CHAPTER 7
THE DEHYDRATION AND SWEETENING OF NATURAL GAS

Natural gases either from natural production or storage reservoirs contain water, which condense and form solid gas hydrates to block pipeline flow and especially control systems. Natural gas in transit to market should be dehydrated to a controlled water content to avoid hydrate as well as to minimize the corrosion problems.

Often hydrogen sulfide is present in field gases and has to be removed to a specific level (0.1 to 0.25 grain per 100 scf) because of its toxicity. Carbon dioxide is a corrosive diluent, but it has a value for some enhanced oil recovery processes and is included in acid gas removal processes.

7.1 DEHYDRATION

Dehydration of natural gas is the removal of the water that is associated with natural gases in vapor form. The natural gas industry has recognized that dehydration is necessary to ensure smooth operation of gas transmission lines. Dehydration prevents the formation of gas hydrates and reduces corrosion. Unless gases are dehydrated, liquid water may condense in pipelines and accumulate at low points along the line, reducing its flow capacity. Several methods have been developed to dehydrate gases on an industrial scale.

The three major methods of dehydration are 1) direct cooling, 2) adsorption, and 3) absorption. Molecular sieves (zeolites), silica gel, and bauxite are the desiccants used in adsorption processes. In absorption processes, the most frequently used desiccants are diethylene and triethylene glycols. Usually, the absorption/stripping cycle is used for removing large amounts of water, and adsorption is used for cryogenic systems to reach low moisture contents.

7.1.1 Direct Cooling

The saturated vapor content of natural gas decreases with increased pressure or decreased temperature (Figure 4.1). Thus, hot gases saturated with water may be partially dehydrated by direct cooling. Gases subjected to compression are normally "after cooled", and this cooling may well remove water from the gas. The cooling process must reduce the temperature to the lowest value that the gas will encounter at the prevailing pressure to prevent further condensation of water.

7.1.2 Absorption of Water in Glycols

Absorption dehydration involves the use of a liquid desiccant to remove water vapor from the gas. Although many liquids possess the ability to absorb water from gas, the liquid that is most desirable to use for commercial dehydration purposes should possess the following properties:

     1. High absorption efficiency.
     2. Easy and economic regeneration.
     3. Non-corrosive and non-toxic.
     4. No operational problems when used in high concentrations.
     5. No interaction with the hydrocarbon portion of the gas, and no contamination by acid gases.

The glycols, particularly ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T4EG) come to closest to satisfying these criteria to varying degrees. Water and the glycols show complete mutual solubility in the liquid phase due to hydrogen-oxygen bonds, and their water vapor pressures are very low. One frequently used glycol for dehydration is triethylene glycol, or TEG:

$$CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$
$$|$$
$$CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$
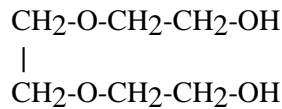
The flow sheet of a TEG dehydration unit is shown in Figure 7.1. This is mainly an absorption/stripping type process, similar to the oil absorption process. The wet gas is dehydrated in the absorber, and the stripping column regenerates the water-free TEG. The glycol stream should be recharged constantly because some TEG may react and form heavy molecules, which should be removed by the filter shown in Figure 7.1 or by distillation of a slip stream.

7.1.3 Adsorption of Water by a Solid

Adsorption (or solid bed) dehydration is the process where a solid desiccant is used for the removal of water vapor from a gas stream. The solid desiccants commonly used for gas dehydration are those that can be regenerated and, consequently, used over several adsorption-desorption cycles.

The mechanisms of adsorption on a surface are of two types; physical and chemical. The latter process, involving a chemical reaction, is termed "chemisorption". Chemical adsorbents find very limited application in gas processing. Adsorbents that allow physical adsorption hold the adsorbate on their surface by surface forces. For physical adsorbents used in gas dehydration, the following properties are desirable.

1. Large surface area for high capacity. Commercial adsorbents have a surface area of 500-800 m^2/g.
2. Good "activity" for the components to be removed, and good activity retention with time/use.
3. High mass transfer rate, i.e., a high rate of removal.
4. Easy, economic regeneration.
5. Small resistance to gas flow, so that the pressure drop through the dehydration system is small.
6. High mechanical strength to resist crushing and dust formation. The adsorbent also must retain enough strength when "wet".
7. Cheap, non-corrosive, non-toxic, chemically inert, high bulk density, and small volume changes upon adsorption and desorption of water.

Some materials that satisfy these criteria, in the order of increasing cost are; bauxite ore, consisting primarily of alumina ((Al_2O_3. x H_2O); alumina; silica gels and silica-alumina gels; and molecular sieves. Activated carbon, a widely used adsorbent, possesses no capacity for water adsorption and is therefore not used for dehydration purposes, though it may be used for the removal of certain impurities. Bauxite also is not used much because it contains iron and is thus unsuitable for sour gases.

Alumina

A hydrated form of aluminum oxide (Al_2O_3), alumina is the least expensive adsorbent. It is activated by driving off some of the water associated with it in its hydrated form ((Al_2O_3.$3H_2O$) by heating. It produces an excellent dew point depression values as low as -100 °F, but requires much more heat for regeneration. Also, it is alkaline and cannot be used in the presence of acid gases, or acidic chemicals used for well treating. The tendency to adsorb heavy hydrocarbons is high, and it is difficult to remove these during regeneration. It has good resistance to liquids, but little resistance to disintegration due to mechanical agitation by the flowing gas.

Silica Gel and Silica-Alumina Gel

Gels are granular, amorphous solids manufactered by chemical reaction. Gels manufactured from sulfuric acid and sodium silicate reaction are called silica gels, and consist almost solely of silicon dioxide (SiO_2). Alumina gels consist primarily of some hydrated form of Al_2O_3. Silica-alumina gels are a combination of silica and alumina gel.

Gels can dehydrate gas to as low as 10 ppm, and have the greatest ease of regeneration of all desiccants. They adsorb heavy hydrocarbons, but release them relatively more easily during regeneration. Since they are acidic, they can handle sour gases, but not alkaline materials such as caustic or ammonia. Although there is no reaction with H_2S, sulfur can deposit and block their surface. Therefore, gels are useful if the H_2S content is less than 5-6%.

Molecular Sieves

These are a crystalline form of alkali metal (calcium or sodium) alumina-silicates, very similar to natural clays. They are highly porous, with a very narrow range of pore sizes, and very high surface area. Manufactured by ion-exchange, molecular sieves are the most expensive adsorbents. They possess highly localized polar charges on their surface that act as extremely effective adsorption sites for polar compounds such as water and hydrogen sulfide. Molecular sieves are alkaline and subject to attack by acids. Special acid-resistant sieves are available for very sour gases.

Since the pore size range is narrow, molecular sieves exhibit selectivity towards adsorbates on the basis of their molecular size, and tend not to adsorb bigger molecules such as the heavy hydrocarbons. The regeneration temperature is very high. They can produce a water content as low as 1 ppm. Molecular sieves offer a means of simultaneous dehydration and desulfurization and are therefore the best choice for sour gases.

Solid desiccants or absorbents are commonly used for dehydrating gases in cryogenic processes. The use of solid adsorbent has been extended to the dehydration of liquid. Solid adsorbents remove water from the hydrocarbon stream and release it to another stream at higher temperatures in a regeneration step. A flow diagram for adsorption is shown in Figure 7.2.

Figure 7.3 illustrates the movement of an adsorption zone front as a function of time. In a dry desiccant bed, the adsorbate components are adsorbed at different rates. A short while after the process has begun, a series of adsorption zones appear, as shown in Figure 7.3-b. The distance between successive adsorption zone fronts is indicative of the length of the bed involved in the adsorption of a given component. Behind the zone, all of the entering component has been removed from the gas; ahead of the zone, the concentration of that component is zero. Note the adsorption sequence: C_1 and C_2 are adsorbed almost instantaneously, followed by the heavier hydrocarbons, and finally by water that constitutes the last zone. Almost all the hydrocarbons are removed after 30-40 min and dehydration begins. Water displaces the hydrocarbons on the adsorbent surface if enough time is allowed. At the start of dehydration cycle, the bed is saturated with methane as the gas flows through the bed. Then ethane replaces methane, and propane is adsorbed next. Finally, water will replace all the hydrocarbons.

For good dehydration, the bed should be switched to regeneration just before the water content of outlet gas reaches an unacceptable level. The regeneration of the bed consists of circulating hot dehydrated gas to strip the adsorbed water, then circulating cold gas to cool the bed down.

7.2 SWEETENING

Many natural gases contain hydrogen sulfide (H_2S) in concentration ranging from barely detectable quantities to over 30 mole percent. Gases containing H_2S or CO_2 are classified as sour, and gases free from H_2S and CO_2 are called sweet. With increasing demands to natural gas, natural gases containing H_2S are also being tapped for utilization after purification. Natural gas that is transported to the fuel market must meet legal requirements, which specify a maximum H_2S content less than 4 ppm in the gas. These requirements are justified, since H_2S is a toxic gas, and its combustion product is sulfur dioxide or trioxide. Besides emitting a bad odor at low concentrations, H_2S is deadly poisonous and at concentrations above 600 ppm it can be fatal in just three to five minutes. Its toxicity is comparable to cyanide. Thus, it cannot be tolerated in gas that would be used as domestic fuel. Further, H_2S is corrosive to all metals normally associated with gas transporting, processing and handling systems, and may lead to premature failure of most such systems.

The removal of H_2S from natural gas is accompanied by the removal of CO_2 and COS if present, since these have similar acid characteristics.

Like dehydration processes, desulfurization processes are primarily of two types: adsorption on a solid (dry process), and absorption into a liquid (wet process). Both the adsorption and absorption processes may be of the physical or chemical type. These processes may also be classified into the following categories:

1. Non-regenerative. The materials used in treating the gas are not recovered in these processes.
2. Regenerative processes with recovery as H_2S. These include the physical absorption processes, the amine processes, molecular sieves, etc.
3. Regenerative processes with recovery as elemental sulfur. With growing environmental concerns regarding sulfur emission, these processes have acquired a prominent role in desulfurization operations.
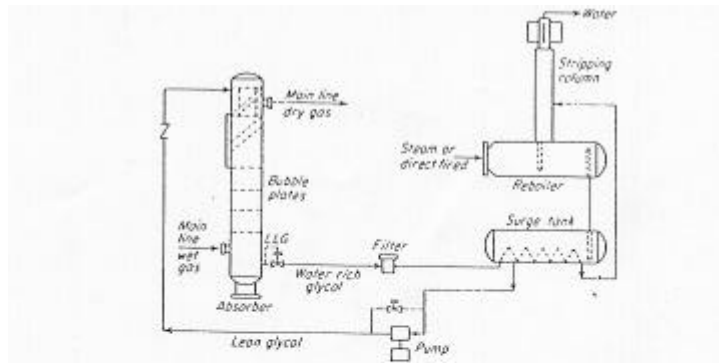
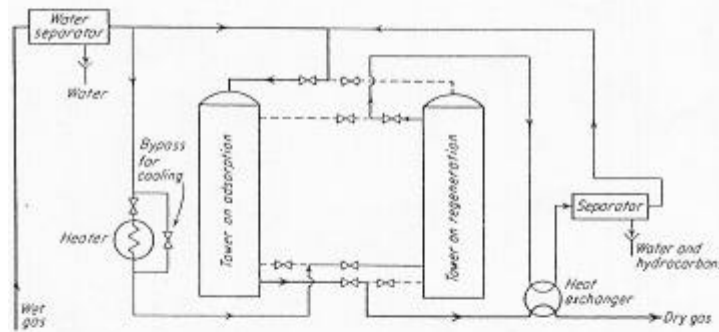Figure 7.1 Flow sheet for TEG dehydration plant.

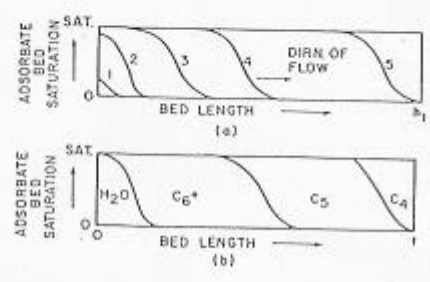Figure 7.2 Flow diagram for solid desiccant dehydration.

Figure 7.3 A schematic representation f the adsorption process.