming - Can be induced by hydrocarbons, salts and degradation products.

Salt precipitation - Can cause problems with reboiler.

Glycol Carryover - Poor tower design

Chimney tray Design - Poor design can lead to re-entrainment.

A simple visual inspection of the glycol can provide clues for identifying many glycol problems. The following conditions can indicate major problems:

- The presence of a finely divided black precipitate is the result of iron corrosion.
- A black viscous glycol solution may be the result of heavy hydrocarbon contamination or glycol polymerization due to thermal breakdown or interaction with hydrocarbons.
- A sweet, aromatic odour may be an indicator of thermal degradation of the glycol.
- A two-phase solution indicates hydrocarbon contamination.

### 5 Adsorption Dehydration

Dehydration with TEG is termed absorption. Adsorption is a phenomenon where a solid surface holds a molecule either by chemisorption or physisorption. The most common industrial application is physisorption where van der Waals forces attract and hold molecules onto a solid surface.

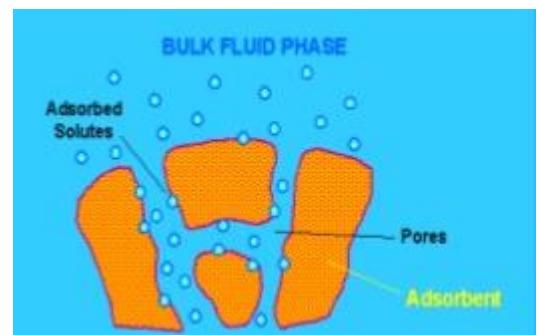
Desiccants in common commercial use fall into one of three categories:

Gels – alumina or silica gels manufactured and conditioned to have an affinity for water.

Alumina – a manufactured or natural occurring form of aluminium oxide that is activated by heating.

Molecular Sieves – manufactured or naturally occurring aluminosilicates exhibiting a degree of selectivity based on crystalline structure in their adsorption of natural gas constituents.

Silica Gel is a generic name for a gel manufactured from sulphuric acid and sodium silicate. It is essentially pure silicon dioxide,  $\text{SiO}_2$ . It is used for gas and liquid dehydration and



hydrocarbon (iC<sub>5+</sub>) recovery from natural gas. When used for dehydration, silica gel will give outlet dewpoints of approximately -60°C.

Alumina is a hydrated form of alumina oxide (Al<sub>2</sub>O<sub>3</sub>). It is used for gas and liquid dehydration and will give outlet dewpoints in the range of -70°C. Less heat is required to regenerate alumina than for molecular sieve, and the regeneration temperature is lower. However, molecular sieves give lower outlet water dewpoints.

### 5.1 Molecular Sieves

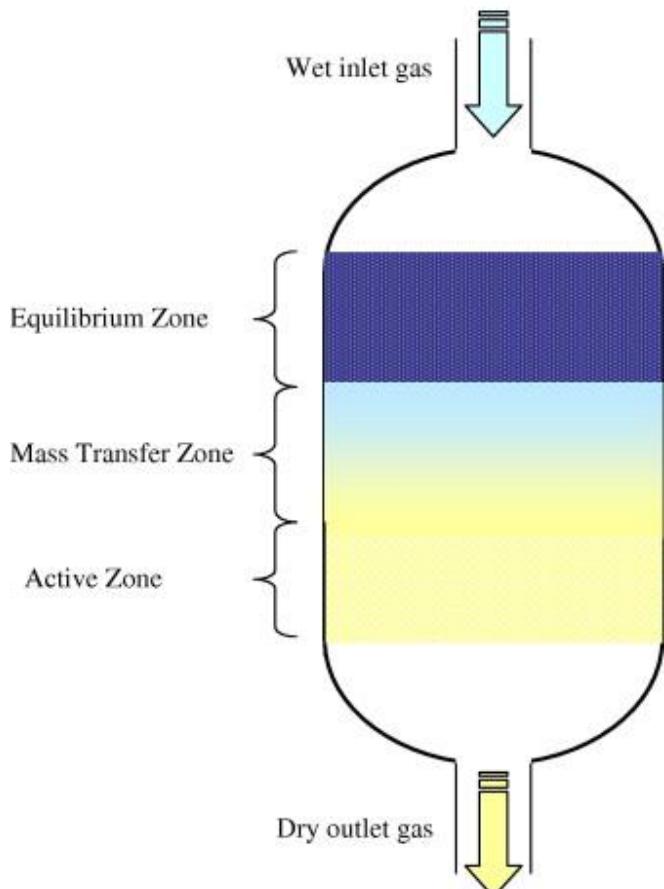
Molecular sieves are the most common industrial adsorption dehydrators. They are a class of aluminosilicates and possess the highest water capacity, will produce the lowest water dewpoints, and can be used to simultaneously sweeten (remove hydrogen sulphide) and dry gases and liquids. Their equilibrium water capacity is much less dependent on adsorption temperature.

They are usually more expensive and find application where a very dry gas is required. Hence molecular sieve dehydrators are commonly used ahead of cold temperature plants – cryogenics, LNG.

These plants typically operate at very cold temperatures and require a very dry feed gas to prevent formation of hydrates and ice. Dehydration to a -100°C dewpoint is possible with molecular sieves.

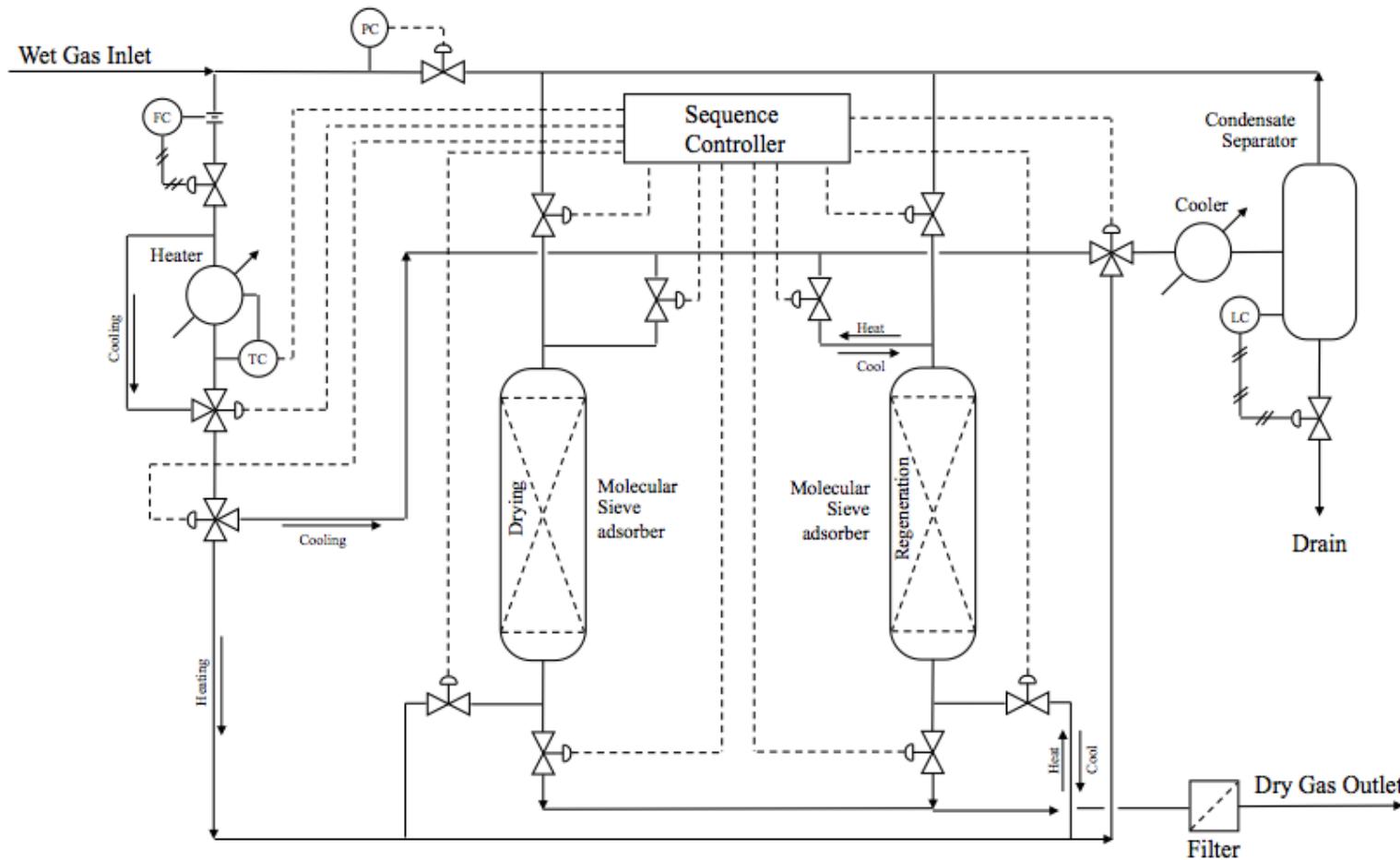
The process is batch requiring two (or more) vessels with one on-line removing water while the other is being regenerated. When the bed is taken off-line, the water is removed by heating the sieve to typically 230-320°C, depending on the desiccant used and the performance specification. The regeneration gas used to heat the bed is a slipstream of dry process gas or the feed gas. The regeneration gas is returned to the process after it has been cooled and the free water removed.

Gas flow during adsorption is typically downflow. This allows higher gas velocities (thus smaller diameter towers) since bed fluidization is avoided. Regeneration gas flow is upflow during the heating cycle. In that way, any residual water left on the



desiccant will be at the top of the bed and will not affect the effluent dewpoint when adsorption is resumed. In addition, upflow heating helps to strip any contaminants from the top of the bed extending desiccant life. Regeneration gas flow during the cooling cycle may be upflow if the gas is completely free of water. This saves two switching valves per tower which can reduce capital costs. If the cooling gas contains water, cooling flow should be downflow to avoid preloading of the desiccant at the bottom of the bed with water.

Typical two bed PFD.



## 5.2 Molecular Sieve Preliminary Design

The allowable bed superficial velocity can be calculated from the accompanying figure.

Once the superficial velocity is estimated the bed cross sectional area and diameter (D) can be readily calculated from the gas volume flowrate.

An absorption cycle time has to be estimated, typical 8 – 12 hours.

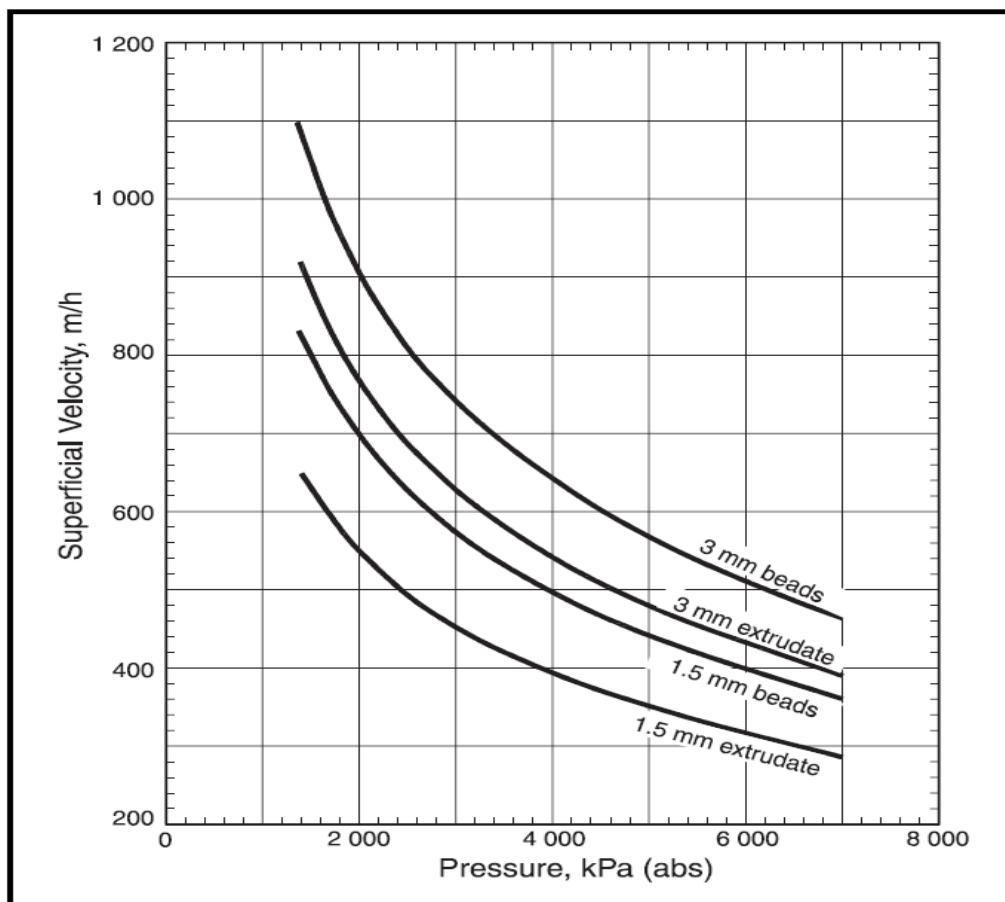
During the adsorption cycle, the bed is operating in the three previously mentioned zones; The top equilibrium zone where the desiccant in this zone is in equilibrium with the wet inlet gas.

The mass transfer zone (MTZ) is where the water content of the gas is reduced from saturation to typically < 1 ppmv. Followed by the bottom unused desiccant active zone.

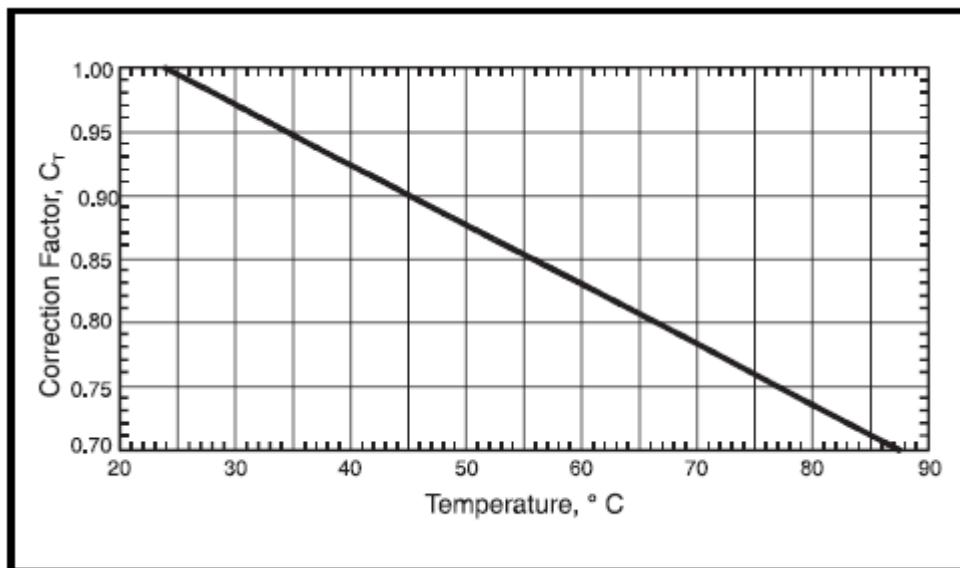
If the bed operates too long in adsorption, the mass transfer zone begins to move out the bottom of the bed causing water breakthrough. At breakthrough, the water content of the outlet gas begins to increase and will eventually reach feed gas water content when the MTZ is completely displaced.

Both water capacity and the rate at which solid desiccants adsorb water decline as the material ages. The object of the design is to install enough desiccant such that after three to five years, the mass transfer zone will be at the bottom of the bed at the end of the adsorption cycle.

**Allowable Velocity for Mole Sieve Dehydrator**



In the saturation zone, molecular sieve is expected to hold approximately 13 kg of water per 100 kg of sieve. New sieve will have an equilibrium capacity near 20kg; 13kg represents the approximate capacity of a 3-5 year old sieve.



To determine the mass of desiccant required in the saturation zone, calculate the amount of water to be removed during the cycle and divide by the effective capacity.

$$S_s = W_r / (0.13 \times C_t)$$

S<sub>s</sub> = molecular sieve material required in sat zone, kg

W<sub>r</sub> = Water removed per cycle, kg

C<sub>t</sub> = Temperature correction factor

Calculate the L<sub>s</sub>, the length of packed bed in the saturation zone from;

$$L_s = S_s \times 4 / (\pi \times D^2 \times \rho)$$

Sieve density is around 700 kg/m<sup>3</sup>

The length of the mas transfer zone can be calculated from:

$$L_{MTZ} = (V/560)^{0.3} \times K$$

V = Superficial vapour velocity

K = 1.7 for 3mm sieve, 0.85 1.5 mm sieve

The total bed height is the sum of the saturation and MTZ lengths.

A further 1.9m is added top and bottom to provide even gas distribution.

### 5.3 Molecular Sieve Overview

Recommended Operating Range:

T < 50°C

T > Hydrate point

Desiccant Service:

3 - 5 years in absence of poisoning. Limited by loss of capacity, dusting and breakage

Dehydration Obtained:

Product is essentially bone dry (water free) gas. Dewpoint: -75 to -125°C (Silica Gel: -60°C)

Length of Cycle: Varies with water loading and gas rate: 4 - 24 hours

Regeneration: Temperature: 175 - 300°C. About 5 to 15% of the total gas stream is used for regeneration. 8 hour cycle: 6 hours heating, 2 hours cooling

Advantages:

Low exit dewpoint

Effective dewpoint depression over a wide range of operating conditions

Compact

Relatively low initial investment for small amounts of gas (batch or semi-batch operation)

Rated capacity may be increased by bypassing some wet gas

Disadvantages:

High initial investment

Desiccant sensitive to poisoning

Rated capacity declines with pressure

Pressure drop is higher than liquid desiccant systems

Regeneration heat load can be high in relation to the amount of gas processed.

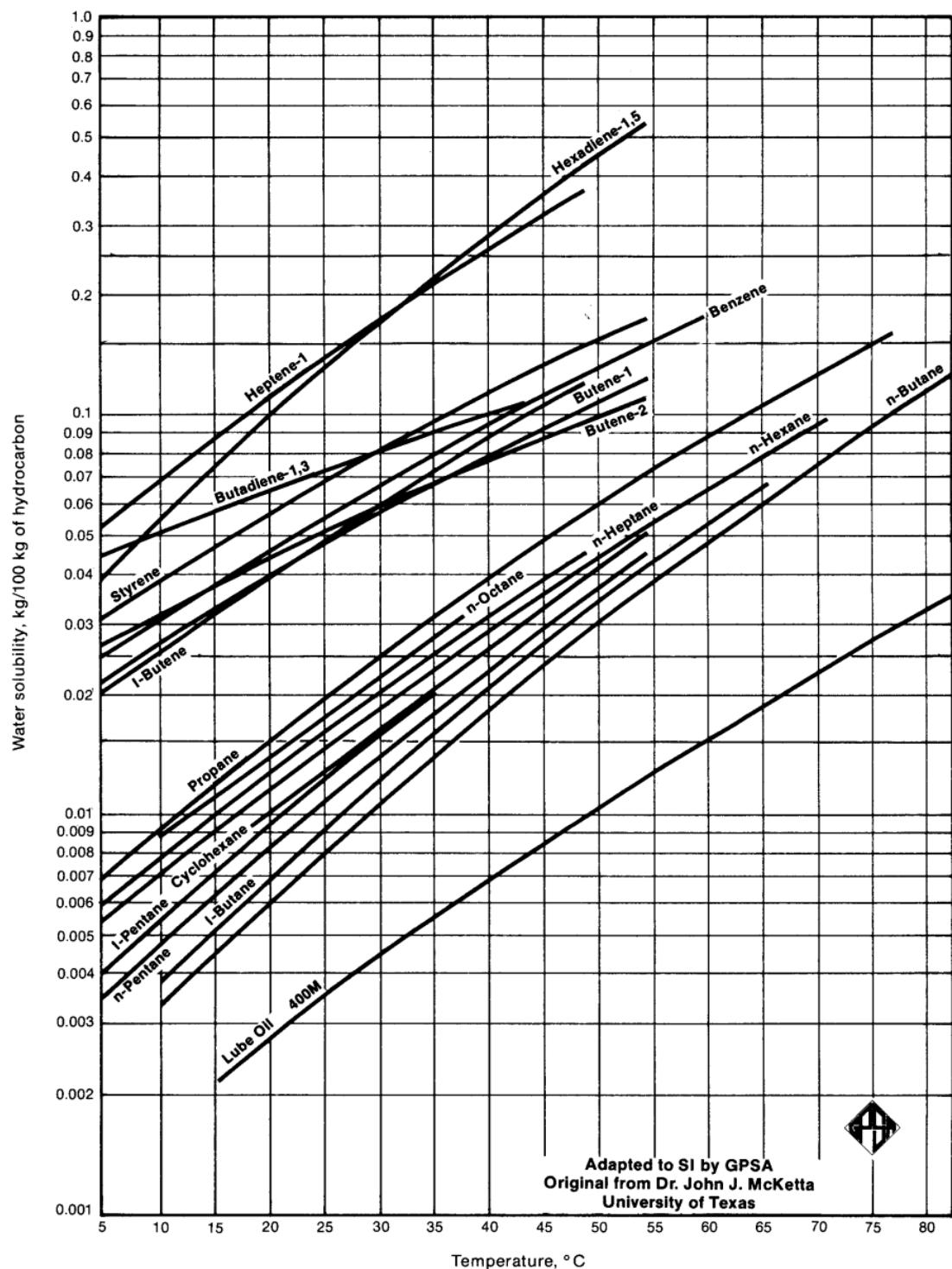
## 6 Liquid Drying

Many liquid streams must be dehydrated to allow further processing or meet requirements of a handling chain to a direct consumer. For example, commercial propane must be dry before entering the fuel market to prevent freezing problems as the liquid vaporizes at temperatures below the hydrate point, or even below the freezing point of any free water that may be present.

The amount of water that can be in solution with light hydrocarbon liquid is very small, even at the saturation point – see following chart.

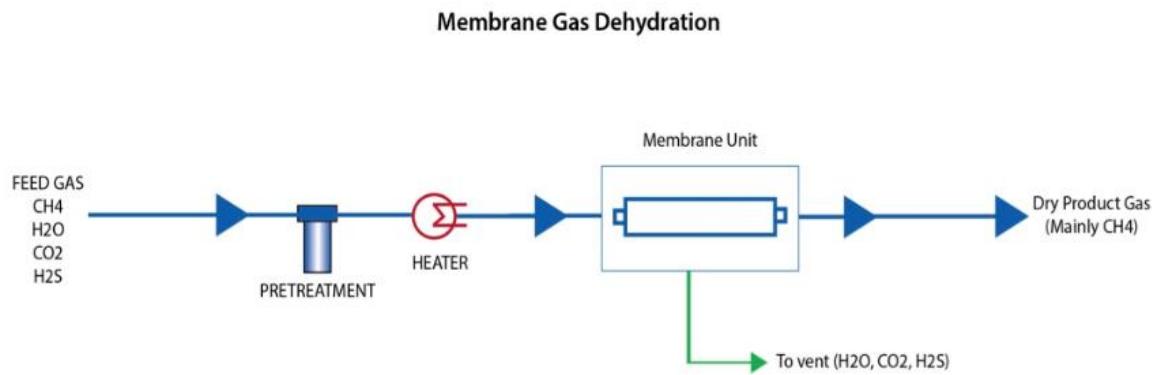
Effective drying to very low levels of moisture is usually required. The desired maximum moisture level for commercial propane is approximately 10 mg/kg. However, liquids exposed to cryogenic temperatures require virtually all the moisture be removed.

Molecular sieves are often used to dry liquid hydrocarbons from gas plants.



## 6.1 Membrane Dehydration

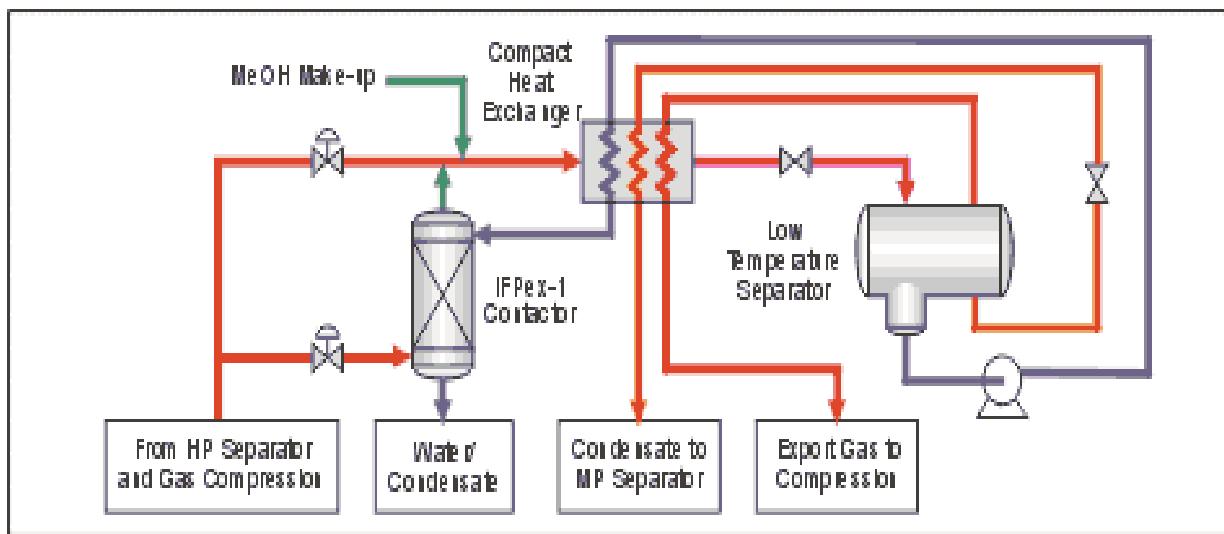
Membrane dehydration is yet to gain widespread acceptance. In a typical membrane gas dehydration system the feed gas is first filtered to remove any entrained liquids. The gas then enters the membrane modules. The H<sub>2</sub>O as well as the CO<sub>2</sub> and H<sub>2</sub>S permeate preferably through the membrane. The non-permeated gas, mainly CH<sub>4</sub>, remains at pressure and is the product gas.



## 6.2 IFPEX Dehydration

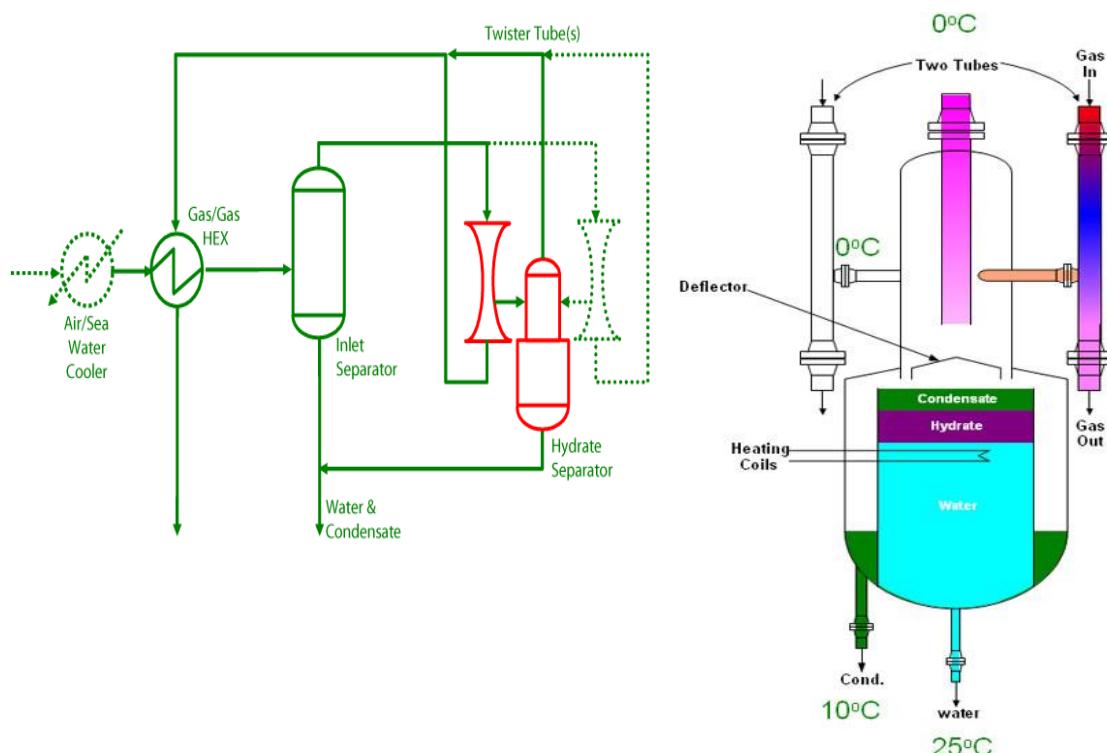
Gas dehydration can be achieved by chilling a gas stream to low temperatures in order to remove water down to a level which is equivalent to the specified water dewpoint. One complication of such a process is the need for a hydrate inhibitor to prevent hydrates forming at low temperatures. Institut Francais du Petrole (IFP) has developed a scheme which uses methanol for such a duty and overcomes the traditional regeneration problems associated with methanol.

The novel regeneration process consists of a packed column to enable a slipstream of the wet gas stream to be contacted with the water/methanol stream from the Low Temperature Separator. The gas effectively strips the methanol out of the water stream producing a discharge water stream containing as low as 50 ppm of methanol (suitable for offshore disposal). Methanol losses from the Low Temperature Separator to the vapour and liquid hydrocarbon streams are accounted for by means of a methanol make-up which is added to the inlet gas stream prior to chilling. The main benefits of the process are the simple, environmentally friendly regeneration (minimal losses) process, small footprint area over conventional dehydration schemes and the ability to dewpoint the gas at the same time as it is being dehydrated. The main drawbacks are the methanol losses to the hydrocarbon phases and the dual dehydration and dewpointing function. This is a drawback, as well as an advantage, as if the water specification is severe whilst the hydrocarbon dewpoint is not, IFPEx-1 will essentially overtreat the gas and produce large amounts of unwanted condensate.



### 6.3 Twister Dehydration

This is a Shell proprietary design. Here the gas is accelerated and the temperature drops resulting in the formation of hydrate crystals. Tangential inflow nozzles swirl the feed stream. The resulting centrifugal forces separate the heavier liquids and hydrates from the vapour, resulting in a high separating efficiency without internals (which could freeze-up with hydrates). Liquids and hydrates are collected in the bottom section, where hydrates are melted by heating coils. CFD modelling, field testing and commercial operation have confirmed a very high separating efficiency (>99%) and stable operation without the use of chemicals. The Hydrate Separator can be designed as either a 2 or a 3-phase separator to suit the specific requirements of each application.



## 7 Natural Gas Liquids Recovery - Dewpointing

In addition to achieving gas sales specification it may be commercially attractive to condense additional NGLs (mainly propane and butane) and export with oil or as a separate stream for treatment and sales. This is often termed dewpointing.

The main schemes for dewpoint control are :

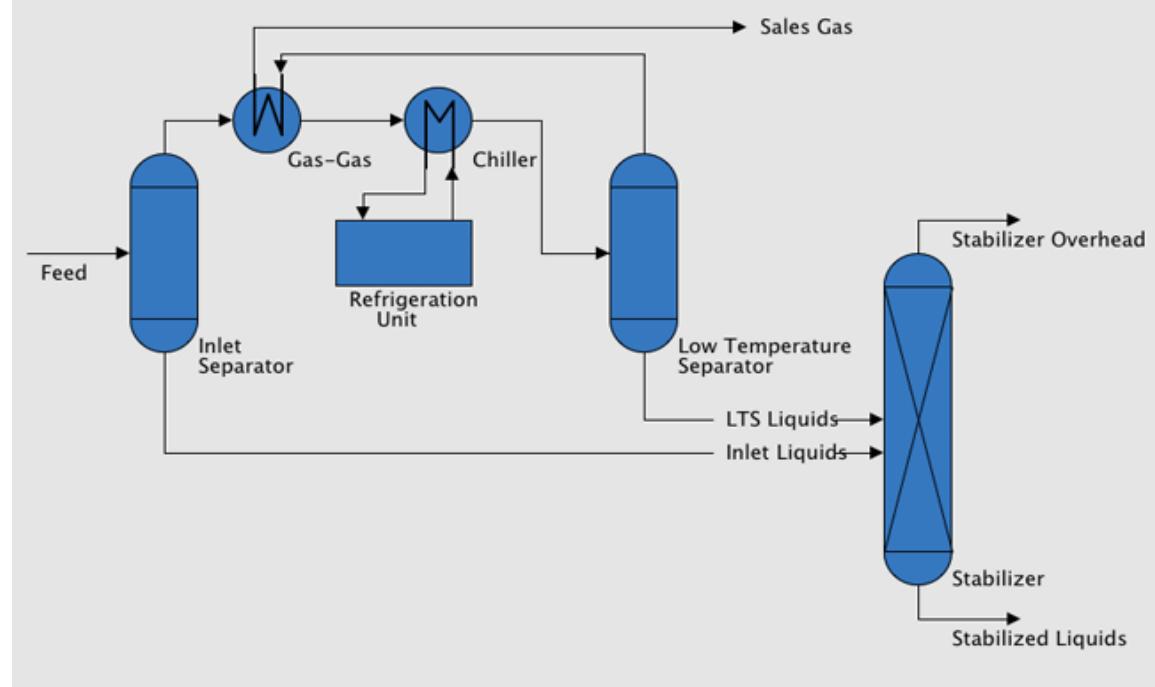
- Refrigeration
- Joule Thomson Expansion
- Turbo Expander

Other schemes include:-

- Silica Gel Beds (as previously mentioned)
- Vortex Tubes

### 7.1 Refrigeration

**Dew Point Control Gas Plant**

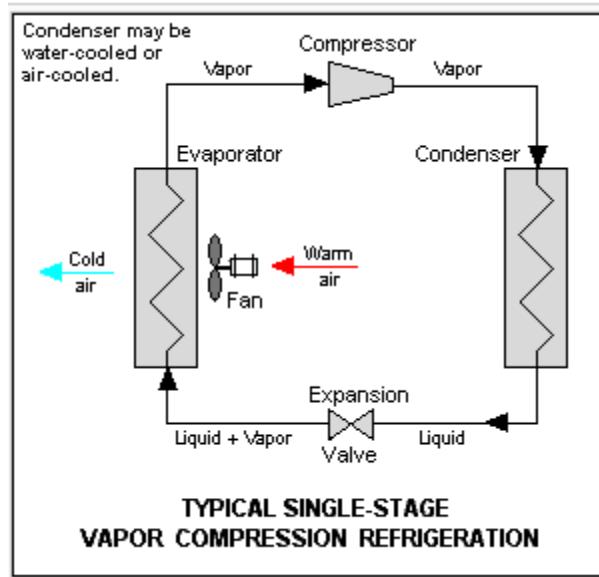


In the above figure the feed is cooled by external refrigeration before passing into the dewpoint separator where the heavier fractions drop out for NGL recovery leaving a low dewpoint gas.

### 7.1.1 Refrigeration Unit

The vapor-compression cycle is used in most household refrigerators as well as in many large commercial and industrial refrigeration systems. The equipment configuration is shown opposite.

In this cycle, a circulating refrigerant enters the compressor as a vapor. The vapor is compressed and exits the compressor superheated. The superheated vapor passes to a condenser which removes the superheat and then condenses



the vapor at essentially constant pressure and temperature. The condensing medium has to be colder than the pressurised refrigerant to affect condensation. The condensing medium is often air or water.

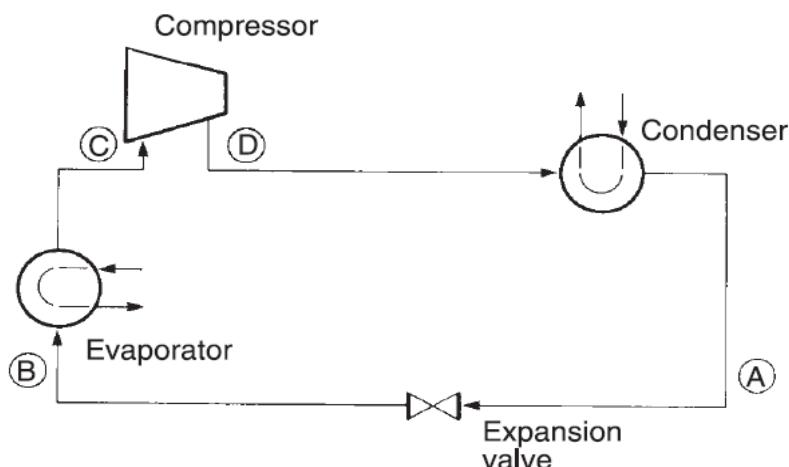
The liquid pressurised refrigerant is expanded across a throttle valve where Joule-Thomson cooling takes place.

The cold liquid-vapor mixture is passed to an evaporator (process cooler) where it is vapourised at essentially constant temperature. The latent heat of vapourisation is the effect which cools the process. The resulting refrigerant vapor returns to the compressor inlet to complete the thermodynamic cycle.

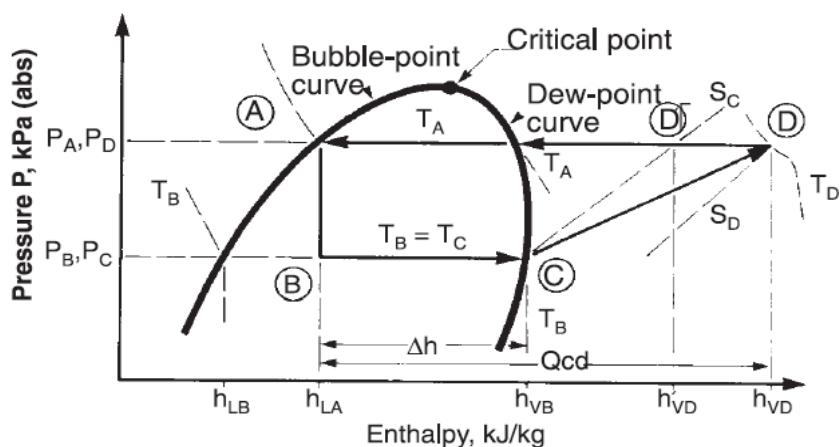
The refrigeration cycle can be broken down into four distinct steps;

- Expansion
- Evaporation – Process Chilling
- Compression
- Condensation

This arrangement is shown together with the associated cycle on a Mollier chart.



Process Flow Diagram



## 7.2 Refrigeration Evaporator/Process Chiller

The most common type of chiller employed in the gas processing industry is the kettle type.

The refrigerant is expanded into the shell of the kettle where a level is maintained to completely submerge the process tube bundle.

When using a kettle type chiller, care should be taken to provide adequate vapour disengaging space above the operating level of liquid refrigerant. This type chiller improperly designed and operated is probably the largest single cause of compressor failure due to liquid carryover.

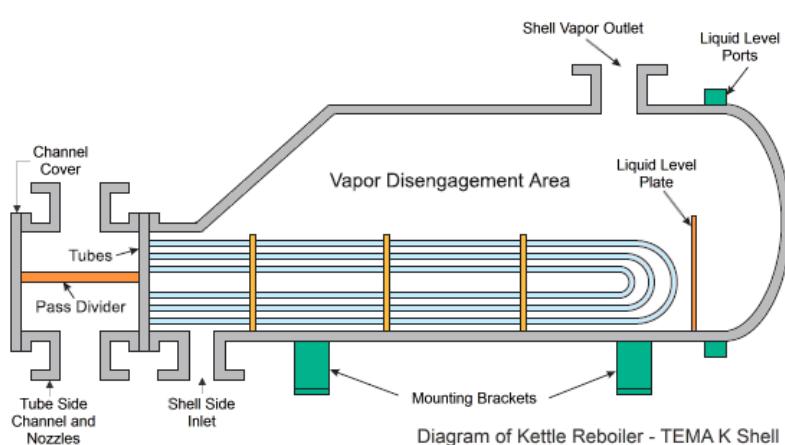


Diagram of Kettle Reboiler - TEMA K Shell

### 7.3 Refrigerants

Selection of the refrigerant is generally based upon temperature requirements, availability, safety, environment and economics. Historical refrigerants are HCFCs (Hydro-chloro-fluro-carbons) and CFCs (Chloro-fluro-carbons) of which Freon R22 is widely used. As a result of ozone depletion effects these chemicals are being replaced with non-ozone depleting refrigerants.

As a Party to the Montreal Protocol, countries must incrementally decrease HCFC consumption and production, culminating in a complete HCFC phase out in 2030. The major milestones that are upcoming for developed countries are a reduction in 2015 to at least 90 percent below baseline HCFC levels and a reduction in 2020 to at least 99.5 percent below baseline.

#### 7.3.1 Classes of Refrigerants

##### Hydrocarbons and Inorganic Compounds

These include ammonia, CO<sub>2</sub>, simple hydrocarbons (propane), and water; they are often referred to as natural refrigerants. They have zero ozone depletion potential (ODP) and low global warming potential (GWP) values. There has been increased interest and application of these refrigerants in recent years, although all of these fluids present one or more drawbacks (such as toxicity, flammability, corrosivity, high pressures, and/or lower efficiency) that require consideration when designing systems.

Ammonia has been used as a refrigerant for more than 150 years. It has excellent thermodynamic characteristics and provides a very high refrigeration effect per unit mass, but the volumetric cooling capacity is similar to many halocarbon refrigerants.

Ammonia is very common in large beverage processing, food storage, and industrial refrigeration systems where its thermodynamic characteristics and low cost are attractive. Absorption chillers with ammonia/water mixture are suitable and cost effective for some specific applications, especially using a waste heat, in Combined Chilling, Heat and Power (CCHP) systems and district cooling.

CO<sub>2</sub> is nonflammable and has low toxicity; its ODP is zero, but it has a GWP. The pressure/temperature characteristics of CO<sub>2</sub>, however, have two major implications for refrigeration system design. It operates at very high pressures, approximately ten times the pressure of halocarbon or ammonia systems. Second, the low critical temperature of 31.0 °C implies a trans-critical cycle in many applications requiring direct heat exchange with the outdoor environment. The high operating pressure makes it a dense refrigerant that requires smaller piping and compressor sizes. Reduced penalties from pressure drops can yield operation and design benefit particularly when evaporator temperatures drop to -30 to -50°C.

CO<sub>2</sub> has been used as a refrigerant since the mid-19th century, but was largely displaced by ammonia and the CFC and HCFC refrigerants by the mid-20th century. There has been a resurgence of interest since the early 1990s as an alternative to the halocarbon refrigerants. It is being used in heat pump water heater applications (primarily in Japan).

Hydrocarbons are constituents of natural gas and petroleum. The most common hydrocarbon refrigerants are propane, butane, and isobutane. They generally have good thermodynamic properties. Hydrocarbons with a wide range of boiling points are available to meet refrigeration requirements over a wide range of temperatures. These refrigerants have zero ODP, low GWP, and are generally of low toxicity. However, they are highly flammable, and this is the major impediment to their wider use. Hydrocarbons have long been used for process refrigeration in the petrochemical industry; here flammability of the refrigerant is not an issue because the products being produced are of similar hazard. Household refrigerators using isobutane as the refrigerant were introduced in Europe in 1992 and now account for more than one-third of global production.

Water could be considered the ultimate in safe and environmentally benign refrigerants, but it has a very low vapor density, requiring large compressors and piping sizes. Pressure drops across components extracts a larger efficiency penalty compared to higher-pressure equipment. The equipment operates under a vacuum posing the problem of drawing air into a system. Development of prototype vapor-compression equipment using water is underway for large chilled-water systems (such as those used in large building air-conditioning).

### **Halocarbon Refrigerants**

The halocarbon refrigerants include one or more of the halogens (i.e., the elements fluorine, chlorine, or much less frequently, bromine or iodine) in a molecule with a carbon backbone. These chemicals were first commercialized in the 1930s and include CFCs (i.e., containing carbon, fluorine, and chlorine), HCFCs (also containing hydrogen), and HFCs (which do not contain chlorine). The most commonly used CFC refrigerants were CFC-12 and CFC-11. The production of these refrigerants was phased out by year end 1995 in developed countries and by year end 2009 in developing countries due to their impact on stratospheric ozone.

The most common HFCs in use are HFC-134a and the blended refrigerants R-410A, R-404A, and R-507. HFC-134a is currently being used for automotive air conditioning, in small refrigeration systems such as home refrigerators and vending machines, and in larger water chillers where screw and centrifugal compressors are employed. R-410A (a blend of HFC-32 and HFC-125) is used in many residential and small commercial air-conditioning systems as the replacement for HCFC-22. It operates at approximately 50% higher pressure, which

dictates redesign of equipment, but this higher pressure does allow for more compact arrangements.

In an attempt to retain the desirable properties of the widely used HFC refrigerants, but with low GWP values, a new class of HFCs has recently been introduced. These incorporate a carbon-carbon double bond into the molecular structure; thus they belong to the chemical class of “olefins” and these new refrigerants are termed HFOs, for “hydrofluoroolefin.” The double bond provides a mechanism for rapid degradation in the atmosphere, leading to low GWP values.

Refrigerant	GWP	ODP	Comments
CFC 12	8100	1	Banned in EU since 2000.
HCFC 22	1500	0.05	Being phased out. Use of these refrigerants should be identified and plans for their replacement developed in accordance with dates set out in regional legislation.
HFC 134a	1300	0	Various HFCs used since mid-1990s as alternatives to ozone-depleting CFCs and HCFCs in a wide variety of stationary and mobile RAC applications. Three examples given here – around 20 others also available. HFC 134a is being phased out in the EU and is proposed to be phased out in the US for mobile air conditioning systems.
HFC 404A	3300	0	High global warming potential and subject to regulation in the EU, with likely regulation in the US. Potential for phase out in the longer term as alternatives become available.
HFC 410A	1725	0	
FC	~10	0	New refrigerants; very low GWP. Not yet commercially available.
CO <sub>2</sub>	1	0	Operates at very high pressure.
Hydrocarbons	3	0	Widely used in very small systems; highly flammable.
Ammonia	0	0	Used in large industrial systems; toxic and combustible.

ODP – ozone depletion potential

GWP – global warming potential

#### 7.4 Staged Refrigeration

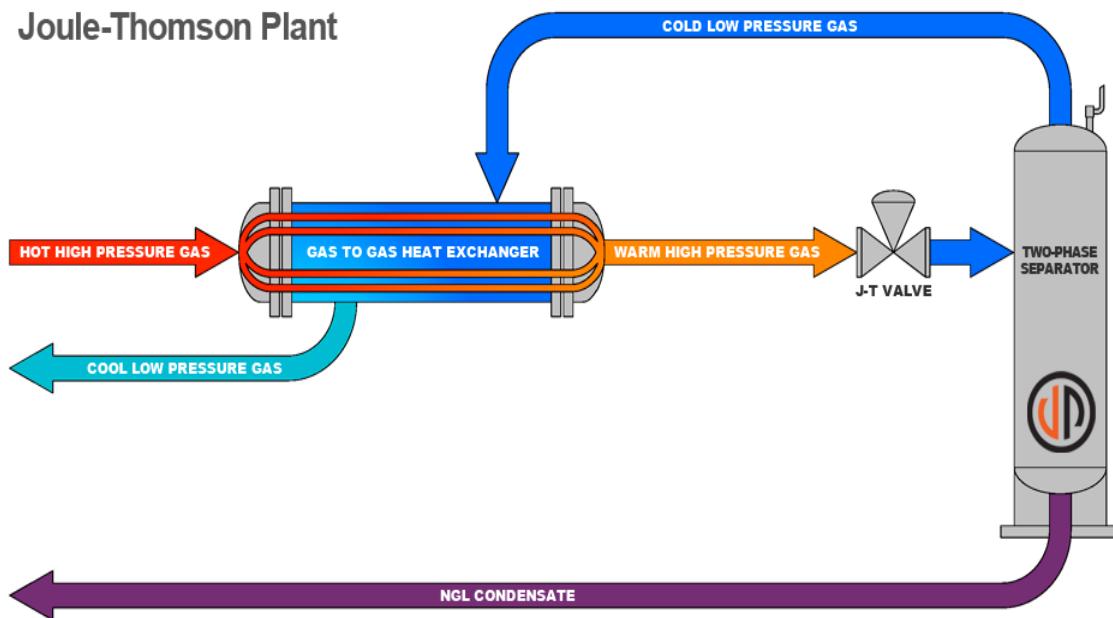
Energy consumption is frequently reduced as the number of stages is increased. However, the installation cost of such refrigeration systems increases as the number of stages increases. The optimum overall cost will be a function of the specific system and has to be determined for a set of economic criteria. This is presented later in the energy efficiency modules.

### 7.5 Joule Thomson Expansion

As a gas expands, the average distance between molecules grows. Because of intermolecular attractive expansion causes an increase in the potential energy of the gas. If no external work is extracted in the process and no heat is transferred, the total energy of the gas remains the same because of the conservation of energy. The increase in potential energy thus implies a decrease in kinetic energy and therefore in temperature.

A second mechanism has the opposite effect. During gas molecule collisions, kinetic energy is temporarily converted into potential energy. As the average intermolecular distance increases, there is a drop in the number of collisions per time unit, which causes a decrease in average potential energy. Again, total energy is conserved, so this leads to an increase in kinetic energy (temperature). Below the Joule–Thomson inversion temperature, the former effect (work done internally against intermolecular attractive forces) dominates, and free expansion causes a decrease in temperature. Above the inversion temperature, gas molecules move faster and so collide more often, and the latter effect (reduced collisions causing a decrease in the average potential energy) dominates: Joule-Thomson expansion causes a temperature increase.

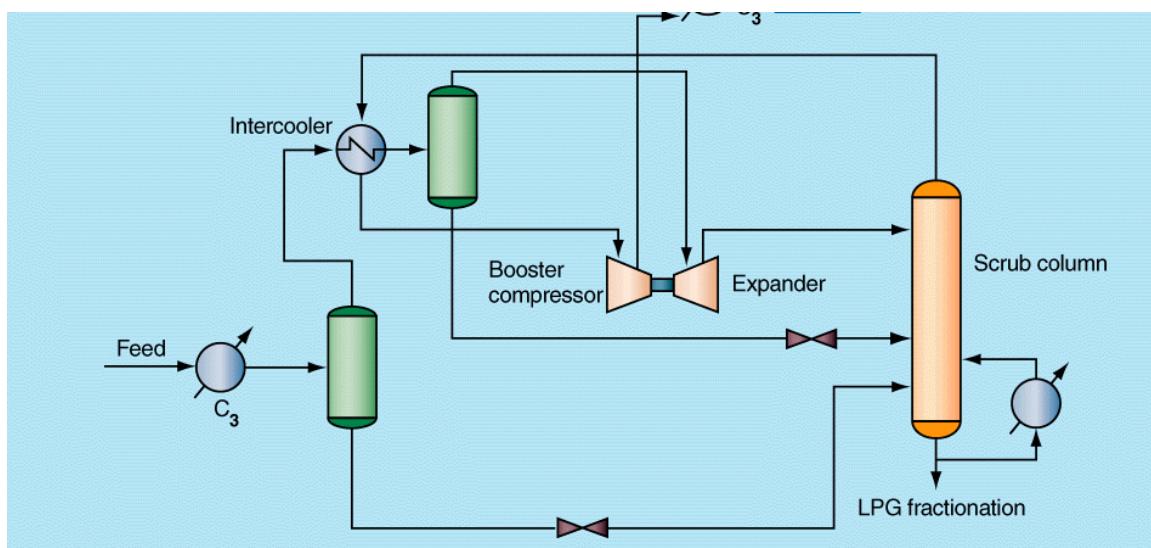
**Joule-Thomson Plant**



The feed is first cooled and then expansion is achieved by pressure let-down through a Joule-Thomson valve. The liquid is taken off in the separator drum.

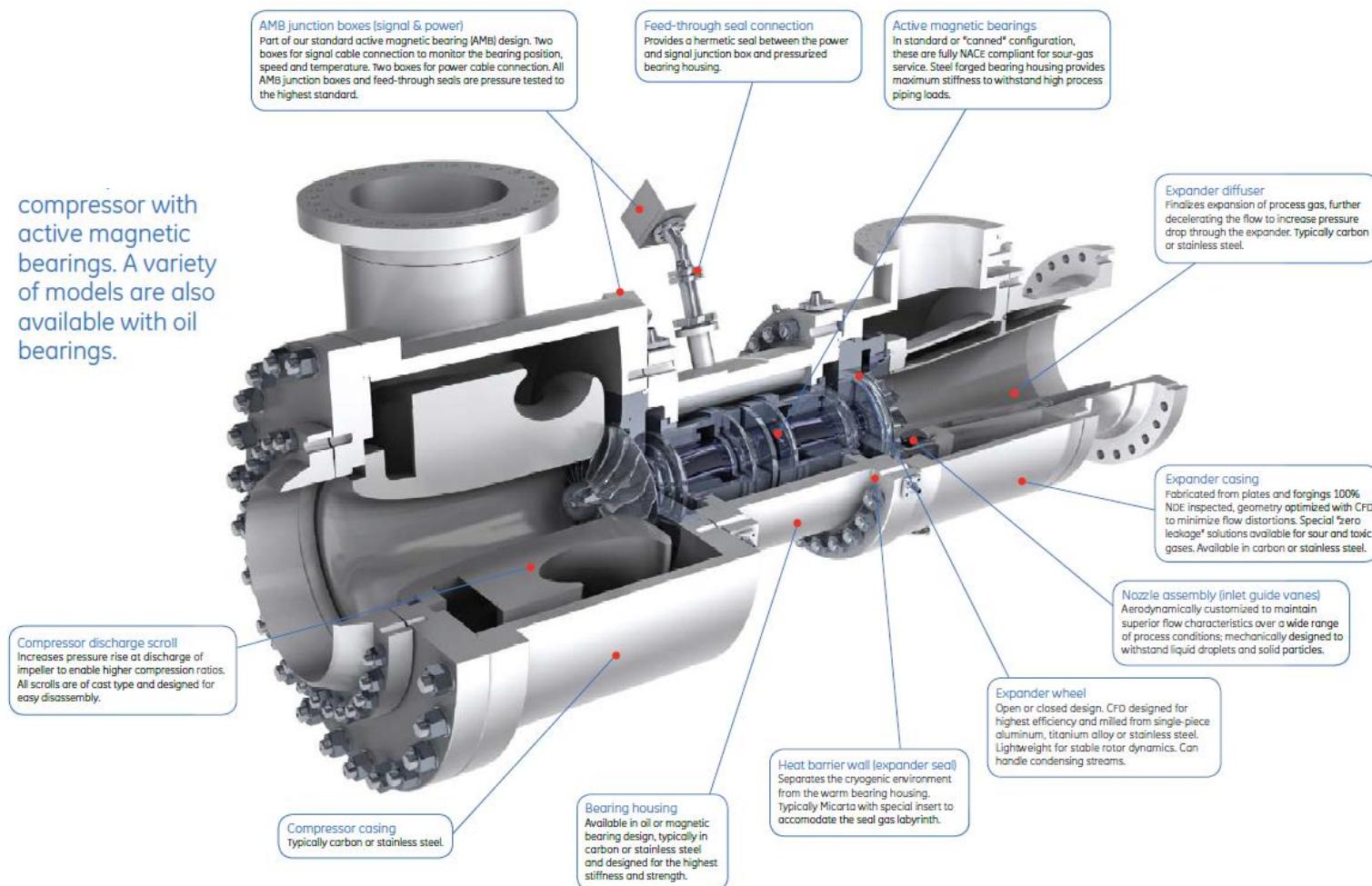
### 7.6 Turbo-Expansion

Here the feed is expanded through an expansion turbine, where the gas cools through pressure let down and the extraction of energy. The liquid is separated and the gas is recompressed by a second compression wheel using the power generated from the original expansion.

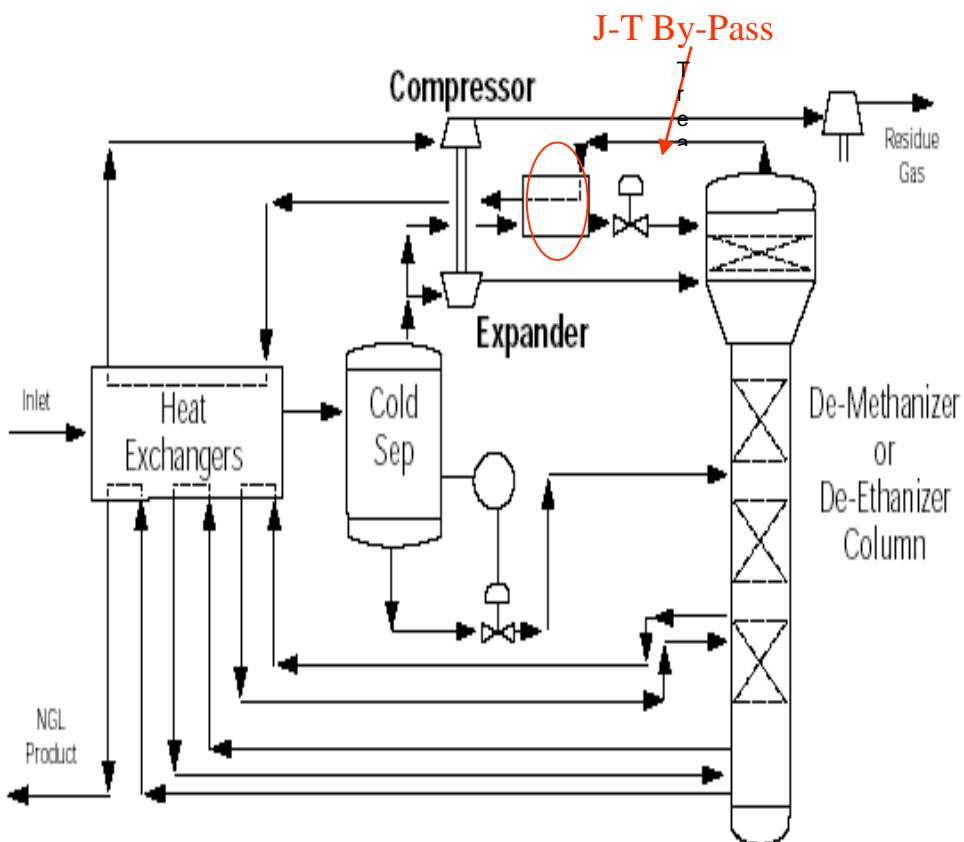


Details of the expander compressor arrangement follow.

compressor with active magnetic bearings. A variety of models are also available with oil bearings.



A typical arrangement is shown;



The above arrangement makes use of the temperature gradient over the column through multiple heat exchange paths with an inlet coldbox.

### Expander Compressor Guidelines

Gas / Gas exchanger approach between hot and cold streams 5 - 10°C,

Refrigeration cooler approach between cold gas and refrigerant streams 5 - 10°C.

These temperature approaches represent initial estimates and should be subject to optimisation as design is developed.

For a turbo expander / recompressor scheme typical polytropic efficiencies are:

Turbo Expander 75%

Recompressor 75%

Other criteria for the turbo expander selection are :

maximum proven machine approx. 5 MW (Check with vendors for latest status)

maximum pressure ratio 2.5 : 1

liquid content of outlet up to 40% wt

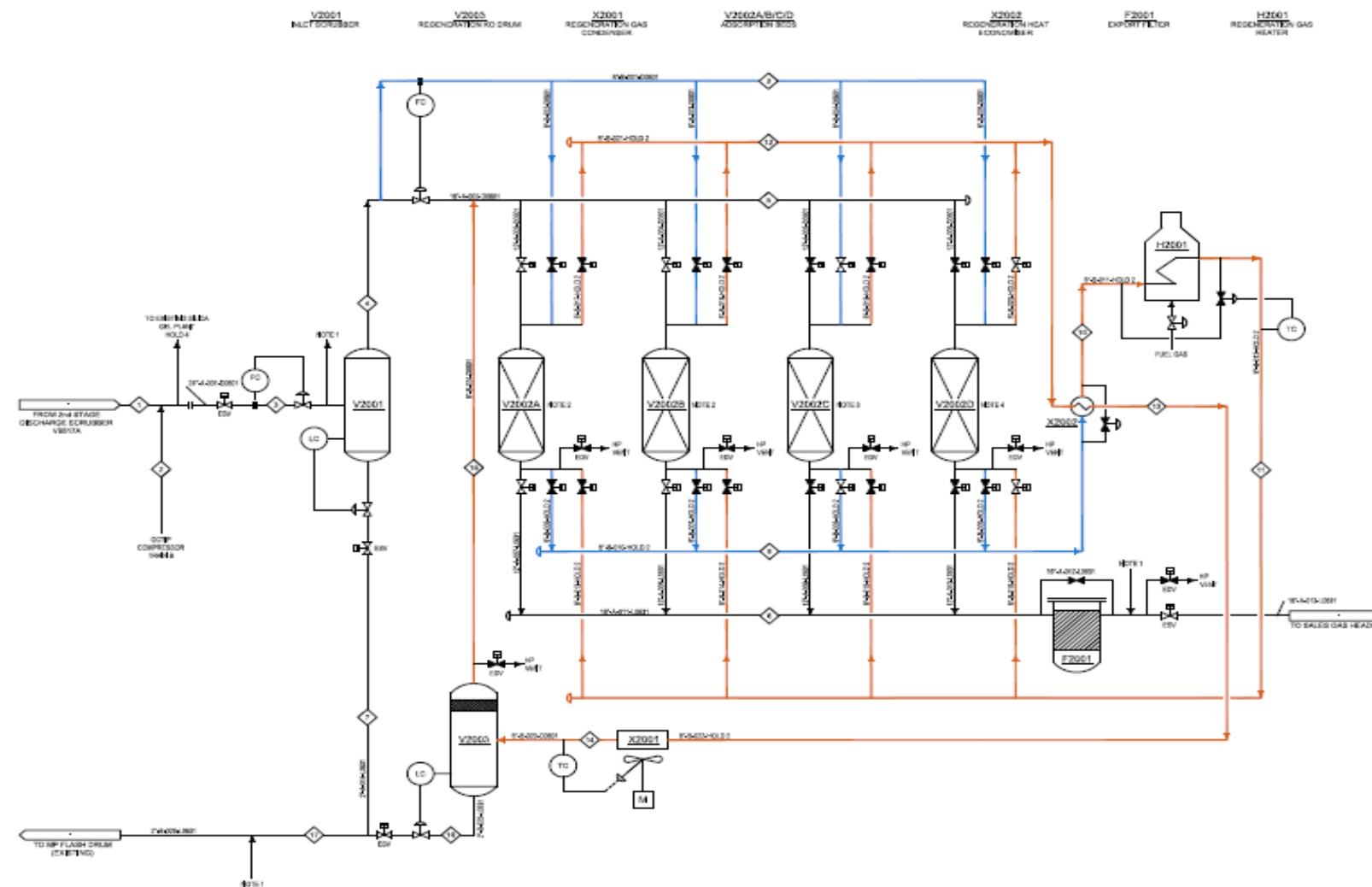
### 7.7 Silica Gel Dewpointing

Silica gel is a porous, amorphous form of silica ( $\text{SiO}_2$ ). Although it has the same chemical composition as sand, silica gel is radically different from other  $\text{SiO}_2$ -based materials, due to its unique internal structure.

The internal structure of silica gel is composed of a vast network of inter-connected microscopic pores that attract and hold water, alcohols, hydrocarbons and other chemicals on their surface through phenomena known as physical adsorption and capillary condensation. This phenomena can be reversed by changing the conditions under which adsorption takes place, pressure reduction.

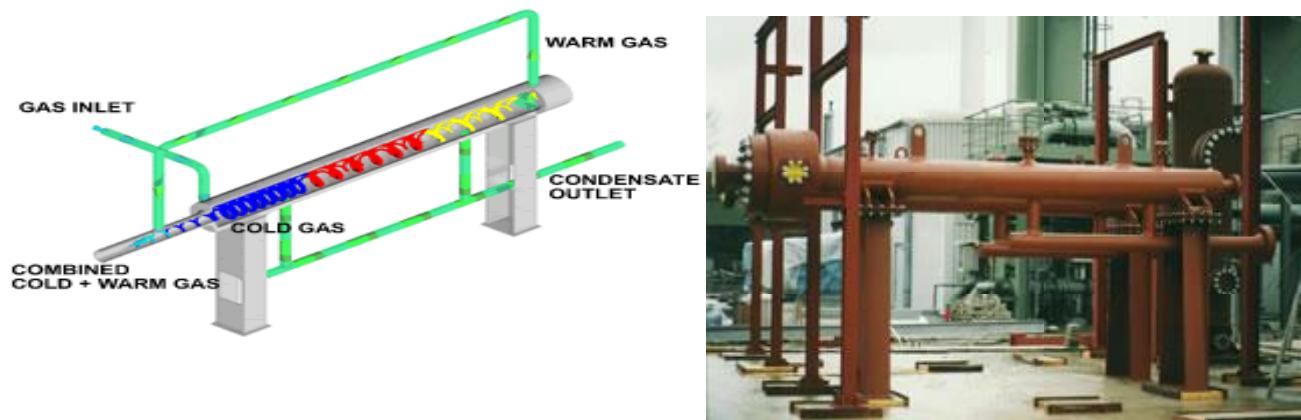
In some circumstances silica gels can be used to adsorb the heavier hydrocarbon components in a gas to meet transportation or treatment specifications.

A typical PFD follows.



## 7.8 Vortex Tube

A vortex tube can be used to produce hot and cold gas plus a liquid using the Hilsch effect. The Hilsch effect refers to the tangential introduction of a gas stream through a nozzle creating a forced vortex which leads to a simultaneous separation of the gas and liquid in the gravitational field of the vortex and at the same time causing a temperature gradient to form across the vortex (the temperature reduces from the wall to the tube centre). Due to the temperature gradient the expansion moves away from a Joule Thomson process (adiabatic expansion) towards a more efficient isentropic expansion. No rotating parts are an advantage but this device has received little interest though Ruhr Gas have some industrial units.



## 7.9 Selection Criteria

Deciding whether to adopt a refrigeration unit, a turbo-expander or a Joule-Thomson valve will involve a multi criteria assessment. When faced with alternative options to provide the same goal, in the case low temperature, the engineer must balance the following areas;

Capital Cost – CAPEX – how much does it cost to buy and install?

Operating Cost – OPEX how much does it cost to operate?

Availability – plant uptime, frequent breakdowns will impact production

Revenue – how much cash flow will the option deliver?

Safety – what are the key safety implications of the competing options?

Environmental – what is the environmental footprint of the competing options?

## 8 Acid Gas Treatment

Hydrogen Sulphide ( $H_2S$ ) and Carbon Dioxide ( $CO_2$ ) are often found with oil and gas fields.

The requirement for acid gas treatment is dependant on various criteria.

### $H_2S$ Removal

Acid gas treatment may be required to limit the concentration of  $H_2S$  in the fuel gas, pipeline and sales specifications. Minimising impact on environment may be another reason for treatment.

## CO<sub>2</sub> Removal

Where economics dictate the requirements i.e. where savings in compression and transportation costs outweigh the cost of the treatment unit.

CO<sub>2</sub> could be used for enhanced oil recovery (EOR) schemes – miscible gas injection.

Like H<sub>2</sub>S, minimising impact on environment may be another reason for treatment.

The CO<sub>2</sub> could be used for carbon capture and sequestration (CCS) schemes.

Other components which may require treatment/consideration are;

- Hydrogen Cyanide (HCN)
- Carbonyl Sulphate (COS)
- Carbon Disulphide (CS<sub>2</sub>)
- Mercaptans (RSH)
- Nitrogen (N<sub>2</sub>)
- Sulphur Dioxide (SO<sub>2</sub>)
- Mercury (Hg)

### 8.1 Hydrogen Sulphide Removal

H<sub>2</sub>S emissions from oil & gas development have the potential to pose a significant health risk and is odourless at concentrations above 0.2ppm because it quickly degrades the sense of smell.

H <sub>2</sub> S Concentration (ppm)	Health Issue
≤ 0.2	Odour threshold
10	Eye irritation
100	Headache, dizziness, vomiting, heavy coughing
200 – 300	Eye & respiratory tract inflammation
500 – 700	Loss of consciousness – <i>death within 30 – 60 minutes</i>
700 – 900	Rapid loss of consciousness – <i>death within 30 minutes</i>

$\geq 1000$	Unconsciousness in seconds – <i>death within minutes</i>
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Note - H<sub>2</sub>S is also an extremely flammable substance - H<sub>2</sub>S vapour can travel considerable distance to a source of ignition and flash back explosively.

Any sulphur components are undesirable as they can poison catalytic processes and cause acid rain when combusted as a fuel.

## 8.2 Amine Gas Treatment

Amine gas treating, also known as gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkanolamines (commonly referred to simply as amines) to remove hydrogen sulphide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) from gases. It is a common process used in refineries, petrochemical plants, natural gas processing plants and other industries.

Processes within natural gas processing plants that remove hydrogen sulphide and/or mercaptans are commonly referred to as sweetening processes because they result in products which no longer have the sour, foul odours of mercaptans and hydrogen sulphide.

There are many different amines used in gas treating:

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Methyl-diethanolamine (MDEA)
- Diisopropylamine (DIPA)
- Aminoethoxyethanol (diglycolamine) (DGA)

The most commonly used amines in industrial plants are the alkanolamines MEA, DEA, and MDEA. Note that the chemical suppliers often increase the reaction efficiency by including proprietary activators with the amine.

A typical amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the downflowing amine solution absorbs H<sub>2</sub>S and CO<sub>2</sub> from the upflowing sour gas to produce a sweetened gas stream (H<sub>2</sub>S-free gas) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H<sub>2</sub>S and CO<sub>2</sub>.

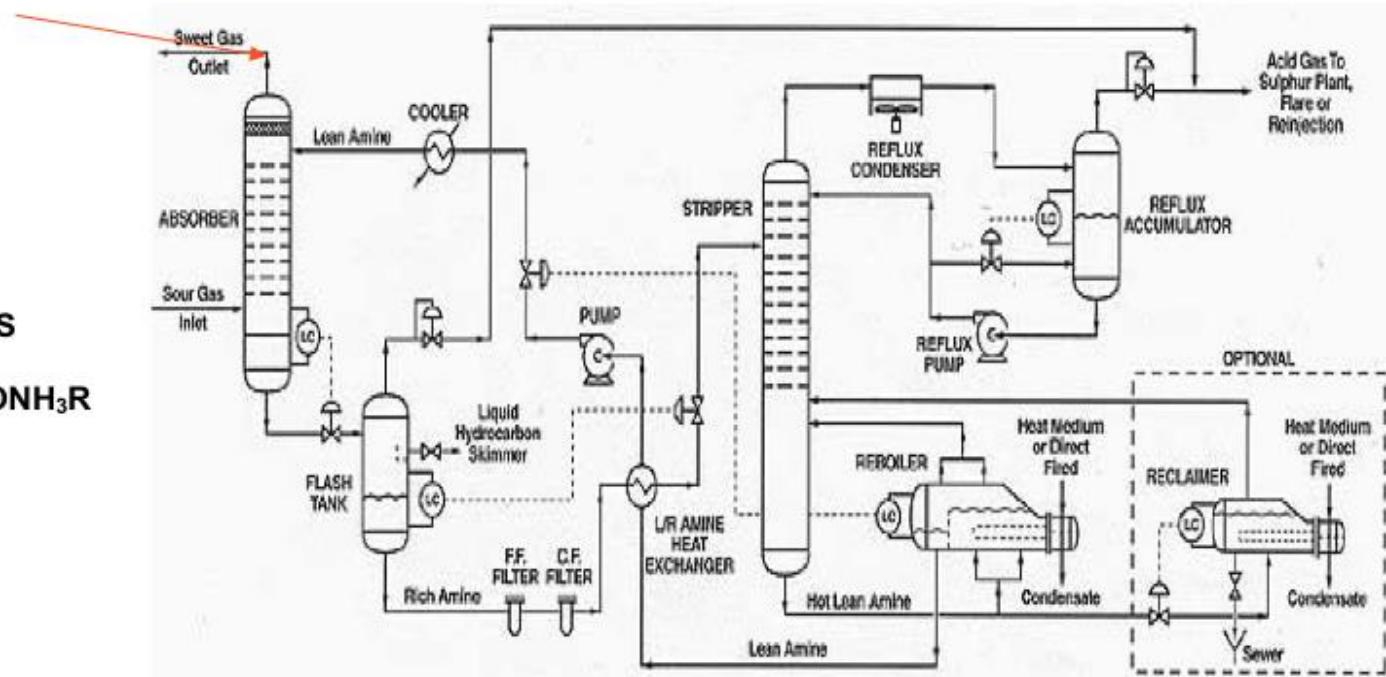
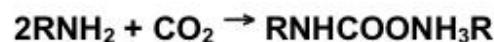
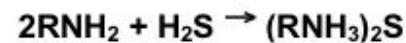
Offshore the stripped gas is usually sent to a flare where the H<sub>2</sub>S is burned to SO<sub>2</sub>. In oil refineries, that stripped gas is mostly H<sub>2</sub>S, much of which often comes from a sulphur-

removing process called hydrodesulphurization. This H<sub>2</sub>S-rich stripped gas stream can be routed into a Claus process to convert it into elemental sulphur.

A typical amine unit PFD follows.

Water Saturated

Basic Amine  
Sweetening Plant



Typical Properties /  
Process Conditions

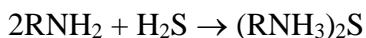
Comp	Pvap @ 38 C mbar	Aq. Sol. wt%	T cont C	T strip C
MEA	1.400	10 - 20	30 - 60	90 - 115
DEA	0.077	10 - 20	30 - 60	90 - 115
DGA	0.213	40 - 70	60 - 85	125 - 140

It should be recognised that amines are aqueous solutions hence the treated gas will be water saturated. Consequently a gas dehydration unit is likely to follow amine treatment.

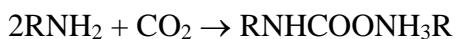
### Amine Chemistry

Amines with stronger base properties will be more reactive towards H<sub>2</sub>S and CO<sub>2</sub> and will form stronger chemical bonds. As the amine reactivity increases, i.e. from tertiary amine to primary amine, then the acid gas vapour pressure over the amine will be lower for a given loading and a higher equilibrium loading may be achieved.

The reactions between an amine and H<sub>2</sub>S and CO<sub>2</sub> occur according to the following equations (shown for a primary amine) are:



CO<sub>2</sub> reacts predominantly via the reaction below, forming a carbamate with primary and secondary amines.



The main difference with tertiary amines compared to primary and secondary amines is that CO<sub>2</sub> does not react to form carbamate.

The reaction of H<sub>2</sub>S is nearly instantaneous with all amines. The reaction rate of CO<sub>2</sub> is much slower and widely variable for different amines. The slowness of the CO<sub>2</sub> reaction with tertiary amines, means that tertiary amines have the highest selectivity to H<sub>2</sub>S. This accounts for MDEA's wide use in H<sub>2</sub>S selective service.

Corrosion occurs in places where the highest concentrations of wet gases encounter the highest temperatures (e.g. lean-rich solvent exchangers, strippers and reboilers).

Solution degradation can occur as air (oxygen), COS, SO<sub>2</sub> and sometimes CO<sub>2</sub> react with the amines and form insoluble salts and corrosion products. These are removed by filters located in the regeneration system.

Some of the materials that can cause foaming problems in amine units include suspended solids, condensed hydrocarbons, amine degradation products and most foreign materials such as corrosion inhibitors, valve grease or even impurities in the make-up water. The installation of a scrubber and/or separator in the feed gas line is essential to reduce degradation and foaming problems.

### 8.3 Flash vessels

A flash vessel may be necessary between the absorber and the regenerator when substantial amounts of hydrocarbons are co-absorbed with the acid gases, or when CO<sub>2</sub> is to be preferentially flashed out from the solvent if it contains high CO<sub>2</sub> to H<sub>2</sub>S ratios. Flashing out CO<sub>2</sub> before the stripper enriches the H<sub>2</sub>S content in the acid gases sent from the regenerator, which improves the operation of any associated sulphur recovery plant.

Flash vessel also reduces erosion in downstream equipment.

In the recent years, MDEA has gained a large share of the gas treating market. Many companies are offering their own version of MDEA (BASF's aMDEA, Union Carbide's UCARSOL, Shell's SCOT process, etc.). It has a relatively low energy requirement, low vapour pressure, degradation resistance and it is selective to H<sub>2</sub>S in the presence of CO<sub>2</sub>. The increasing demand for a selective H<sub>2</sub>S removal process has focused attention to the merits of MDEA. The principle application in recent years has been for the selective removal of H<sub>2</sub>S from CO<sub>2</sub> used for Enhanced Oil Recovery.

A process was developed by BASF Aktiengesellschaft and uses activated MDEA (aMDEA) solution, which is regenerated by flashing rather than steam stripping. The process is mostly used for removing CO<sub>2</sub> from ammonia synthesis gas.

Activated MDEA can be used for the removal of CO<sub>2</sub>, H<sub>2</sub>S and COS from natural gas and other gases.

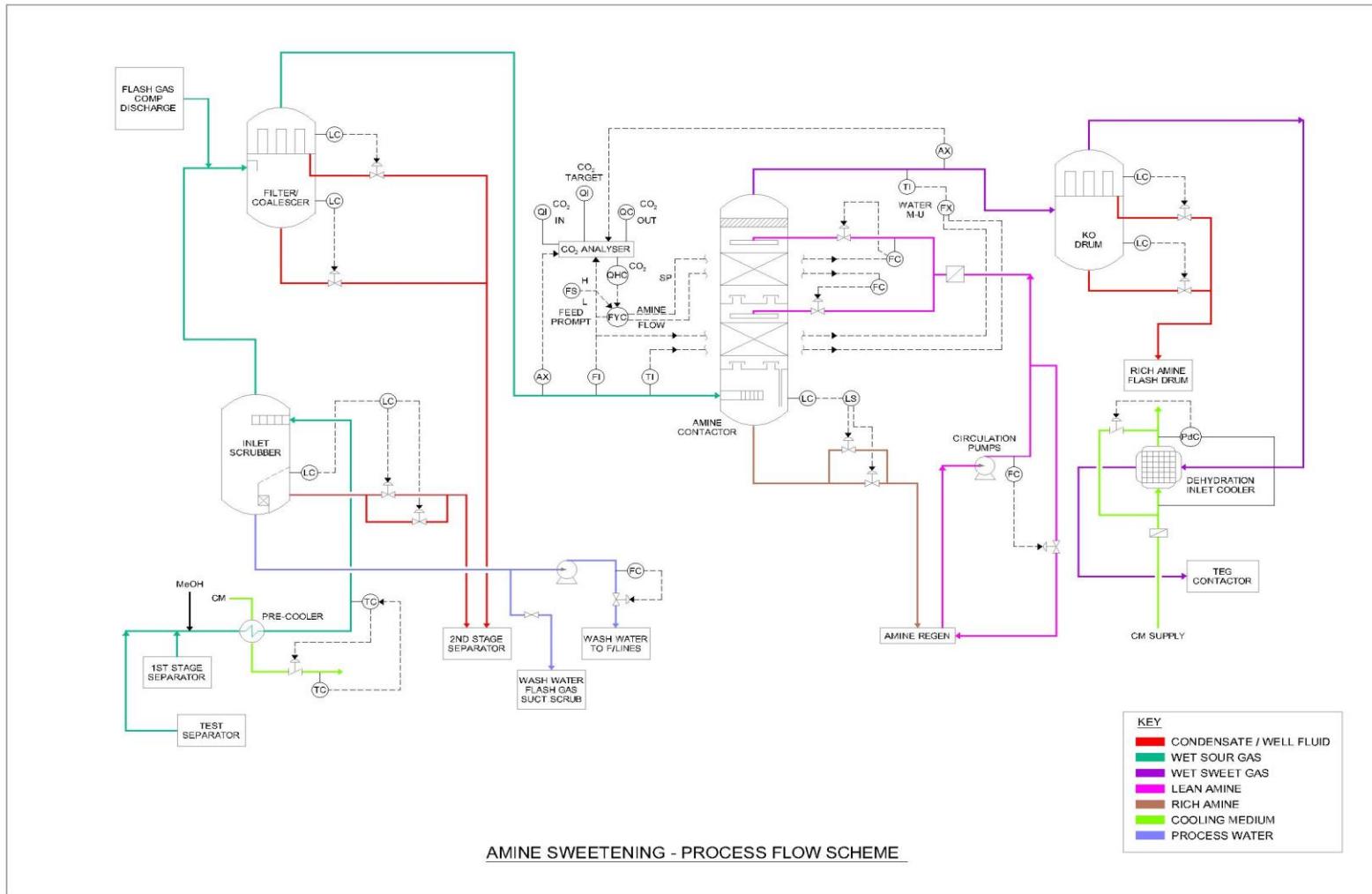
### Amine System Description

The following narrative is for an offshore plant designed to produce a maximum CO<sub>2</sub> limit of 2.0 mol% is often applied to the Sales Gas. A more stringent specification could be met (i.e. the process selected could remove more CO<sub>2</sub>) but it would prove uneconomic for this particular development.

The H<sub>2</sub>S has to be removed to give a maximum limit of 2 ppmv in the Sales Gas. In fact, the design of the plant will remove virtually all the H<sub>2</sub>S to give an export gas content of less than 1ppmv.

Bearing in mind what has been said, the purpose of the sweetening plant is to maximise the removal of H<sub>2</sub>S from the Sales Gas whilst at the same time controlling the CO<sub>2</sub> removal. The economics of the process employed are very closely tied to the CO<sub>2</sub> removal level and also the quantity removed daily. For these reasons the amount of CO<sub>2</sub> left in the gas has to be controlled within a tight band - termed the "CO<sub>2</sub> slippage".

The PFD for the process is shown.



Sour, wet gas from both the first-stage and test separator combines at the inlet of the amine pre-coolers, where it is cooled against cooling medium to 45 °C. This gas stream represents approximately 90% of the total feed to the amine gas sweetening system.

The resultant three-phase mixture from the coolers is separated in the amine inlet scrubber. The two- phase liquid mix is segregated in the base of the vessel into hydrocarbon and aqueous phases. The former is returned to the second-stage separator whilst the water can, in future, be used as wash water. Initially the water will overflow the internal weir and be returned to the second-stage separator.

Gas from the top of the scrubber is routed to the amine inlet filter/coalescer where it is combined with the hot discharge gas from the Flash Gas compressor, which represents the remaining 10% of the total gas flow. This mixing raises the gas temperature to give approximately 5 °C of superheat to prevent liquid condensation and consequent foaming problems in the contactor. The vessel is designed to provide high efficiency separation of virtually all particulate and droplets. Liquids separated in the vessel are returned to the second- stage separator. The gas leaving the filter/coalescer section of the vessel is routed to the inlet of the amine contactor. Amine units are prone to foaming and any liquid carryover is to be avoided.

The contactor consists of three sections; an inlet gas/liquid separation compartment at the base and two beds of structured packing where the gas/amine contact occurs. The sour feed gas at approximately 86 barg and 50 °C is passed upwards through the contactor against a counter-current flow of lean amine solution which is at approximately the same temperature. The amine absorbs the bulk of the H<sub>2</sub>S and approximately half of the CO<sub>2</sub>. The sweetened gas passes out of the top of the contactor through a demister section.

The absorption process is exothermic which results in a rise in gas temperature such that it is at approximately 70 °C at the outlet. The outlet gas is routed to a KO drum, where any amine carryover is removed, before being passed on to the dehydration plant. Any liquid accumulating in the KO drum is routed to the inlet of the amine regeneration plant.

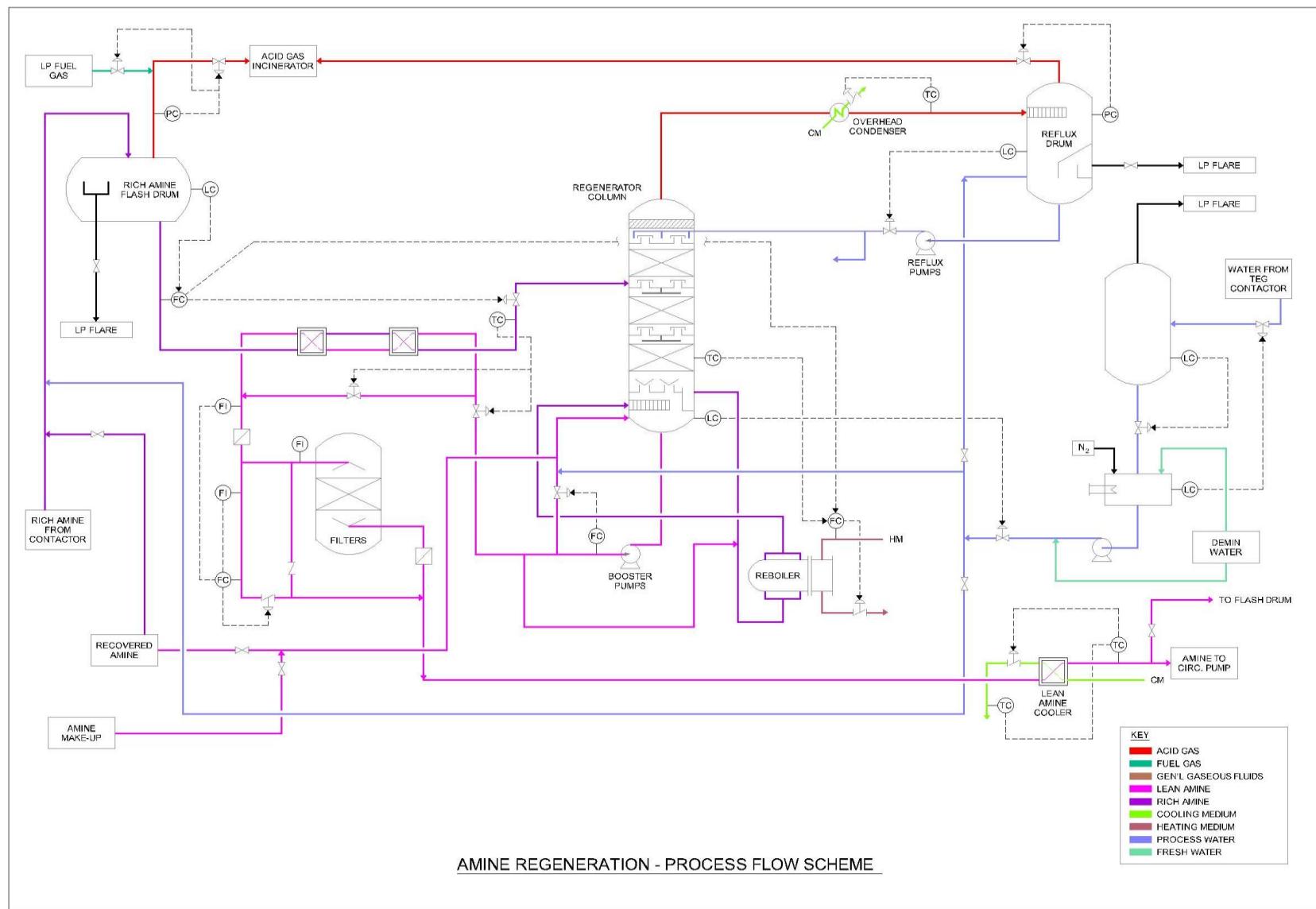
Typical droplet capture is around 0.3-0.5 microns.

The temperature of the gas is finally reduced to 26 °C at the inlet to the dehydration plant by cooling it against cooling medium in the dehydration inlet cooler.

Efficient and economic operation of the amine plant requires matching the amine flowrate to acid gas load and consequently the level of CO<sub>2</sub> in the contactor outlet. The contactor control system has, therefore, been designed to control lean amine flow to meet a desired CO<sub>2</sub> outlet

concentration (slippage) with an element of feed forward control based on the acid gas loading (i.e. inlet flowrate and inlet CO<sub>2</sub> concentration). The required turndown ratio for the contactor to achieve the desired CO<sub>2</sub> slippage over a wide range of inlet flows has been achieved by giving the operator the ability to select either a single or double bed contactor configuration. Either amine feed point can be used for a wide range of conditions. However, the upper feed point will always give greater contact time and the possibility of excessive absorption of acid gas. Use of the lower point will always involve a higher amine flowrate. Amine, rich in reaction products, leaves the bottom of the amine contactor at 54 °C under level control and passes to the regeneration system.

The regeneration system PFD follows



The regeneration process involves reversing the absorption reaction chemistry. Since the absorption process is exothermic, it follows that the reverse reactions must be endothermic.

The regeneration process therefore involves reduction in the pressure to slightly above atmospheric and then heating the rich amine solution.

The rich amine is first routed to a low-pressure rich amine flash drum operating at 5.2 barg.

The pressure let down from contactor pressure allows entrained gas to be flashed off under vessel pressure control, whilst the residence time afforded by the vessel acts as a buffer to attenuate flow variations into the regenerator. The flashed gas is rich in acid gas and is routed to an acid gas incinerator for safe disposal.

The rich amine liquid is released on level control to the regenerator column. The rich amine feed is heated to approximately 100 °C by exchange with the lean amine return to the contactor in the rich/lean amine exchangers. Downstream of the heat exchangers the pressure of the system is reduced to regenerator pressure of 0.6 barg across the rich amine control valve. The valve is placed close to the inlet nozzle of the column to minimise pressure loss in the piping system and hence reduce pipe diameter.

The regenerator consists of four sections. Bottom to top they are; a bottom reboil section; two beds of structured packing – the lower and upper stripping beds; and a top bed of structured packing - the rectifying bed. On top of each stripping section a chimney type draw-off tray collects liquid from above and redistributes it across the bed below. This improves contact efficiency and hence regeneration efficiency. A total draw-off tray with chimney risers is located below the bottom bed where the amine solution is accumulated and fed to the thermosyphon reboiler. A two-phase reboiler return enters the tower below the total draw-off. The rich amine feed enters the column at the chimney tray above the upper stripping bed and travels down the column until it reaches the total draw-off. It picks up heat from the ascending vapour (essentially water saturated CO<sub>2</sub>) and is at approximately 119 °C at the draw-off. The liquid flows by gravity to the reboiler where it is heated to generate steam and provide the energy to reverse the absorption reactions. Heat input for the reboiler is provided by the heating medium system with the flowrate controlled to maintain the desired regeneration temperature of 118 °C at the mid height of the lower stripping bed. The reboiler returns a two-phase mixture back into the column. The column base is sized to act as the inventory hold-up capacity for the system (including drain-down during shutdowns).

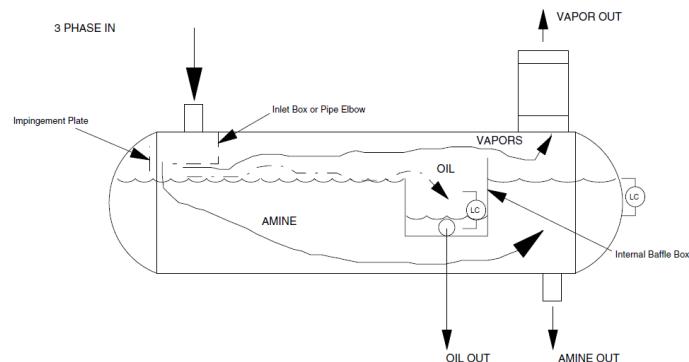
Flash steam and hot acid gases generated in the reboiler travel upwards through the beds, stripping more gases from the downflowing amine. The amine solution at the base of the column is essentially free of acid gas reaction products and is pumped from the regenerator to

the rich/lean amine exchangers by the amine booster pumps where it is cooled to 58 °C by exchange with the incoming rich amine stream.

The cooled, lean amine is slipstream filtered to remove particulate and dissolved residual hydrocarbons in a series configuration of filters consisting of cartridge/carbon/cartridge filters in that order. Amine systems become contaminated with organic and inorganic solids, this can lead to foaming in the contactor and stripper. The cleaned-up amine is then cooled in the lean amine cooler to 52°C by exchange with cooling medium. Finally, the amine pressure is increased for re-entry to the amine contactor by the amine circulation pumps.

The demand rate for amine is set by the desired CO<sub>2</sub> slippage, the feed gas flowrate and acid gas loading as previously mentioned. In steady state and with negligible losses the level in the base of the regenerator should remain constant. This is not practical and losses do occur which leads to a depletion in inventory. The primary loss is that of water from the top of the column. The level in the regenerator is, therefore maintained by a make-up system. The primary source of water make-up is the aqueous phase produced in the dehydration inlet cooler and separated out in the bottom gas/liquid separation section of the TEG contactor. Fresh amine make-up and recovered amine is routed to the base of the regenerator. Amine solutions degrade in the presence of air to form acidic compounds such as acetic acid. To avoid this, the design of the system attempts to exclude air in the regeneration system. The water and amine make-up tanks are nitrogen blanketed as is the amine drainage sump tank. The water saturated stripped acid gases pass overhead from the regenerator column through a demister and are cooled to 35 °C in the overhead condenser. The acid gases are separated in the reflux drum and released under pressure control to the acid gas incinerator for safe disposal. The condensed water contains dissolved acid gases - sour water. The water is returned to the column as reflux pumps and enters the column above the rectifier bed. The reflux can be diverted to the rich amine flash drum in instances where foaming occurs in the regenerator.

The flash drum operates as a typical three phase separator as indicated.



## 8.4 Operational Issues

Many issues are linked to the production or introduction of contaminants. Amine contaminants can be grouped into five distinct categories; (1) heat stable salts, (2), degradation, (3) injection chemicals, (4) hydrocarbons and (5) particulates. All of these contaminant categories can typically be present in any given amine system at the same time, although the amount of each one can vary from insignificant to several per cent.

### **Heat Stable Salts:**

Strong acid anions such as formate, acetate, thiosulphate, thiocyanate, and chloride can tie up an amine molecule to form a salt that is not capable of being regenerated by the addition of heat, and are thus referred to as Heat Stable Salts. Not only do they tie up the amine and thereby reduce the acid gas carrying capacity, but they are also considered corrosive.

However, there is still a considerable amount of confusion in the industry over the term “Heat Stable Salt”. Many times the term is used in a generic sense to mean “contaminant”, while in fact it is only one type of amine contaminant, and may not even be the most offensive contaminant. New engineers assigned to amine and sulphur plant areas, then often assume that the only contaminants in their amine system are the Heat Stable Salts. This idea can be reinforced when lab analyses show only Heat Stable Salt contaminants, but do not report other types of contaminants such as degradation products.

### **Degradation:**

Degradation products are contaminants in solution that are derived from the breakdown of the base amine molecule itself, often irreversibly, to form totally different chemical species.

Examples of degradation products are the ethylenediamine derivatives which can form when CO<sub>2</sub>, COS or O<sub>2</sub> are in an amine system. Degradation products continue to be the target of ongoing research as to any negative effects on amine solutions (corrosivity and other physical properties). Because they have only recently been considered important to measure, degradation products, such as bicine, are difficult for labs to consistently measure in small quantities, and can add to analysis expense.

### **Injection Chemicals:**

Corrosion inhibitors from upstream pipeline operations and amine system injections, such as anti-foam chemicals can concentrate in amine systems. While these chemicals are excellent in controlling operating problems, their injection into an amine system over the months and years between turnarounds can build up to a substantial percentage of the amine concentration. A large build up of injection chemicals can eventually lead to fouling and can cause changes in solution physical properties, such as viscosity and mass transfer.

**Hydrocarbons:**

Heavy hydrocarbons from natural gas streams can condense in the contactor, and lubrication oil from upstream reciprocating compression can build up in amine systems over time. These hydrocarbons can cause foaming, and at high enough concentrations can change amine solvent physical properties.

**Particulates:**

Typical insoluble particulates include iron sulphates, metals from equipment corrosion, charcoal from amine filters, and catalyst fines from upstream units. Amine manufacturers and suppliers stress overall solvent quality. When thinking about overall amine hygiene, it should be kept in mind that any compounds in an amine system that are not either (1) amine or (2) water are considered contaminants, and should be removed when they exceed recommended levels.

**Feed Gas Contaminants:**

In natural gas service, contaminants entering with the feed gas are generally less troublesome than refinery feed gas contaminants. Contaminants in natural gas feeds that typically cause the most problems in amine systems are oxygen, carbonyl sulphide, and carbon dioxide, and hydrocarbons. It is not uncommon for small amounts of oxygen to be drawn into the suction side of low-pressure field compressors in natural gas gathering systems. The oxygen molecule will then react to provide a number of contaminants in amine solutions. For instance, oxygen will react with hydrogen sulphide to eventually form thiosulphate and sulphate salts, which are heat stable. Oxygen will also react with amines to form formic, glycolic and oxalic acids, the ions of which form Heat Stable Salts.

**Derived Contaminants:**

Carbon dioxide, which is often a component of sour natural gas feeds, will also react to form contaminants that can then react with the amine molecule to form degradation compounds. Amine degradation chemistry is more complex than salt formation, because a series of intermediate compounds are formed that continue to react to eventually form ethylenediamines.

**8.5 Physical Solvent Processes**

These processes differ to amine absorption as the binding reaction of the solvent is very weak. They are characterised by;

- Low heats of solution
- Low utility requirements

- Co-absorption of heavy hydrocarbons (C<sub>3</sub>+ ) from the gas stream
- Sensitivity of treated gas specification and solvent circulation rate to the absorption pressure

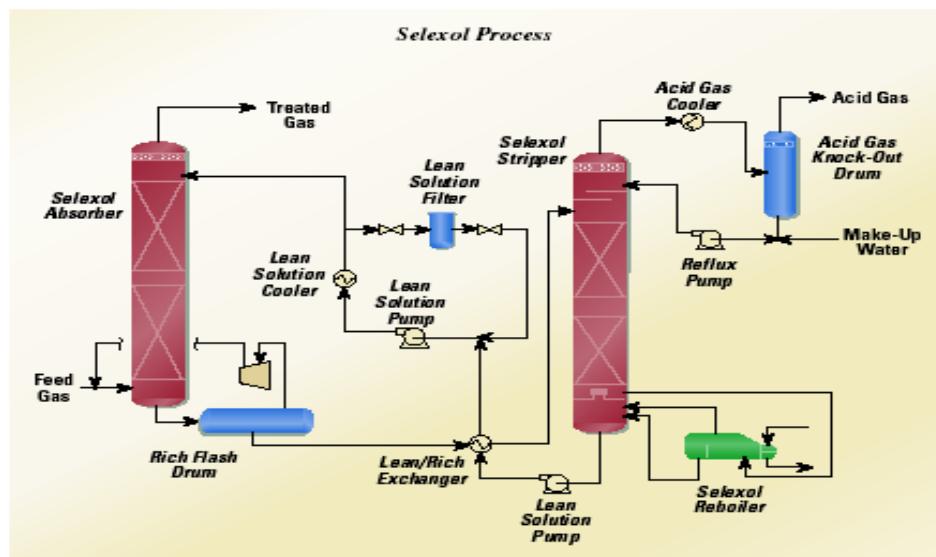
In general, the physical solvent process should be considered when:

- The partial pressure of acid gas is above 4 bar
- The heavy hydrocarbon concentration in the feed gas is low
- Bulk removal of the acid gas is desired
- Selective removal of H<sub>2</sub>S is desired

The solution loading and treated gas specification are directly proportional to the acid gas partial pressure in the feed gas. Hence physical solvent processes show advantages over chemical solvent processes at high absorption pressures. They are relatively non-corrosive so lower cost materials can be utilised.

One of the most common physical solvents goes under the trade name Selexol. It was developed by the Allied Chemical Corporation and now licensed by Union Carbide, the Selexol process can be used for selective or combined removal of H<sub>2</sub>S, RSH, CS<sub>2</sub>, COS, CO<sub>2</sub>, BTX, water, hydrocarbons, VOC, and chlorinated and oxygenated hydrocarbons from gas or air by physical absorption.

The process uses a solvent dimethyl ether or polyethylene glycol. Generally, it is applicable for bulk removal of carbon dioxide (and hydrogen sulphide) for high acid gas partial pressures. Most commercial applications have been for bulk carbon dioxide only.



As physical solvent Selexol absorbs various acid gas compounds in proportion to their partial pressure. Solvent regeneration is by pressure letdown of rich solvent. The solvent is

essentially regenerated without heat. However, to reduce treated gas contaminants to low ppm, the solvent can be regenerated by stripping medium, such as gas, air, or heat.

Feed gas enters the absorber where contaminants are absorbed by Selexol solvent. Absorption takes place at low temperatures (-5 °C to 0 °C). Rich solvent from the bottom of the absorber then flows to a recycle flash drum to separate and recompress any co-absorbed product gas back to the absorber. Pressure reduction in a further flash drum releases offgases. In most applications, the solvent is regenerated in a stripper column. The regenerated solvent is then pumped through a cooler and recycled back to the absorber.

Selexol units have the economic advantage that a single unit simultaneously controls the treated gas water and hydrocarbon dewpoints along with the acid gas content.

The main disadvantage of the Selexol process is the product losses incurred. Also, Selexol will absorb heavy hydrocarbons (C3+) from the feed gas which are not easily regenerated and can build up over time in the solvent. Typically water and hydrocarbons need to be recovered using a water wash and small fractionation tower.

## 8.6 Molecular Sieves

Molecular sieves can be used for gas treating, both for H<sub>2</sub>S and for CO<sub>2</sub> removal. CO<sub>2</sub> removal via these sieves is more attractive when the product requires a very low CO<sub>2</sub> content and if the feed contains less than 1.5 vol % of CO<sub>2</sub>.

Molecular sieves are commonly applied for CO<sub>2</sub> removal from hydrogen rich gases (e.g. Pressure Swing Adsorption (PSA) systems such as in many hydrogen plants). Active carbon can also be used, though its application is mostly restricted to the removal of trace quantities. Crystalline sodium-calcium silicates can be used for the selective removal of H<sub>2</sub>S and other sulphur compounds from natural gas streams. The activated crystalline material is porous, with pore openings in a given structure having exactly the same size.

Pore size	Type of Molecular Sieve	Application
3A	Potassium variation of sodium alumina silicate	Commercial dehydration of unsaturated hydrocarbon streams, including cracked gas, propylene, butadiene, acetylene; drying polar liquids such as methanol and ethanol. Adsorption of molecules such as NH <sub>3</sub> and H <sub>2</sub> O from a N <sub>2</sub> /H <sub>2</sub> flow. Considered a general-purpose drying agent in polar and nonpolar

		media.
4A	Sodium alumina silicate	Preferred for static dehydration in closed liquid or gas systems, e.g., in packaging of drugs, electric components and perishable chemicals; water scavenging in printing and plastics systems and drying saturated hydrocarbon streams. Adsorbed species include SO <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> S, C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , and C <sub>3</sub> H <sub>6</sub> . Generally considered a universal drying agent in polar and nonpolar media
5A	Calcium variation of sodium alumina silicate	Separation of normal paraffins from branched-chain and cyclic hydrocarbons; removal of H <sub>2</sub> S, CO <sub>2</sub> and mercaptans from natural gas. Molecules adsorbed include nC <sub>4</sub> H <sub>10</sub> , nC <sub>4</sub> H <sub>9</sub> OH, C <sub>3</sub> H <sub>8</sub> to C <sub>22</sub> H <sub>46</sub> , and dichlorodifluoro-methane (Freon 12®).
13X	Sodium alumina silicate with X crystal structure	Commercial gas drying, air plant feed purification (simultaneous H <sub>2</sub> O and CO <sub>2</sub> removal) and liquid hydrocarbon/natural gas sweetening (H <sub>2</sub> S and mercaptan removal).

The adsorption of components on the sieve is:

- Directly proportional to molecular weight.
- Inversely proportional to vapour pressure.
- Directly proportional to dipole moment (polarity).

Adsorption in order of retention:

- Water (strongest).
- Methanol (co-adsorbs with water).
- Heavier mercaptans.
- Light mercaptans, H<sub>2</sub>S.
- CO<sub>2</sub>.

- COS (weakest).

A common use of molecular sieves is mercaptan removal. Molecular sieves are also used for H<sub>2</sub>S removal to about 1000 ppm.

Plants may also be designed to adsorb H<sub>2</sub>S and water whilst leaving CO<sub>2</sub> in the gas stream.

## 8.7 Batch Solvents

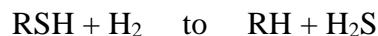
Batch solvents or adsorption beds are often used as a final polishing stage to remove the final traces of sulphur.

### Chemsweet

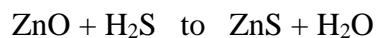
Chemsweet is a process that removes hydrogen sulphate from natural gas using a slurry suspension of fine zinc oxide particles in zinc acetate solution.

Mercaptans and carbonyl sulphate are also removed by reaction with the slurry to form zinc sulphate and zinc mercaptide. A dispersant is added to the slurry to keep solid particles in suspension, spent slurry passes to a degassing tower and is dumped.

Desulfurization of organic sulphur compounds is typically accomplished, by first, hydrogenating these compounds to form hydrogen sulphate:



Then, the hydrogen sulphate reacts with the zinc oxide adsorbent to form zinc sulphate, effectively trapping the sulphur:



### Sulfatreat

Sulfatreat is a fixed bed process designed to remove hydrogen sulphate and mercaptans from natural gas. Equipment is simple and consists of an upstream separator and the reactor itself. The catalyst is disposed when exhausted and as feed concentration is increased up to 2800 ppm, catalyst life is reduced. Almost 350kg of H<sub>2</sub>S can be adsorbed before change-out is required.

The catalyst is non-toxic, non-phosphoric and environmentally safe. PH control is not required and the process generates no toxic or corrosive gas.

There is little chance of methane hydrate formation due to low pressure drop across the bed.

## Puraspec

The puraspec process licensed by Synetix, can be used for removal of ppm concentrations of H<sub>2</sub>S and COS from hydrocarbon gases and liquids to meet pipeline or petrochemical specifications as required. Fixed beds of chemical absorbants provide effectively total irreversible selective removal of impurities from wet or dry hydrocarbons without feedstock losses. The operating conditions can range from: temperatures of -7°C to 204 °C; and pressures of atmospheric to 138 bar. Typically the process uses two separate reactors so that continuous production can be maintained even when one bed is being recharged.

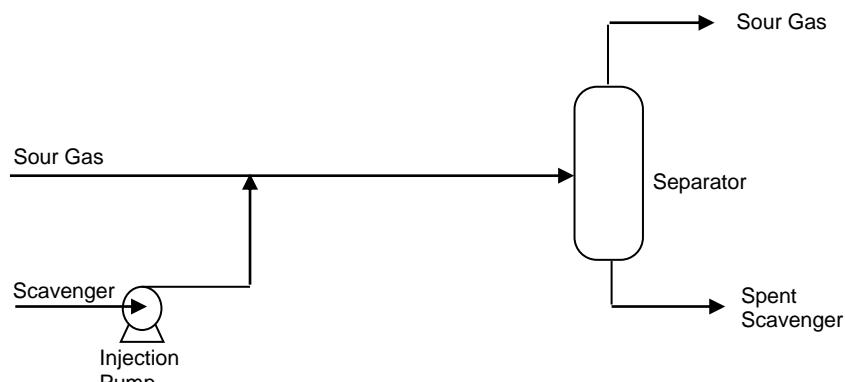
Puraspec can be used to remove mercury.

## 8.8 H<sub>2</sub>S Scavengers

A direct injection H<sub>2</sub>S scavenging system for natural gas is very simple consisting simply of an injection pump, injection point, a length of pipe for scavenger-gas contact, and a means of separating the spent scavenger (normally provided by existing equipment).

The method of introducing the scavenger into the gas line may either be piping tee, injection quill, or atomising nozzle. In-line mixers have also been used downstream of the injection point in order to ensure proper gas – scavenger contact. Most scavenging agents are designed to treat gas over a wide range of temperature, pressure and flow conditions. However, there are a number of issues which limit the suitable injection locations:

- Water content of gas. Many water-based scavenging agents require the gas to be water-saturated in order to prevent the formation of unwanted solid by-products. This may affect the selected injection point, or even require the injection of additional water.
- Temperature of gas. Low temperatures result in slow reaction rate, affecting the H<sub>2</sub>S removal performance. Conversely, excessively high temperatures can cause the scavenger to degrade and form corrosive products.
- Length of available piping runs to ensure adequate contact time. In offshore applications, the availability of piping runs of adequate length can be limited.



In view of the above factors, injection of a multi-phase scavenger at the wellhead, or vapour scavenger at separator outlets can prove to be the most effective location. The disposal method for the spent scavenger varies. However for offshore applications, if the correct scavenging agent is selected it is possible to dispose to sea, along with the produced water. Liquid scavenging is most suitable when the amount of H<sub>2</sub>S is relatively small, around 100kg/day or below. For example, Champion's 'Gas Treat' chemical is quoted to be effective in the range of 1 to 90 kg/day H<sub>2</sub>S removal.

## 8.9 Membrane Processes

Membrane separation is based on the selective diffusion of gases through a permeable membrane. Gas mixtures are separated on the basis of their different solubility and diffusivity through the membrane barrier when under an imposed partial pressure gradient, with the feed gas at high pressure and the permeate gas at low pressure. The components of the natural gas diffuse at different rates, i.e. H<sub>2</sub>O vapour, CO<sub>2</sub> and H<sub>2</sub>S have high permeation rates, methane has a medium rate and heavier hydrocarbons like butane have a much lower permeation rate. For commercial applications, feed pressure between 25 - 100 bara is required and the permeate (acid gas) pressure is low (maximum 4.1 bara). Membranes are not as effective at lower feed gas pressures (i.e. below 25 bara) due to the reduced partial pressure driving force of the acid gases. Feed gas is generally cooled for water and HC removal then heated above its dew point. In some cases further dehydration may be required.

Lean sales gas CO<sub>2</sub> content of 2-3 mole% can be obtained at high pressure but the CO<sub>2</sub> rich gas is produced at low pressure between 2-3 bara needing recompression for reinjection. Even with this limitation, membranes are ideally suited for bulk removal of CO<sub>2</sub> at high pressures. Membranes work on a pressure differential and there will be a Joule-Thomson temperature change for the permeate (although not as great as a J-T effect through a valve). As a result of this, there is a chance of free water or heavier hydrocarbons condensing. Free water is detrimental to a cellulose acetate-based membrane, as it will dissolve the membrane. The newer polyamid membranes exhibit better water resistance. In some cases there is a large heat transfer area between feed and permeate so the permeate stays warm.

Permeation rates for water vapour through membranes is many times higher than for methane and therefore membranes can be sized for dehydration of the sales gas to pipeline specification (100mg/sm<sup>3</sup>). For specs lower than this membrane units are not practical due to the area required.

Liquid hydrocarbons are not detrimental to membranes, but they can coat the membrane surface and significantly reduce their efficiency. For feed gases containing significant amounts of heavy HCs, a precooler is recommended upstream of the membranes to knock out the heavy HCs. If there is only a small amount of HCs present, the membrane module can be designed to prevent liquid HCs collecting on the membrane surface. In any event, to avoid any condensation, it is recommended that the feed gas temperature be raised 5 -7 °C above the dewpoint of the gas immediately upstream of the membrane unit.

## 9 Mercury Removal

Mercury in natural gas is present predominantly as elemental mercury. It can also be present in other forms – inorganic, organic and organic ionic where the mercury is contained in very small discrete droplets independent of the other phases.

The primary reason for removing mercury is to protect downstream aluminium heat exchangers and equipment, such as those used in cryogenic hydrocarbon recovery and LNG plants. Mercury may also poison the catalysts used in many refinery processes.

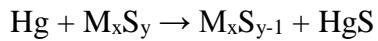
When mercury contacts an aluminium surface the aluminium diffuses from the surface – mercury absorbs into the aluminium causing structural failure.

It is also hazardous to personnel if present in equipment.

Absorbents (pre-activated; sulphated) are by their nature active material. They consist of a high porosity, spherical mixed-sulphate absorbent of different diameters. The absorbents are loaded into a mercury-removal vessel where the mercury is irreversibly bound to them.

These absorbents remove small quantities of contaminants from a wide variety of liquid and gas streams, with high efficiency and effectiveness. The absorbent unit is designed to remove mercury from typically an average inlet concentration of about 200 µg/std m<sup>3</sup> to about 0.1 µg/std m<sup>3</sup>.

Mercury vapor reacts with the metal sulphate to form a stable mercuric sulphate:



The reactive metal (mercury) is incorporated in an inorganic support and the absorbent is supplied with the reactive sulphate present or formed in situ by reaction with H<sub>2</sub>S in the hydrocarbon to be treated.



## 10 Process Selection

A summary of the key considerations for selecting the appropriate treatment process are listed.

- air pollution regulations regarding sulphur disposal
- type and concentration of impurities in the process gas
- specifications for the residue gas
- specifications for the acid gas
- temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered
- volume of gas to processed
- hydrocarbon composition of the process gas
- selectivity required for acid gas removal
- capital and operating cost

## 11 H<sub>2</sub>S Removal from Oil streams

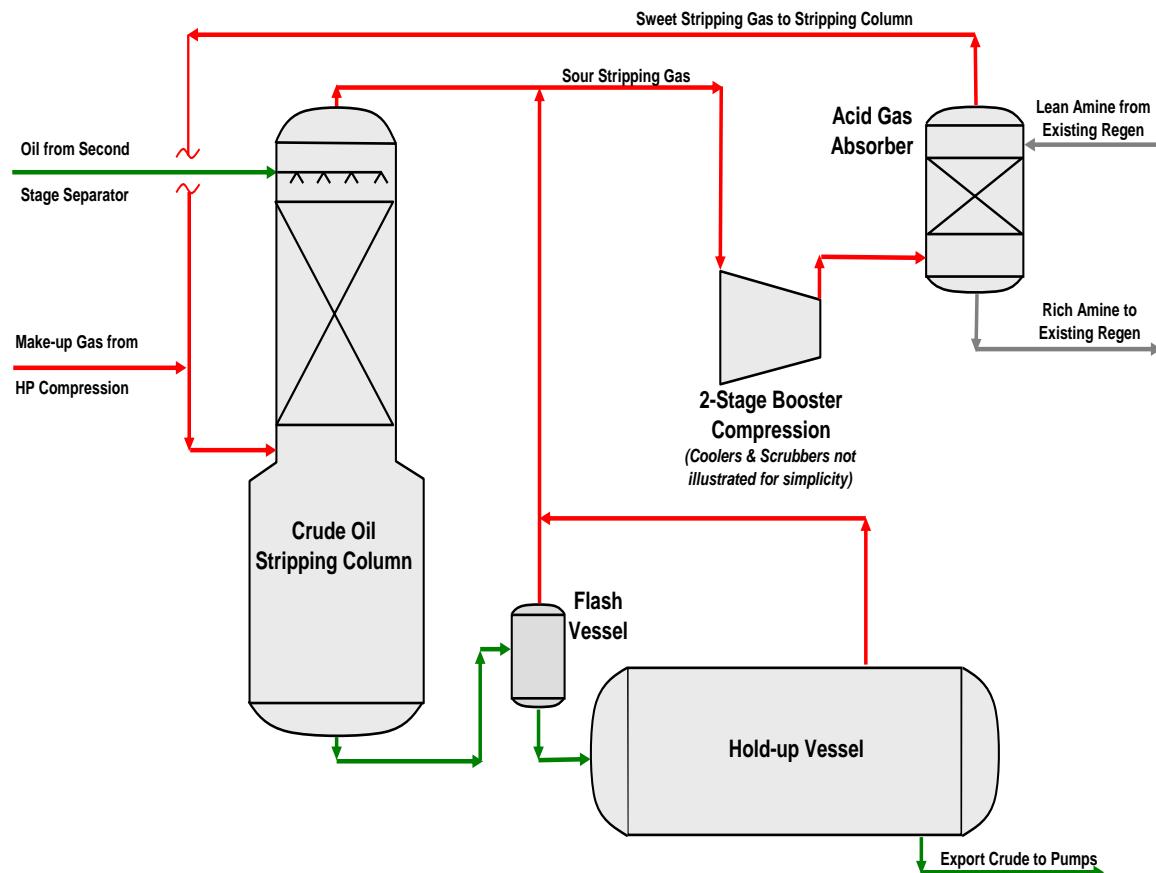
Gas stripping is the unit operation most commonly used for removal of H<sub>2</sub>S from oil streams.

H<sub>2</sub>S removal is required for corrosion control and terminal specifications.

The equipment configuration is as follows.

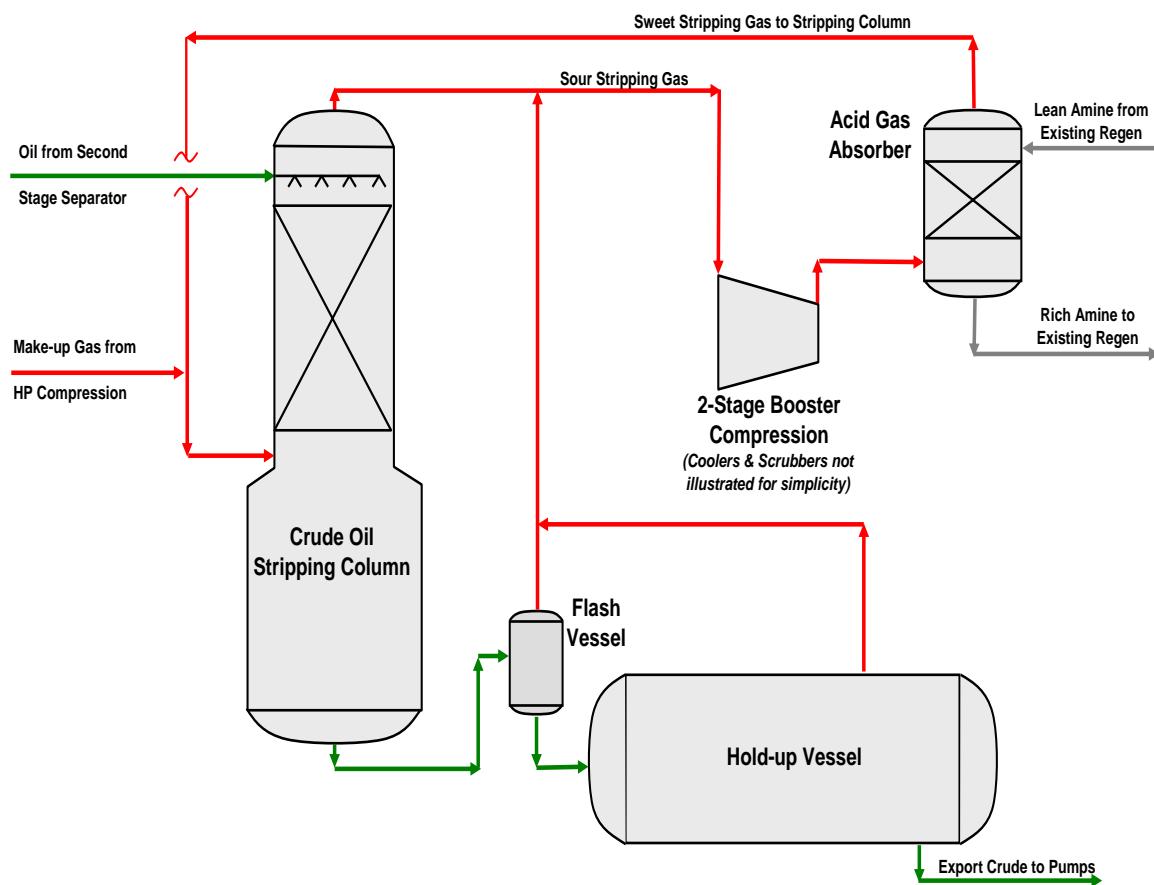
Oil Flow Path:

1. The Oil is fed into the desorption column via a nozzle array.
2. Oil then progresses through the plate / packing section and is contacted counter-currently with stripping gas to remove H<sub>2</sub>S.
3. Treated sweet oil ( $\leq 11\text{ppm}$ ) is collected at the bottom of the desorption column.
4. Oil passes through the flash vessel to provide the gas analysers with an H<sub>2</sub>S sample.
5. The oil is then stored in the hold-up vessel for approximately 3 minutes whilst the gas analysers recorded the results of the sample.
6. Oil stored in the hold up vessel is then exported to the Oil Pipeline.



#### Gas Flow Path:

1. Production gas (considered to be sweet) is fed into the system.
2. Gas passes up through the desorption column and is contacted counter-currently with the crude oil along the active tray area.
3. Sour stripping gas exits the desorption column and passes through the 2-stage booster compression.
4. Sour stripping gas is sent to the acid gas absorber to remove H<sub>2</sub>S using Amine.
5. Note - Designed outlet specification is 10ppm H<sub>2</sub>S.
6. The sweet stripping gas is recycled back into the desorption column and if required secondary supply of stripping gas is available from existing gas production.



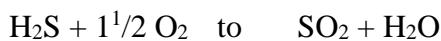
## 12 Sulphur Recovery

Sulphur is present in natural gas principally as hydrogen sulphide. The H<sub>2</sub>S present is removed from natural gas by means of one of the acid gas treatment processes described earlier. The resulting H<sub>2</sub>S containing acid gas from the regeneration system can be converted to elemental sulphur by means of the Claus process.

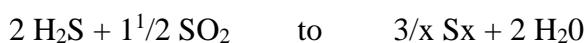
## 12.1 Claus Process

The Claus process is split into two parts.

1. A thermal or combustion reaction section in which most of the overall heat of reaction (from burning  $\frac{1}{3}$  of the H<sub>2</sub>S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed



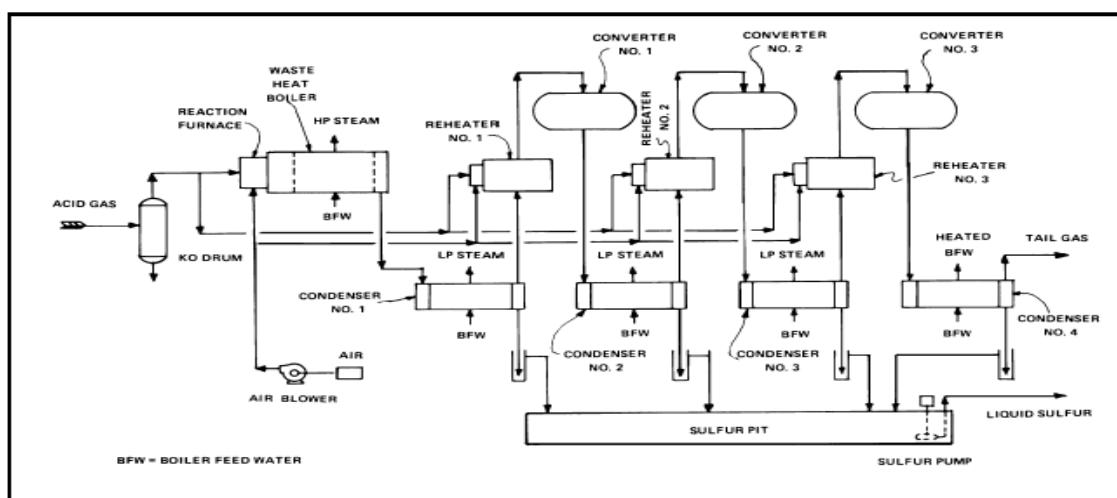
2. A moderately exothermic catalytic reaction section in which sulphur dioxide ( $\text{SO}_2$ ) formed in the combustion section reacts with unburned  $\text{H}_2\text{S}$  to form elemental sulphur.



The Claus sulphur recovery process includes the following process operations:

- Combustion - burn hydrocarbons and other combustibles and 1/3 of the H<sub>2</sub>S in the feed

- Waste Heat Recovery - cool combustion products. Because most Claus plants produce 1030-3450 kPa steam at 185-243°C, the temperature of the cooled process gas stream is usually about 315-370°C.
  - Sulphur Condensing - cool outlet streams from waste heat recovery unit and from catalytic converters. Low pressure steam at 345-480 kPa is often produced and the temperature of the cooled gas is usually about 177°C or 127-149 °C from the last condenser.
  - Re-heating- Reheat process stream, after sulphur condensation gas separation, to a temperature high enough to remain sufficiently above the sulphur dewpoint, and generally, for the first converter, high enough to promote hydrolysis of COS and CS<sub>2</sub> to H<sub>2</sub>S and CO<sub>2</sub>.
  - COS + HO to CO<sub>2</sub> + H<sub>2</sub>S
  - CS<sub>2</sub> + 2 HO to CO<sub>2</sub> + 2 H<sub>2</sub>S
  - Catalytic Conversion - Promote reaction of H<sub>2</sub>S and SO<sub>2</sub> to from elemental sulphur
  - Overall Sulphur Recovery does not exceed 96-97% due to equilibrium limitations
- A three stage Claus process is shown.



In Canada there is not a market for all the sulphur produced and the sulphur accumulates as sulphur fields.



**13 Key Learnings**

1. Gas specifications – water, cricondenbar, calorific value, wobbe index
2. Water content of gas
3. Hydrate formation
4. Principles of glycol dehydration and construction of operating and equilibrium lines
5. Principles of molecular sieve
6. Refrigeration, Joule-Thomson and Turbo-expansion processes
7. Use of Mollier chart to estimate refrigeration system components
8. Principles of amine absorption for CO<sub>2</sub> and H<sub>2</sub>S removal.
9. Principles of Mercury Removal