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## Abstract

Sour natural gas contains carbon dioxide or hydrogen sulfide or both. In addition, sour gas often contains other sulfur species such as mercaptans and carbonyl sulfide. The carbon dioxide and sulfur components of the natural gas have to be removed to meet the sales gas specifications. The removed components are called acid gas. There are different ways of dealing with acid gas: it can be flared, used for sulfur production or injected into a geological formation. Because of environmental constraints, only sulfur production or injection are viable options. This paper deals with various aspects of sour gas sweetening that makes the injection of acid gas more economical. To look at sour gas sweetening from the point of view of acid gas injection (AGI), one has to understand the variables that affect AGI. The most important variable is the wellhead injection pressure which determines the AGI compressor discharge pressure. The wellhead injection pressure depends on reservoir pressure and temperature, reservoir depth, the density of the acid gas, the acid gas flowrate and the size of the injection tubing. The paper presents the required wellhead injection pressure for different compositions of acid gas at various acid gas injection temperatures for the same reservoir conditions, injection tubing diameter and acid gas flowrate. The paper compares estimated densities for pure hydrogen sulfide, carbon dioxide and mixtures of the two at various temperatures and pressures. In general, the density of pure hydrogen sulfide at various pressures and temperatures is higher than that of carbon dioxide, which means that the higher the H<sub>2</sub>S content in the acid gas the higher the density of the mix and the lower the required wellhead injection pressure. Another important aspect of AGI is the water content of acid gas. The higher the water content the higher the hydrate formation temperature. The saturated water content of acid gas is a function of acid gas pressure and temperature as well as the gas composition. The paper discusses the water content of acid gas and its effect on hydrate formation temperature. There are a number of technologies for sweetening of natural gas, such as absorption, adsorption, membranes, liquid redox, scavenging, biological, and cryogenic. This paper concentrates on absorption technologies, which include chemical, physical and mixed (hybrid) solvents. Depending on H<sub>2</sub>S and CO<sub>2</sub> concentrations in the feed gas to the absorption unit and the type of the absorption medium, the acid gas can have H<sub>2</sub>S and CO<sub>2</sub> in various proportions. Acid gas with high CO<sub>2</sub> to H<sub>2</sub>S ratio or low H<sub>2</sub>S concentration will require acid gas enrichment to be suitable as feed to a Claus plant. No such enrichment is required for AGI; acid gas with any proportions of H<sub>2</sub>S to CO<sub>2</sub> is suitable for disposal into a geological formation. The acid gas phase envelopes and the acid gas densities discussed in the paper were calculated using VMGSim software offered by Virtual Materials Group. Water content of acid gas was calculated using AQUAlibrium software and wellhead injection pressures were calculated using GLEWPro software.

## 1. Introduction

There are a number of technologies for sweetening of sour natural gas, such as absorption, adsorption, membranes, liquid redox, scavenging, biological, and cryogenic. Absorption technologies are most widely used. They use chemical, physical and mixed (hybrid) solvents for the removal of acid components of sour gas. Most often, the solvents are alkanolamines, often just called amines. The processing units for the removal of acid components of natural gas are often called AGRs – Acid Gas Removal units. Depending on H<sub>2</sub>S and CO<sub>2</sub> concentrations in the feed gas to the AGR unit and the type of the absorption medium, the acid gas can have H<sub>2</sub>S and CO<sub>2</sub> in various proportions.

If the intent is to produce sulfur from acid gas, high CO<sub>2</sub> to H<sub>2</sub>S ratio or low H<sub>2</sub>S concentration will require acid gas enrichment (AGE) – acid gas with less than approximately 30% H<sub>2</sub>S may not be good for a straight-through Claus process and various ways of AGE might be required. An AGE process uses a selective solvent to reject as much CO<sub>2</sub> as

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possible and to recover most H<sub>2</sub>S. It is basically another AGR unit, where the acid gas from the first AGR unit is further processed to concentrate the H<sub>2</sub>S content in the acid gas.

If the intent is to produce CO<sub>2</sub> for enhanced oil recovery (EOR), the CO<sub>2</sub> product has to meet Quality Specifications for Industrial CO<sub>2</sub> Use for CO<sub>2</sub>-EOR published by the Global CCS Institute, which is minimum 95% CO<sub>2</sub>, maximum 5% hydrocarbons and less than 10 – 200 ppm H<sub>2</sub>S. No specifications are required for AGI; acid gas with any proportions of H<sub>2</sub>S to CO<sub>2</sub> is suitable for disposal into a geological formation.

Figure 1 shows the block flow diagram for possible ways of handling acid gas from a sweetening unit. Sour gas is sweetened in a regenerable liquid solvent sweetening unit. The acid gas, depending on the composition and processing objective, can be sent directly to a Sulfur Plant, to an AGI unit or to an AGE unit for either increasing the H<sub>2</sub>S content of the acid gas before it is sent to the Sulfur Plant or for increasing CO<sub>2</sub> concentration for EOR.

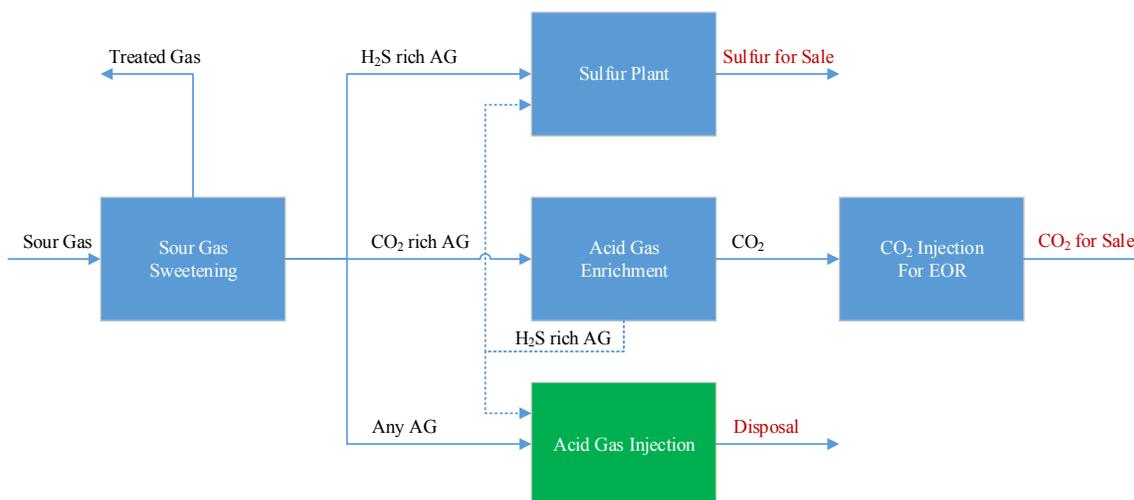


Figure 1. Block flow diagram for handling acid gas

The sour gas sweetening itself can be accomplished in two stages: in the first, H<sub>2</sub>S is removed with maximum CO<sub>2</sub> slippage, and in the second, CO<sub>2</sub> is removed to be sold for EOR. Such a processing scheme is depicted in Figure 2.

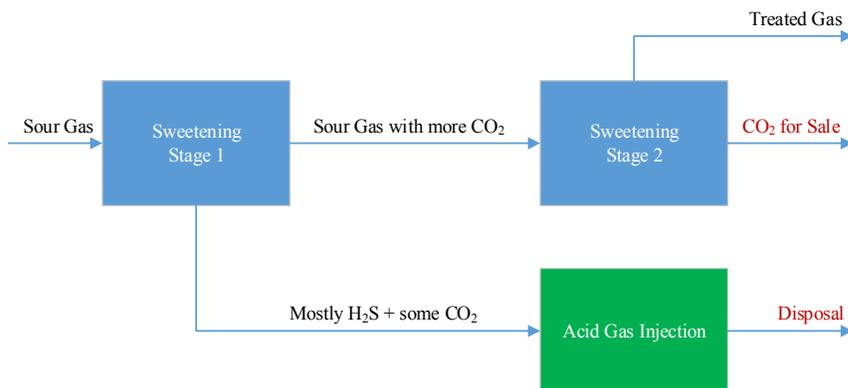


Figure 2. Block flow diagram for two-stage sweetening

In AGI, the density of acid gas plays an important role because the higher the density the lower the required wellhead injection pressure and consequently, the lower the compression costs. For the acid gas temperature and pressure ranges encountered in acid gas injection, the density of acid gas increases with H<sub>2</sub>S concentration.

Given the above, when choosing a solvent for the sweetening of sour natural gas, one should select a solvent which maximizes CO<sub>2</sub> slippage, or, in other words, a solvent, or an amine that does not absorb or reacts with CO<sub>2</sub>. There are primary, secondary and tertiary amines. Primary amines have one functional group attached to the nitrogen atom, secondary amines have two, and tertiary amines have three. H<sub>2</sub>S reacts readily with any amine, whereas for CO<sub>2</sub> the reactions with amines are more complex. There are two reaction mechanisms, a fast one that leads to the formation of a carbamate and a slow one that leads to the formation of bicarbonate and carbonate. The first one requires a

hydrogen atom in the amine structure, that is why  $\text{CO}_2$  reacts fast with primary and secondary amines, but does not react with tertiary amines. The other requires the presence of water but it involves all the amines. Since we are interested in maximizing the density of acid gas, we should try to slip as much  $\text{CO}_2$  as possible, which means we should use tertiary amines for sweetening the sour natural gas. The most popular tertiary amine used for sweetening is MDEA, methyldiethanolamine. There is another group of amines that do not react with  $\text{CO}_2$  called sterically hindered amines. Those are amines with bulky functional groups that make it difficult for  $\text{CO}_2$  to access and react with the nitrogen to form a carbamate. DIPA, di-isopropanolamine, is a secondary amine, but at the same time it is considered a sterically hindered amine because of two large isopropyl groups. Another example of a sterically hindered amine is AMP, 2-amino-2-methyl-1-propanol, a primary amine. AMP is offered by ExxonMobil as FLEXSORB. Other means of slipping  $\text{CO}_2$  involve shortened contact time with the amine, achieved by using fewer trays in the amine contactor. Yet another method is taking advantage of the fact that  $\text{CO}_2$  reacts with amines of higher density more slowly. The density of the amines can be increased by decreasing their temperature and increasing their concentration.

## 2. Densities of $\text{CO}_2$ , $\text{H}_2\text{S}$ and Their Mixtures

It would be beneficial to start the discussion of acid gas densities with the review of acid gas phase envelopes. Figure 3 shows the phase envelopes of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and their mixtures. The critical point of  $\text{H}_2\text{S}$  lies at 8.97 MPa and 100.2°C. The critical point of  $\text{CO}_2$  lies at 7.38 MPa and 31°C. At a given temperature, up to 31°C,  $\text{H}_2\text{S}$  becomes liquid at much lower pressures than  $\text{CO}_2$  when compressed. At a given pressure,  $\text{CO}_2$  has to be cooled down to a much lower temperature than  $\text{H}_2\text{S}$  to become liquid. These conditions favor  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}$ -rich acid gas in acid gas injection since such an acid gas can be liquefied at higher temperatures and lower pressures than  $\text{CO}_2$  and  $\text{CO}_2$ -rich acid gas.

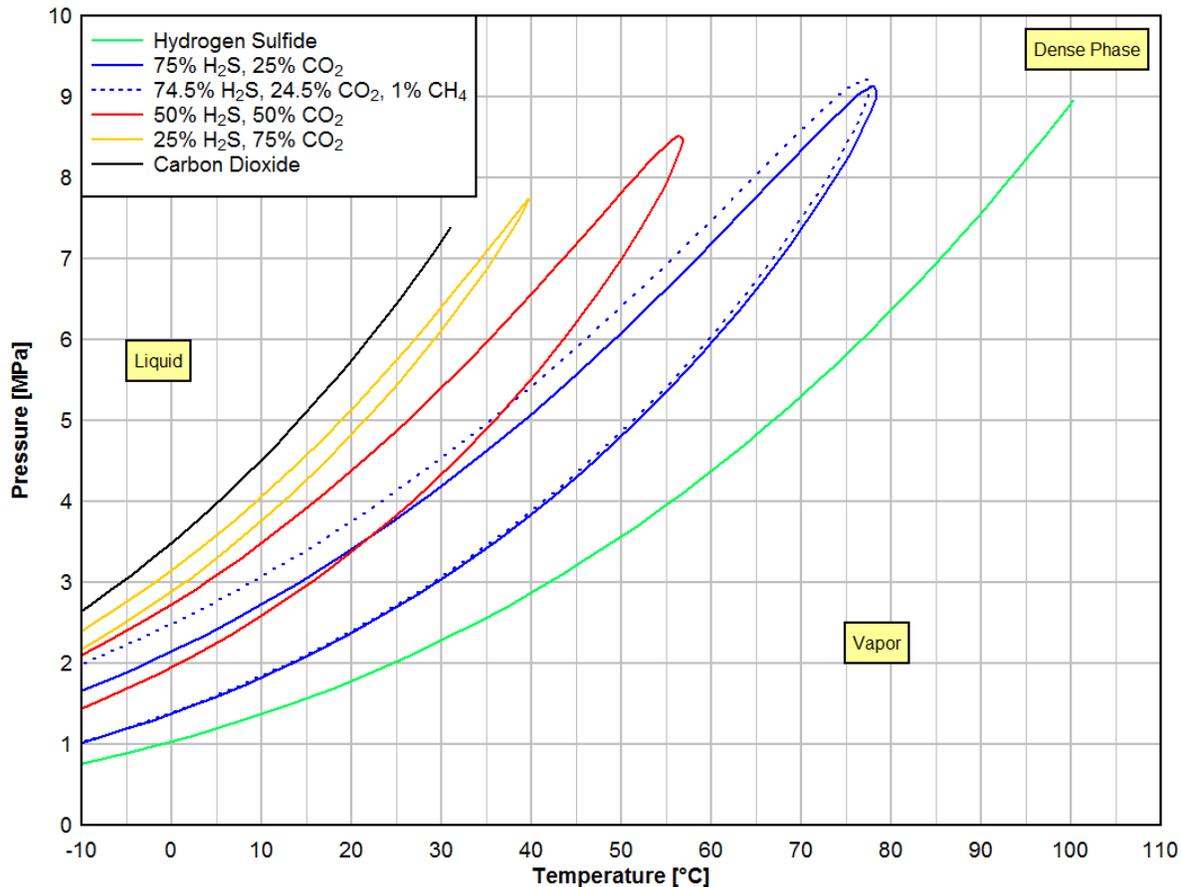


Figure 3. Phase envelopes of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and their mixtures

The density of pure  $\text{H}_2\text{S}$  and pure  $\text{CO}_2$  as a function of pressure is shown in Figure 4. As could be expected, the higher the pressure, the higher the density and the higher the temperature, the lower the density of both gases. In general, densities of gaseous  $\text{CO}_2$  are higher than those of gaseous  $\text{H}_2\text{S}$ . However, with increasing pressure, when the two gases become liquids,  $\text{H}_2\text{S}$  is denser than  $\text{CO}_2$ .

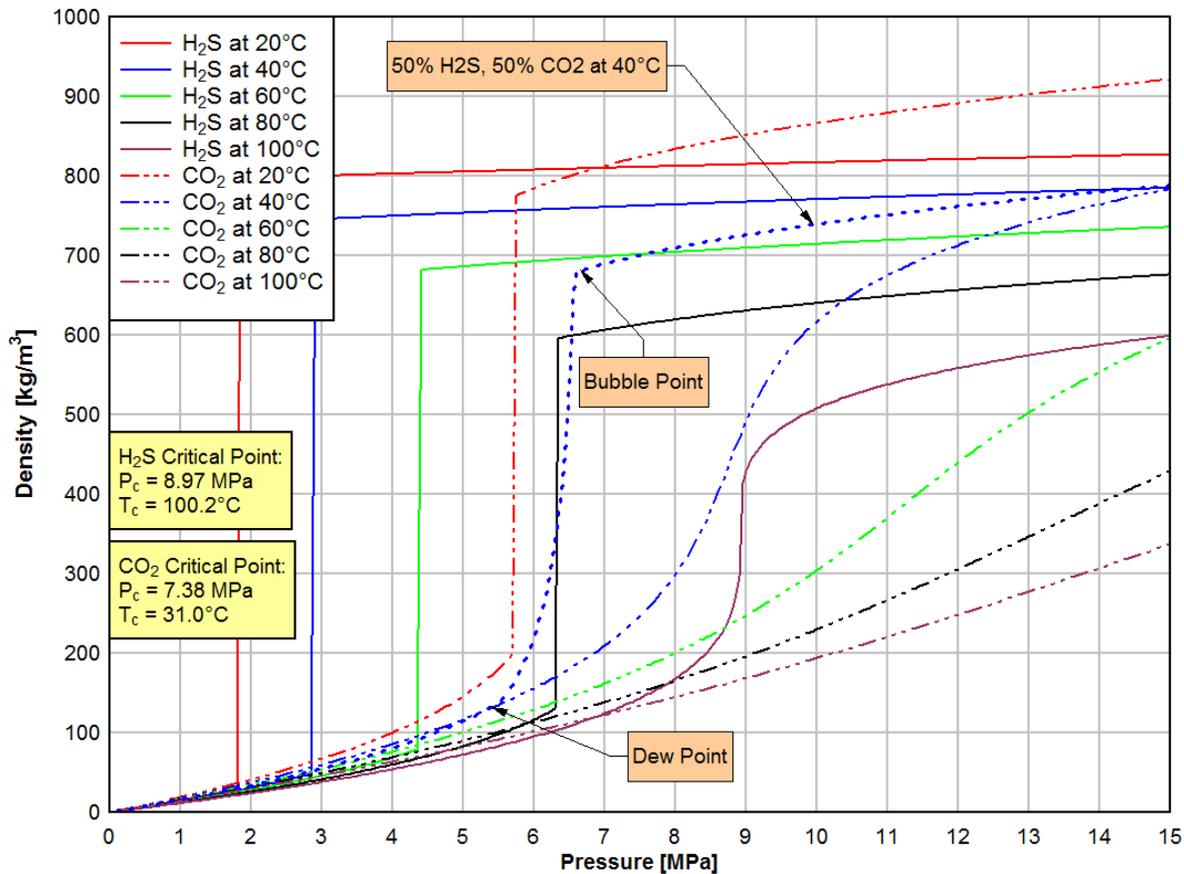


Figure 4. Pressure dependent densities of H<sub>2</sub>S and CO<sub>2</sub> at various temperatures

The densities of H<sub>2</sub>S and CO<sub>2</sub> as functions of temperature are shown in Figure 5. At lower temperatures, the density of CO<sub>2</sub> is higher than that of H<sub>2</sub>S. At higher temperatures, above 30 - 40°C, depending on the pressure, the density of H<sub>2</sub>S becomes higher than that of CO<sub>2</sub>. This is the temperature range to which acid gas can be cooled down in an aerial cooler during compression. The densities of acid gas were calculated using the VMGSim software.

**2.1. Effect of Impurities on the Density of Acid Gas**

In reality, acid gas is not composed of H<sub>2</sub>S or CO<sub>2</sub> or a mixture of the two components only. It has a number of impurities, the most important being water and methane. Figure 3 shows the effect of methane on the shape of the phase envelope of acid gas. It moves it to the left and makes it wider which means that the acid gas has to be cooled to a lower temperature to liquefy it. Methane decreases the density of acid gas, which means that a higher pressure is required to liquefy it. Water, on the other hand, increases the density of acid gas and decreases the required wellhead injection pressure. Table 1 compares the wellhead injection pressures for acid gas with methane and with water. The calculations are based on acid gas flowrate of 30,000 Sm<sup>3</sup>/d, the wellhead flowing temperature of 37.8°C, the well depth of 2500 m, the reservoir pressure of 25 MPa and the injection tubing inside diameter of 5.07 cm (1.995 inch).

Table 1. Wellhead injection pressure as a function of acid gas composition

Composition	Wellhead Injection Pressure (MPa)	Density at Wellhead (kg/m <sup>3</sup> )
75% H <sub>2</sub> S, 25% CO <sub>2</sub> , dry basis	7.242	749.4
75% H <sub>2</sub> S, 25% CO <sub>2</sub> , water saturated at 3.4 MPa (after the 3 <sup>rd</sup> stage of compression)	6.805	766.4
74.5% H <sub>2</sub> S, 24.5% CO <sub>2</sub> , 1% CH <sub>4</sub>	7.538	737.2

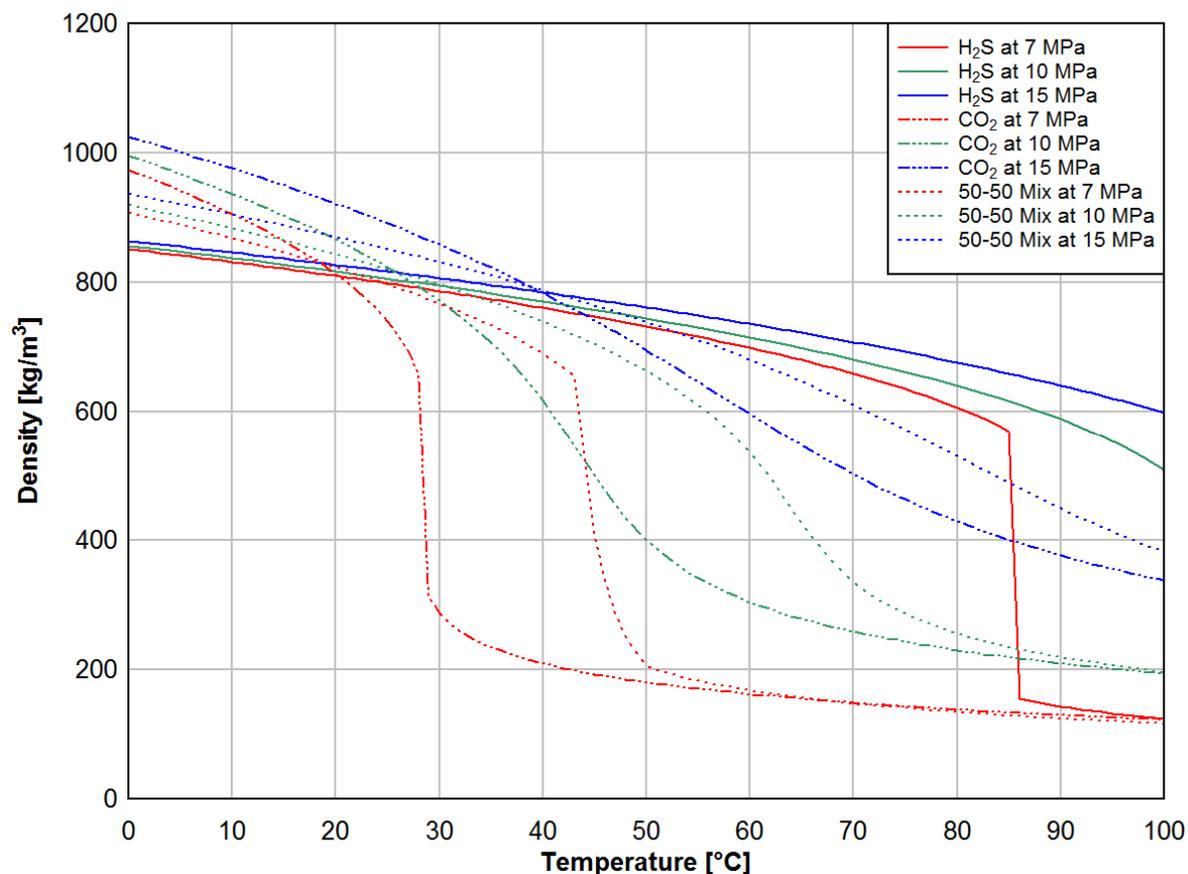


Figure 5. Temperature dependent densities of H<sub>2</sub>S and CO<sub>2</sub> at various pressures

### 3. Water Content of Acid Gas

Figure 6 shows saturated water content of H<sub>2</sub>S and CO<sub>2</sub> at various temperatures. The saturated water content curves for mixtures of H<sub>2</sub>S and CO<sub>2</sub> lie between the curves for pure H<sub>2</sub>S and CO<sub>2</sub>. The curves presented in the graph were calculated using AQUALibrium software. At low pressures, the water content of the acid gas is essentially independent of composition. It is also a decreasing function of the pressure. But acid gas exhibits a minimum in the water content, which is not the case with the hydrocarbons. With increasing pressure, when acid gas changes from vapor to liquid, its saturated water content increases – the increase is considerable in case of pure H<sub>2</sub>S and is slight in case of pure CO<sub>2</sub>. The higher the temperature of the acid gas the higher the saturated water content of the acid gas. The presence of hydrocarbons in the acid gas decreases its saturated water content slightly.

Acid gas is generated in the amine regenerator column and leaves the column saturated with water. Acid gas cannot be injected “as is” and must be dehydrated to a certain degree to prevent corrosion of the equipment and piping and to avoid hydrate formation. Corrosion is enhanced by the presence of free water but free water does not have to be present for hydrates to form.

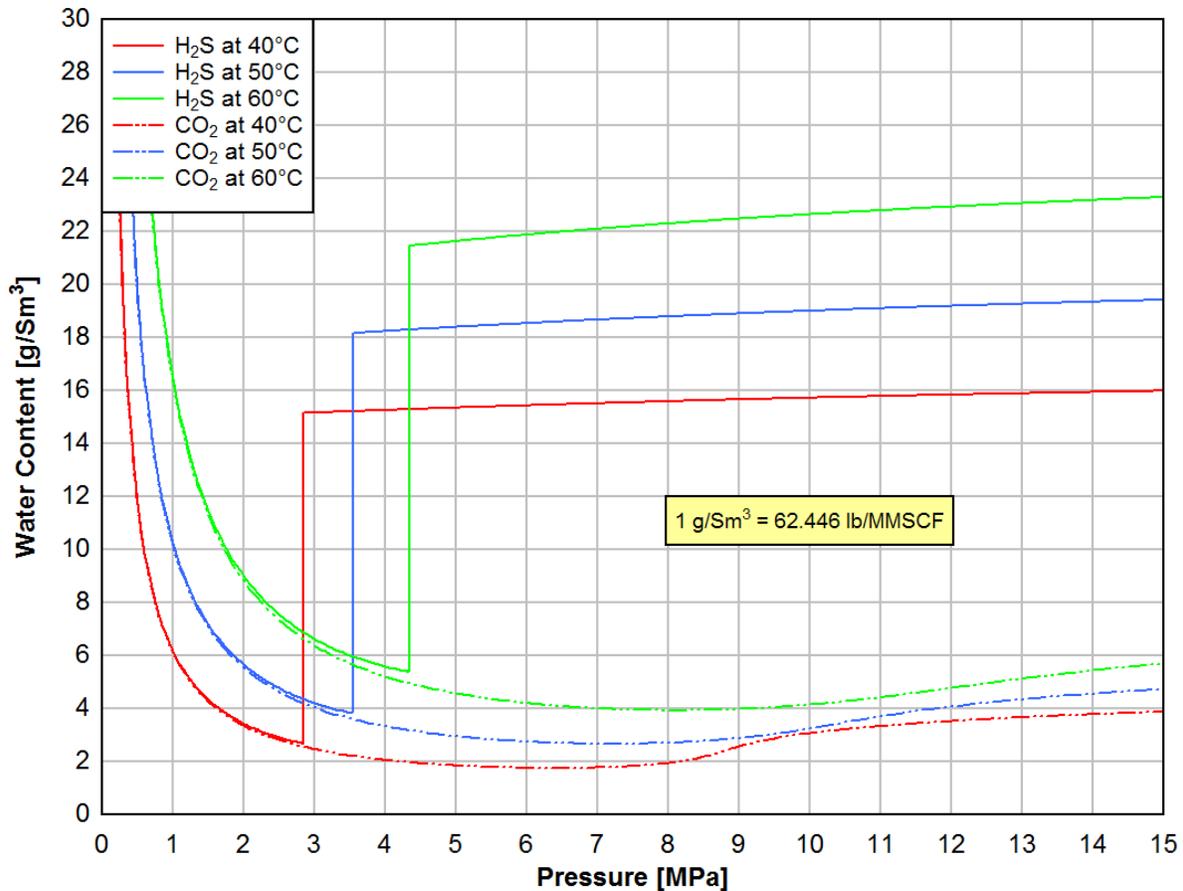


Figure 6. Water content of H<sub>2</sub>S and CO<sub>2</sub> at various temperatures

### 3.1. How to Dehydrate Acid Gas?

In many injection schemes acid gas does not require dehydration beyond that achievable by compression and cooling alone. In some circumstances additional dehydration is required. As can be seen in Figure 7, the acid gas compressed to 3.4 MPa and cooled to 48.9°C (120°F) contains approximately 3.6 g/Sm<sup>3</sup> of water. Compressing the acid gas to 10 MPa in the last stage of compression does not change its water content. But at 10 MPa, the saturated water content of pure H<sub>2</sub>S is approximately 18.6 g/Sm<sup>3</sup> and the saturated water content of pure CO<sub>2</sub> is approximately 3.2 g/Sm<sup>3</sup>. This means that pure H<sub>2</sub>S at 10 MPa is well undersaturated with respect to water and does not need dehydration, whereas pure CO<sub>2</sub> at 10 MPa is oversaturated with water and definitely requires additional dehydration to prevent corrosion and hydrate formation issues. As a rule of thumb, it can be said that the acid gas with 25% H<sub>2</sub>S and more does not need additional dehydration.

There are a number of methods commonly used to dehydrate the acid gas. The most popular is absorption of water with triethylene glycol (TEG). Other methods include adsorption, e.g. on molecular sieves or silica gel, or proprietary methods like the patented Dexpro process, in which a small slipstream (typically 10-20%) of the dense phase final acid gas fluid is passed through a temperature control JT valve and reinjected into the Dexpro module upstream of the final stage suction scrubber. The effect of TEG dehydration is shown in Figure 7, where the acid gas, after the third stage of compression, was dehydrated from 3.6 g/Sm<sup>3</sup> to approximately 0.3 g/Sm<sup>3</sup>. With this degree of dehydration, even the pure CO<sub>2</sub> is well below the saturated water content at 10 MPa. The benefit of dehydrating acid gas is lowering the hydrate formation temperature. Without TEG dehydration, the hydrate formation temperature at 10 MPa is +30°C for pure H<sub>2</sub>S and +10°C for pure CO<sub>2</sub>. With TEG dehydration as shown in Figure 7, the hydrate formation temperature drops to -39°C and -32°C respectively. The hydrate formation temperature becomes important when acid gas is transported to the injection wellhead in a long pipeline, where the acid gas temperature may drop to the ground temperature.

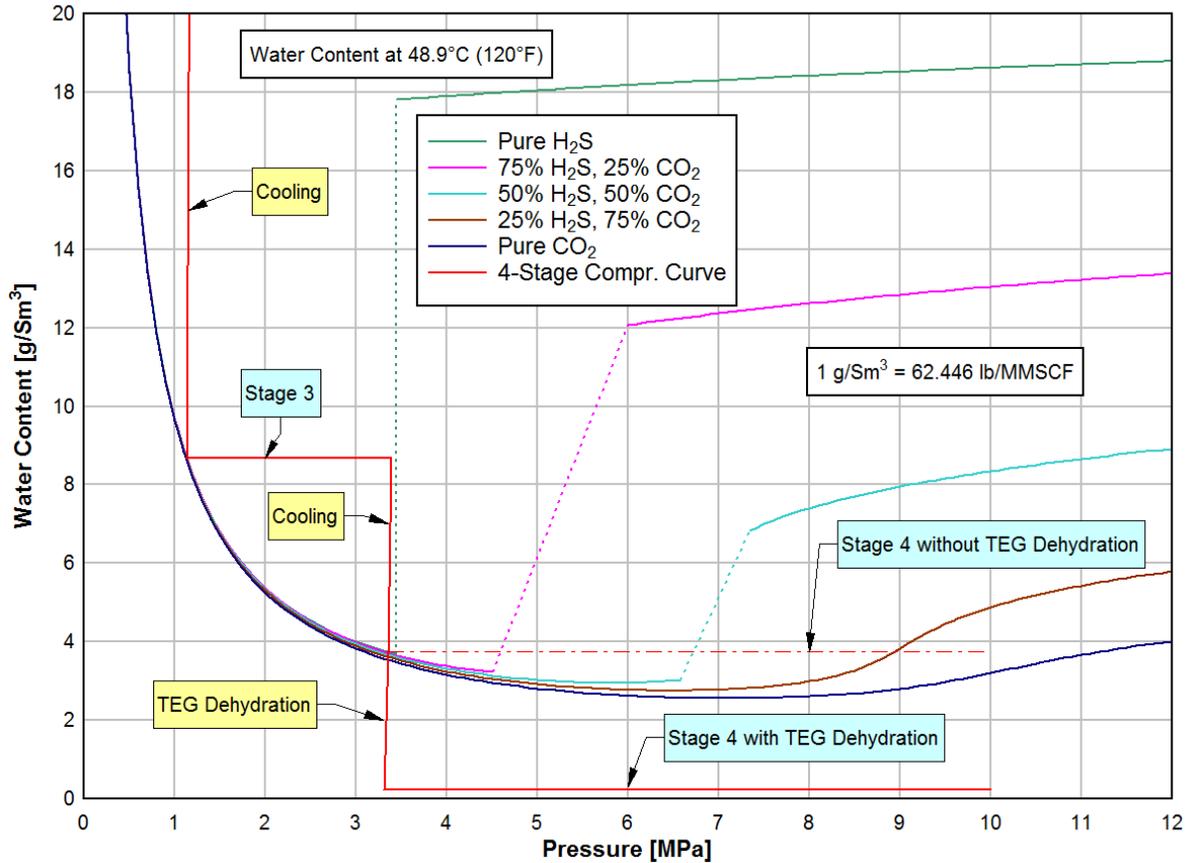


Figure 7. Acid gas dehydration with and without TEG

#### 4. Estimating Wellhead Injection Pressure

The most important variable affecting AGI is the wellhead injection pressure which determines the AGI compressor discharge pressure. The wellhead injection pressure depends on:

1. Reservoir pressure
2. Reservoir temperature
3. Reservoir depth
4. The density of the acid gas
5. The acid gas flowrate
6. The size and wall roughness of the tubing in the injection well

The designer of an AGI scheme does not have any influence over the first three. The density of the acid gas is affected by the temperature and composition of the acid gas. It is also affected by the pressure, but the acid gas injection pressure is calculated using the variables mentioned in points 1, 2, 3, 5 and 6 above.

The wellhead injection pressure  $P_{inj}$  can be expressed using equation (1):

$$P_{inj} = P_{res} + \Delta P_{por} + \Delta P_{sd} + \Delta P_{per} - P_{sh} + P_f \tag{1}$$

- Where:
- $P_{res}$  = reservoir pressure (bottomhole pressure)
  - $\Delta P_{por}$  = pressure drop due to formation porosity and permeability
  - $\Delta P_{sd}$  = pressure drop due to skin damage
  - $\Delta P_{per}$  = pressure drop through the perforations
  - $P_{sh}$  = static head of tubing fluid
  - $P_f$  = frictional pressure drop

For small acid gas injection schemes the reservoir pressure and static head terms are the only ones of significance. Gas Liquids Engineering uses its own in-house program, called GLEWPro, for the calculation of the required wellhead pressure.

Figure 8 shows the wellhead injection pressure as a function of acid gas composition. It was assumed for simplicity, that the acid gas is composed of H<sub>2</sub>S and CO<sub>2</sub> only. The presence of methane in acid gas decreases its density. The presence of water in acid gas increases its density.

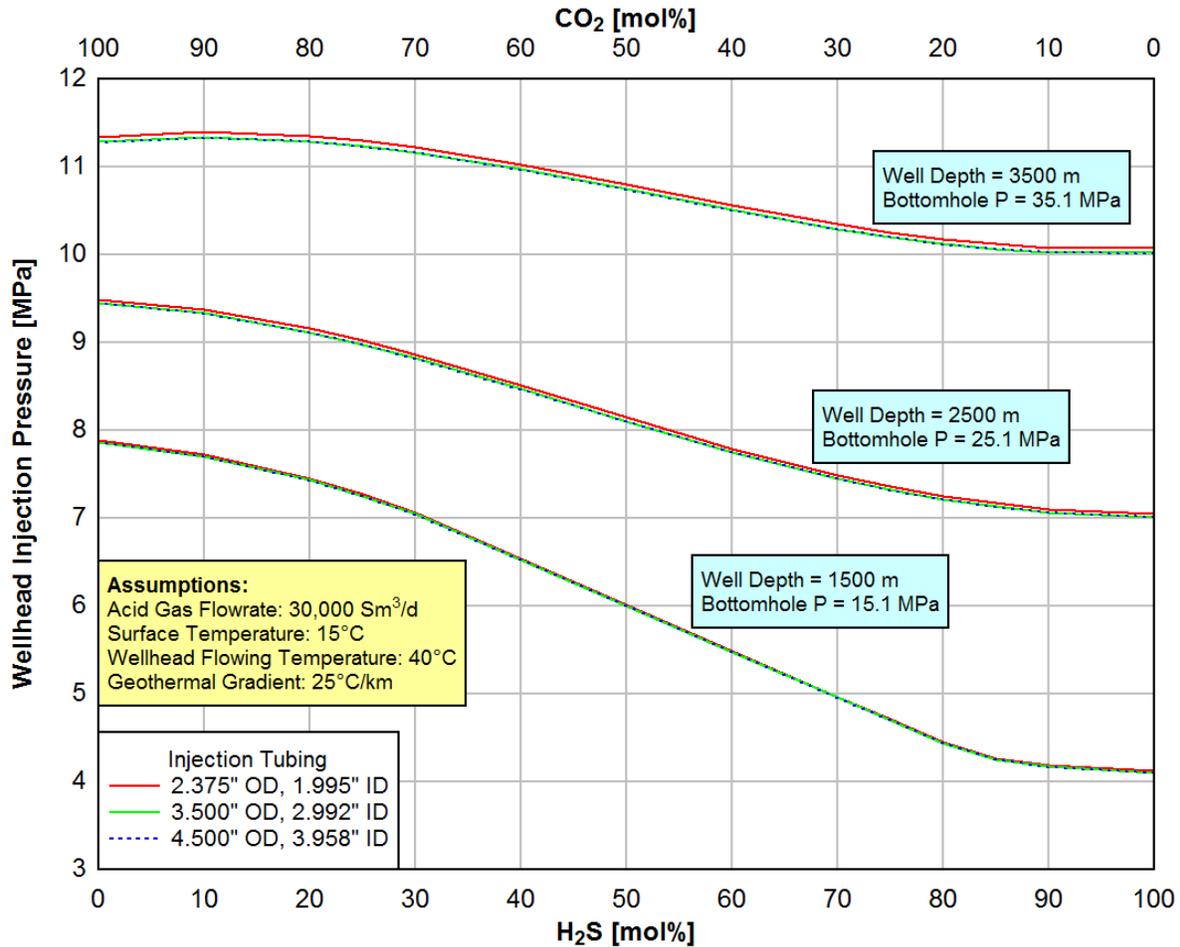


Figure 8. Wellhead injection pressure as a function of acid gas composition

The wellhead injection pressures presented in Figure 8 are for acid gas temperature of 40°C at the wellhead. The acid gas temperature plays an important role in the calculation of the wellhead injection pressure. Figure 9 shows the wellhead injection pressure as a function of acid gas temperature at the wellhead. The higher the temperature of acid gas the higher the wellhead injection pressure. This could be expected as higher temperature decreases the density of acid gas. It would obviously be desirable to cool down the acid gas as low as possible but it is rarely possible for two reasons; first – most often air coolers are used for compressor interstage cooling and the ambient temperature dictates the achievable cooling temperature, second – when cooling acid gas, care should be taken not to condense acid gas before the final stage of compressing because we want to separate water from acid gas and not acid gas from acid gas, and, as can be seen in Figure 3, some acid gas phase envelopes make it impossible to cool down the acid gas below 50 – 60°C.

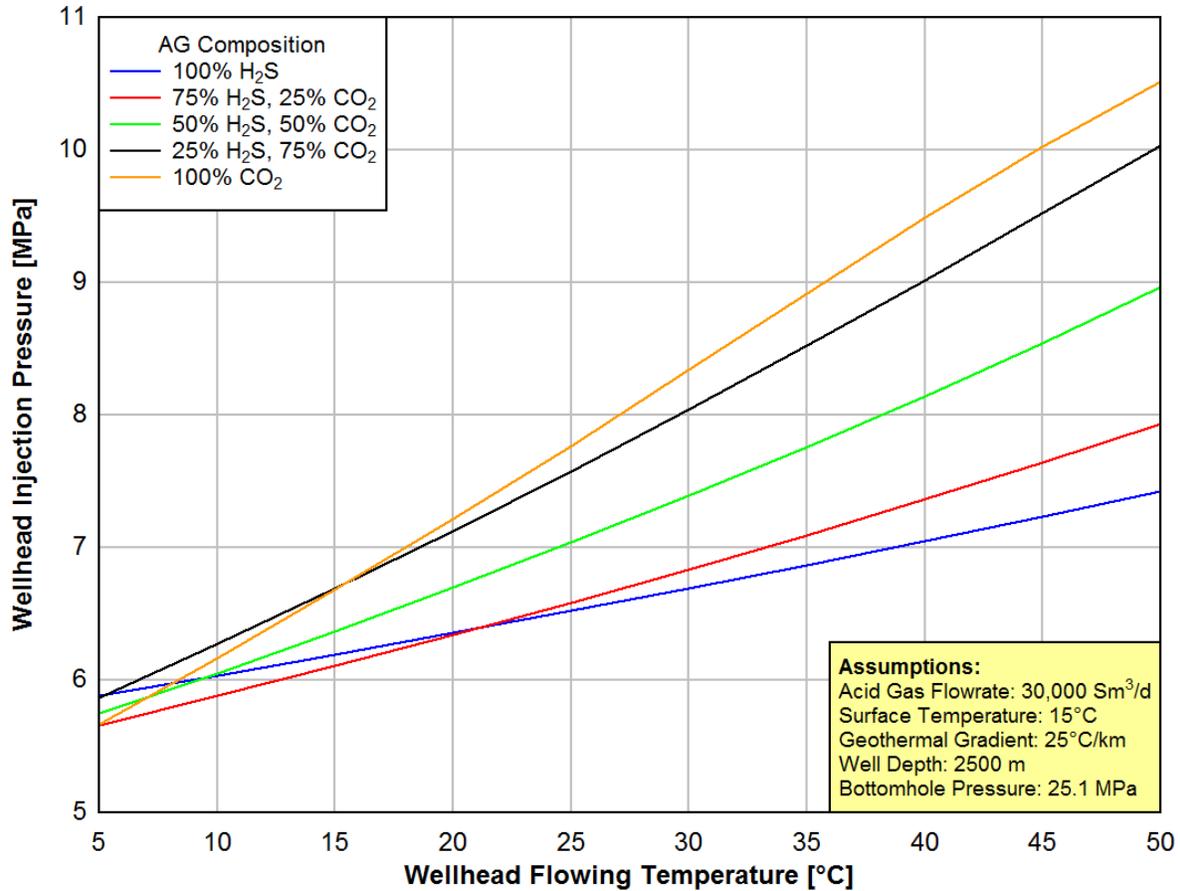


Figure 9. Wellhead injection pressure as a function of acid gas temperature

Wellhead injection pressure depends on the composition of the acid gas, but compressor power also depends on the composition of the acid gas, albeit to a much lesser extent. Table 2 shows the compressor power required to compress 30000 Sm<sup>3</sup>/d of acid gas from 0.156 MPa to 11 MPa (after the last cooler). The temperature of acid gas at the inlet to the AGI compressor is 50°C. It was assumed that the interstage cooling temperatures are the same for all gas compositions shown in Table 2. The results show that the difference in compressor power between pure H<sub>2</sub>S and pure CO<sub>2</sub> is only 3%. Analyzing wellhead injection pressures presented in Figure 7, one can say that the difference in wellhead injection pressures between pure CO<sub>2</sub> and pure H<sub>2</sub>S could be as high as 90%.

Table 2. Acid gas composition vs compressor power

Acid Gas Composition (mol%)	Compressor Power (kW)
100% H <sub>2</sub> S	226.1
75% H <sub>2</sub> S, 25% CO <sub>2</sub>	229.2
50% H <sub>2</sub> S, 50% CO <sub>2</sub>	231.3
25% H <sub>2</sub> S, 75% CO <sub>2</sub>	232.4
100% CO <sub>2</sub>	232.8

### 5. Conclusions

Injection into a geological formation is a suitable method of disposing of unwanted acid gas. The main cost of injection is the acid gas compression. The compression power is a function of the wellhead injection pressure. The wellhead injection pressure is a function of the reservoir pressure and temperature, reservoir depth, acid gas flowrate, acid gas density, and the diameter of the injection tubing. Once the injection reservoir has been selected, the only variables that can still be changed are the acid gas density and the injection tubing diameter. Acid gas density has a major impact on the wellhead injection pressure; injection tubing diameter plays a lesser role in the wellhead injection pressure.

Acid gas density is a function of the composition of the acid gas, its pressure and temperature. The main components of acid gas are hydrogen sulfide, carbon dioxide, and to a lesser extent – hydrocarbons, mainly methane, and water. The higher the H<sub>2</sub>S content of the acid gas and the lower its temperature - the higher the density of acid gas. The H<sub>2</sub>S concentration can be increased by using selective amines which absorb H<sub>2</sub>S but do not absorb much CO<sub>2</sub>. This means that if one wants to minimize the required wellhead injection pressure, one should try to generate acid gas with the highest H<sub>2</sub>S concentration and the lowest possible temperature. Methane in the acid gas decreases acid gas density, so to minimize methane content in acid gas, the amine plant should be equipped with a flash tank which enables methane and other volatile components to separate from rich amine before it reaches the regenerator column. Water on the other hand increases acid gas density but water is detrimental in the process of acid gas injection because of corrosion of equipment and piping if free water is present and because of potential for hydrate formation even if no free water is present.

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