

Tikrit University

College of Petroleum Processes Engineering

**Department of Petroleum and Gas Refining
Engineering**

Gas Technology

Forth Class

Lecture 14

By

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ACID GAS TREATING

Sulfinol Process

The *Sulfinol process* is a regenerative process developed to reduce H₂S, CO₂, COS and mercaptans from gases. The sulfur compounds in the product gas can be reduced to low ppm levels. This process has been developed specifically for treating large quantities of gas, such as natural gas, which are available at elevated pressures. The Sulfinol process is *unique* in the class of absorption processes because it uses a mixture of solvents, which allows it to behave as both a chemical and a physical absorption process.

Features

- Removal of H₂S, COS and organic sulfur to natural gas pipeline specification.
- Low steam consumption and solvent circulation.
- Low corrosion rate.
- Selective removal of H₂S in some natural gas applications.
- Smaller equipment due to low foaming tendency.

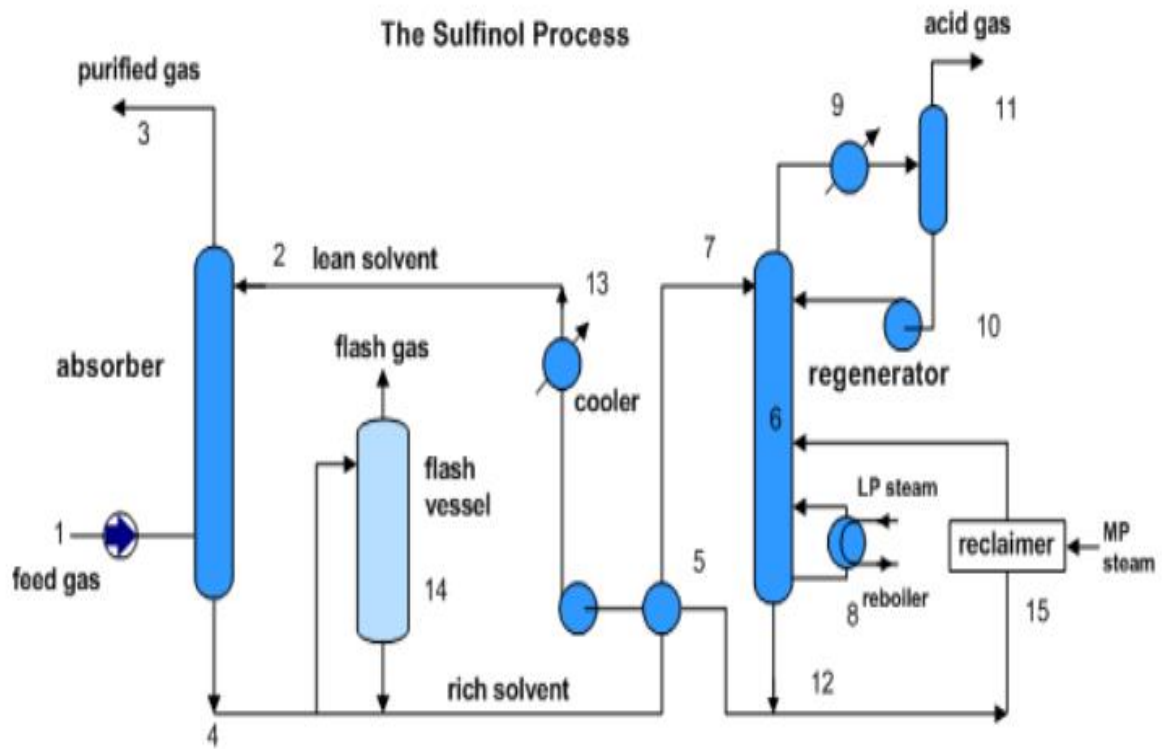


Figure 1: Sulfinol Process

SULFUR RECOVERY PROCESSES

- ✚ The side stream from acid gas treating units consists mainly of hydrogen sulfide/or carbon dioxide.
- ✚ Carbon dioxide is usually vented to the atmosphere but sometimes is recovered for CO₂ floods.
- ✚ Hydrogen sulfide could be routed to an incinerator or flare, which would convert the H₂S to SO₂. The release of H₂S to the atmosphere may be limited by environmental regulations.
- ✚ Most sulfur recovery processes use chemical reactions to oxidize H₂S and produce elemental sulfur. These processes are generally based either on the reaction of H₂S and O₂ or H₂S and SO₂. Both reactions yield water and elemental sulfur. These processes are licensed and involve specialized catalysts and/or solvents.
- ✚ There are two common methods of sulfur recovery: liquid redox and Claus sulfur recovery processes.

Liquid redox sulfur recovery processes

Liquid redox sulfur recovery processes are liquid-phase oxidation processes that use a dilute aqueous solution of iron or vanadium to remove H₂S selectively by chemical absorption from sour gas streams. These processes can be used on relatively small or dilute H₂S stream to recover sulfur from the acid gas stream or, in some cases, can be used in place of an acid gas removal process. The mildly alkaline lean liquid scrubs the H₂S from the inlet gas stream, and the catalyst oxidizes the H₂S to elemental sulfur. The reduced catalyst is regenerated by contact with air in the oxidizer(s). Sulfur is removed from the solution by flotation or settling, depending on the process.

Claus sulfur recovery processes

Hydrogen sulfide (H₂S) is a smelly, corrosive, highly toxic gas. It also deactivates industrial catalysts. H₂S is commonly found in natural gas and is also made at oil refineries, especially if the crude oil contains a lot of sulfur compounds. Because H₂S is such an obnoxious substance, it is converted to non-toxic and useful elemental sulfur at most locations that produce it. The process of choice is the **Claus Sulfur Recovery process**.

Description of the Claus Process

First the H₂S is separated from the host gas stream using *amine absorption*. Then it is fed to the Claus unit, where it is converted in two steps as shown in Figure 2.

Thermal Step: The H₂S is partially oxidized with air. This is done in a reaction furnace at high temperatures (1000-1400 °C). Sulfur is formed, but some H₂S remains unreacted, and some SO₂ is made.



Catalytic Step: The remaining H₂S is reacted with the SO₂ at lower temperatures 450 °F (about 200-350 °C) > dew point of S to prevent condensation on the catalyst, to make more sulfur. A catalyst is needed in the second step to help the components react with reasonable speed. Unfortunately the reaction does not go to completion even with the best catalyst. For this reason two or three stages are used, with sulfur being removed between the stages. Engineers know how

different factors like concentration, contact time and reaction temperature influence the reaction, and these are set to give the best conversions.



Condenser outlet must be $350^{\circ}F >$ melting point of S to prevent the formation of solid S. Inevitably a small amount of H_2S remains in the tail gas. This residual quantity, together with other trace sulfur compounds, COS and CS_2 , formed in the burner side reaction, is usually dealt with in a *tail gas unit*. The latter can give overall sulfur recoveries of about 99.8%.

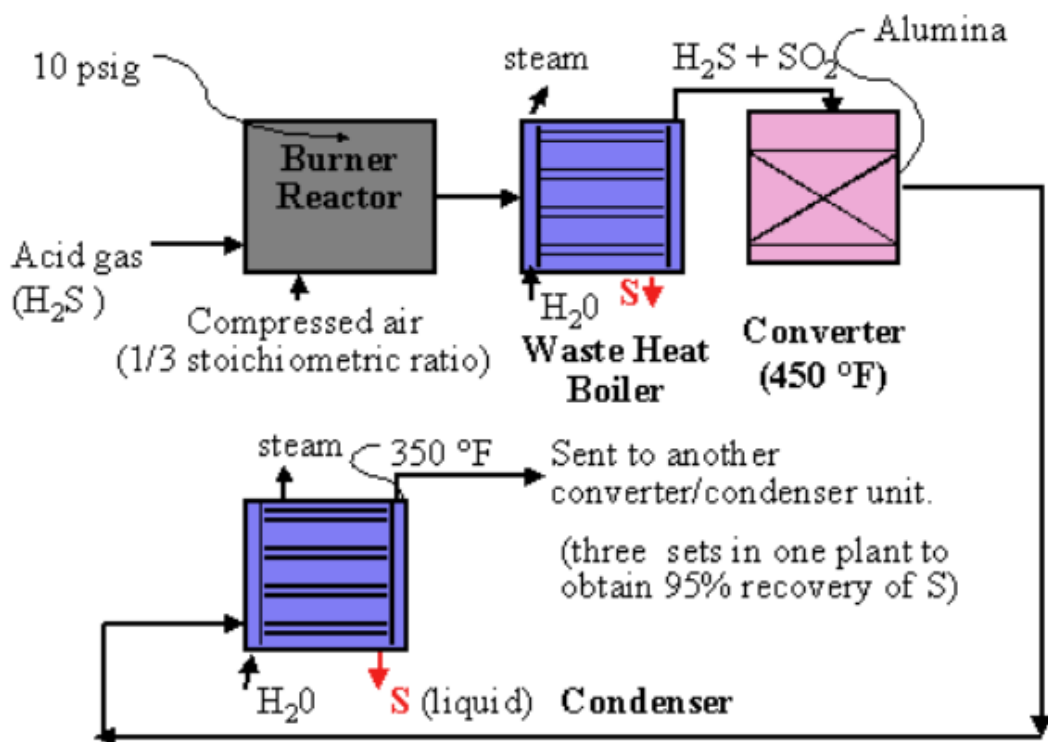


Figure 2: Claus Process

The SCOT Process

Because of the more stringent requirements of pollution control, requirements for tail gas clean-up processes are developed. *The SCOT* process is an example. In the first stage, the Claus tail gas is heated to about 570 OF and reacted with H₂ over a cobalt molybdenum catalyst. All the COS, CS₂, S and SO₂ in the Claus unit off gas are converted to H₂S (Figure 3) by the following reaction



These reactions are highly exothermic. The hot gas from the reactor is cooled in a waste heat boiler and finally quenched in a water cooling tower. The final stage involves the selective absorption of H₂S in an amine solution, normally DIPA. The vent gas from the SCOT absorber typically contains 200–500 ppmv of H₂S. This vent is normally incinerated before discharging to the atmosphere. The rich amine is stripped in a conventional manner, and the H₂S rich stream is recycled back to the front of the Claus plant.

The Claus + SCOT processes combine to remove 99.5% of the S

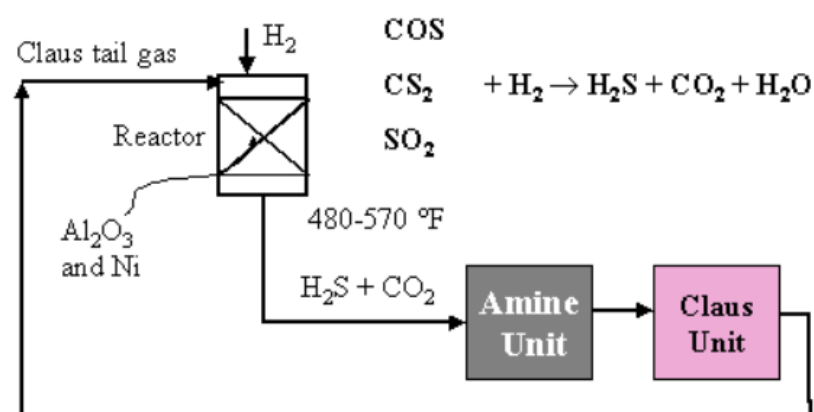


Figure 3: The SCOT Process

GAS DEHYDRATION

Introduction

Water with natural gas can generate a great number of problems.

- One serious problem is that it could form solid hydrates at certain pressures and temperatures, which can plug facilities and pipelines.
- When pressure and temperature drop, water vapor condenses and can cause slug flow and possible erosion and corrosion in the system, especially when acid gases are present.
- Water vapor increases the total volume and decreases the heating value of gas, which subsequently, cannot meet gas stream specifications.

Most free water is removed after the gas-liquid separation is at or near the wellhead. However, there are still small amounts of water vapor associated with the main stream of natural gas that requires further treatment to remove (**dehydration**). Natural gas dehydration is the process of **removing water vapor from the gas stream to lower the dew point of that gas**. The dew point is defined as the temperature at which water vapor condenses from the gas stream. The sale contracts of natural gas specify either its dew point or the maximum amount of water vapor present. There are three basic reasons for the dehydration of natural gas streams:

- To prevent hydrate formation.
- To avoid corrosion problems.
- Downstream processing requirements.

Water Content of Hydrocarbons

In any mixture, where both the gas and liquid phases are in equilibrium, each component, i , in the mixture obeys the relationship

$$x_i \gamma_i P_i^{Sat} = y_i \phi_i P$$

However, reasonably good estimates of the concentration of water in the vapor phase in equilibrium with liquid water can be made at pressures below 500 psia (35 bar). If we make the good assumption of negligible hydrocarbon in the liquid water phase, which, thus makes both x_i and ϕ_i unity for water and assume the gas phase to be ideal, which makes ϕ_i unity, we obtain

$$y_{H_2O} = \frac{P_{H_2O}^{Sat}}{P}$$

Several methods are available to estimate the water content of sweet. One of the most commonly used is the Mcketta and Wehe (1958) approach. They developed a chart (Figure 4) to estimate the water content for sweet natural gas.

- Since salts dissolved in the liquid water in equilibrium with natural gas have a tendency to reduce the water content of the gas, an inset chart is provided in Figure 4 to correct for the effects of salinity.
- This approach is applicable for pressure up to 10,000 psi, temperatures from 50 to 300°F, gas gravity in the range of 0.6 to 1.8, and a brine salinity up to 3%.
- Figure 4 is not applicable to sour natural gas. Wichert and Wichert (2003) developed an updated chart based

(using Figure 4 and augmented by Figure 5) correlation to calculate the equilibrium water content of a sour gas. This approach is applicable for pressure up to 10,000 psi, temperature from 50 to 350°F, and H₂S content up to 55%.

The calculation procedure using the Wichert and Wichert (2003) approach is outlined below.

1. At given pressure and temperature, determine the water vapor content of sweet gas from Figure 4:

1.1- Get the water content at 14.7 psi and 60°F from the general chart of Figure 4, assuming 0.6 gravity gas contacting with pure water, W in lb/MMcf.

1.2- Get the gravity correction factor, C_G, from the inset chart, “Correction for Gravity”, where

$$C_G = \frac{\text{lbs. water in gas of gravity, } \gamma_g}{\text{lbs. water in gas of gravity of 0.6}}$$

1.3- Get the salinity correction factor, C_S, from the inset chart, “Correction for Salinity,” where

$$C_S = \frac{\text{lbs. water in gas if gas had been in contact with brine}}{\text{lbs. water in gas if gas had been in contact with water}}$$

1.4- The water content for the sweet natural gas is

$$W_{\text{sweet}} = W \times C_G \times C_S.$$

2. Determine the mole% of H₂S equivalent concentration of the sour gas by

$$\text{mole\% of H}_2\text{S equivalent} = \text{mole\% of H}_2\text{S} + 0.7 \times (\text{mole\% of CO}_2).$$

3. Determine the ratio of water in sour gas to water in sweet gas by using Figure 5:

3.1- Locate the point that represents the “mole% of H₂S equivalent” and the given temperature in the lower part of Figure 5.

3.2- From this point, move to the upper chart to the given pressure, and move to the left to get the ratio.

4. Determine the saturated water content of the sour gas (W_{sour}) at the given pressure and temperature by multiplying the value from Step 1 (water vapor content of sweet gas) and the ratio from Step 3 (correction).

Example 1: Determination of equilibrium water vapor content in a sour gas
Assume a natural gas mixture with 66% hydrocarbon gas, 21 mole% H₂S, and 13 mole% CO₂ contacting with an aquifer that contains 3% of NaCl. $\gamma_g = 0.86$. The conditions are $p = 2,000$ psi and $T = 100^\circ\text{F}$.

Solution:

Follow the procedure outlined above.

1. Determine water vapor content of sweet gas from Figure 4.

1.1 From general chart: $W = 62$ lb/MMcf.

1.2 From the inset chart “Correction for Gravity”: $C_G = 0.90$.

1.3 From the inset chart “Correction for Salinity”: $C_S = 0.93$.

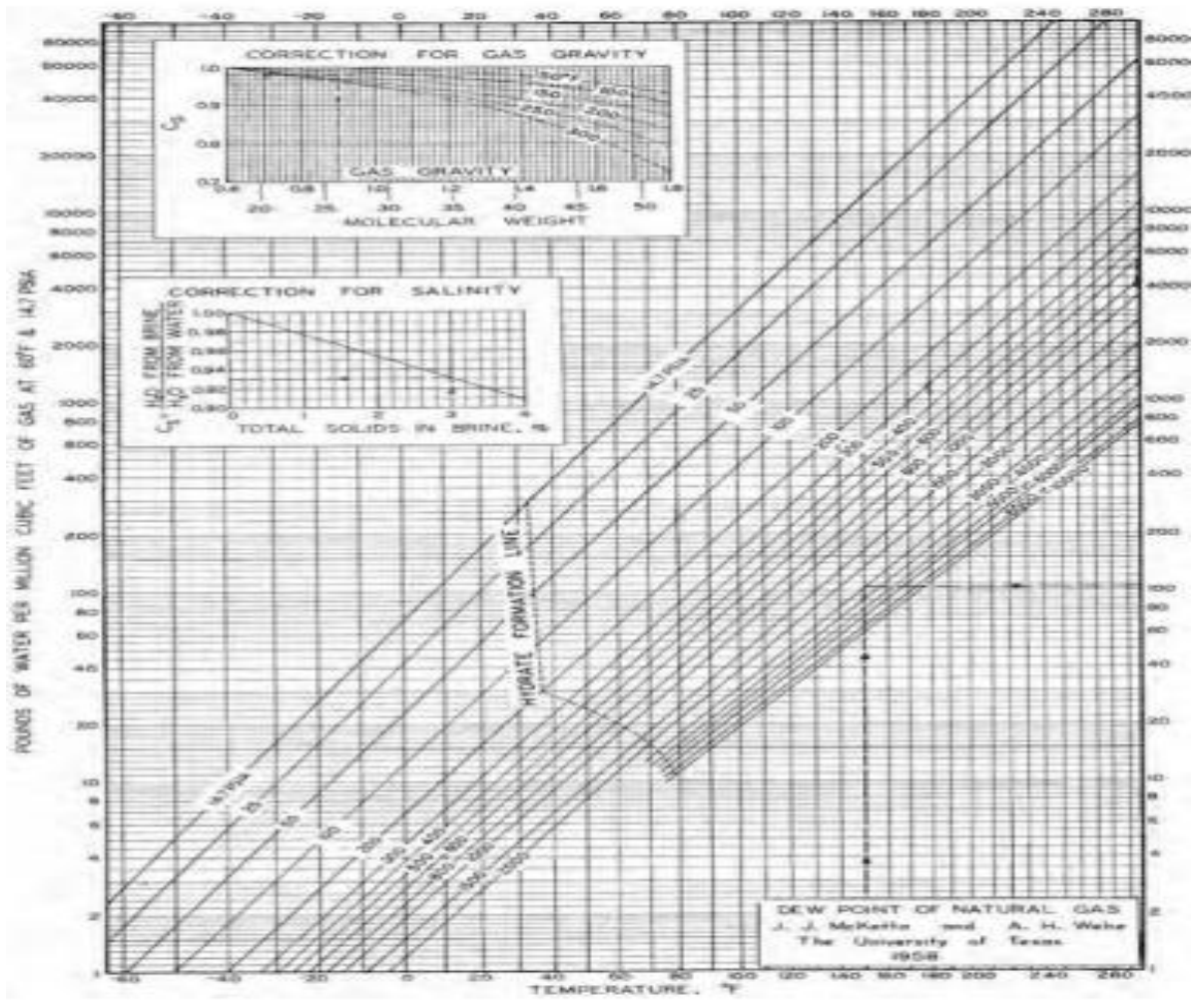


Figure 4: Water content of sweet natural gas.

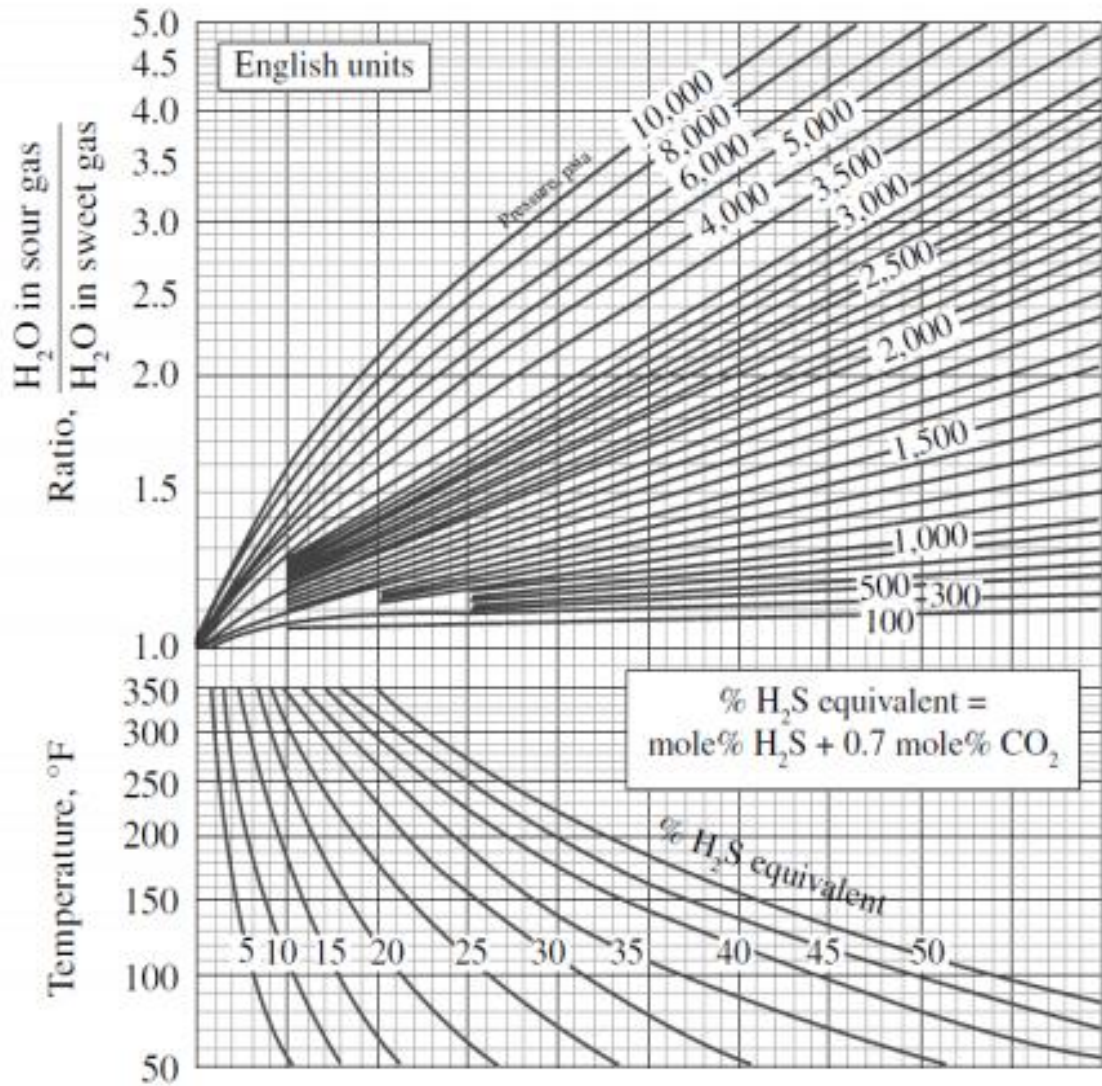


Figure 5: Water content correction for sour natural gas.

1.4 The water content for the sweet natural gas is

$$W_{\text{sweet}} = 62 \times 0.9 \times 0.93 = 51.9 \text{ lb/MMcf/d.}$$

2. Determine the mole% of H₂S equivalent concentration of the sour gas, mole% of H₂S equivalent = 21 mole% of H₂S + 0.7 × (13 mole% of CO₂) = 30%.

3. Determine the ratio of water in sour gas to water in sweet gas by using Figure 4. With 30 mole% H₂S equivalent, p = 2,000 psi and T = 100°F, ratio = 1.53.

Determine the saturated water content of the sour gas (W_{sour}) at the given pressure and temperature by multiplying the value from Step 1 (water vapor content of sweet gas) and the ratio from Step 3 (correction):

$$W_{\text{sour}} = 51.9 \times 1.53 = 79.4 \text{ lb/MMcf/d.}$$

Natural Gas Hydrates

Natural gas hydrates are solid crystalline compounds formed by the chemical combination of natural gas and water under pressure at temperature considerably above the freezing point of water. The chemical formulae for natural gas hydrates are.

Methane	CH ₄ •7H ₂ O
Ethane	C ₂ H ₆ •8H ₂ O
Propane	C ₃ H ₈ •18H ₂ O
Carbon Dioxide	CO ₂ •7H ₂ O

Hydrates tend to form when there is:

- Free water present and temperature decreases below that of hydrate-formation. This usually happens in the flow string or surface line;

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- Sudden pressure drop due to expansion. This usually happens when fluids flows through orifices, back pressure regulators, or chokes.
- If a small “seed” crystal of hydrate or acid gas (H₂S or CO₂) is in the system and the flow rate is high with agitation, it will definitely promote the formation of natural gas hydrates.

Example 2: (from Figure 6), if a natural gas mixture exists with $\gamma_g = 0.9$ and $T = 60$ °F, natural gas hydrate might form when the pressure is above 500 psi; if a natural gas exists with $\gamma_g = 1.0$ and $p = 90$ psi, then natural gas hydrate might form when the temperature is below 40°F. If the natural gas contains acid gases (H₂S or CO₂), the hydrate-formation envelope will expand as acid gases will increase the possibility of hydrate formation.

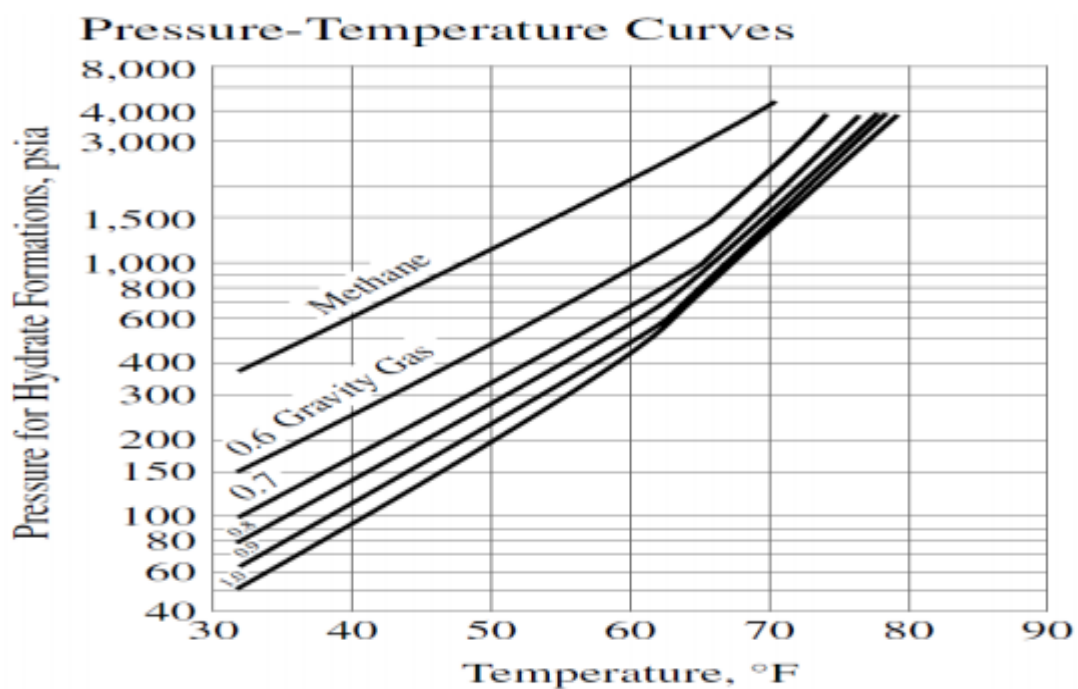


Figure 6: Hydrate formation prediction

Solution:

Figure 4 also can reveal one of the greatest potential future resources of natural gas. For example, at the ocean floor at a depth of 7,000 ft the pressure would be over 3,000 psi. This means that if the temperature is less than 72°F (from Figure 4) hydrates will form.

There are four ways to dehydrate the natural gas : direct cooling, compression followed by cooling, absorption, and adsorption. The last two approaches are more commonly used

Dehydration Methods

Two processes, absorption and adsorption, are the most common for drying natural gas

Absorption (Glycol Dehydration Process)

In this process (Figure 7), a hygroscopic liquid is used to contact the wet gas to remove water vapor from it. Triethylene glycol (TEG) is the most common solvent used.

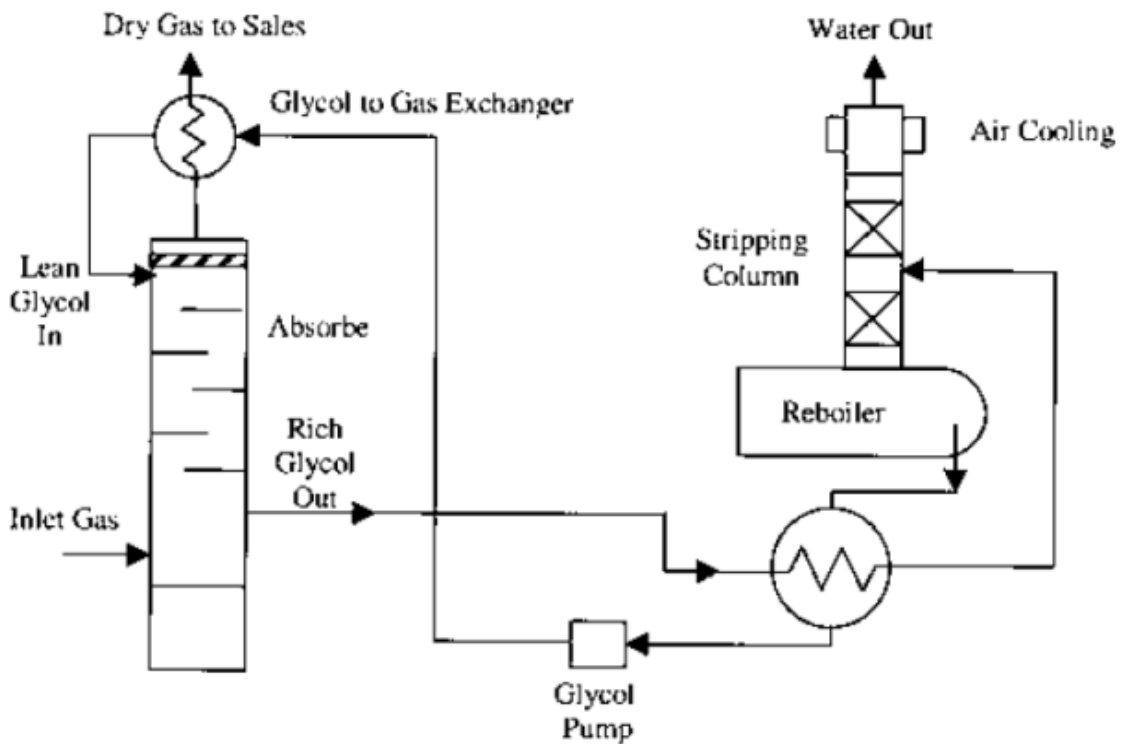


Figure 7: Flow Diagram of TEG Dehydration

Adsorption: Solid-Bed Dehydration

- Solid desiccant dehydration systems work on the principle of adsorption.
- Adsorption involves a form of adhesion between the surface of the solid desiccant and the water vapor in the gas.
- The water forms an extremely thin film that is held to the desiccant surface by forces of attraction, but there is no chemical reaction.
- Solid desiccant dehydrators are typically more effective than glycol dehydrators, as they can dry a gas to less than 0.1 ppmV (0.05 lb/MMcf).
- However, in order to reduce the size of the solid desiccant dehydrator, a glycol dehydration unit is often used for bulk water removal. The glycol *Natural Gas* unit would reduce the water content to around 60 ppmV, which would help reduce the mass of solid desiccant necessary for final drying.

- Using desiccant dehydrators as alternatives to glycol dehydrators can yield significant economic and environmental benefits, including reduced capital cost, reduced operation and maintenance cost, and minimal VOC and hazardous air pollutants (BTEX).

Three types of commercial adsorbents are in common use in gas processing plants:

- Silica gel, which is made of pure SiO_2
- Activated alumina, which is made of Al_2O_3
- Molecular sieves, which are made of alkali aluminosilicates and can be altered to affect adsorption characteristics.

Silica gels: Are used mostly where a high concentration of water (>1 mol%) vapor is present in the feed, and low levels of water in the dehydrated gas are not needed. They are relatively noncatalytic compounds.

Aluminas: Are very polar and strongly attract water and acid gases. They are used for moderate levels of water in the feed when low levels of water in the product are not required. They have the highest mechanical strength of the adsorbents considered here.

Molecular sieves: For gas going into cryogenic processing, the only adsorbent that can obtain the required dehydration is a molecular sieve. The system as shown in Figure 8 may consist of two-bed, three-bed, or Multi-bed operation. In the three-bed operation, if two beds are loading at different stages, the third one would be regenerated. The operation of the process is controlled by opening valve and closing valve. After the bed has been used and loaded with water, then it is regenerated by hot gas (say 6 h, as heating time) and then cooled by switching to cold gas (say for 2 h).

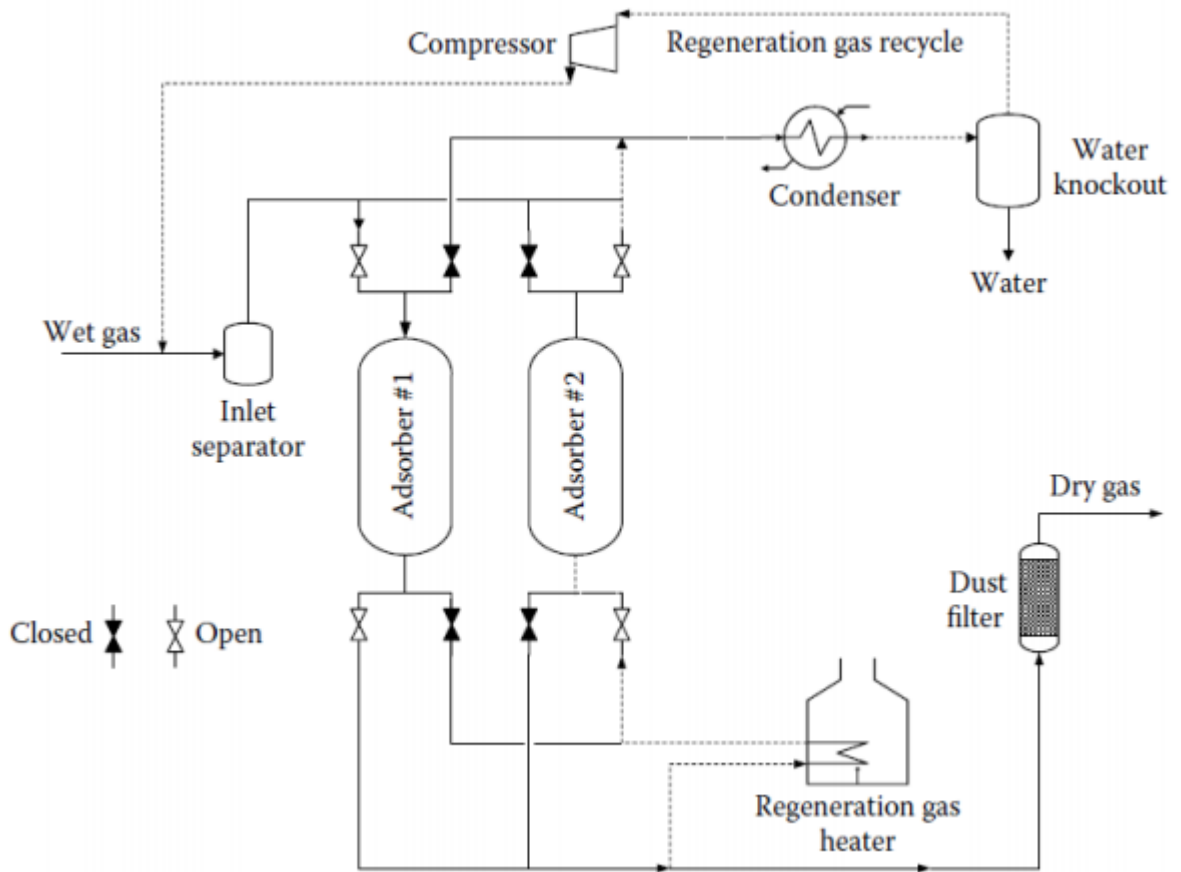


Figure 8: Solid-Bed Dehydration Process