DEHYDRATION OF ACID GAS PRIOR TO INJECTION Eugene W. Grynia, John J. Carroll, Peter J. Griffin, Gas Liquids Engineering, Calgary, Canada

Acid gas is a mixture of hydrogen sulfide and carbon dioxide, with small amounts of other components, and usually saturated with water, which is the by-product of the sweetening of sour gas. Acid gas injection is an environmentally friendly and economically viable option for dealing with unwanted acid gas and in particular small quantities of acid gas. Basically acid gas injection involves the compression of the gas to a sufficient pressure, transport of the compressed gas and injection into a disposal well.

In many injection schemes the gas does not require dehydration beyond that achievable by compression and cooling alone. In some circumstances additional dehydration is required. There are a number of methods commonly used to dehydrate the acid gas. The most popular is absorption of water with triethylene glycol (TEG). This paper discusses the design considerations for application of both methods of dehydrating acid gas: by compression and cooling alone, and by TEG.

1. Introduction

Acid gas is a mixture of hydrogen sulfide and carbon dioxide with a small amount of lower molecular weight hydrocarbons, mainly methane. Acid gas is most often produced in sour natural gas sweetening units, during regeneration of the sweetening chemical, usually an amine. Acid gas liberated from rich amine leaves the amine regeneration tower at a low pressure, typically below 200 kPa, and at about 50°C, the typical temperature downstream of the regeneration tower overhead condenser. In addition, the acid gas is saturated with water. This is not produced water, which contains dissolved salts, which can cause additional problems but rather this is condensed water which should contain virtually no dissolved solids.¹

If acid gas is to be injected into a subsurface formation such as an aquifer or a depleted reservoir, it must be compressed and sent to an injection well through a pipeline. Water present in acid gas can contribute to corrosion of the compression equipment and the pipeline, and it may facilitate hydrates formation. All main constituents of acid gas: H₂S, CO₂ and methane, are hydrate formers. Hydrates can form in acid gas without the presence of free water; however free water is required in the acid gas to cause corrosion of carbon steel. It is recommended to keep the relative water saturation of the acid gas mixture considerably below 100% in order to avoid condensation of water in the piping, facilities, pipeline or well.

In some cases acid gas dehydration by compression and cooling alone is sufficient to avoid corrosion and hydrate issues. If this is insufficient, an additional dehydration process is required. The most popular method of dehydrating acid gas prior to injection, other than compression and cooling is the use of triethylene glycol (TEG).

2. Acid Gas Phase Diagrams

Before any discussion of water content of acid gas and acid gas dehydration can commence, one needs to look at the phase diagrams of acid gas mixtures.

Fig. 1 shows phase diagrams of acid gas components, hydrogen sulfide and carbon dioxide, as well as some mixtures of the two gases. As methane is the most common impurity present in acid gas, its effect on the shape of the phase envelope is also shown on the graph for the 75% H₂S and 25% CO₂ mixture.

Of all the acid gases shown in Fig. 1 pure hydrogen sulfide liquefies most readily; at $48.9^{\circ}C(120^{\circ}F)$, the typical air cooler design temperature, H₂S liquefies at around 3500 kPa. Pure carbon dioxide can be liquefied only below 32°C. The phase diagrams of the mixtures of the two gases, possibly including some impurities like methane, are called phase envelopes. Most of the phase envelopes of acid gas lie between the phase diagrams of carbon dioxide and hydrogen sulfide. The higher the H_2S content of acid gas the closer its phase envelope lies to the phase diagram of pure H_2S .

Phase envelopes of acid gas are used in the design of acid gas compression and injection schemes. As it is important not to liquefy acid gas during compression, phase envelopes help determine the lowest safe interstage cooling temperatures. The cooling temperatures also affect the degree to which acid gas is dehydrated. Acid gases with a high concentration of $CO₂$ can be cooled in the interstage coolers to a lower temperature than acid gases with a high concentration of H_2S .

3. Water Content of Acid Gas

Let's start with the water content of sweet natural gas – natural gas that contains no H₂S. As the pressure increases the water content decreases. This is the case for all pressures of concern to the natural gas production and processing industries, that is for pressures up to about 100 MPa (14 500 psi).

The water content of acid gas mixtures is significantly different from that of sweet gas. Water is significantly more soluble in acid gas than it is in sweet gas. In addition, the water content of acid gas mixtures exhibits a minimum. Another important aspect of the water content is that acid gases tend to liquefy much more readily than sweet gas. Furthermore, the water content of the liquefied acid gas increases dramatically. That is, the water content of liquid acid gas is significantly greater than the vapor acid gas at the same conditions.

Fig. 2 shows saturated water content for pure hydrogen sulfide, pure carbon dioxide and three different mixtures of the two compounds at 48.9°C (120°F), a common design temperature of interstage air coolers. The saturated water content of methane is shown for comparison. The calculations were made using AQUAlibrium 3.1, a software developed by John Carroll, Gas Liquids Engineering.

Fig. 2: Saturated Water Content at 48.9°C (120°F)

At 48.9°C and 41.4 kPa (120°F and 6 psig), assumed to be the compressor suction conditions, the saturated water content of acid gas is approximately 63 $g/Sm³$ (3934 lb/MMSCF) and is practically independent on the composition of acid gas. With the increasing pressure, the water content decreases to a certain minimum and then it starts to increase. The dotted lines represent the transition from the gas phase to the liquid phase. Pure $CO₂$ and the mixture of 25% H_2 S and 75% CO₂ do not liquefy at 48.9°C. This can be compared with the CO₂ phase diagram in Fig. 1.

4. Water Content of Acid Gas for Different Isotherms

Figures 3, 4, and 5 show water content of pure H₂S, 50% H₂S and 50% CO₂ mix, and pure CO₂ at three different temperatures, 40° C, 48.9° C (120 $^{\circ}$ F), and 60 $^{\circ}$ C.

Fig. 3: Saturated Water Content of Pure Hydrogen Sulfide

Pure hydrogen sulfide liquefies at all the temperatures plotted on the above graph. The dotted lines represent the transition from the gaseous state to the liquid state. The transition pressures correspond to the vapor pressures shown for pure hydrogen sulfide in Fig. 1.

The water content of pure hydrogen sulfide is summarized below:

If acid gas were to be compressed just a little bit, from the pressure of the minimum water content of the gas to the pressure of the minimum water content of the liquid, than the relative water saturation of the liquid hydrogen sulfide would be as shown in the above table. The actual relative water saturation, however, depends on the pressure of the

gas from which the gas is compressed, and the discharge pressure, but it is not much different from the numbers presented in the table. As the relative water saturation of liquid pure hydrogen sulfide is well below 100%, dehydration by compression and cooling alone is sufficient to prevent corrosion.

Fig. 4: Water Content of 50% H2S and 50% CO2 Mix

The minimum water content of the mixture of 50% H_2S and 50% CO_2 is as follows:

Acid Gas Temperature	Minimum Water Content of Gas	Minimum Water Content of Liquid	Minimum Relative Water Saturation Of Liquid
\circ	g/Sm`	/Sm	
40	2.01	6.44	31%
48.9	2.95	6.82	43%
$60*$	4.57	8 94	51%

* The 50% H₂S and 50% CO₂ acid gas does not liquefy at 60°C. The relative water saturation was calculated for the minimum water content and the water content at 10000 kPa.

It is not always possible to design acid gas compression with the interstage discharge pressure close to the minimum water content of the gas. Let's assume that the acid gas pressure after the 3^{rd} stage cooler is 3400 kPa and 10000 kPa after the $4th$ stage cooler. The numbers would then look like this:

The relative water saturation of the 50% H_2S / 50% CO_2 acid gas mixture is below 100% therefore no corrosion is expected.

Fig. 5: Saturated Water Content of Pure CO²

At the temperatures plotted in Fig. 5 carbon dioxide does not liquefy. Only at temperatures below about 32°C will a CO2-rich liquid form (compare with the $CO₂$ phase diagram in Fig. 1). This is in contrast to the isotherms shown for hydrogen sulfide in Fig. 3, which show a distinct break at the liquefaction point.

Since carbon dioxide does not liquefy at the temperatures shown on the graph above, the calculation of the minimum water saturation does not apply here. Instead, it was assumed that the acid gas pressure after the $3rd$ stage cooler is 3400 kPa and 10000 kPa after the $4th$ stage cooler. The results are presented below:

It is evident that compression and cooling alone is not able to dehydrate carbon dioxide by compression and cooling to the temperatures above 45°C or so. At 48.9°C and 60°C, free water would be present at 10000 kPa. Hence, additional dehydration for these temperatures is required.

5. Effect of Impurities on Water Content of Acid Gas

The main impurity in the acid gas is methane. It has an effect on the water capacity of the acid gas. At high pressure, a hydrocarbon rich stream holds less water than an acid gas stream. The presence of methane in the acid gas therefore reduces the water holding capacity of the stream.

Fig. 6 shows the saturated water content of pure H₂S, pure CO₂ and, for comparison, pure methane at 48.9°C (120 \textdegree F). The addition of 1% methane has a bigger effect on the water content of H₂S than it has on the water content of CO₂. For example, at 48.9°C and 10000 kPa H₂S has a saturated water content of 18.62 g/Sm³, and CO₂ has a saturated water content of 3.20 $g/Sm³$. If the two gases contain 1% methane then the water content is reduced to 17.84 g/Sm³ and 3.09 g/Sm³ respectively. Thus, the presence of 1% methane in H_2S and CO_2 has reduced their water holding capacity by 4.2% and 3.4% respectively. Higher methane content reduces the water holding capacity of acid gas mixtures even more.

Even though methane affects saturated water content of high H_2S acid gases more than that of low H_2S acid gases, the presence of methane in acid gas containing a high percentage of $H₂S$ does not create a problem because the relative water saturation of liquid hydrogen sulfide is still low. The relative water saturation of pure H_2S compressed from 3400 kPa to 10000 kPa is 19.9% and for H2S with 1% methane it is 20.7%. On the other hand, methane effect on relative water saturation of liquid acid gas containing relatively low concentrations of H2S is more pronounced. For an acid gas composed of 25% H_2S and 75 % CO_2 , the saturated water content is 3.58 g/Sm³ at 3400 kPa and 4.88 g/Sm³ at 10000 kPa. The same acid gas with 1% methane has the saturated water content of 3.57 g/Sm³ at 3400 kPa and 4.56 g/Sm³ at 10000 kPa. Thus, if these two gases are compressed from 3400 kPa to 10000 kPa, the relative water content would be 73.4% and 78.3% respectively.

Fig. 6: Saturated Water Content at 48.9°C (120°F)

Ethane affects the water content of acid gas even more than methane. To compare it with methane, at 48.9°C and 10000 kPa H₂S containing 1% ethane has a saturated water content of 17.62 $\frac{g}{Sm^3}$. However, since ethane content of acid gas is usually much less than 1%, its effect on water holding capacity of acid gas can be neglected.

6. Acid Gas Dehydration

As mentioned in the Introduction, the presence of water in the acid gas poses several problems, including corrosion and hydrate formation. There are a number of ways water can be removed to various degrees from acid gas, including:

- Compression and cooling alone
- TEG dehydration
- Refrigeration
- Mole sieves
- Thermodynamic phase separation (Dexpro process, patent pending) 2

Dehydration of acid gas by compression and cooling is always used since the acid gas needs to be compressed and cooled anyway. If additional dehydration is required then water absorption with TEG is the most popular method.

6.1 Compression and Cooling Alone

Acid gas is usually compressed from a suction pressure of less than 200 kPa to a discharge pressure dictated by the reservoir pressure, injection well depth and the length of the acid gas injection pipeline. The number of compression stages depends on the required injection pressure, but usually does not exceed five. If more stages are required, acid gas is typically condensed after the last stage of compression and a pump is used to increase the acid gas pressure to the required value.

Fig. 7 shows a four-stage compression curve superimposed on saturated water curves at 48.9°C (120°F). The compression ratio for each stage is approximately 3, including interstage cooler pressure drops.

Fig. 7: Dehydration by Compression and Cooling to 48.9°C (120°F)

In this particular example, acid gas was dehydrated from 63 $g/Sm³$ to approximately 3.73 $g/Sm³$. At 10000 kPa saturated water content and relative saturation after compression of acid gas mixtures shown in Fig. 7 are as follows:

* Oversaturated, free water present.

Pure carbon dioxide cannot be dehydrated to relative water saturation below 100% if the $3rd$ stage discharge pressure is around 3400 kPa, as in the above example. However, if the next to last compression stage discharge pressure is increased to 5000 kPa, at which pressure the saturated water content is 2.80 $g/Sm³$, the relative water saturation of this particular acid gas decreases to 87.5%. If this acid gas contains 1% methane, the relative water saturation at 10000 kPa increases to 90.6%. To increase the pressure from the suction pressure of 142.7 kPa (6 psia) to 5000 kPa in three stages, the compression ratio would have to be around 3.4, including pressure drops across the interstage coolers.

When setting the interstage pressures to optimize acid gas dehydration by compression and cooling alone, one needs to check whether the interstage discharge temperatures do not exceed the limits recommended by the compressor vendor. If the limit is exceeded, the compression ratio needs to be lowered.

Based on the above analysis, a rule of thumb can be proposed which says that if the $H₂S$ content of acid gas is 25 mole% or more, dehydration by compression and cooling alone is sufficient to prevent corrosion. Otherwise additional dehydration may be required.

The above rule of thumb can be used for short injection pipelines and excludes situations when acid gas injection is suspended and acid gas sits in the pipeline for a long period of time, reaching the ground temperature. If the temperature of the acid gas falls to 2°C, assumed to be the ground temperature, the relative water saturation increases as follows:

* Oversaturated, free water present.

6.2 Acid Gas Dehydration with TEG

Triethylene glycol (TEG) is commonly used in dehydration of natural gas due to its relatively low vapor pressure. However, above 48.9°C (120°F) in the contactor, the TEG losses to the dry gas are high enough to justify cooling the inlet gas to or below 48.9°C. Another possibility would be to use tetraethylene glycol (TREG). It is more expensive than TEG but its losses to the dry gas are lower at high contactor temperatures due to its low vapor pressure. On the other hand pumping costs are higher because TREG is more viscous than TEG.³

The lower the temperature of the inlet gas at constant pressure the smaller the amount of water in the gas and smaller the required diameter of the contactor, since the density of the gas and consequently its actual velocity in the contactor is lower. However, the limiting factors in the selection of the gas temperature are the availability of the cooling media and hydrate formation, with the most important: the avoidance of acid gas condensation in the compressor interstage coolers.

The higher the pressure of the inlet gas at constant temperature the smaller the amount of water in the gas and smaller the required contactor diameter since the actual velocity of the gas in the contactor is lower. However, the acid gas feed pressure is determined earlier, in the design of the compressor interstage pressures.

Figure 8 shows a typical gas dehydration equipment configuration.

Fig.8: Acid gas dehydration with TEG.

The acid gas from the stage of compression prior to last flows through the Inlet Separator and enters the TEG Contactor at the bottom. It then flows upward through a number of trays or a layer of random or structured packing. The gas comes in contact with TEG flowing from the top of the Contactor. The dried gas leaves the Contactor at the top, cools down the lean TEG in the Dry/Lean Exchanger, and flows to the suction scrubber of the last stage of compression. The TEG, rich in water, leaves the Contactor and flows into the Flash Tank, where the pressure is lowered, usually to approximately 345 kPag (50 psig) or lower, to flash off some of the gas that was absorbed at high pressure in the Contactor. The TEG is then directed to the Rich/Lean Exchanger (glycol-glycol preheater) before being fed to the Still Column on top of the Reboiler, operating at the pressure close to atmospheric. The Still Column and the Reboiler are shown on Fig. 8 as the TEG Regenerator. Sometimes, the rich glycol is preheated in the Rich/Lean Exchanger first, and then it is sent to the Flash Tank.

The number of trays or the height of the packing depends on the required degree of dehydration. A typical number is 6 to 12 trays (real trays, not ideal stages). Since the acid gas does not have to be dehydrated to the same level as sales gas, a smaller number of trays might be sufficient. It is worth noting that the number of trays can have a greater effect on the amount of water removed than the circulation rate. The concentration of the TEG depends on the required degree of dehydration. If deeper dehydration is required, stripping gas is used to increase the concentration of lean glycol. In the case of acid gas dehydration there is no need for deep dehydration and stripping gas is not normally used in TEG units for acid gas dehydration.

The higher the glycol circulation rate at the constant gas flow rate the more water is removed from the gas. Normally, the glycol circulation rate is given as gallons of TEG per pound of water removed. A typical design is 2 to 7 gallons of glycol per pound of water to be removed, or, to simplify the design, per pound of water in the wet feed gas. Less than two gallons of glycol per pound of water may affect the gas-glycol contact and more than 7 gallons of glycol per pound of water may decrease the reboiler temperature and lean glycol concentration, which in turn decreases the glycol water absorption capacity.

Since the acid gas feed to the TEG Contactor is still wet, the feed lines are usually made from a corrosion resistant 316 stainless steel. The vessels, equipment, and piping on the TEG rich side are usually made from carbon steel, however there are specific areas where gas breakout is possible. In these instances - 316 stainless steel or 316 clad carbon steel is usually specified. Carbon steel is the material of choice for the lean side.⁴ If the feed is predehydrated with glycol upstream of the TEG Contactor then the contactor itself can be made of carbon steel instead of stainless steel.⁵

VMGSim, the trademark software of Virtual Materials Group, Calgary, Alberta, was used to simulate the dehydration of acid gas with TEG. Three theoretical stages were used in the TEG Contactor; this is equivalent to approximately 12 real trays. The flow rate of acid gas is 1 million SCMD on a dry basis, TEG circulation assumed to be the minimum recommended for good gas-glycol contact, which is 2 gallons (US) of glycol per pound of water in the feed gas. It was also assumed that rich glycol is heated up to 300°F in the Rich/Lean Exchanger before being fed to the Still Column. TEG is heated to 400°F in the Regenerator. The concentration of lean TEG is 98.7 wt. %.

Table 1 summarizes the results of the simulation.

Table 1: Results of the simulation of TEG dehydration for three different compositions of acid gas.

The flash gas from the Flash Tank and the offgas from the Still Column have a high concentration of hydrogen sulfide. Instead of sending the two streams to the flare or incinerator, they can be recycled to the first stage of compression to minimize emissions.

Fig. 9 presents the bottom part of the compression curve to better show how much TEG dehydration lowers the water content of acid gas compared to dehydration by compression and cooling alone.

Fig. 9: TEG Dehydration After 3rd Stage of Compression

The water content of acid gas shown in Fig. 9 is for 48.9°C (120°F). When the acid gas is transported in a long injection pipeline to the injection well, or if the injection operation is suspended for a period of time, the temperature of the acid gas may drop to the ground temperature. Since the saturated water content of acid gas decreases with decreasing temperature, the relative water saturation of the acid gas in the pipeline increases.

Table 2 compares relative water saturation of acid gas dehydrated with TEG after the third stage of compression. Again, the acid gas pressure after the third stage is 3400 kPa, the compressor discharge pressure is 10000 kPa. The comparison is for 48.9°C and for 2°C, assumed to be the ground temperature.

Table 2: Relative water saturation of TEG dehydrated acid gas at 48.9°C and 2°C

Acid gas dehydrated with TEG remains undersaturated with respect to water when the temperature of acid gas drops from 48.9°C to the ground temperature of 2°C.

It was suggested before that acid gas containing 25% or more of H2S does not have to be dehydrated beyond compression and cooling alone. It would be interesting to know how this rule of thumb is implemented in practice.

Table 3 shows some examples of acid gas injection schemes in Western Canada showing the composition of acid gas and the type of dehydration, if any.⁶

Injection	Acid Gas	Inj. Rate	Dehydration	Pipe	Line Length
Start Date	% H_2S/CO_2	$10^3 \text{ m}^3/\text{d}$	Type	Material	m
June 1989	12/88	6	TEG	CS	2 2 0 0
May 1995	20/80	120	TEG	CS	4 0 0 0
April 1996	65/35	16.9	Refrigeration	CS	2 200
May 1996	5/95	28	TEG	CS	1460
Nov. 1996	42/58	12	None	SS	150
Dec. 1996	60/40	5	Mole Sieve	CS	4 300
Dec. 1996	50/50	114	TEG	CS	1 200
March 1997	60/40	69	None	CS	4 800
July 1997	51/48		Refrigeration	CS	16 000
Nov. 2000	80/20	18.3	None	CS	
August 2001	50/50	15	TEG	CS	2420
Nov. 2001	74/25	90	TEG	CS	10 000
March 2002	1.5/98	130	TEG		
Oct. 2002	78/20	820	None		14 450
Dec. 2002	80/19	338	Refrigeration	CS	20 000

Table 3: Acid gas injection schemes in Western Canada (excerpts)

There are more than 60 acid gas injection schemes in North America and only 15 are listed in the above table. But based on the schemes listed, TEG dehydration was used in all cases where acid gas contains less than 25% H2S. Some operators decide for various reasons to dehydrate the acid gas with higher content of H_2S .

Table 3 also shows the material of construction of the injection pipelines. Most of the lines are made of carbon steel because acid gas is already sufficiently dehydrated. For non-dehydrated acid gas, the line can be carbon steel or 316L stainless steel. Stainless steel is more expensive so, if the line cost exceeds the dehydration unit cost, then perhaps it is more economical to dehydrate the acid gas.

7. Hydrates of Acid Gas

Corrosion is not the only concern when there is water in the acid gas stream. Hydrates formation temperatures will also need to be checked when designing an acid gas injection scheme. Fig. 10 shows hydrate formation curves for a number of acid gas compositions. The highest hydrate formation temperatures are for pure hydrogen sulfide, the lowest – for pure carbon dioxide.

Fig. 10: Acid Gas Hydrates

Table 4 summarizes the hydrate formation temperatures for 5 acid gases of different composition.

Table 4: Summary of hydrate formation temperatures for various acid gases.

If acid gas is cooled to 50°C or so, then, depending on the length of the pipeline, it may reach the injection well before it cools below the hydrate formation temperatures shown in Table 4. However, in case of long pipelines, the temperature of acid gas may reach the ground temperature which may be lower than the hydrate formation temperature. In such cases dehydration with TEG should be considered for any acid gas, not only the one that contains less than 25% H₂S. Another consideration is an interruption of acid gas injection during which acid gas remains in the pipeline and slowly cools down to the ground temperature that may be below the hydrate formation temperature. A remedy would be to dehydrate the acid gas anyway or if dehydration is not considered, inject the acid gas remaining in the injection pipeline with dry sweet gas.

8. Conclusions

Acid gas has to be compressed prior to injection. The process of compressing and interstage cooling is often sufficient to dehydrate acid gas below 100% relative water saturation thus avoiding corrosion problems. Otherwise other means of dehydrations are required, most often by using triethylene glycol (TEG). TEG units are installed before the last stage of compression. No stripping gas is required. TEG circulation rate can be kept to a minimum but to ensure good contact between the gas and the glycol, the circulation rate has to be at least 2 gallons (US) of glycol per pound of water in the acid gas being fed to the TEG contactor.

There are cases where dehydration of acid gas by means other than compression and cooling alone should be considered even if the relative water saturation of the acid gas is below 100%. Additional dehydration is required if the acid gas injection pipeline is long enough to allow cooling the acid gas to ground temperature or the temperature below hydrate formation, or if the operating philosophy of the acid gas injection scheme allows for suspension of injection with the acid gas sitting in the injection pipeline until the acid gas temperature reaches ground temperature or the temperature below hydrate formation.

Literature

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