

Fundamentals of Acid Gas Injection (AGI)

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1: PHASE BEHAVIOR AND PHYSICAL PROPERTIES RELEVANT TO ACID GAS INJECTION

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The foundation of a good process design is accurate physical property and phase equilibrium calculations. This is no less true for acid gas injection than for any design. The design of an acid gas injection scheme requires knowledge of the density, enthalpy, entropy, viscosity, thermal conductivity, and other properties of the acid gas mixture. This paper presents a discussion of the various phenomena in general and a review of specific tools for calculating the properties and phase behavior.

For density calculations simple corrections to the Peng-Robinson and Soave-Redlich-Kwong equations are accurate to within about 3%, except in the region near a critical point. Correlations are provided in this paper for estimating the viscosity and thermal conductivity of acid gas mixtures. These are significantly less accurate than the density predictions, one should anticipate errors on the order of 20% or more.

For phase equilibrium calculations in the absence of an aqueous phase, the commonly-used cubic equations of state can be used with excellent accuracy. However, they are much less accurate for predicting the phase equilibrium involving a water-rich phase, notably the water content of the acid gas. Extreme caution is recommended for calculating the water content of acid gas. Simple models, and even some of the more advanced models, can result in large errors. Many of these models do not show the correct qualitative behavior, notably the minimum in the water content.

Among the components commonly found in natural gas mixtures, none forms a hydrate more readily than hydrogen sulfide. In addition, mixtures containing hydrogen sulfide form hydrates more readily than similar mixtures without H₂S. Thus hydrates are potentially a problem in the design and operation of an acid gas injection scheme. Models are available for predicting the formation of hydrates in acid gas systems. In systems where there is plenty of water, one can anticipate errors as large as 3 Fahrenheit degrees. In water reduced situations, the design engineer should be cautious. Many models, even the advanced models, are not designed to handle this situation.

In the natural gas business it is common to predict the physical properties of a sour gas stream by calculating the properties for a sweet gas and then correct for the presence of acid gas components. In general, these corrected sweet gas methods *should not be used for acid gas*.

Introduction

Let's begin with a few definitions. Strictly speaking "sour gas" is natural gas that contains significant amounts of sulfur compounds – so much that it has to be treated in order to produce a saleable product. The most important of these sulfur compounds is hydrogen sulfide. Carbon dioxide is often associated with hydrogen sulfide and processes for removing these compounds are very similar. Thus gas that contains CO₂ but no sulfur compounds is often also called sour gas, but this is strictly not the case.

"Sweet gas" is therefore the opposite of sour gas, in as much as it contains only very small amounts of sulfur compounds or none at all. The processes for producing sweet gas from sour gas are called sweetening.

Finally, in the natural gas business "acid gas" is a mixture which contains hydrogen sulfide and carbon dioxide, but may contain small amounts of other gases. The term acid gas comes from the fact that when dissolved in water H₂S and CO₂ form weak acids. An acid gas stream is the by-product of the sweetening

process. Typically aqueous solvents are used to sweeten sour gas. Thus the acid gas produced is usually saturated with water and water can be problematic. Also, the acid gas contains some hydrocarbons. The amount and type of hydrocarbons in the acid gas depends upon the solvent used in the sweetening process. With chemical solvents (those that react chemically with the acid gas), methane tends to be the most significant hydrocarbon present in the acid gas. With physical solvents and mixed solvent (a combination of a chemical and a physical solvent), there tends to be more heavier hydrocarbons in the acid gas.

Acid gas injection has quickly becoming the method of choice for disposing of small quantities these gases. Basically, the acid gas is compressed to high pressure, transported via pipeline to an injection well, and injected into a suitable subsurface formation. In addition, with the current depressed market for sulfur, some larger producers are considering acid gas injection as an alternative for dealing with unwanted sulfur.

Physical Properties: Density, Viscosity, Thermal Conductivity

Physical Properties of Pure H₂S and pure CO₂

Carbon dioxide is one of the most often studied industrial compounds, possibly only second to water. A rather large database exists for the physical properties of carbon dioxide. There is significantly more data available for carbon dioxide than for hydrogen sulfide, particularly for transport properties. One reason for this is that carbon dioxide is significantly easier to deal with than hydrogen sulfide. Hydrogen sulfide is toxic and requires special precautions when used in the lab. In addition, carbon dioxide has a much lower critical point making the interesting critical region in the range of more experimenters. The vicinity of critical point is attractive to researchers because of the nature of the physical properties in that region – the properties change dramatically with small changes in either the temperature or the pressure.

Pure CO₂

Over the years, there have been several tables of properties published for carbon dioxide. The thermodynamic properties of CO₂, including the density, were reviewed by Angus et al. (1976) and tables of thermodynamic properties were constructed. However, the latest tables for the thermodynamic properties of CO₂ are those of Span and Wagner (1996).

Vukalovich and Altunin (1968) reviewed both the thermodynamic and transport properties. As a part of their study, Vukalovich and Altunin (1968) reviewed 15 studies reporting measurements of the viscosity of CO₂ under pressure for dates up to 1965. They noted differences as large as 20% between the various experimental investigations.

The data for the viscosity and thermal conductivity were reviewed, correlated, and tabulated by Vesovic et al. (1990). Vesovic et al. (1990) listed 27 studies of the viscosity of dense carbon dioxide, mostly studies undertaken after 1965. Among their selected data set agreement was generally better than 10%, and often much better.

Vesovic et al. (1990) listed almost 60 investigations of the thermal conductivity of CO₂, both at low pressure and under pressure. Deviations among their selected data set for the high-pressure regions typically agree to with better than 5%, with the exception of the critical region. Vesovic et al. (1990) confirm that in general the thermal conductivity is a strong function of the density, except in the critical region.

The viscosity of saturated liquid CO₂ can be estimated from the correlation:

$$\ln \mu = -15.43217 + 0.165216 T - 3.35203 \times 10^{-4} T^2 \quad (1)$$

where μ is in $\mu\text{Pa}\cdot\text{s}$ and T is in K and $260 < T < 302 \text{ K}$ ($-8.3 < t < 87.5^\circ\text{F}$). This equation reproduces the saturated liquid CO_2 values from Vesovic et al. (1990) to within $\pm 3\%$. This correlation should not be extrapolated beyond the given temperature range, especially to higher temperatures where CO_2 liquid does not exist.

Pure H_2S

Goodwin (1983) reviewed the thermodynamic properties of hydrogen sulfide, including the density. Using an advanced equation of state a table of properties was constructed over a wide range of pressures and temperatures. These tables are useful for estimating the density and thermodynamic properties of pure H_2S .

There is only a very small data set for the viscosity of hydrogen sulfide. There have been three experimental investigations of the viscosity of liquid hydrogen sulfide: Steele et al. (1906), Hennel and Krynicki (1959), and Runovskaya et al. (1970). The temperature ranges for the three sets of data are given in Table 1. For the two low-temperature studies, Steele et al. (1906) and Runovskaya et al. (1970), the pressure was probably 1 atm (14.696 psia), whereas the study of Hennel and Krynicki (1959) was at the vapor pressure of pure H_2S . In spite of their age, the data of Steele et al. (1906) have been used in many reference books including the *DIPPR Data Book* (Daubert et al., 1999).

Table 1 Summary of Measurement of the Viscosity of Liquids Hydrogen Sulfide

Reference	Temperature Range
Steele et al (1906)	-82.2 to -63.4°C -116.0 to -82.1°F
Hennel and Krynicki (1959)	-11.5 to +50.0°C +11.3 to +122.0°F
Runovskaya et al. (1970)	-83.1 to -61.4°C -117.6 to -78.5°F

Figure 1 shows a plot of the three data sets for the viscosity of liquid hydrogen sulfide. The plot reveals the discrepancy between the data of Steele et al. (1906) and Runovskaya et al. (1970). Also shown on this plot is a correlation of the data. This is based on all three sets of data and represents a reasonable agreement, especially for the low temperature data. The equation is:

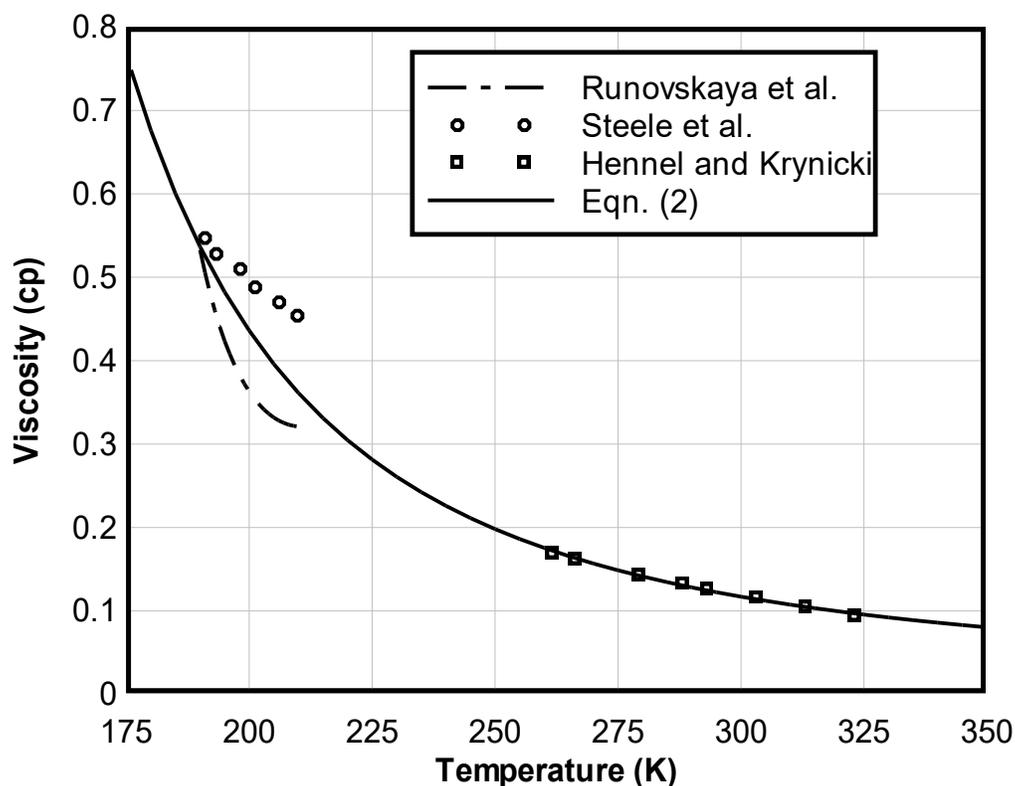
$$\ln \mu = 2.13461 + \frac{788.636}{T} \quad (2)$$

where μ is in $\mu\text{Pa}\cdot\text{s}$ and T is in K and $180 < T < 324 \text{ K}$ ($-135 < t < 124^\circ\text{F}$). It should not be extrapolated beyond the given temperature range.

The only experimental data for the low-pressure viscosity of vapor hydrogen sulfide are those of Rankine and Smith (1921). Furthermore, there are no data for the viscosity of H_2S under pressure.

There are even less data available for the thermal conductivity of hydrogen sulfide than there are for the viscosity. To the best of the author's knowledge, the only measured data for the thermal conductivity of H_2S are those of Barua et al. (1968). These data are for low-pressure gas in the temperature range – 78.5° to 200°C. Any data in the literature for the liquid or high-pressure gas regions were undoubtedly based on generalized correlations.

Fig. 1 Viscosity of Liquid Hydrogen Sulfide



Physical Properties of Mixtures

Although tabulated data are highly useful for pure components, they are less useful for mixtures. In addition, the equations of state used to generate the tables are very complicated and not easily extended to mixtures. It would be impossible to tabulate properties for all mixtures of industrial interest. Thus limited amounts of experimental data are obtained and correlations are developed to cover the range of conditions of interest in industrial practice.

Density

There are limited data for the physical properties of mixtures of H_2S and CO_2 . In a study of the phase behavior and volumetric properties of sour gas mixture Robinson et al. (1960) reported the densities for three mixtures of carbon dioxide and hydrogen sulfide. These data were for mixtures containing 17.75%, 20.35% and 60.25% hydrogen sulfide at 160°F for pressures from 150 to 1800 psia. All of these data are in the gaseous region (compressibility factors in the range 0.95 to 0.45). In a more thorough investigation of the binary system H_2S+CO_2 Kellerman et al. (1995) measured the densities of four mixtures: 6.07%, 9.55%, 29.33%, and 49.99% hydrogen sulfide. Temperatures in this study ranged from -9.7° to 350.3°F and pressures up to 2900 psia. These measurements included both liquid and vapor regions.

For the calculation of thermodynamic properties, including the density, the cubic equations of state have become the workhorse of the process simulation business. In particular, the equations of state of Soave (1972) [SRK] and of Peng and Robinson (1976) [PR] and modifications of these original forms are the most commonly used. Boyle and Carroll (2002) performed a detailed study investigating the accuracy of cubic equations of state for estimating the density of acid gas mixtures. Except in the region near a critical point, they showed that a volume-shifted SRK or PR equation is sufficiently accurate for engineering calculations in the gas, liquids, and supercritical regions. Typically errors for the volume-shifted equations

of state were less than 3% over the range of temperature and pressure of interest in acid gas injection, where errors as large as 15% were observed.

If the mixture is a liquid, then a simple correlation, based on the pure components densities, can be used to estimate the density:

$$v_{\text{mix}} = \sum_{i=1}^{\text{NC}} x_i v_i^{\text{pure}} \quad (3)$$

where v_{mix} is molar volume of the mixture, v_i^{pure} is the molar volume of pure i , x_i is mole fraction of component i , and NC is the number of components in the mixture. Then the density is then calculated from:

$$\rho = \frac{M}{v} \quad (4)$$

A significant problem with this approach is how do we apply this equation if all of the substances are not liquids at the conditions of interest? For example, consider a mixture containing 20% carbon dioxide and 80% hydrogen sulfide at 120°C and 1000 psia. At these conditions the mixture is a liquid as is H₂S, but pure CO₂ is not. At this temperature, carbon dioxide is supercritical. What value should be used for the specific volume of pure CO₂ in the above equation in order to obtain the specific volume of the mixture? To avoid this problem we need some mixture information from which we could extract a mixture-specific pure pseudo-property. Such a problem does not arise when using an equation of state approach.

For example, from Span and Wagner (1996), the density of pure CO₂ at 120°F and 1088 psia is 12.3 lb./ft³ and from Goodwin (1983) the density of pure H₂S is 45.7 lb./ft³. Using the simple model given above [Eqn. 3 and (4)] the estimated density for a mixture containing 20% carbon dioxide and 80% hydrogen sulfide is 27.5 lb./ft³. Using the volume-shifted PR equation the density is estimated to be 43.8 lb./ft³. In this case the equation of state yields a better estimate of the true density.

Viscosity

The availability of viscosity for the pure components was discussed earlier. In addition, no data are available in the scientific literature for the transport properties (viscosity and thermal conductivity) of mixtures of H₂S and CO₂.

The *DIPPR Data Book* (Daubert et al., 1999) provides a relatively simple correlation for the low pressure viscosity of many compounds. Their equation is given below:

$$\mu^* = \frac{A T^B}{1 + C/T + D/T^2} \quad (5)$$

where μ^* is the low pressure viscosity in Pa·s, T is the absolute temperature in K, and A , B , C , and D are empirical constants. The constants for the components of interest in this study are given in Table 2.

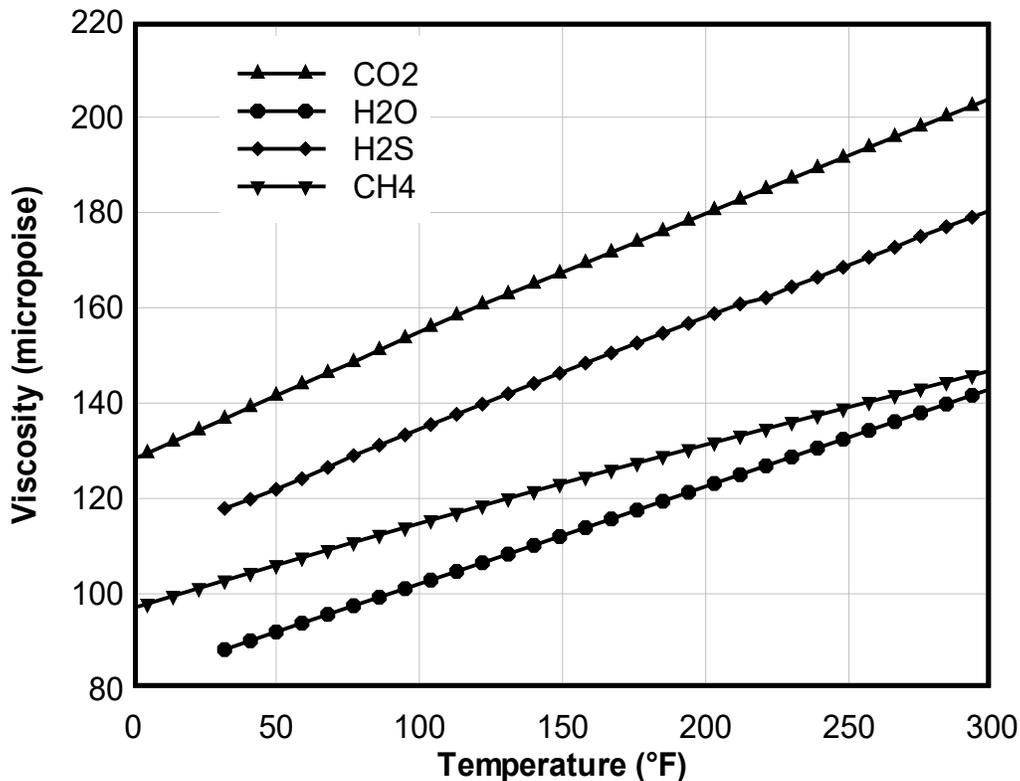
Table 2 Coefficients for the DIPPR Equation for Low Pressure Viscosity

	A	B	C	D
Water	6.1839×10 ⁻⁷	6.7779×10 ⁻¹	8.4723×10 ⁺²	-7.3930×10 ⁺⁴
hydrogen sulfide	4.2860×10 ⁻⁷	6.7150×10 ⁻¹	1.6710×10 ⁺²	0.0000×10 ⁺⁰

carbon dioxide	2.1480×10^{-6}	4.6000×10^{-1}	$2.9000 \times 10^{+2}$	$0.0000 \times 10^{+0}$
Methane	1.3230×10^{-5}	1.7980×10^{-1}	$7.1800 \times 10^{+2}$	$-8.9000 \times 10^{+3}$
Ethane	7.8170×10^{-6}	2.7300×10^{-1}	$9.8100 \times 10^{+2}$	$-3.0300 \times 10^{+4}$
propane	2.2090×10^{-6}	3.8240×10^{-1}	$4.0500 \times 10^{+2}$	$0.0000 \times 10^{+0}$

Figure 2 shows the viscosity of H₂S, CO₂, water, and methane at low pressure calculated using Eqn. (5). Note, for a gas at low pressure, the viscosity increases with increasing temperature, which is contrary to the behavior of a liquid. As can be seen from the plot, the low pressure viscosity of the acid gas components is greater than that for either water or methane. Although not shown in this figure, the low pressure viscosity of ethane and propane are less than methane, which is the trend for light hydrocarbon gas viscosity which decreases with increasing gravity. Also note that of the four components shown in Fig. 2, water has the lowest low pressure viscosity.

Fig. 2 Viscosities of Several Gases at Low Pressure



Although kinetic theory can be used to predict the viscosity of mixtures of gases, the equations are very complicated. If some additional assumptions are made, the following simplified mixing rule is obtained:

$$\mu_{\text{mix}}^* = \sum_i \frac{y_i \mu_i^*}{\sum_j y_j \phi_{ij}} \quad (6)$$

where y_i is the mole fraction of component i , μ_i^* is the low pressure viscosity of pure i . Most correlations use this approach and the problem becomes one of estimating the parameters ϕ_{ij} . For example, Wilke (Reid et al., 1987) gives the following expression:

$$\phi_{ij} = \frac{\left[1 + (\mu_i^*/\mu_j^*)^{1/2} (M_i/M_j)^{1/4}\right]^2}{\left[8(1 + M_i/M_j)\right]^{1/2}} \quad (7)$$

where M_i is the molar mass of component i and M_j is the molar mass of component j .

As an example of a generalized correlation for viscosity at high pressure consider the method developed by Jossi et al. (1962). The corresponding states method of Jossi et al. (1962) can be used to correct for the high density:

$$\left[(\mu - \mu^*)\xi + 1\right]^{1/4} = 1.0230 + 0.23364 \rho_R + 0.58533 \rho_R^2 - 0.40758 \rho_R^3 + 0.0923324 \rho_R^4 \quad (8)$$

where μ^* is low pressure viscosity (from above) and ρ_R is the reduced density ($\rho_R = \rho/\rho_C$). Note that this correlation indicates that the high pressure viscosity is a function of the density alone. All other parameters in this equation are either scaling factors or constants. The ξ is calculated using:

$$\xi = \left[\frac{RT_C N_A^2}{M^3 P_C^4} \right]^{1/6} \quad (9)$$

where R is the universal gas constant, T_C is the critical temperature, N_A is Avogadro's number, $6.022 \times 10^{23} \text{ mol}^{-1}$, M is the molar mass, and P_C is the critical pressure. It is not obvious from either the equation or the constant in the equation, but ξ has units of reciprocal viscosity.

The correlation of Jossi et al. (1962) is reported to be valid for the range $0.1 \leq \rho_R \leq 3$. Actually for reduced densities less than 0.1, it is probably safe to use the low pressure viscosity. In the author's experience, you can expect to have errors larger than 30% when using this correlation for acid gas mixtures, especially in the region near a critical point.

One problem with correlations that are based on the reduced density is our inability to accurately calculate the density of the mixture. Another problem with this approach is the need for mixture critical properties: 1. critical density which is a parameter in the main correlation and 2. the critical temperature and critical pressure which are required to evaluate ξ . Lacking additional information, which is clearly lacking in this case, the pseudo-critical properties can be used.

Figure 3 shows the viscosity of saturated liquid carbon dioxide with values from Vesovic et al. (1990) and the prediction from the correlation of Jossi et al. (1962) with densities calculated using a volume-shifted PR equation. One's initial reaction to this plot is that the errors seem quite large. However they are approximately 30%, which is within the range stated earlier. In addition, these values are quite close to the critical pressure for pure CO_2 (in this case $0.91 < T_R < 0.99$), and thus a significant portion of the error may be attributed to relatively poor estimates of the density.

Fig. 3 Viscosity of Saturated Liquid Carbon Dioxide

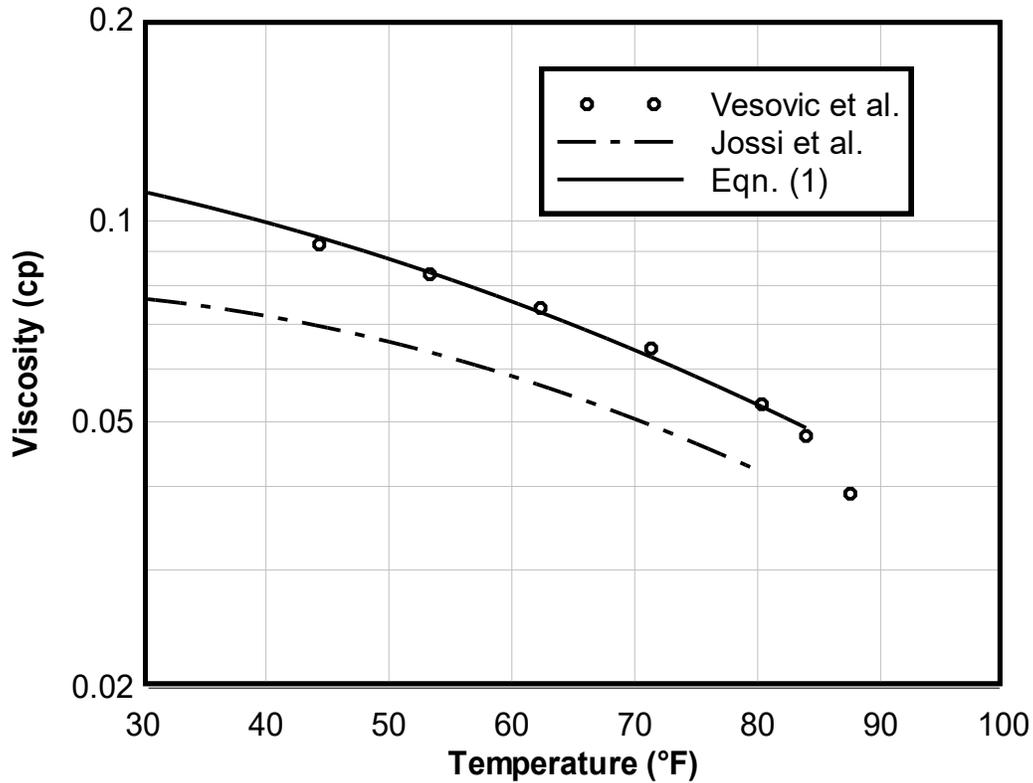


Figure 4 shows the viscosity of saturated liquid H₂S along with the data presented earlier. In this case the correlation of Jossi et al. (1962) is surprisingly good with errors typically less than 15%.

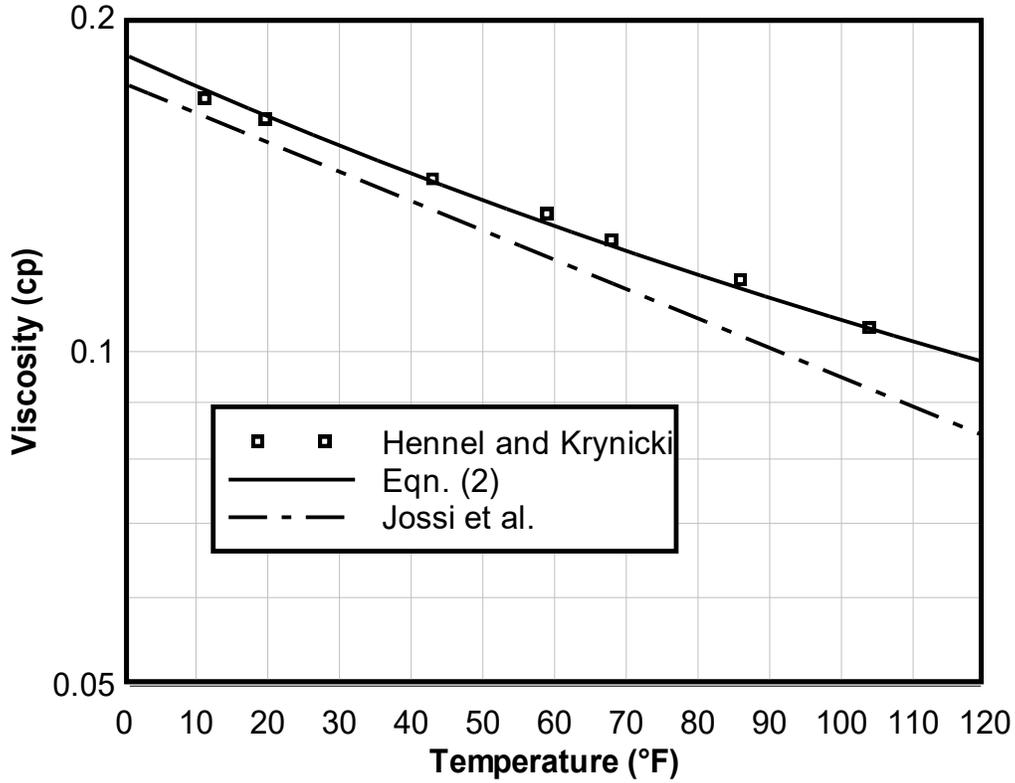
For liquid mixtures, the following simple correlation is often applied:

$$\ln \mu_{\text{mix}} = \sum_{i=1}^{\text{NC}} x_i \ln \mu_i \quad (10)$$

where μ_{mix} is the mixture viscosity, x_i is the mole fraction of component i , and NC is the number of components in the mixture. This method has similar limitations to those noted for Eqn. (3) – most notably, it is only applicable if all components are in the liquid phase in the pure state at the temperature and pressure. Thus for acid gas mixtures such a model cannot be used to estimate the effect of methane on the viscosity of the liquid mixture. Over the range of temperatures and pressures of interest in acid gas injection, methane is always a gas.

For example, from Eqn (1) the liquid viscosity of CO₂ at 41°F is 98 $\mu\text{Pa}\cdot\text{s}$ and from Eqn (2) that for H₂S is 144 $\mu\text{Pa}\cdot\text{s}$. Using Eqn (10), the estimated viscosity for an equimolar mixture is 119 $\mu\text{Pa}\cdot\text{s}$. Using the Jossi et al approach outlined above and assuming the mixture is at its bubble point, the estimated viscosity is 101 $\mu\text{Pa}\cdot\text{s}$. One should not be surprised by a difference of this magnitude.

Fig. 4 Viscosity of Liquid Hydrogen Sulfide



Thermal Conductivity

The availability of thermal conductivity for CO₂ and H₂S was discussed earlier. As with the viscosity, no data are available for the thermal conductivity of mixtures of H₂S and CO₂. As with the viscosity, the starting point for calculating the high pressure thermal conductivity is the thermal conductivity at low pressure. For this we will again use the DIPPR correlation (Daubert et al., 1999):

$$\lambda^* = \frac{AT^B}{1 + C/T + D/T^2} \quad (11)$$

where λ^* is the low pressure thermal conductivity in W/m·K, T is the absolute temperature in K, and A, B, C, and D are empirical constants. The constants for the components of interest in this study are given in Table 3. All of these values were taken from the DIPPR data book (Daubert et al., 1999) with the exception of hydrogen sulfide. The constants for H₂S were obtained by fitting the data of Baura et al. (1968).

Thermal conductivities of gaseous mixtures can be estimated in a similar fashion to the viscosity of these mixtures. This is true because both mixture approximations are based on the kinetic theory. Thus:

$$\lambda_{\text{mix}}^* = \frac{\sum_i y_i \lambda_i^*}{\sum_j y_j A_{ij}} \quad (12)$$

Table 3 Coefficients for the DIPPR Equation for Low Pressure Thermal Conductivity

	A	B	C	D
water	2.1606×10^{-3}	7.6839×10^{-1}	$3.9405 \times 10^{+3}$	$-4.4534 \times 10^{+5}$
hydrogen sulfide	7.6552×10^{-8}	$1.9200 \times 10^{+0}$	$3.6839 \times 10^{+2}$	$4.6973 \times 10^{+4}$
carbon dioxide	$3.6900 \times 10^{+0}$	-3.8380×10^{-1}	$9.6400 \times 10^{+2}$	$1.8500 \times 10^{+6}$
methane	1.2260×10^{-3}	8.0310×10^{-1}	$9.6000 \times 10^{+2}$	$-6.1200 \times 10^{+4}$
ethane	$8.2180 \times 10^{+0}$	-7.0120×10^{-1}	$-1.4189 \times 10^{+3}$	$9.6230 \times 10^{+5}$
propane	6.1500×10^{-5}	$1.1696 \times 10^{+0}$	$4.9760 \times 10^{+2}$	$0.0000 \times 10^{+0}$

where the following can be used to estimate A_{ij} :

$$A_{ij} = \frac{\left[1 + (\lambda_i/\lambda_j)^{1/2} (M_i/M_j)^{1/4}\right]^2}{\left[8(1 + M_i/M_j)\right]^{1/2}} \quad (13)$$

which is again, similar to the viscosity equation.

The effect of water on the density

At low pressure the presence of water tends to reduce the density of an acid gas mixture. For example, Table 4 presents some calculated densities for an equimolar mixture of H₂S and CO₂ in the presence of water. These calculations were performed using a volume-shifted PR equation. The difference between the density of the dry gas and the density of the gas containing 5 mol% water is only about 2.5% at these pressures. This density change is largely due to the differences in the molar masses of the acid gas versus that of water. Thus the density reduction is larger for pure CO₂ than it is for pure H₂S. The interested reader should compare these result with those obtained using the ideal gas law.

Table 4 Effect of Water on the Density (lb./ft³) of an Equimolar Mixture of Hydrogen Sulfide + Carbon Dioxide at 120°F and Low Pressure

Pressure (psia)	0% water 0 lb./MMCF	2.5% water 1190 lb./MMCF	5% water 2370 lb./MMCF	Saturated†
15	0.0949	0.0936	0.0924	0.0886
30	0.190	0.188	0.185	0.184

† - at 15 psia water saturation is 11.4% (5450 lb./MMCF) and at 30 psia it is 5.7% (2700 lb./MMCF)

At higher pressure the effect of water on the density of an acid gas mixture is less significant. This is due to two factors. The first of these is that under pressure the acid gas mixture tends to contain less water (typically less than 1 or 2%). The second is that the water simply does not have a large influence on the density, as was clear for the low pressure mixtures. Table 5 shows some calculated densities for an equimolar mixture of H₂S and CO₂ both with and without water at 120°F. Again, these densities were calculated using the volume-shifted PR equation. For the five pressures shown, the difference between the densities is less than 1%.

Table 5 Effect of Water on the Density (lb./ft³) of an Equimolar Mixture of Hydrogen Sulfide + Carbon Dioxide at 120°F and High Pressure

Pressure (psia)	Density with 0% Water (lb./ft ³)	Saturated Water Content (mol%)	Density (lb./ft ³)
900	9.51	0.39	9.55
700	6.15	0.40	6.15
500	3.88	0.47	3.87
300	2.11	0.68	2.11
100	0.650	1.80	0.644

Table 6 shows the effect of water on the density of liquefied hydrogen sulfide. These are liquids mixtures because the pressures in the table are above the bubble point for these mixtures at 120°F. As with the gas mixtures under pressure, the water has a relatively small effect on the density of the liquefied acid gas.

Table 6 Effect of Water on the Density (lb./ft³) of Liquid Hydrogen Sulfide at 120°F and 1088 psia

	Tables/Simple	Volume-shifted PR
Pure H ₂ S	45.7	45.5
1% water	45.8	45.7
2.4% water (sat'd)	45.8	46.0

The effect of hydrocarbons on the density

Table 7 shows the effect of a small amount of light hydrocarbon on the density of an acid gas mixture, which is in the gas phase. Methane tends to reduce the density of the acid gas, and probably more so than one might anticipate. From Table 7 it can be seen that 1% methane in an equimolar mixture of H₂S and CO₂ can reduce the mixture density by as much as 2%. The effect of ethane and propane is predicted to be much less.

Table 7 Estimated Density (lb./ft³) of Equimolar Mixtures of H₂S and CO₂ at 120°F in the Gas Phase and Demonstrating the Effect of Hydrocarbons

Pressure (psia)	No hydrocar.	1% methane	2.5% methane	1% ethane	1% propane
900	9.52	9.32	9.07	9.48	9.61
700	6.15	6.08	5.97	6.14	6.18
500	3.88	3.85	3.79	3.87	3.89
300	2.11	2.10	2.08	2.11	2.12
100	0.650	0.647	0.641	0.647	0.652

In the liquid phase, the effect of methane is predicted to be slightly larger. Table 8 shows the density of liquefied acid gas mixtures including the effect of the addition of light hydrocarbons. One per cent methane in the liquid mixture reduces the density by more than 2%. Again the effect of ethane and propane is significantly less.

Table 8 Estimated Density (lb./ft³) of Equimolar Mixtures of H₂S and CO₂ at 100°F in the Liquid Phase and Demonstrating the Effect of Hydrocarbons

Pressure (psia)	No hydrocar.	1% methane	2.5% methane	1% ethane	1% propane
1100	43.4	42.3	40.3	42.8	42.7
1200	44.3	43.2	41.4	43.7	43.6
1500	46.4	45.4	43.8	45.8	45.7

The effect of impurities on the viscosity

In order to demonstrate the effect of impurities, the viscosity of several acid gas mixtures at low pressure were calculated using the model outlined above. Again the base case is an equimolar mixture of H₂S and CO₂ and the results are presented in Table 9. From this table it can be seen that a small amount of impurity has a very small effect on the low pressure viscosity.

Table 9 Estimated Viscosity (cp) of Equimolar Mixture of H₂S and CO₂ at Low Pressure and Demonstrating the Effect of Impurities

Temp. (°F)	H ₂ S+ CO ₂	1% water	5% water	1% methane	2.5% methane
80	0.0138	0.0138	0.0136	0.0138	0.0137
100	0.0143	0.0143	0.0141	0.0143	0.0142
120	0.0148	0.0148	0.0146	0.0148	0.0147
150	0.0155	0.0155	0.0153	0.0155	0.0155

To extrapolate the viscosity from low pressure to high pressure requires the density. As was demonstrated, these impurities do not have a large effect on the density of the acid gas mixture. So we can anticipate only a relatively small effect of these impurities on the viscosity at high pressure.

Vapor-Liquid Equilibrium

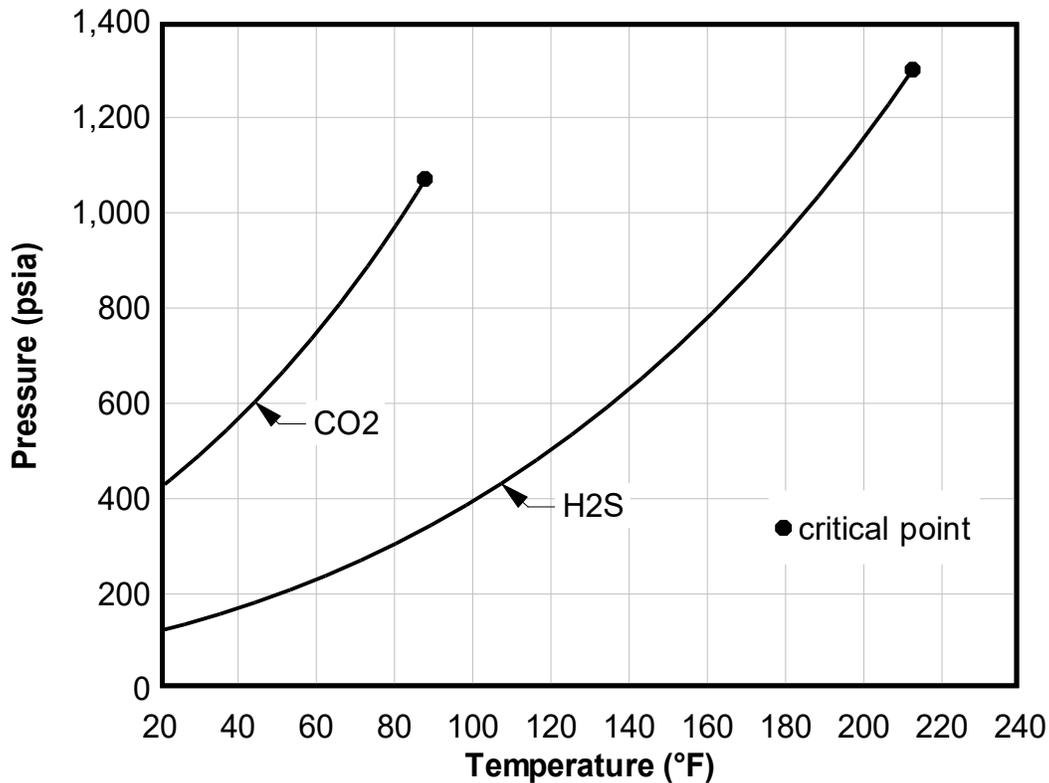
Another of the important aspects of the design of an acid gas injection scheme is the non-aqueous phase equilibrium. Fluid phase equilibrium involving water, which is also very important, and hydrates will be discussed later. In the design of an acid gas injection scheme, it is important to identify the conditions at which the acid gas will liquefy. Therefore, the construction of a phase envelope is usually the first step in the analysis of an acid gas injection scheme.

The Vapor Pressure of H₂S and CO₂

Figure 5 shows the vapor pressure of pure hydrogen sulfide and carbon dioxide. These curves terminate at the critical point. If, and only if, the temperature and pressure of interest fall exactly on the curve in the plot then the fluid exists in two phases. Otherwise the fluid is single phase.

For a system containing only a single component these are the boundaries between the vapor and the liquid. For the substance to be in the liquid phase, the temperature must be less than the critical temperature and the pressure must be greater than the vapor pressure. To be in the gas phase, the pressure must be less than the critical pressure and the temperature must be less than the vapor pressure. If the pressure is less than the critical pressure, but the temperature is greater than the critical temperature, this is still in the gas region.

Fig. 5 Vapor Pressures of Carbon Dioxide and Hydrogen Sulfide



Binary Mixtures of H₂S and CO₂

The most important non-aqueous system involved in acid gas injection is the binary mixture hydrogen sulfide + carbon dioxide, since acid gas is composed almost exclusively of these components.

Two early studies of the phase equilibrium in the system hydrogen sulfide + carbon dioxide were Bierlein and Kay (1953) and Sobocinski and Kurata (1959). Bierlein and Kay (1953) measured vapor-liquid equilibrium (VLE) in the range of temperature from 30° to 212°F and pressures to 1300 psia and they established the critical locus for the binary mixture. For this binary system the critical locus is continuous between the two pure component critical points. Sobocinski and Kurata (1959) confirmed much of the work of Bierlein and Kay (1953) and extended it to lower temperatures, down as low as -140°F, which is where solids are formed. Furthermore, liquid phase immiscibility was not observed in this system. Liquid H₂S and CO₂ are completely miscible.

Robinson and Bailey (1957) and Robinson et al. (1959) studied the VLE in the ternary mixtures of hydrogen sulfide + carbon dioxide + methane. These investigations also included a few points for the binary system H₂S+CO₂. The points for the binary mixtures were at temperatures between 40° and 160°F and at pressures from 600 to 1200 psia.

Recently Kellerman et al. (1995) reported data for the thermodynamic properties, including VLE, for the system H₂S+CO₂. Their measurements of the phase boundary were for temperatures between -13° and 140°F and pressures up to 1300 psia.

The design engineer can use the experimental investigations listed above to verify the accuracy of the model selected for performing the phase equilibrium calculations.

Effect of Hydrocarbons

One of the interesting features of the system hydrogen sulfide + methane is liquid-phase immiscibility. The H₂S-rich and CH₄-rich liquids are immiscible. However, this occurs at temperatures well below those of interest in acid gas injection. However, unusual looking phase diagrams are often obtained for mixtures rich in H₂S and CH₄ because the algorithms typically are not designed for multiple liquid phases and they get “confused” (as does the design engineer generating them).

Among the interesting equilibria observed in these systems is that ethane and carbon dioxide exhibit azeotropy. This makes separation of these two components by binary distillation impossible.

An interesting investigation of the ternary mixture H₂S+CO₂+CH₄ was performed by Ng et al. (1985). Although much of this study was at temperatures below those of interest in acid gas injection, they provide data useful for testing phase behavior prediction models. The multiphase equilibrium they observed for this mixture, including multiple critical points for a mixture of fixed composition, should be of interest to all engineers working with such mixtures. It demonstrates that the equilibria can be complex, even for relatively simple systems.

Calculation Methods

Phase equilibrium calculations are usually based on the concept of the K-factor. The K-factor is defined as follows:

$$K_i = y_i/x_i \quad (14)$$

where x_i is the mole fraction component i in the liquid and y_i is the mole fraction component i in the vapor. The K-factors are a function of the pressure, temperature and composition; although in simpler models the effect of composition is neglected.

There are three basic phase equilibrium calculations: (1) a flash calculation – phase split at specified conditions, (2) bubble point calculation, and (3) dew point calculation. For bubble and dew points, there are two types of calculations. First, the temperature is specified and the pressure is calculated with the alternative being the pressure is specified and the temperature is calculated.

Raoult's Law

In its most general form, Raoult's law says that the partial pressure of a component in the gas phase is equal to the mole fraction of that component in the liquid phase times its vapor pressure. Mathematically:

$$x_i P_i^{\text{sat}} = y_i P$$

where P_i^{sat} is the vapor pressure of component i and P is the total pressure. This is a very simple model, which neglects non-idealities in both the liquid and vapor phases. Substituting this equation into the K-factor expression yields:

$$K_i = \frac{P_i^{\text{sat}}}{P}$$

While such an approach may provide reasonable estimates for acid gas, this can only be expected at low pressure (less than 50 psia). Therefore, over the region of temperature and pressure of interest in acid gas injection, this model is clearly not applicable.

Another problem with this approach is what do you use for the vapor pressure if a component is supercritical. In particular how would you use this method to determine the effect of methane on the phase equilibrium?

K-Factor Charts

The K-factor method is designed for hand calculations. The *GPSA Engineering Data Book* has long contained a series of K-factor charts for estimating phase equilibrium. These are fairly accurate for hydrocarbon mixtures, but their application to non-hydrocarbons is less accurate. The data book does not include a chart for carbon dioxide, but recommends that the K-factor for carbon dioxide can be approximated as the geometric mean of the K-factors for methane and ethane.

$$K_{\text{CO}_2} = \sqrt{K_{\text{CH}_4} \times K_{\text{C}_2\text{H}_6}} \quad (3-5)$$

The charts provide estimates of the K-factors given the temperature and the pressure, but the engineer must do iterative calculations in order to obtain actual estimates of the equilibrium. A single calculation is quite time consuming; thus repeated calculations are frustrating and take a considerable amount of time. The construction of a phase envelope based on such methods is almost hopeless.

Equations of State

The cubic equations of state have become the workhorse of the process industry, particularly for natural gas. Most designs in the natural gas business are based on such equations.

The equations of state, commonly used for the calculation of phase equilibrium in natural gas systems, are applicable for acid gas mixtures as well. Clark et al. (1998) in a study of equilibrium in a single system claimed that equations of state were not applicable to acid gas systems. Subsequently, Carroll (2002a) demonstrated that Clark et al. (1998) were probably incorrect. Carroll (2002a) performed a thorough review of the phase equilibria for these systems, which cover many systems including acid gas, and hydrocarbon systems.

One of the often-stated advantages of equations of state, and the cubic equations of state in particular, is their simplicity. However, the calculation of phase equilibrium with an equation of state is too difficult to be performed by hand. Such calculations require a computer. Fortunately many software packages are available for such calculations.

Calculations

Several calculations will be presented both to demonstrate the accuracy of the equation of state approach and to show the effect of impurities on the vapor-liquid equilibrium. Although all of the calculations presented here were performed using the PR equation, equivalent results would be obtained using the SRK equation. For vapor-liquid equilibrium calculations in natural gas systems there is little to choose one equation over the other.

The most important systems in the design of an acid gas injection scheme is the binary mixture of H₂S and CO₂. Figure 6 shows the phase envelopes for four mixtures of H₂S and CO₂. The curves are from a relatively simple version of the PR equation. The version used here was as described in the original paper of Peng and Robinson (1976), including the simple mixing rules. The interaction parameter for the H₂S-CO₂ binary was 0.0974. The phase envelopes show the banana shape characteristic of acid gas mixtures. They show little or no retrograde region, which is commonly encountered in mixtures of hydrocarbons.

Fig. 6 Phase Envelopes for Four Mixtures of Carbon Dioxide and Hydrogen Sulfide

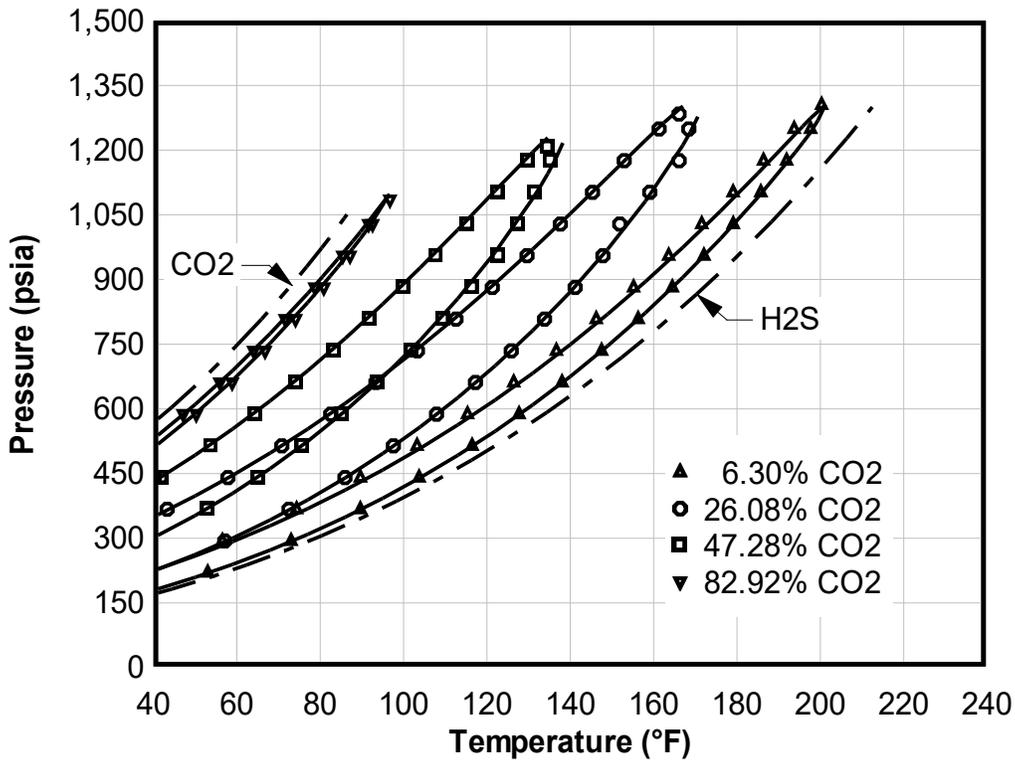
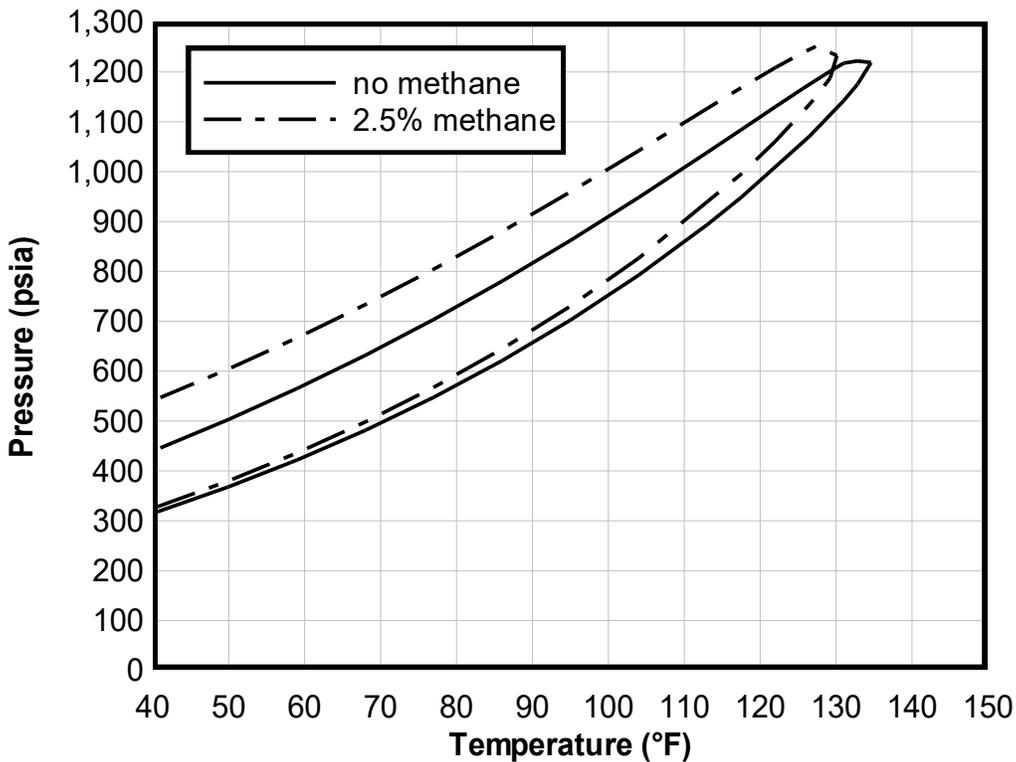


Fig. 7 Two Phase Envelopes for Mixture of Hydrogen Sulfide and Carbon Dioxide and Demonstrating the Effect of Methane



The most common impurity in an acid gas mixture, other than water, is probably methane. Figure 7 shows two phase envelopes – one for an equimolar mixture of H₂S and CO₂ and one for a mixture of H₂S (48.75 mol%) + CO₂ (48.75%) + CH₄ (2.50%). The phase envelope for the mixture containing methane is broader than the one without. In essence the dew point loci are the same for the two mixture (some deviations near the critical point). This is because the dew point is more dependent of the less volatile components (CO₂ and H₂S). On the other hand, the bubble point has increased significantly. The methane is harder to liquefy than the CO₂ or H₂S and this tends to increase the bubble point.

In addition to the calculations presented here, Carroll (2002a) demonstrates the applicability of the PR equation to predict the vapor-liquid equilibrium for many systems of interest in the design of an acid gas injection scheme.

Vapor-Liquid Equilibrium with Water

Water is perhaps the most significant impurity in an acid gas mixture. The formation of a water-rich condensed phase, be it aqueous liquid, hydrate, or ice, all pose potential problems in the operation of the injection scheme.

With sweet gas the water content of the gas continually decreases with increasing pressure. The water content of gaseous acid gas mixtures, on the other hand, goes through a minimum.

An important aspect of acid gas injection is the water content of the acid gas mixture. In addition, it is important to know the effect of the state (gas or liquid) of the acid gas on the water content of the mixture.

The Water Content of Acid Gas

The study of Selleck et al. (1952) is considered the benchmark investigation of the system hydrogen sulfide + water. They published tables of smoothed data, which are commonly quoted. However, these tables are based on relatively few and highly scattered experimental data points. Carroll and Mather (1989a) re-evaluated the phase behavior in this system showing a clearer picture of the equilibria and accurately reflecting all of the available experimental data.

There have been many investigations of the water content of CO₂-rich fluids. In general there is reasonable agreement amongst the various sets of data in the low and moderate pressure regions. The benchmark investigation of the phase behavior in the system carbon dioxide water was that of Wiebe and Gaddy (1939,1940,1941).

For many years there were two sets of conflicting data for the VLE in the system CO₂+H₂O at high pressure (up to 300 MPa). These were Tödeheide and Franck (1963) and Takenouchi and Kennedy (1964). Although these studies agreed qualitatively, they differed significantly quantitatively. Recent results by Mather and Franck (1992) indicate that the data of Tödeheide and Franck (1963) are the correct ones.

Finally, the author of this paper has performed thorough reviews of the literature and is unaware of any experimental data for the water content for binary mixtures of H₂S+CO₂ in the public domain. Such data, if available, would be very useful for constructing and evaluating models.

Estimating the Water Content of Acid Gases

There are several models available for calculating the water content of natural gas. Only a few of them will be examined here.

In the ideal model, the water content of a gas is assumed to be equal to the vapor pressure of pure water divided by the total pressure of the system. This yields the mole fraction of water in the gas and this is value converted to lb./MMSCF by multiplying by 47484. Mathematically this is:

$$w = 47484 \frac{P_{\text{water}}^{\text{sat}}}{P_{\text{total}}} \quad (18)$$

where w is the water content, lb./MMSCF. Clearly this model is very simple and should not be expected to be highly accurate except at very low pressures, less than about 50 psia.

In 1958 McKetta and Wehe published a chart for estimating the water content of sweet natural gas. This chart has been modified slightly over the years and has been reproduced in many publications, most notably the *GPSA Engineering Data Book*. The McKetta-Wehe chart is quite accurate to all gases (sweet, sour, and acid) for pressure up to about 200 psia. However, it is not applicable to sour gas at high pressure. Fortunately, most engineers who work in the natural gas industry are aware of this limitation. There have been corrections proposed to make the chart applicable to these systems. Two will be discussed in the next section of this chapter.

Maddox (1974) developed a method for estimating the water content of sour natural gas. His method assumes that the water content of sour gas is the sum of three terms: 1. a sweet gas contribution, 2. a contribution from CO_2 , and 3. a contribution from H_2S . Charts are provided to estimate the contributions for CO_2 and H_2S . Although these charts have the appearance of being useful for calculating the water content of pure H_2S and pure CO_2 the author advises that they should not be used for this purpose. Therefore this method is not applicable to acid gas mixtures.

Wichert and Wichert (1993) proposed a relatively simple correction based on the equivalent H_2S content of the gas. The equivalent H_2S content, $y_{\text{H}_2\text{S,equiv}}$, used in this correlation is that defined by:

$$y_{\text{H}_2\text{S,equiv}} = 0.7y_{\text{CO}_2} + y_{\text{H}_2\text{S}} \quad (19)$$

This method was recently revised to account for new observations (Wichert and Wichert, 2003).

They presented a single chart where given the temperature pressure and equivalent H_2S one could obtain a correction factor, F_{corr} . Revised correction factors range from 1.0 to 5.0. The correction factors tend to increase with increasing H_2S equivalent and increasing pressure, and decrease with increasing temperature. This method is limited to an H_2S equivalent of 55 mol% and thus is not applicable to acid gas mixtures.

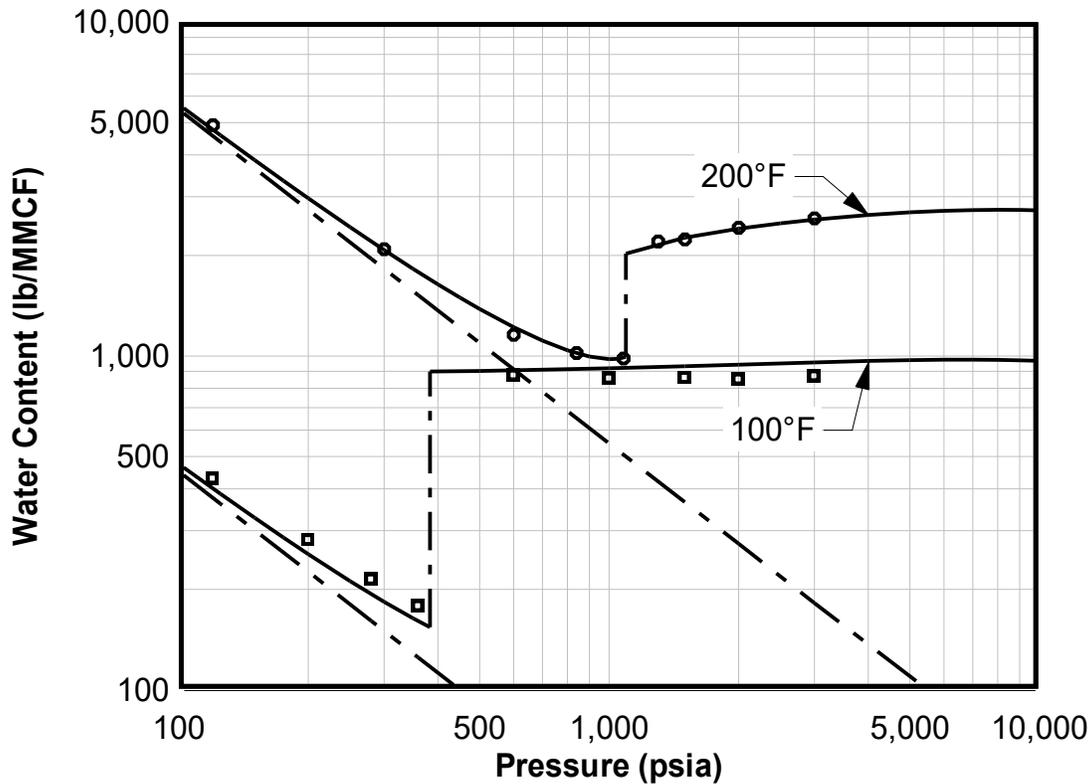
None of the methods outlined above is applicable for calculating the water content of acid gas. Theoretically, a properly construct equation of state model can be used for such calculations. However, the original SRK and PR equations are not applicable. As a starting point an equation of state for this application would have to accurately predict the vapor pressure of pure water, which neither the PR nor SRK equations do. Next an advanced mixing rule would be required. Carroll and Mather (1989c) describe such a model for the system $\text{H}_2\text{S}+\text{H}_2\text{O}$.

Carroll (2002b) and Carroll (2002c) reviewed the water content of sour gas and acid gas mixtures. Those papers demonstrate the accuracy of several methods for predicting water contents for these mixtures. It is demonstrated that even with the best available models errors of about 10% (or more) are expected. Although much of this error is due to the model themselves, there is also a large error associated with the experimental data, as will be demonstrated.

Calculations

Figure 8 shows two isotherms for the water content of hydrogen sulfide. This plot shows the experimental data of Gillespie et al. (1980, 1984) and the predictions from a two-fluid model and from the ideal model. Note, the vertical broken lines indicate a three-phase point (aqueous liquid+H₂S-rich liquid + vapor). From this graph it is clear that the two-fluid model is an excellent qualitative model of the experimental data.

Fig. 8 Water Content of Hydrogen Sulfide at 100 and 200°F
(Data from Gillespie et al., 1984, solid curves from Two-Fluid Model, and sloping broken curves from Ideal Model)



The ideal model is a good prediction in the low-pressure limit (less than about 200 psia) but at high pressure it is grossly in error. Furthermore, the ideal model cannot predict the phase change and the effect of that change on the water content.

Figure 9 shows two more isotherms for the water content of hydrogen sulfide (120° and 220°F) showing the raw data of Selleck et al. (1952) and the calculation from the two-fluid model. The description shown in this figure is different from that believed by Selleck et al. (1952).

Figure 10 shows the water content of CO₂ at 122° and 167°F. On this plot are shown data from three sources and the prediction from the two-fluid model. At 122°F the model is in excellent fit of the experimental data from both Wiebe and Gaddy (1939,1940,1941) and Coan and King (1971). However, at 167°F there appears to be some disagreement. The data point of Wiebe and Gaddy (1939,1940,1941) at about 350 psia is clearly in error – it is almost half the value compared with the other two sets of experimental data at approximately the same pressure. In addition from Fig. 10 the minima in the water content are clear. At 122°F the minimum is at about 1000 psia, whereas at 167°F the minimum is at about 1500 psia.

Fig. 9 Water Content Hydrogen Sulfide at 120° and 220°F
 (Data from Selleck et al., 1952, curves from Two-Fluid Model)

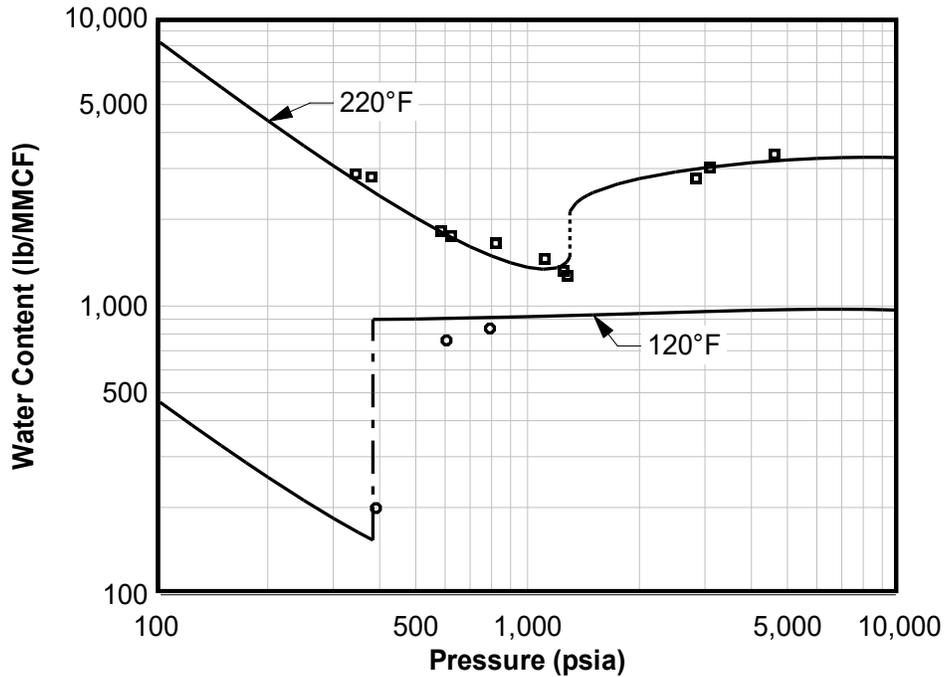
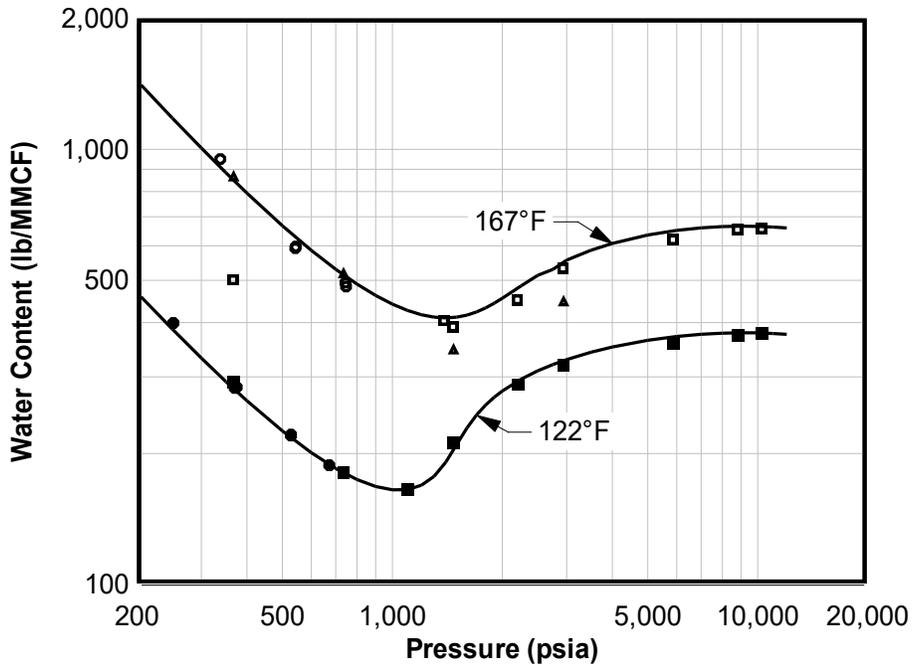


Fig. 10 Water Content of Carbon Dioxide at 122°F and 167°F
 (Data points: squares - Weibe and Gaddy, circles - Coan and King, and triangles - Gillespie et al. Curves from Two-Fluid Model)



The Solubility of Acid Gas

Another important aspect in the design of an acid gas injection scheme is the solubility of the acid gas in water and brine. In the design of the surface equipment it is useful to know the amount of acid dissolved in the water removed in the interstage scrubbers. From a reservoir engineering point of view, it is

important to know the solubility of the acid gas in the formation water. The water removed in the interstage scrubbers does not contain any dissolved solids because it is water of condensation.

Pure Water

At low pressure the solubility of the acid gas components in the vapor phase can be calculated using the simple Henry's law.

$$x_i H_{ij} = y_i P \quad (20)$$

where x_i is the mole fraction of component i in the liquid, H_{ij} is the Henry's constant for solute i in solvent j , y_i is the mole fraction of component i in the gas, and P is the total pressure.

Carroll and Mather (1989) demonstrated that a relatively simple extension of Henry's law could be used to model the solubility of H_2S in water up to about 150 psia. Their model was:

$$x_i H_{ij} = y_i P \hat{\phi}_i^V \quad (21)$$

where $\hat{\phi}_i^V$ is the fugacity coefficient for component i in the vapor. To keep their model relatively simple the authors used the original Redlich-Kwong equation of state to estimate the fugacities. Subsequently Carroll et al. (1991) showed that a similar model work for carbon dioxide over the same range of pressures.

At higher pressure, it is necessary to account for the non-idealities in the liquid phase as well as the vapor. Carroll and Mather (1992) used the following model for the solubility of CO_2 in water:

$$x_i H_{ij} \exp\left(\frac{\bar{v}_i^\infty [P - P_j^\circ]}{RT}\right) = y_i P \hat{\phi}_i^V \quad (22)$$

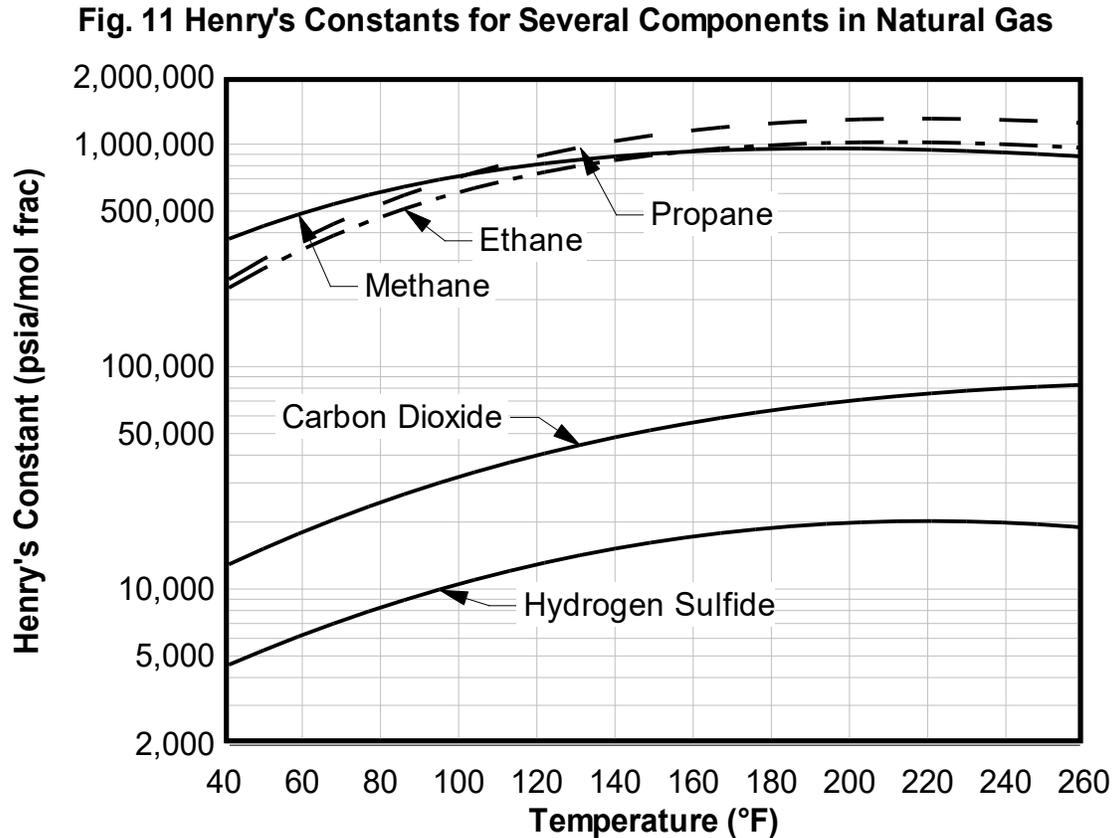
where \bar{v}_i^∞ is the partial molar volume of i in solvent j at infinite dilution, P_j° is the vapor pressure of the solvent, R is the universal gas constant, and T is the absolute temperature. The exponential term is the Poynting correction, which is the effect of pressure on the reference fugacity, and is only important at high pressure. For carbon dioxide this model was found to be reasonably accurate up to about 15,000 psia. Carroll and Mather (1997) used the same model to calculate the solubilities of light hydrocarbons in water.

For the solubility of hydrogen sulfide under pressure it is necessary to include additional contribution to the non-idealities in the liquid phase. This is because H_2S is more soluble than CO_2 . Carroll and Mather (1993) used the following extension of Henry's law to model the high pressure solubility of H_2S in water:

$$\gamma_i x_i H_{ij} \exp\left(\frac{\bar{v}_i^\infty [P - P_j^\circ]}{RT}\right) = y_i P \hat{\phi}_i^V \quad (23)$$

where γ_i is the activity coefficient for the solute in the aqueous phase and is a rather complex function of the aqueous phase composition.

Figure 11 shows the Henry's constants for H₂S, CO₂, and three light hydrocarbons in water. The larger the Henry's constant the lower the solubility. For the five components shown in Fig. 11 hydrogen sulfide is the most soluble, whereas the three hydrocarbons are the least soluble.



The extension of these models to mixtures of gases to a single solvent is quite simple. The appropriate equation is for each of the components in the mixture and the resultant series of equations is solved simultaneously.

The interested reader can learn more about Henry's law from the series of papers by Carroll (1991, 1992, 1999a).

Estimating the Effect of Dissolved Solids

For most gases the solubility in a brine solution is less than the solubility in pure water. This is called "the salting-out effect". The following equation, proposed by Sechenov more than a century ago, can be used to approximate the salting-out effect:

$$\log(S_{\text{water}}/S_{\text{electrolyte}}) = k I \tag{24}$$

where S_{water} is the solubility in pure water, $S_{\text{electrolyte}}$ is the solubility in the electrolyte solution, I is the concentration of the electrolyte, and k is the salting-out coefficient. Various units could be used for the solubilities, but the valuables given in the next section, the solubilities of both the acid gas components and the NaCl must be in molality (moles of salt per kilogram of solute). The salting-out coefficient is a function of the temperature, but it is approximately independent of the pressure and assumed to be independent of the nature of the phase of the solute.

There is a relatively large database of experimental data for the solubility of carbon dioxide in water, much of which is at low pressure. Clever (1996) critically reviewed the data and generated salting-out coefficients. He separated the data into low pressure and high pressure regions.

There are significantly less data for the solubility of hydrogen sulfide in sodium chloride solutions (and even less for the solubility in other electrolyte solutions). Sulemeimenov and Krupp (1994) measured some solubilities at high temperature and reviewed the existing data for the solubility of H₂S in NaCl solutions.

Gas Hydrates

What are gas hydrates?

Gas hydrates are solid ice-like materials that form at relatively high temperature. That is, they form at temperatures above the freezing point of water (32°F or 0°C).

In a gas hydrate, water forms a hydrogen-bonded cage and different molecules reside inside the cage. Water is called the “host” and the other molecule is called a “guest” or a “hydrate former”. The guest must of sufficient size to fit inside the lattice formed by water molecules. Hydrate formers include: methane, ethane, propane, hydrogen sulfide, carbon dioxide, and nitrogen.

In order for a hydrate to form, three conditions must be met:

1. The right combination of temperature and pressure
2. A sufficient amount of water
3. A hydrate former must be present

Hydrate formation is favored by low temperature and high pressure, but the actual hydrate formation condition is a function of the gas under consideration. Different gases form hydrates at different conditions.

It may seem obvious that some water must be present; however, just having “some” water present is not enough. There must be enough water to form the hydrate phase. Ironically, if there is too much water present, a hydrate will not form either. If the hydrate former is present in too low a concentration, then it will merely dissolve in the water. Some acid gas disposal schemes take advantage of this property.

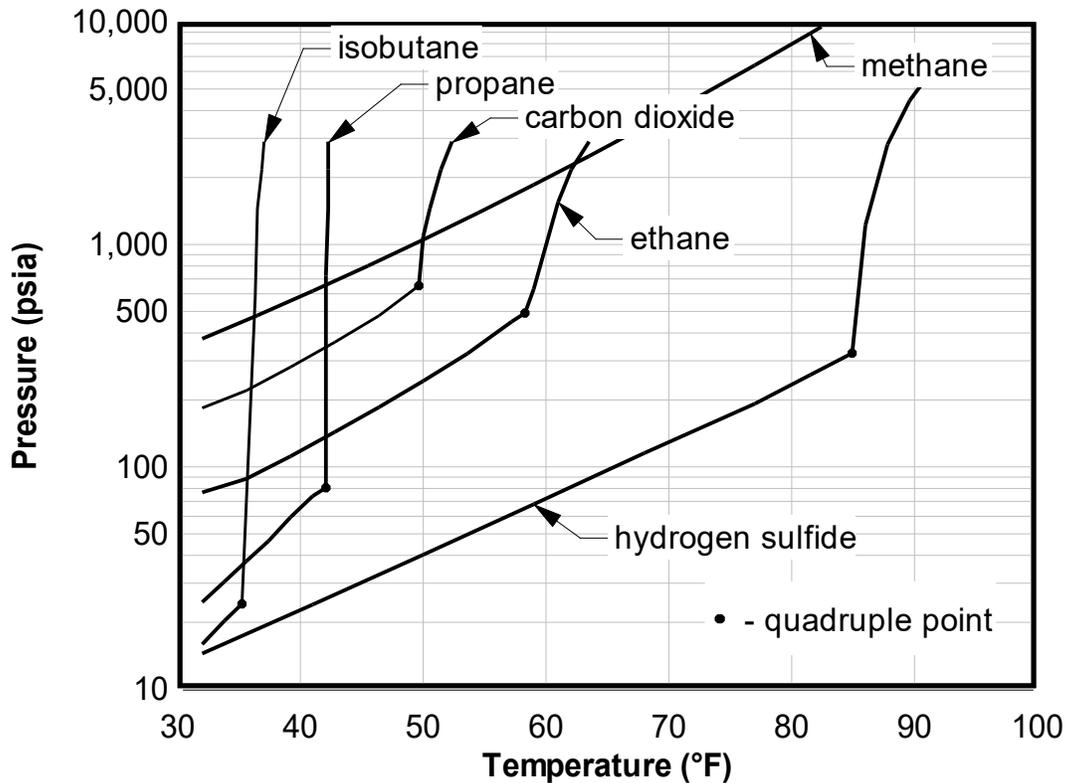
Hydrates of CO₂, H₂S, and Light Hydrocarbons

Of the components commonly found in natural gas, none forms a hydrate as easily as hydrogen sulfide. The hydrate of H₂S forms at the lowest pressures and persists to the highest temperatures.

The literature for the formation of hydrates in the system H₂S has been thoroughly reviewed by Carroll and Mather (1991). This review covers all investigations back to the middle of the 19th century. A good review of the carbon dioxide hydrate was presented by Bakker et al. (1996).

Figure 12 shows the pressure and temperature at which a hydrate will form for hydrogen sulfide, carbon dioxide, and light hydrocarbons. These curves represent the maximum conditions at which a hydrate can form for these pure components. From this figure it can be seen that the hydrate for hydrogen sulfide forms at temperatures greater than 85°F. It is difficult to imagine, *a priori*, that a solid water phase could form at 85°F!

Fig. 12 The Hydrate Loci For Several Components Found In Natural Gas



The chart presented in Fig. 12 is useful for pure components, but is less useful for mixtures. It is important to be able to predict at what conditions a hydrate will form in the mixtures encountered in acid gas injection.

Shortcut Calculation Methods

The *GPSA Engineering Data Book* provides three methods for performing hand calculations of the hydrate formation. Although these methods are not recommended for acid gas mixture, they will be reviewed here briefly.

The first of these is based on the gas gravity. A simple chart is provided that plots the temperature-pressure locus with the gas gravity as the third parameter. The first reason why the chart method is not recommended for acid gases is that the chart is limited to gases with gravities less than 1.0. Typical acid gas mixtures have gravities greater than 1.1. The second reason is the chart was developed for sweet gas and is not even applicable to sour gas mixtures.

The second simple calculation method is a K-factor approach. This method is slightly more rigorous, but also requires more time to perform the calculations. Using the K-factor charts requires an iterative procedure. Carroll (2004) showed that this method is not very accurate for sour gas mixtures. It predicts the hydrate temperature to within 3 Fahrenheit degrees only about 40% of the time. It is anticipated that this method would be at least this poor for acid gases and possibly significantly worse.

The final method presented in the *GPSA Engineering Data Book* is the chart method of Baillie and Wichert (1987). This method, although designed for sour gas mixtures, is limited to about 55% H₂S and therefore is not applicable to acid gas mixtures.

Mann et al. (1989) proposed a more advanced K-factor method, which among other things accounted for the different types of hydrates. This method has not gained wide acceptance in the process business. It was probably hoped that they would develop a method that would rival the original K-factor method in its simplicity, but the method turns out to be too complex for hand calculations. On the other hand, Carroll (2004) showed that this method was quite accurate for sour gas mixtures and thus it should work reasonably well for acid gas mixtures as well.

Rigorous Methods

For accurate prediction of the hydrate formation conditions for acid gases, the advanced methods are preferred. The more advanced methods for predicting hydrate formation are based on the work of van der Waals and Platteeuw (1959). This is a statistical thermodynamic model.

Several software packages are available commercially for predicting hydrate formation, including the multipurpose process simulation programs. These programs use a van der Waals- Platteeuw-type model. These methods are applicable to sweet gas, sour gases, and acid gases. They represent the best available approach to this problem.

Methods of Hydrate Control

Once we have concluded that hydrates are a potential problem, we must address the question of what can be done to alleviate the problem?

Earlier, the three criteria for hydrate formation were presented. These give us some insight into methods for battling their formation. Of the three criteria, the one that we can do nothing about is the presence of a hydrate former. Obviously in an acid gas injection scheme a hydrate former will be present. This is unavoidable.

Dehydration

Another method of combating hydrate formation is to remove the water from the stream. No water, no hydrate – it is that simple.

Figure 13 shows the effect of reduced water on the hydrate of CO₂ at 300 and 500 psia. The plot shows the raw experimental data from Song and Kobayashi (1987). Unfortunately a similar set of data do not exist for H₂S. The curves on these plots merely represent “best fits” through the data points. At higher temperatures the equilibrium is between hydrate and vapor, whereas at lower temperatures the equilibrium is between a CO₂-rich liquid and a hydrate. The broken vertical lines on the plot are the transition from one phase regime to the other. Because water is more soluble in liquid CO₂ than it is in gaseous CO₂ there is a significant inhibition in the hydrate formation.

If the stream has a sufficient amount of water (greater than about 25 lb./MMCF) then at 500 psia a hydrate will form at about 46°F (see Fig. 12). However, if the water content is reduced to 12 lb./MMCF, the hydrate does not form until about 36°F if the fluid is a gas and about -2°F if the fluid is a liquid. This reduction in the hydrate formation temperature is due solely to the dehydrated state of the fluid.

There are other reasons for dehydrating a stream. In the natural gas business, the gas should be “dry”, relatively free of water, in order to prevent hydrates and to prevent the formation of an aqueous phase, especially during transportation. In acid gas injection, this becomes more important since aqueous solutions of acid gases are highly corrosive.

Figure 14 shows the phase envelope and two hydrate loci for an acid gas mixture. The first curve labeled “Saturated” assumes that there is plenty of water present. The other hydrate locus is labeled “200 lb./MMCF” and this is the hydrate curve for the acid gas containing the specified amount of water. For both cases the hydrate curve for the vapor is essentially the same. And typical of an acid gas, the hydrate can form at fairly high temperatures; in this case up to about 79°F.

**Fig. 13 Water Content of Carbon Dioxide Low Temperature
(Data Points from Song and Kobayashi, 1987)**

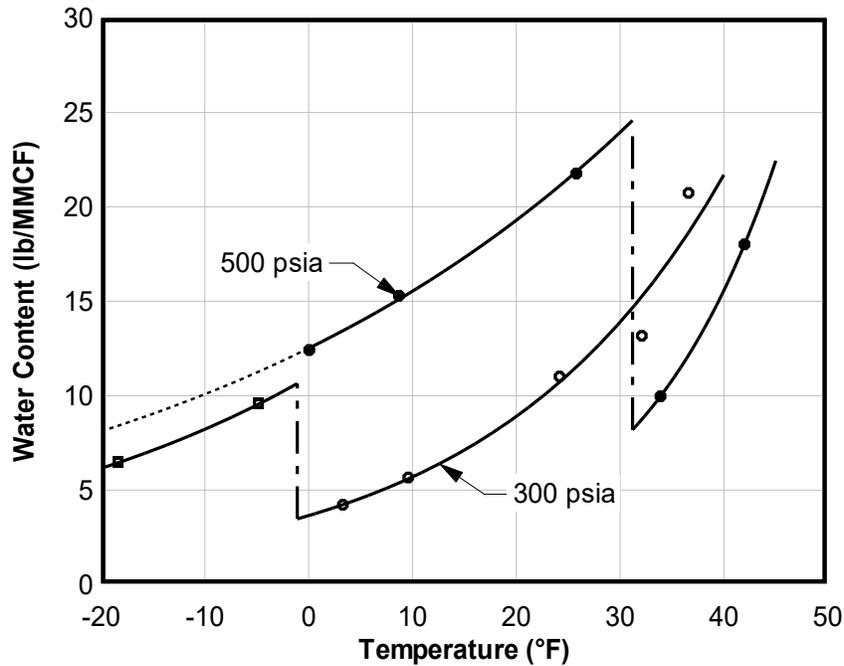
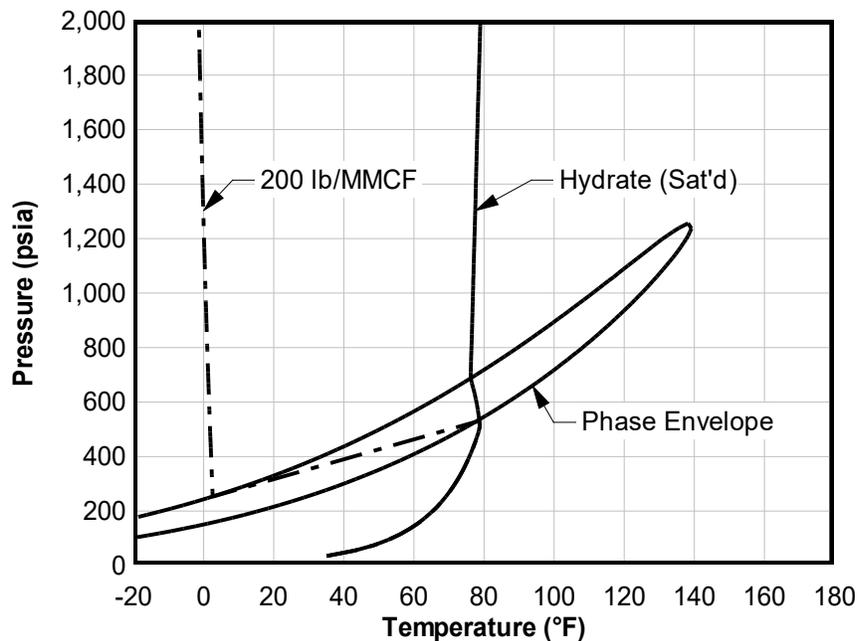


Fig. 14 Phase Envelope and Hydrate Loci for an Acid Gas Mixture



On the other hand, for the liquefied acid gas reducing the water content to 200 lb./MMCF has a dramatic effect on the hydrate temperature. For the case where there is plenty of water, the hydrate forms at between 75° and 79°F. On the other hand, the reduced water case, the hydrate forms at less than +3°F.

Heating

Another method used to combat hydrates is the use of heat. In this scheme we alter the temperature such that a hydrate will not form. From an earlier example, this means that the temperature must be such that it moves the conditions to the right of the hydrate formation curve.

In pipelines, heat is usually supplied with a line heater. In the design of a line heater, sufficient heat must be supplied to the fluid such that it is never at a temperature where a hydrate will form. That means the fluid must be heated well above the hydrate formation temperature. As it flows through the line it will cool, losing energy to the environment. Once it arrives at its destination, usually the plant site, it must be warmer than the hydrate temperature. It may be necessary to use more than one line heater.

Heat tracing can also be used; however it is usually best used if the problem is localized, for example around a valve. Points notorious for freezing in the acid gas injection scheme are the dump valves from the interstage knockout drums.

Methanol Injection

Perhaps the most common method to combat hydrate formation in the natural gas business is the use of methanol, although other inhibitors could be used as well (such as glycols). Methanol is inexpensive and very effective.

Figure 15 shows the inhibiting effect of methanol on the hydrate of hydrogen sulfide. The experimental data shown in this figure are from Ng et al. (1985). The solid curve on this plot is the same as that on Fig. 12 but appears slightly different because of the different axes on the two plots.

The simplest method of estimating the inhibiting effect is from the Hammerschmidt equation:

$$\Delta T = \frac{2355 W}{M(100 - W)} \quad (25)$$

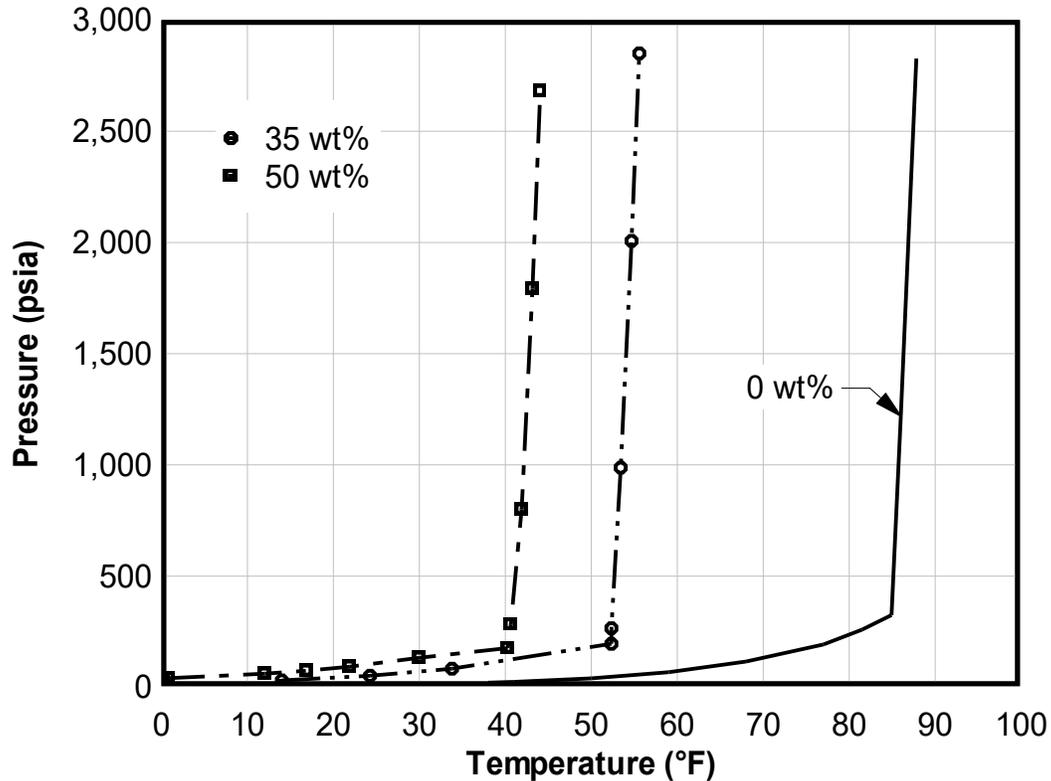
where ΔT is the temperature depression, °F, M is the molar mass of the inhibitor, g/mol, and W is the concentration of the inhibitor in the aqueous phase, weight per cent. This concentration is on an inhibitor plus water basis (that is, it does not include the other components in the stream). Typically methanol is used as the inhibitor and the molar mass of methanol is 32.042 g/mol. For methanol Eqn. (25) can be used for concentration up to about 35 wt.%.

Again, it is also important to note that these methanol concentrations are based on the aqueous phase. The 35 and 50 wt.% noted in Fig. 15 are not the concentrations in the total mixture, but only in the aqueous phase.

To use the Hammerschmidt equation you must first estimate the hydrate conditions without an inhibitor present. The Hammerschmidt equation only predicts the deviation from the temperature without an inhibitor present, not the hydrate forming conditions themselves.

The advanced models based on the van der Waals and Platteeuw (1959) have been adapted for use with inhibitors.

Fig. 15 The Inhibiting Effect of Methanol on the Hydrate of Hydrogen Sulfide



Summary

The design of an acid gas injection schemes requires an understanding of a significant amount of physical property and phase behavior.

Depending upon the composition, conditions, and the phase of the mixture, densities of acid gas mixtures range from less than 1 lb./ft³ to up to as much as 60 lb./ft³; the low densities corresponding to the gas phase and the higher densities to the liquid. Typically liquid densities of acid gas mixture range from 0 to 55 lb./ft³.

Based on the pure component data and models for the viscosity, acid gas viscosities range from about 0.01 to 0.2 cp over the range of temperature and pressure of interest to acid gas injection. This is true regardless of the phase of the mixture.

Although not discussed in this paper, equations of state can also be used to calculate enthalpy departures and entropy departures. Thus, in combination with ideal gas heat capacities, equations of state can be used to calculate the enthalpies and entropies of acid gas mixtures. These thermodynamic properties are required for the design of compressors and coolers.

Recommendations

This paper reviews many of the important properties of acid gas mixtures and gives some recommendations as to how to best estimate the properties. Below are a series of tables that summarize these recommendations.

Table 10 Recommendations for Estimating Density of Acid Gas Mixtures

	Gas	Liquid
Ideal Gas	less than 50 psia	NO
Soave-Redlich-Kwong	Yes	NO
SRK – volume shift	Yes	Yes
Peng-Robinson	Yes	Yes
PR – volume shift	Yes	yes
Average molar volume [†]	NO	yes
Tabulated data [‡]	Yes	Yes

† - with restrictions noted in the text

‡ - for pure components only

Table 11 Recommendations for Estimating Vapor-Liquid Equilibria (Non-aqueous) in Acid Gas Mixtures

Raoult's Law	NO
K-factor	NO
Soave-Redlich-Kwong	Yes
Peng-Robinson	Yes
other EOS	Yes

- in order to model such VLE the EOS require only a single interaction parameter, which is standard for natural gas applications

Table 12 Recommendations for Estimating Water Content of Acid Gas Mixtures

	Gas	Liquid
Ideal Model	less than 50 psia	NO
McKetta-Wehe Chart	less than 200 psia	NO
Maddox correction	NO	NO
Wichert correction	NO	NO
Original Soave-Redlich-Kwong	NO	NO
Original Peng-Robinson	NO	NO
Modified EOS [†]	Yes	Yes

† - the design engineer would be wise to verify that the selected package is appropriate for this application (see discussion in paper)

Table 13 Recommendations for Estimating Hydrate Formation in Acid Gas Mixtures

	Maximum	Water reduced
Gas gravity	NO	NO
K-factor	NO	NO
Baillie-Wichert Chart	NO	NO
Mann et al.	Yes	NO
computer methods	Yes	yes [†]

† - provided the software was constructed for this situation

Testing Models

One message should have been clear throughout this paper – the design engineer should verify that his/her models are applicable for these systems. And with respect to the software vendors, users should not rely solely on the opinions of the software companies.

The first step in testing a model is to determine if it is qualitatively correct. For example, does it predict that there is liquid phase immiscibility in acid gas + water systems? Does it predict that there is no such immiscibility in systems such as H₂S + CO₂, H₂S + light hydrocarbons, and CO₂ + light hydrocarbons? In the absence of a phase change in the acid gas mixture, does the model predict a minimum in the water content of the acid gas? Furthermore, when the acid gas liquefies, does the model show an increase in the water content from the vapor phase to the liquid phase?

The next step is a quantitative survey, which requires experimental data. As we have seen, data are not available for all situations; however one of the reasons for noting the available data is to give the design engineer some references to test the models.

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SECTION 2: COMPRESSORS IN AGI PERFORMANCE – SELECTION – DESIGN – MATERIALS - CONTROL

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Introduction

Acid Gas Injection (AGI) involves disposal of a mixture of different gases with two bulk constituents; carbon dioxide (CO₂) and hydrogen sulfide (H₂S). The ratio of these gases that are present will vary from one facility to another depending on how sour the natural gas entering the processing facility is and how much of the acid gas needs to be removed to make a saleable product or a product that meets downstream treating specifications. Acid gas from natural gas processing facilities is a byproduct stream that:

- Usually has little or no economic value, although there is a growing market for capturing CO₂ that is dependent upon oil, gas, dry ice and other industrial market conditions, government incentives, or corporate initiatives.
- Cannot be vented or flared in large quantities due to environmental regulations.
- Usually is saturated with water from upstream processes and flows out of the vent stack at low temperature and low pressure (typically slightly above atmospheric pressure).

Injecting the acid gas stream into a nearby injection well for permanent underground storage is an attractive means of disposal since it disposes of the entire stream, is not subject to market conditions, does not generate SO₂, H₂SO₄, elemental sulfur, or other sulfur compounds, does not require third parties to come to the facility to remove and transport large quantities of sulfur, and is generally regarded as an environmentally responsible practice.

The heart of the acid gas injection system is the acid gas compressor. Many acid gas injection (AGI) system processes share some similar characteristics:

- The quantity of acid gas to be injected is usually small, i.e. less than 10 MMSCFD.
- The gas is produced by the upstream acid gas removal unit saturated with water at a low pressure, i.e. less than 10 psig.
- The required injection pressure is high, i.e. greater than 1,000 psig.
- Dehydration of acid gas is common with H₂S fractions < 30 vol. % (mol. %), but above 30 vol. % H₂S, the compression and cooling steps are typically sufficient to remove enough water prior to sending the acid gas to the injection well.

These flow rate and suction and discharge pressure characteristics make reciprocating compressors an ideal AGI compression technology, and specifically packaged reciprocating compressors are widely used for AGI throughout the gas treating industry. This section of the fundamentals of AGI will use an example acid gas injection system based on the following conditions:

- Feed flow rate of 6 MMSCFD on a wet basis.
- Gas composition on a dry basis of 95 vol. % CO₂ and 5 vol. % H₂S, saturated with water at the feed pressure and temperature.
- Feed conditions of 10 psig and 120 °F at the compressor package inlet flange.
- Discharge conditions of 2,500 psig at the compressor discharge flange and (assumed nearby) injection wellhead inlet.
- Air cooling of the compressor is required and during summer can cool to 120 °F.

Figure 1 and Figure 2 are photographs taken from AGI Compressor sites that Trimeric designed.

Compressor Performance & Selection Considerations

The previous section of this fundamentals paper dealt with the physical properties of acid gas mixtures and the importance of knowing the properties of the acid gas across the entire range of operating conditions. This is true when specifying an acid gas compressor, especially one that compresses acid gas to a pressure higher than the critical pressure. The critical pressure of a mixture of H₂S and CO₂ falls between the pure component critical pressures as a function of the H₂S fraction. The critical pressure for pure H₂S is 1,300 psia and it is 1,071 psia for pure CO₂. Compressor manufacturers usually maintain their own modeling programs that are either used internally or also made available to external users. As part of the selection process, independent confirmation of the accuracy of the physical property package used to specify and design the compressor is recommended.

Suction and discharge conditions are set by the system designer and need to encompass the entire operating window of the acid gas system. Some important things to consider when defining the suction and discharge conditions include:

1. The entire range of possible acid gas flow rates. The upstream acid gas removal unit may be built to operate on a defined inlet gas specification, but in practice receive gas that has far less acid gas in it than the specification allows. As a result, the total acid gas flow rate may be less than what the acid gas removal unit was designed to remove. A maximum, minimum, and normal flow condition should be provided to the compressor designer.

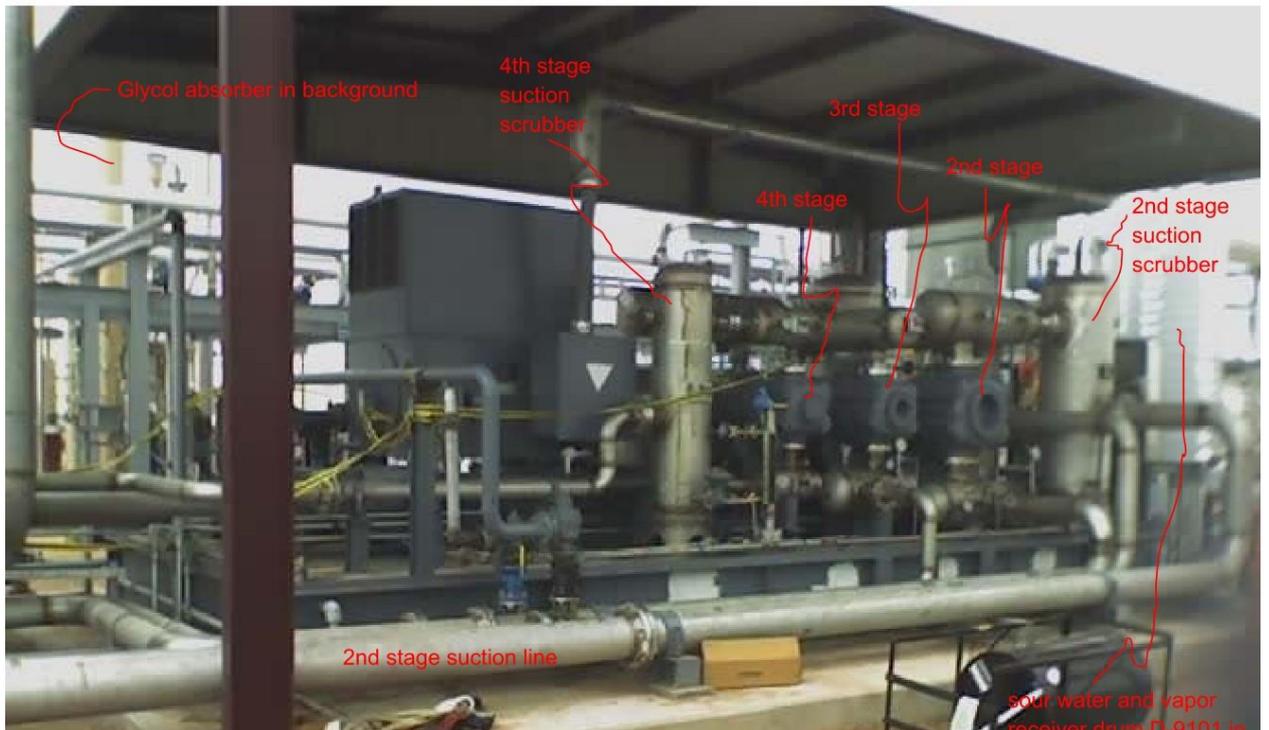


Figure 1 and Figure 2 are photographs taken from AGI Compressor sites that Trimeric designed.



Figure 1 and Figure 2 are photographs taken from AGI Compressor sites that Trimeric designed.

2. Discharge pressure conditions may not be well known if the acid gas injection well is not already designed or if it is being drilled into a formation with few existing wells in it. If the acid gas compressor needs to be ordered before the well is fully characterized, it may be prudent to design the acid gas compressor for a lower discharge pressure than the maximum and allow for a downstream boosting unit, like a dense phase pump to be installed in the future if necessary.
3. Winter conditions and summer conditions will also have a larger impact on the acid gas compressor design than on some other gases. The interstage coolers of the acid gas compressor will most likely be air-cooled and therefore the acid gas temperatures will be subject to diurnal temperature swings unless the system is designed to maintain temperatures in the compressor. Hydrate formation considerations, liquefaction of the acid gas at moderate pressures, and different gas densities at compressor stages are all things that have to be considered in the compressor system design.

The reliability of the acid gas compressor is critical for the gas treating facility to be able to operate normally. When the compressor shuts down, upstream operations may need to be curtailed or flaring of the acid gas may be necessary, which can have a substantial financial penalty associated with it. Maintaining an acid gas compressor is also difficult; each shut down requires a blow down and purge of the compressor system. The compressor is specified to minimize the chances of unintended maintenance, and the system designer should include reliability requirements in the request for bid package that is sent to compressor designers. Compressor packagers operate in a competitive business environment with tight margins and in the absence of clear reliability and performance requirements, they may design a lower capital cost compressor that has a higher overall cost of ownership with more downtime for scheduled and unscheduled maintenance. Some specifications to include on the compressor design and bid request are as follows:

1. Limiting piston speed to less than 850 ft/min. Piston speed is set by the RPM of the compressor, multiplied by the stroke length, and multiplied by 2.
2. Lower RPM speed compressors will reduce the total cycles of the compressor valves proportionally and thereby increase their lifespan. Acid gas is a high molecular weight gas and high molecular weight gases are more likely to cause suction valves in the compressor to stay open past the end of the suction stroke of the piston and then the valves are slammed closed as the compression stroke starts. This can lead to premature valve failure and is more likely in high RPM compressors.
3. Lower discharge temperatures on each stage will increase the reliability of compressor valves. Discharge temperature is largely set by the compression ratio across a given stage, which also sets the rod load of the compressor. The speed of the compressor will also have an impact on the discharge temperature of the gas; slower machines will have a lower discharge temperature for the same gas flow rate, but this is a lower impact than the compression ratio. Discharge temperatures should always be kept below 300 °F and ideally even below 280 °F.

For the example listed above, the compressor selected for this service is a six cylinder, five stage compressor. The first stage of compression has the highest volumetric flow

rate and this sets the processing capacity of the compressor, is made up of two cylinders operating in parallel, and each subsequent stage of compression is done with one cylinder. Figure 3 shows a run sheet for the selected compressor.

	Company: Ariel Corporation	Ariel Performance	Customer: AGI	
	Quote:		Inquiry:	
7.7.16.0	Case 1:		Project: LRGCC - AGI Example	

Compressor Data:	Elevation,ft: 50.00	Barmtr,psia: 14.669	Ambient,F: 100.00
Frame: (ELP) KBK/6	Stroke, in: 6.00	Rod Dia, in: 2.000	
Max RL Tot, lbf: 92000	Max RL Tens, lbf: 46000	Max RL Comp, lbf: 50000	
Rated RPM: 1200	Rated BHP: 5520.0	Rated PS FPM: 1200.0	
Calc RPM: 698.3	BHP: 1702	Calc PS FPM: 698.3	
<u>SOUR GAS-2 CO2 PACKING COOLING</u>		Driver Data:	
Services		Type: <u>VFD</u>	
Service 1		Mfg: Model: 60 Hz - 8 Po	
Gas Model VMG-APRNL2		BHP: 0	
Stage Data:		Avail: 0	
	1	2	3
Target Flow, MMSCFD	6.000	6.000	6.000
Flow Calc, MMSCFD	6.074	5.822	5.725
BHP per Stage	385.6	373.4	386.4
Specific Gravity	<u>1.4419</u>	<u>1.4773</u>	<u>1.4918</u>
Polytropic Exponent (N)	1.2711	1.2679	1.2894
Comp Suct (Zs)	0.9922	0.9818	0.9544
Comp Disch (Zd)	0.9898	0.9764	0.9428
Pres Suct Line, psig	10.00	N/A	N/A
Pres Suct Flg, psig	9.75	44.39	133.38
Pres Disch Flg, psig	46.24	138.06	406.33
Pres Disch Line, psig	N/A	N/A	N/A
Pres Ratio F/F	2.494	2.586	2.844
Temp Suct, F	120.00	120.00	120.00
Temp Clr Disch, F	120.00	120.00	120.00
	4	5	6
Temp Suct, F	120.00	130.00	130.00
Temp Clr Disch, F	120.00	120.00	120.00
	1	2	3
Cylinder Data:	Throw 1	Throw 2	Throw 3
Cyl Model	22K:20	20-1/8K:20	12-1/2K:23
Cyl Bore, in	22.000	19.625	12.500
Cyl RDP (API), psig	259.1	313.6	740.9
Cyl MAWP, psig	285.0	345.0	815.0
Cyl Action	DBL	DBL	DBL
Cyl Disp, CFM	1835.6	1459.1	587.4
Pres Suct Intl, psig	8.18	41.43	126.20
Pres Disch Intl, psig	49.81	144.77	424.37
Temp Disch Intl, F	272	275	290
HE Suct Gas Vel, FPM	5852	5073	4929
HE Disch Gas Vel, FPM	5014	4285	4224
HE Spcrrs Used/Max	0/0	0/0	0/4
HE Vol Pkt Avail	0.69+44.63	No Pkt	No Pkt
Vol Pkt Used	12.00 (V) %	No Pkt	No Pkt
HE Min Clr, %	14.82	17.53	17.31
HE Total Clr, %	20.87	17.53	17.31
CE Suct Gas Vel, FPM	5804	5020	4803
CE Disch Gas Vel, FPM	4973	4240	4115
CE Spcrrs Used/Max	0/0	0/0	0/0
CE Min Clr, %	15.27	18.00	18.38
CE Total Clr, %	15.27	18.00	18.38
Suct Vol Eff HE/CE, %	73.6/79.5	75.7/75.2	72.1/70.7
Disch Event HE/CE, ms	16.7/20.5	16.7/19.6	15.8/18.4
Suct Pseudo-Q HE/CE	4.7/4.6	4.0/4.0	4.2/4.0
Gas Rod Ld Comp, %	31.7 C	62.8 C	74.0 C
Gas Rod Ld Tens, %	34.0 T	66.9 T	76.6 T
Gas Rod Ld Total, %	34.3	67.6	78.5
Xhd Pin Deg/%RvrsI lbf	146/90.7	170/92.2	171/90.0
Flow Calc, MMSCFD	3.037	5.822	5.725
Cyl BHP	192.8	373.4	386.4

Figure 3. Example Acid Gas Compressor Run Sheet.

To stay close to the parameters for reliability, while allowing for some additional capacity in the acid gas system, the compressor motor has a maximum rotational speed of 891 RPM, but will be driven by a variable frequency drive so that it normally operates at a slower speed. This also allows for a further reduction in capacity that will be discussed later in this section of the fundamentals.

The compression process mapped out on a pressure vs. enthalpy diagram is shown in Figure 4.

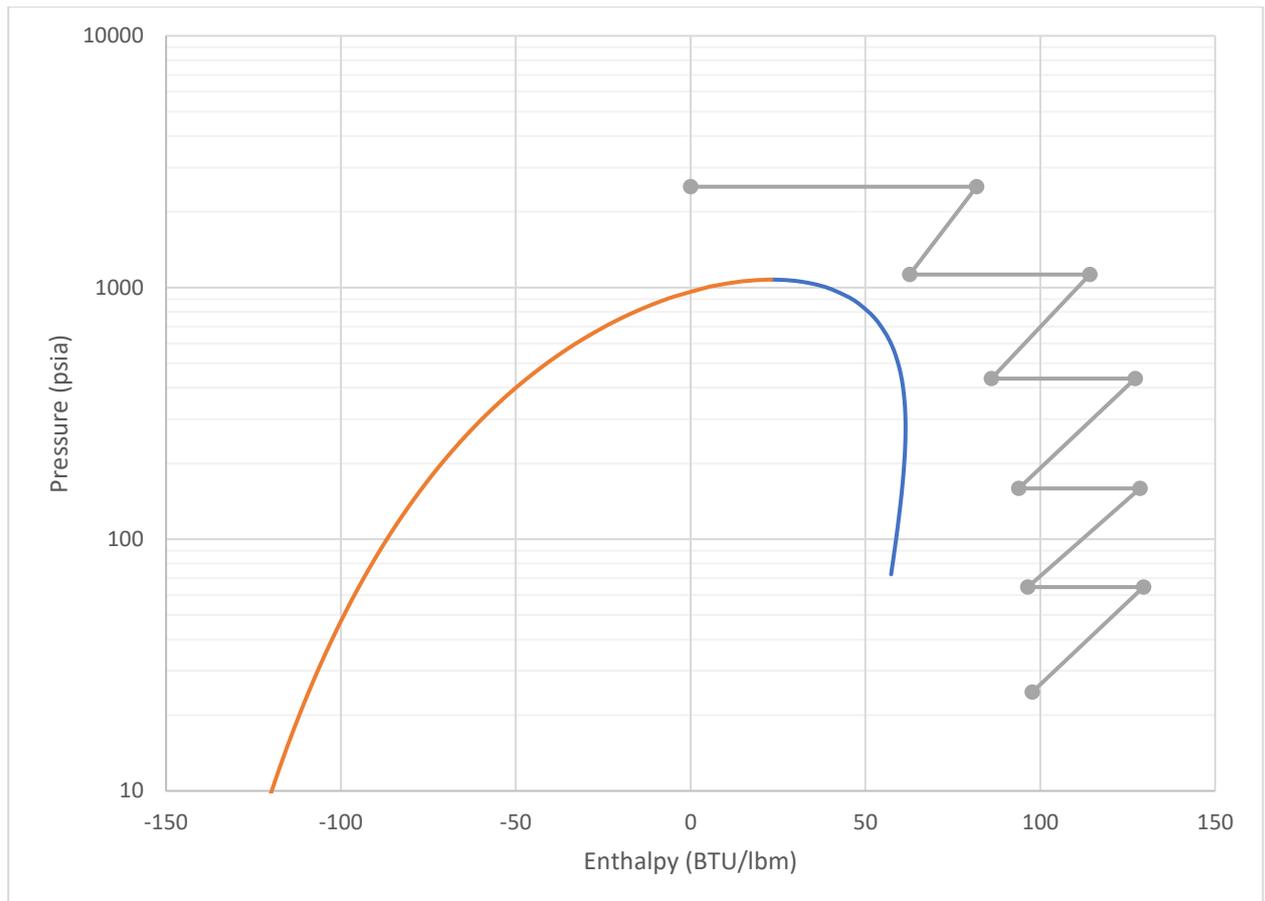


Figure 4. Pressure vs. Enthalpy (PH) Diagram of Acid Gas Compression Process.

Figure 4 shows several key considerations for the acid gas compression process. The compression process happens well-away from the two-phase region of the fluid so there is little or no chance for liquids to form in the process as long as interstage temperatures are properly controlled. Staying away from the right side of the dome (or the dew point of the gas) also reduces the risk of solid hydrates forming as these usually in a gas temperature range between 32 and 60 °F. Temperature is not shown in Figure 4, but cooling after Stages 1 through 3 is done to 120 °F in this example. The inlet to Stage 5 is at or near the critical pressure of the fluid, which by itself is not a major issue but as the fluid approaches the critical point (i.e. the critical pressure and critical temperature), the physical properties of the fluid can change substantially and this may cause the compressor to operate differently or even cause damage to the compressor. As a result, it is important to operate the compressor away from the critical point and in this example, the Stage 4 discharge gas is not cooled all the way to 120 °F but instead just to 130 °F, so that the compression process maintains an

adequate margin away from the critical point. Some compressor manufacturers recommend staying 40-50 °F above the critical temperature to ensure stable physical properties. Compressor system designers often design the transition through the critical pressure to occur midway through a compression step, so that the suction scrubber and pulsation bottle and the discharge pulsation bottle will not be subject to large changes in volumetric flow rate that can occur with small changes in temperature or pressure near the critical point. That would be another concern with cooling the Stage 4 discharge / Stage 5 suction gas closer to its critical temperature. It is also important to maintain the fluid's compressibility above 0.5 for the compressor to be able to compress the fluid (Ariel Corporation, 2025).

Compressor Design and Materials

Reciprocating compressors are well known in the oil and gas industry. Their function and general makeup are well understood. However, it is the application in which the compressor is applied in that defines most of its enigmatic internal processes. AGI applications are one of the most demanding. Compressing a corrosive, toxic gas composed mostly of hydrogen sulfide and carbon dioxide, from relatively low suction pressures to discharge pressures up to 3000 psig, requires significant attention to materials of construction and system design. There are industry standards such as API 618 and NACE MR0175/ISO 15156 that provide guidance on the shall/shall nots, however, it is the field experience that ultimately proves success.

As with any piece of rotating machinery, there is a source of power and a source consuming that power. A reciprocating compressor is the consumer. A driver provides torque as well as the rate the torque is applied, horsepower. The driver in AGI applications is almost always an electric motor with variable frequency drive (VFD). The horsepower required mostly depends on the flow requirement and compression ratio. AGI applications tend to have flow requirements of approximately 0.5 to 10 MMSCFD and a total compression ratio exceeding 100, requiring about 250 to 2500 HP. Lastly, a compressor's cylinder configuration and frame size are also determined based on this flow, power, and compression ratio.

The running gear of a reciprocating compressor will remain much the same regardless of the application, as depicted below in

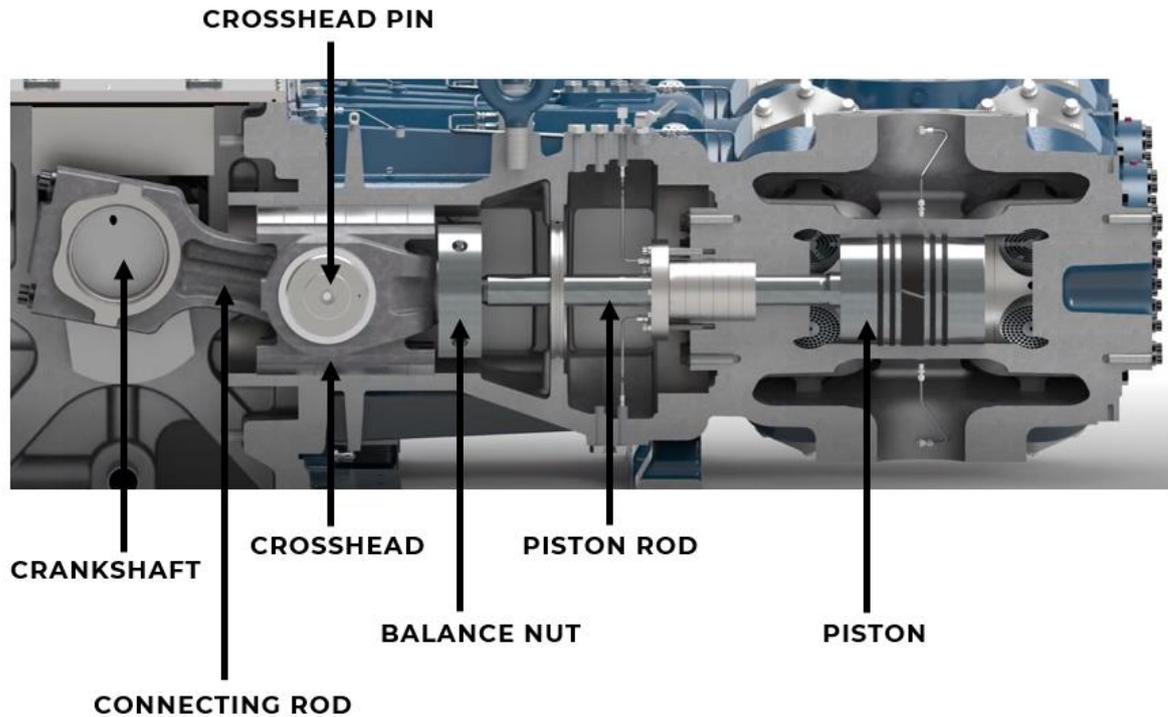


Figure 5. Utilizing a slider-crank mechanism, composed of a crankshaft, connecting rod, and crosshead, the rotational motion of the driver provides a torque which is then translated into a linear motion and force. The resultant force is composed of the inertia of the reciprocating components (crosshead, balance nut, piston rod assembly) and the gas force due to compression, referred to as crosshead pin load per API 618. The crankshaft will dictate the stroke of the piston and the speed of the driver will determine the piston speed ($2 \times \text{stroke} \times \text{RPM}$). The lower the piston speed, the lower the wear rate on consumable components such as seals/bearings, increasing reliability which is paramount in AGI applications. However, reduced speed inherently reduces throughput or capacity. Lower piston speeds also provide better flow dynamics of the heavy gas within a compressor cylinder, this will be discussed later.

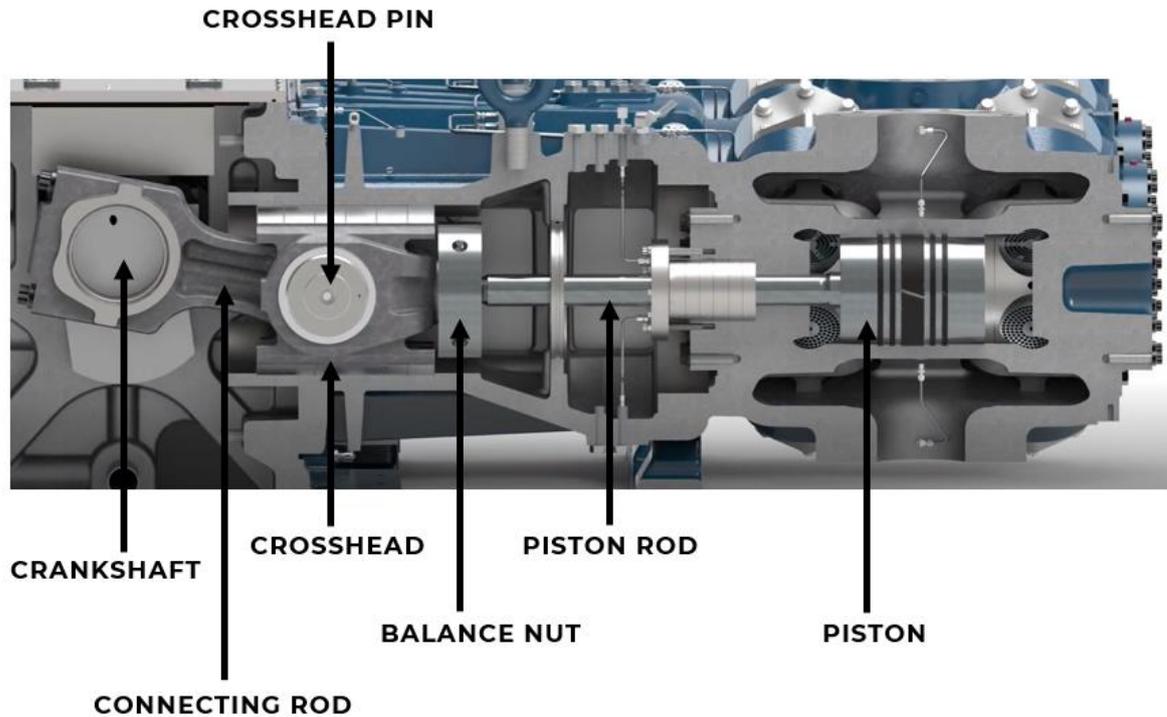


Figure 5: Reciprocating Compressor Running Gear.

There appears to be a generational influence, as well as recommendations from industry standards, demanding no yellow metals within the frame, or crankcase of the compressor, for AGI applications due to the high concentration of hydrogen sulfide in the process gas. Yellow metals (copper alloys) are found in the half-shell bearings of the frame mains and big-end of the connect rods, as well as the bushings within the small-end of the connecting rods and crossheads. Hydrogen sulfide will react with the copper alloys creating a black surface layer of copper sulfide. Applying no yellow metals requirements means bearings/bushings made of aluminum. Furthermore, aluminum is not as robust as the tri-metal bearings or the bronze bushings it replaces, and thus, derates of the compressor and increased service intervals may follow. Also, larger frames rated at higher rod loads may not allow the use of aluminum bearings altogether. In a properly designed system, no process gas will be exposed to the crankcase and yellow metals may still be used.

Safety moment: If process gas enters the crankcase of a reciprocating compressor, it will ultimately be exposed to the external environment surrounding the compressor as the crankcase contains a breather vent and crankshaft dust seal. Neither are designed to hold pressure. A hydrogen sulfide concentration of 500 ppm is enough to be deadly within minutes.

One also has to consider, if process gas enters the crankcase, then it will be exposed to the compressor's lube oil, the life blood for the running gear. Unless the oil is formulated to handle such situations, oil contamination and degradation may follow, potentially leading to a breakdown in oil viscosity which spells disaster for bearings/bushings.

So, what is a properly designed system to prevent process gas from entering the crankcase for AGI applications with high concentrations of hydrogen sulfide and

carbon dioxide? It is applying two compartment distance pieces with nitrogen or sweet natural gas purge at positive pressure to the piston rod seals, applying the latest technology in piston rod seals, routing distance piece vents/drains into individual manifolds with little-to-no backpressure and piping them to a collection system for further disposal. Each of these will be discussed in detail below but first, one has to consider where the main source of process gas leakage occurs and how it can enter the frame.

Regardless of the compressor application, the main seal to prevent process gas leakage into the crankcase is the packing depicted as item 5 in Figure 6. The packing is a dynamic seal comparable in nature to that of a mechanical seal of a rotating pump, but rather, instead of sealing a rotating shaft, it is sealing a reciprocating shaft or piston rod. Typically lubricated, and most certainly in AGI applications, a packing case is composed of a number of single acting seal ring sets that are meant to seal in one direction (towards the cylinder), incrementally breaking down the pressure. The last ring set in the packing is a double-acting ring that seals in both directions. The double-acting ring encourages any remaining gas from the cylinder to enter the packing vent/drain and prevents intrusion of gas from the distance piece in the event of back pressure. For AGI applications, this last seal ring set must have a positive pressure purge gas applied to enhance its sealing capability.

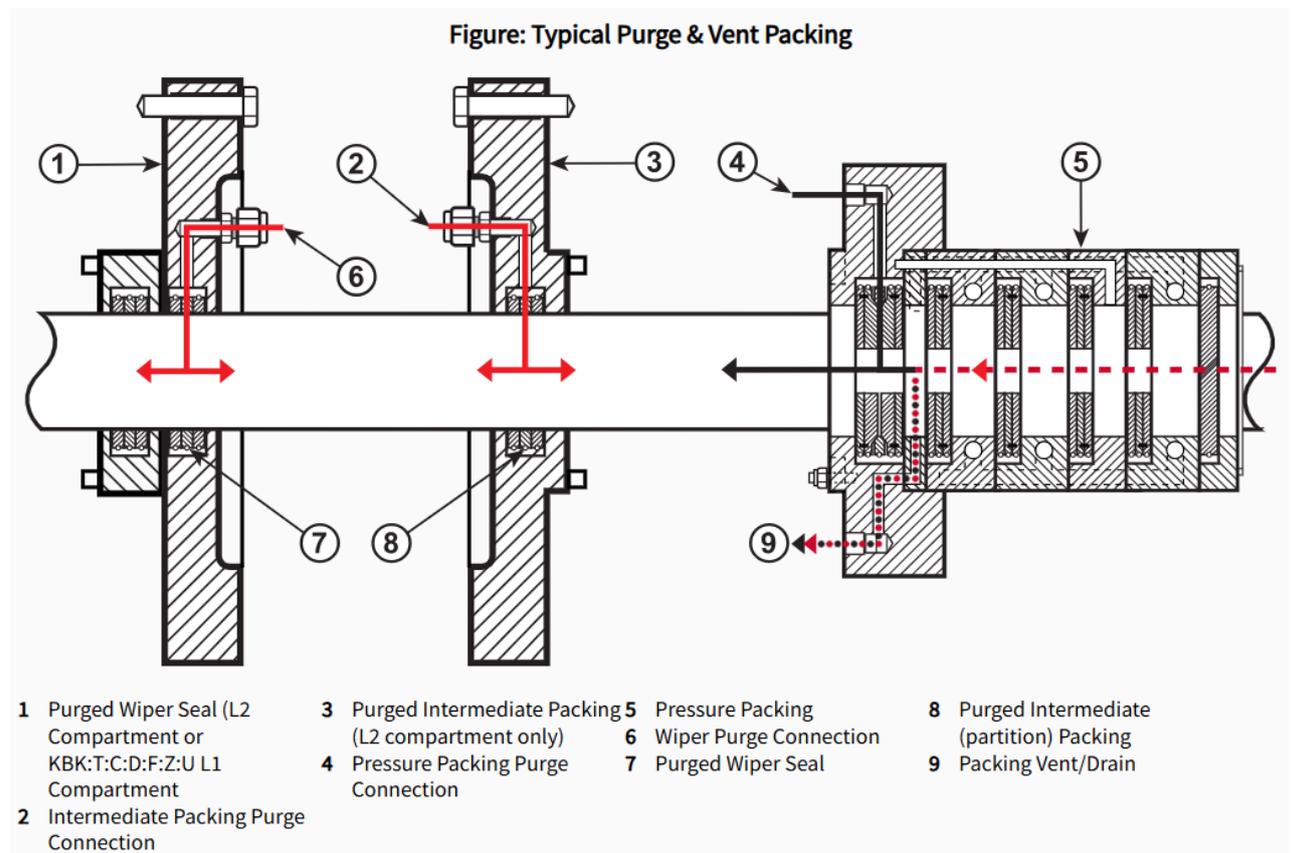


Figure 6: Typical Purge & Vent Packing Configuration in a Long Two Compartment Distance Piece.

Side Note: Regulatory agencies, most notably the EPA, call out leakage thresholds and service intervals on the packing as it is the primary source of emissions for reciprocating compressors, aside from blow down events. The seals within the case

are typically spring energized, non-metallic, although a combination of metallic/non-metallic is also common. Most packing seals still reflect early 20th century designs, however, spurred by increased regulatory pressure and advancements in material science, the design and performance of these seals have improved drastically in recent years. In some applications, achieving near-zero emissions. The seals will eventually wear and will need to be replaced, although lower piston speeds will prolong the wear life of the seals.

In addition to the main packing seal, a two-compartment distance piece arrangement has additional barriers to further prevent process gas leakage into the crankcase. The additional barriers are an intermediate packing and wiper gland, both having purge capabilities, depicted as item 1 and 3 of Figure 6. The intermediate packing seals between the outboard and inboard compartment while the wiper gland wipes frame oil off the rod, preventing oil migration from the frame to the inboard compartment. There is also a seal ring set located in the wiper gland to help prevent back pressure in the compartment from entering the frame. This is a likely source if process gas leakage is observed in the crankcase. Legacy style sealing technology in the wiper was not designed to seal against much back pressure, however, advancements in sealing technology have been applied successfully in this area.

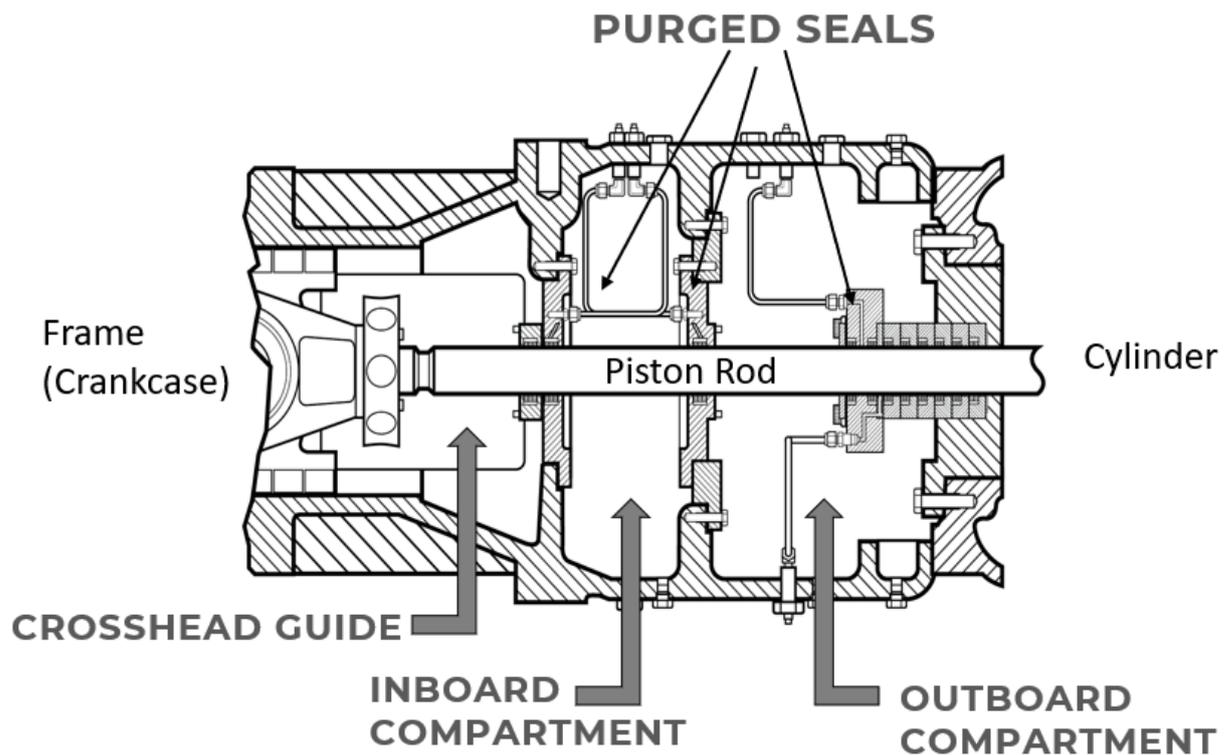


Figure 7: Two Compartment Distance Piece, Type 3 ISO 13631, Type C API 618.

The purge gas to the packing, intermediate packing, and wiper gland is supplied at a pressure of 5-10 psi above the back pressure of the vent/drain system. Each compartment has a vent at the top and a drain at the bottom. The packing case has its own dedicated vent/drain line (seen in Figure 7 as the tube to the bottom of the outboard compartment or item 9 in Figure 6). These three areas are the beginning of the vent/drain system. This system is ideally at atmospheric pressure, or as low as

possible, simply to encourage any process gas leakage to enter the system. Or else, it may find the path of least resistance elsewhere.

Each of these vent/drains must be manifolded separately to prevent cross communication with one another. Connecting them together in any way defeats the purpose of a two-compartment distance piece as it allows gas to flow between compartments. The combined line size should equal the added areas of the incoming two lines. For example, if two 3/4-inch lines meet, a 1-inch line is appropriate after the connection. Lines need to be appropriately sized to prevent restrictions to drain both oil and gas, such as increasing to minimum 3/8-inch tubing from 1/4-inch NPT connections that are provided on the bottom of the distance piece by the OEM. It is common to join the vent and drain of the same compartment to a manifold as the source of these two lines are the same. Internal/external tubing for vent/drains, and lubrication lines, are typically 304 stainless materials although 316 stainless tubing/fittings is commonly applied as an option due to the corrosive process gas. Figure 8 depicts a properly configured vent/drain system with separate manifolding that collectively leads to a separation pot.

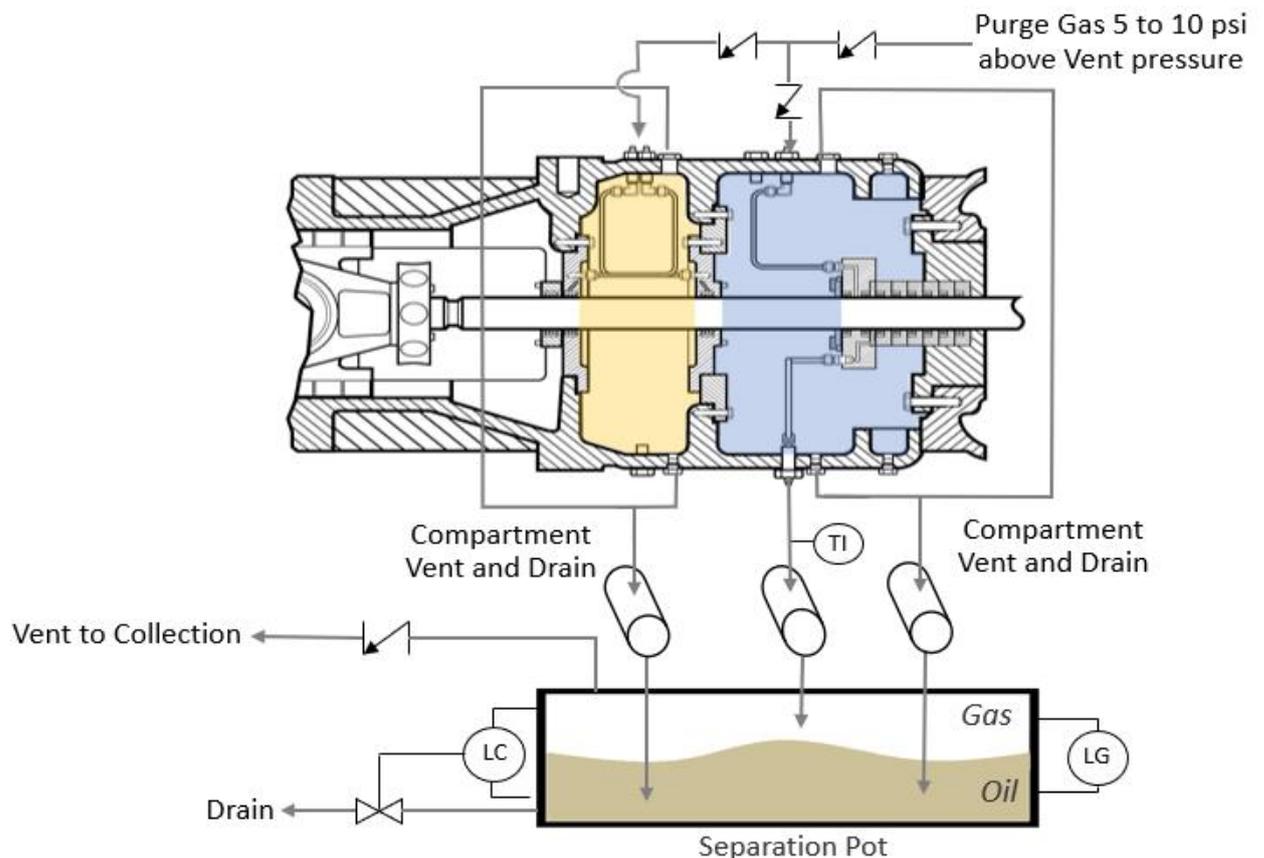


Figure 8: Long Two Compartment Distance Piece Schematic

The separation pot separates lubricating oil and process gas for further disposal to a collection system. Its design is important such that no three manifolds cross communicate with one another. As shown in Figure 8, a liquid level is utilized as a liquid check valve for the compartment manifolds as their lines enter the separation pot and conclude below the liquid level. Oil level is maintained/verified with a controller/gauge and a drain is present to take away excess. Lastly, process gas leakage is vented to its own collection system. This may be to a plant vent system

leading to flare or reinjected into the process by means of a small emission recovery unit (ERU) compressor.

Although the distance piece vent/drains are necessary to collect process gas and lube oil leakage, the goal is to minimize or prevent this leakage in the first place. Steps to prevent this are lower piston speeds, applying appropriate materials of construction to piston rods, applying OEM specified lube oil grade in the cylinders/packing, and water cooling in the packing which will depend on mean cylinder pressure and piston speed.

Due to the corrosive nature of high concentrations of hydrogen sulfide and carbon dioxide, at high partial pressures, stainless steel piston rods may be required. NACE MR0175 defines acceptable materials of construction, for example, a 17-4PH material for piston rods in the double H1150 condition, UNS S17400, Rc 33 maximum. Other grades of stainless may also be acceptable. The piston rod will be exposed to the process gas as it enters into the cylinder on the suction stroke of the crank end side of the cylinder. In addition to surface hardening by means of heat treating, such as ion nitriding, a surface coating of the piston rod is commonly applied in the packing travel region as this is the section of the rod that the seal rings are energized. If a coating is not applied, accelerated wear of the piston rod is likely. Tungsten carbide and chromium nitride coatings are common. To prolong the life of the seal rings and piston rod, a lube oil is injected into the packing case. Ideally, the oil will coat the surface of the rod so the rings will seal along a film of oil, increasing sealing effectiveness and wear life. The lube oil will be exposed to the process gas so it is of the utmost importance to adhere to OEM specifications on lube oil grade. It is not uncommon to see an ISO 220 or ISO 460 grade oil applied. These grades are too heavy to be utilized in the frame lube oil system, so an independent oil supply is required, as seen in Figure 9 below.

Figure: Force Feed Lubrication System Independent Oil Supply

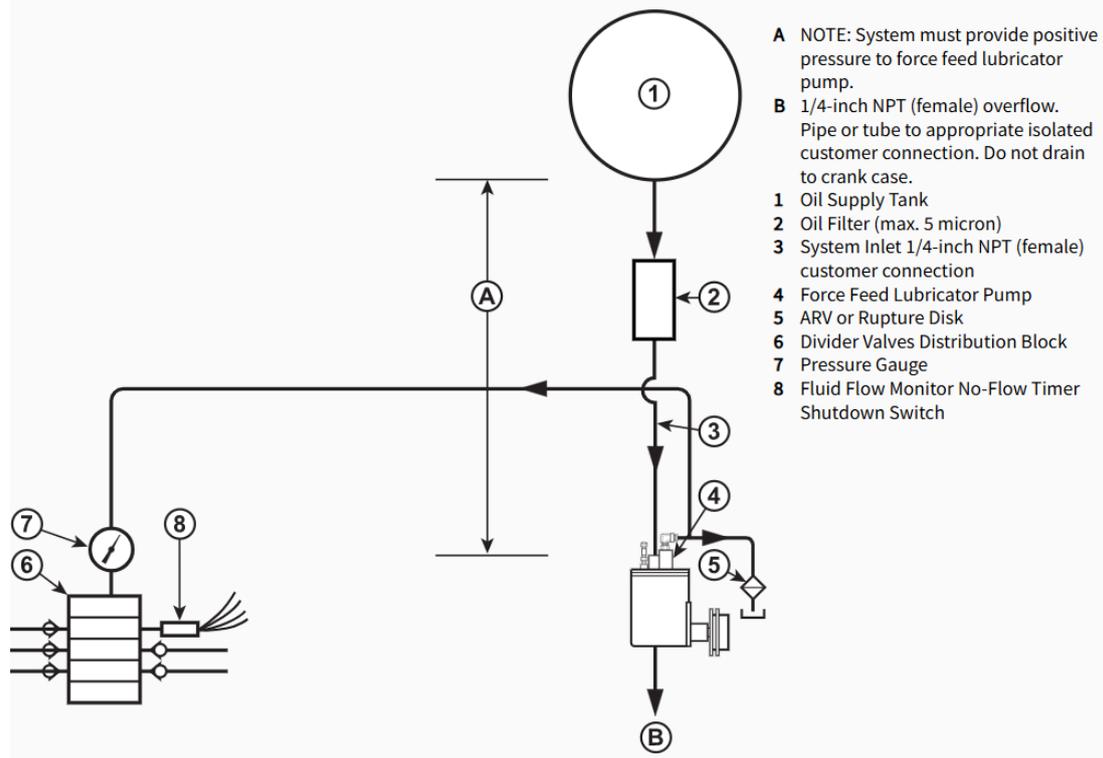


Figure 9: Force Feed Lubrication System Independent Oil Supply

Oil provided by the independent supply lubricates both the packings and cylinder bores. The rate of oil delivery will be specified by the OEM. A newly commissioned compressor will typically be set to a “break in” oil delivery rate of 1.5x the normal lube rate. After a set number of operating hours, usually ~200 hours, the oil delivery is adjusted back to the normal lube rate. The break in period is just that, sealing components will wear to conform to the surface they are sealing against.

Reciprocating compressor cylinders for AGI applications are commonly double-acting, compression occurs on both ends of the cylinder, and made of ductile iron of ASTM A395 grade 60-40-18 suitable per NACE standards. The OEM and/or end user may take exception to NACE standards in the grade of cast iron for AGI applications as field experience would take precedence. The last stage of compression may require the use of forged steel, or block-style, cylinders. The maximum allowable working pressure (MAWP) of ductile cylinders is limited to about 2500psi. AGI applications typically operate at or above pressures in which forged steel is then necessary to achieve higher MAWP. For example, forged steel of AISI 4340 softened to 22 RC or a 17-4PH stainless steel material, as defined in NACE MR0175. Stainless bolting is an option that may be applied external to the cylinder at the flanges, valve caps and heads, however, these surfaces are not “wetted” or exposed to the process gas directly at operating pressures, so standard bolt materials of a grade 8 material might be applied, depending on the compressor OEM.

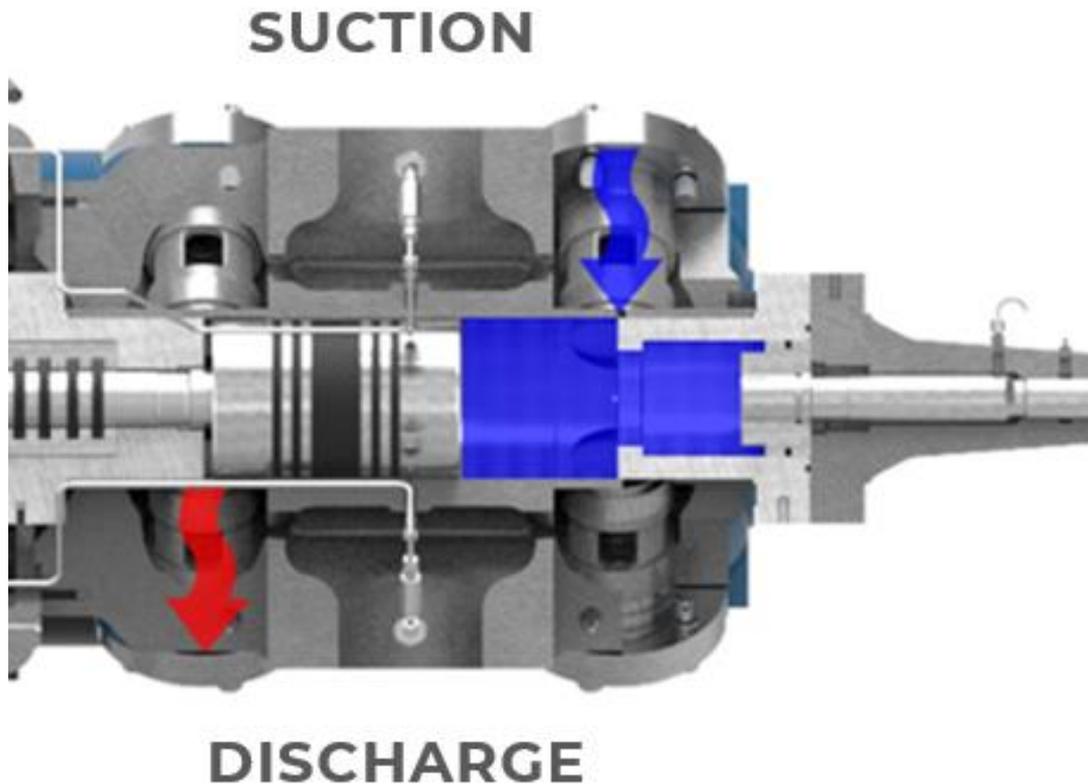


Figure 10: Compression Process of a Double-Acting Cylinder

Cylinders are typically orientated with suction on the top and discharge on the bottom. As seen in Figure 10, when one end of the piston is compressing, the other end is intaking a fresh charge of gas. This process will repeat on both ends as the piston reciprocates back and forth, at the piston speed determined by stroke and operating RPM. It may seem like a continuous flow of gas but the cylinder actually “burps” gas out in pulses at a high frequency.

Process gas can only flow in one direction due to the plate-style valves that act similarly to check valves. Valve body material will be directly influenced by the process gas similarly to piston rods, so a 17-4PH material is commonly applied in AGI applications and meets NACE specifications, though there is field experience suggesting a 400 series stainless material is suitable. Valve plates are mostly non-metallic PEEK material, blending rigidity with a touch of conformability. However, depending on operating pressures of the valve, alternative valve plate materials may be required to maintain sealing effectiveness. Also, valve timing, or the closing event of the valve plate, is thoroughly reviewed for each stage of compression to further confirm valve performance and reliability. The valve timing is adjusted by the use of springs of different stiffness.

Side Note: A flushing lube may be applied to the inlet nozzle on the suction side of the cylinder as a means to coat the valve in oil to prevent corrosion due to the high concentrations of hydrogen sulfide and carbon dioxide. The thought process behind applying flushing lube is the discharge valves will inherently be coated due to cylinder lube by the flow of gas and suction valves miss out on that opportunity. However, there is a sizable sentiment from end users suggesting flushing lube is the cause of decreased valve reliability due to stiction of the valve plate. Similarly to

lifting a cold beverage with its coaster still attached, the valve plate may delay opening during the intake stroke due to it sticking to the seat and causing it to slam open.

Valves operate based on differential pressure. On the suction stroke, the piston retracts and any remaining gas inside the cylinder expands. Eventually the pressure internal to the bore reduces below suction pressure and gas is drawn into the cylinder by the opening of the suction valves (the blue portion of Figure 10). Discharge pressure will hold the discharge valves closed at that time. When the piston reverses, compression will begin forcing the suction valves closed. Once internal bore pressure meets and exceeds discharge pressure, the discharge valves will open and gas will exit the cylinder.

In AGI applications, the heavy gas, typically 1.2 – 1.5 specific gravity, may struggle to exhaust from large bore cylinders due to tight internal clearances and the long distance between suction/discharge valves. Essentially, the compressed gas is not given enough time for it to travel across the face of the piston and out the cylinder. This phenomenon coined by an OEM is called “Instationary Flow”. What ensues is decreased capacity and efficiency. The legacy style solution was to reduce operating RPM and/or reduce stroke (not an easy task if an existing unit). However, there have been recent improvements to large bore cylinder designs to remedy this phenomenon.

Figure 11 is a real-world example of a 1750 hp six throw 5 stage acid gas injection unit. The configuration displayed has two first stage cylinders and one cylinder for each of the remaining stages. The first 4 stages utilize ductile iron A395 cylinders while the 5th stage utilizes AISI 4140, 22 Rc forged steel. The gas analysis mainly contains hydrogen sulfide and carbon dioxide with specific gravity of 1.4. Inlet pressure is 6 psig with a discharge pressure range of 2400-3700 psig. Required flow is 4 MMSCFD.

The reason for many stages, and thus many throws, is partly due to the high compression ratio of 120-180 (discharge pressure absolute / suction pressure absolute) and due to the required flow rate. As the old saying goes, “there’s no replacement for displacement,” when discussing power for an engine. This saying can also be applied to reciprocating compressors, as flow and power are proportional to an extent. To achieve more flow, then any of the following are required: longer stroke, larger cylinders, more cylinders, increased speed, increased inlet pressure, and sometimes, more stages. In AGI applications, longer stroke, increased speed, and increased inlet pressure have traditionally not been easily achieved. This is in part due to the source of the acid gas and the acid gas properties. That leaves larger cylinders, more cylinders, and more stages as the main solution, although as mentioned above, recent changes to an OEM’s cylinder designs may unlock higher piston speeds.

Each stage then takes a bite out of the total compression ratio, at most around 4 ratio per stage. This limit exists so discharge temperatures, suction volumetric efficiency, and gas rod load remain within compressor limits. The process gas will be cooled on the interstage, to some degree, before being introduced into the next stage. The intricacies of interstage cooling of acid gas injection applications will not be discussed here and are discussed elsewhere in the document.

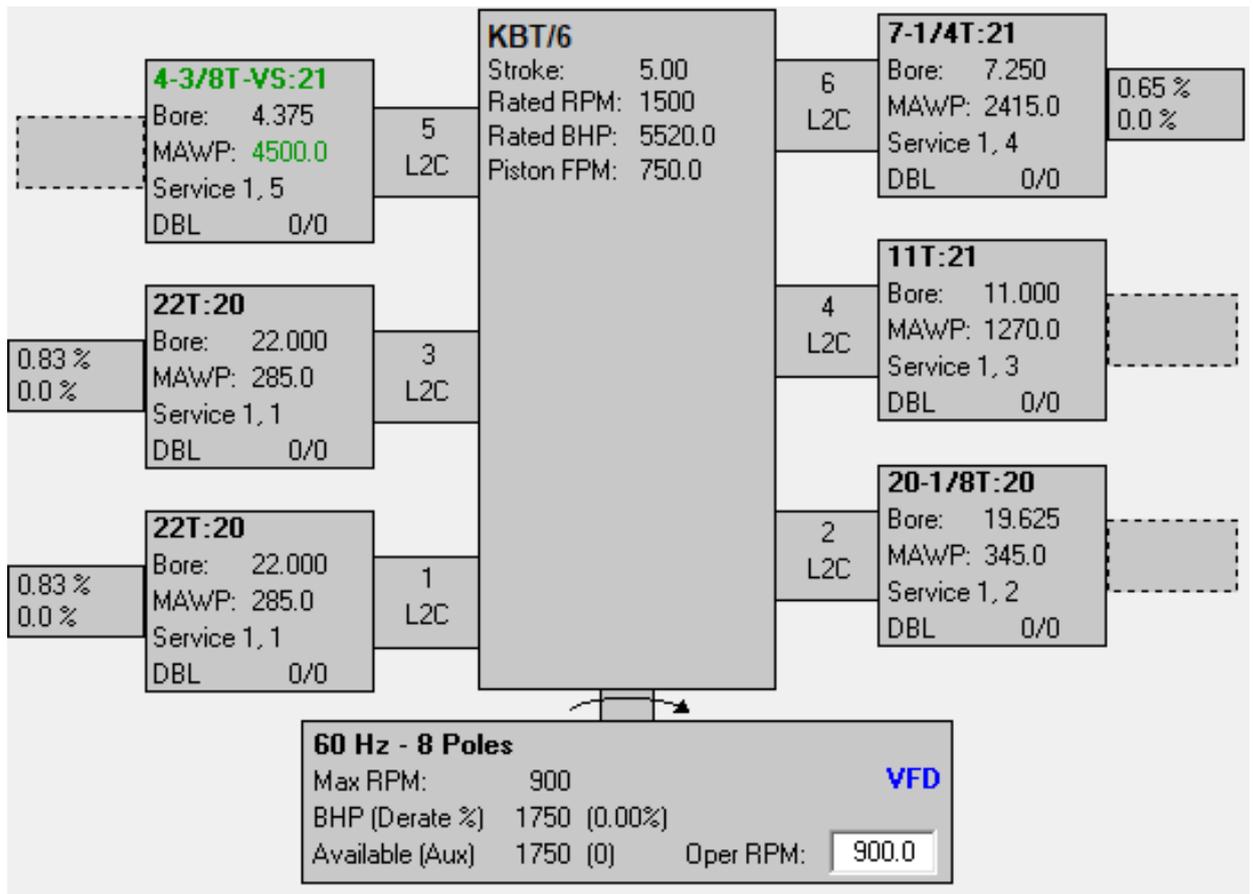


Figure 11: Example of an Acid Gas Injection Unit.

Compressor Package Design and Materials

Packaging of acid gas compressors requires that special attention be paid to material selections, components and design features.

Material Selections

Acid gas coming to the compressor is typically saturated with water by the upstream acid gas removal unit. As the acid gas is compressed and cooled downstream of each compressor stage, the ability of the gas to hold water is reduced and water condenses. At higher pressures above the critical pressure, acid gas regains capacity to hold more water as the pressure is increased. The pressure of minimum water content varies with the gas mixture and is the subject of various papers previously presented at LRGCC and will not be repeated here. The condensed water contains hydrogen sulfide and carbon dioxide and is acidic and corrosive. It is removed from the gas stream in the inlet separator for the next compressor stage.

For many years, the industry standard for acid gas compressors was to utilize austenitic stainless steel (304L, 316L, etc.) on the cold side or suction of each compressor stage and carbon steel on the hot side, or discharge. Cooler tubes, piping to the next stage, suction separator, inlet pulsation drum would all be fabricated from stainless steel materials. Discharge pulsation drum and piping to the cooler would be carbon steel because the gas is well above its water dew point (superheated) during operation. Cooler headers are the same material as the cooler tubes. This met the

requirements of older versions of NACE MR-0175. Subsequent editions of NACE MR-0175 limit the use of 304L and 316L materials to the extent that, in practice, they cannot be used in an acid gas application except for the first stage. However, there are many successful installations using the above materials and some purchasers continue to specify these materials instead of defaulting to compliance with the latest edition of NACE MR-0175. Note that austenitic stainless steel not typically suitable if there are chlorides present in the gas stream.

If compliance with the latest edition of NACE is required, the cold side piping and vessels can be made from carbon steel (see below) or high nickel alloys such as Alloy 825 or Super Duplex. Even if carbon steel is resistant to sulfide stress cracking and hydrogen induced cracking, it is still subject to corrosion from acidic condensation. The addition of an inhibition system or using coated carbon steel can control this corrosion and permit the use of carbon steel. Purchasers who do not have the experience to support going against the latest NACE recommendations, and do not want the added operational cost of a corrosion inhibition system or coated piping, are specifying the more exotic materials. Not only are these materials expensive and require long lead times, but the specialized weld procedures needed are slow when compared to more conventional materials. Additionally, many compressor packagers do not have approved weld procedures for these materials and so they need to develop them or subcontract this work out to a specialist. Either way, equipment deliveries are much longer and the cost of the compressor package is greatly increased.

When carbon steel materials are used, it is important to keep stresses low and hardness below Rockwell C 22. Hardness should be checked in the base metal, Heat Affected Zone and weld metal. Carbon steels should have a uniform and fine grain structure. For large diameter vessels, use HIC tested ASTM 516-60 or 516-70 normalized plate. For smaller diameter vessels and nozzles, use A-333 Grade 6 seamless pipe. Pipefittings should be ASTM A-350 LF2 or ASTM A-420 WPL6. Note that some clients specify 516-60N plate, based on internal research that shows it is less susceptible to stress corrosion cracking than 516-70N under the same conditions. Post-weld heat treatment is required for all carbon steel to eliminate localized stresses caused by welding. A minimum of 1/8" (3 mm) corrosion allowance should be included, but the purchaser should specify what is required based on their experience. Note that if more than 1/4" (6mm) corrosion allowance is specified, drain lines and other small-bore connections may have to be made from corrosion resistant material. Alternatively, they could be made larger in order to have sufficient wall thickness after the corrosion allowance to withstand the design pressure.

100% radiography of all butt welds and UT examination of other pressure retaining welds, is normally specified to ensure the weld integrity no matter what materials are selected.

Hydrogen sulfide reacts with the iron in steel to produce iron sulfide (FeS), and carbon dioxide reacts in a similar way to form iron carbonate (FeCO₃). Both of these form a barrier that actually helps protect the steel from further corrosion. Add to this the thin coating of oil that comes from the cylinder lubrication being carried by the gas stream and in practice the corrosion rates on carbon steel vessels and piping in compressor packages are not as high as predicted by most corrosion prediction

software programs. This is helped if gas velocities are reduced from the normal rule of thumb of 3000 feet per minute (15 m/s) for natural gas applications to 2000 feet per minute (10 m/s). These lower velocities reduce erosion of the protective layer and also ensure that pressure drops are similar to natural gas applications.

The traditional cooler material selection is carbon or stainless steel headers and stainless steel tubes, and coolers are still being purchased this way. For latest NACE compliance, if carbon steel is acceptable, the headers can be fabricated from HIC tested ASTM 516-70N plate with SA 179 seamless carbon steel tubes. Since it is not practical to include a corrosion allowance in the cooler tubes, some purchasers use the less expensive carbon steel headers, with a corrosion allowance and Super Duplex or Alloy 825 tubes.

As can be seen from the above discussion, there are many different opinions on the best material selections. There is no industry standard or theory as good as practical experience with like gas under like conditions. Experienced end-user input is essential in order to come up with a practical, reliable, and safe solution.

When using austenitic stainless steel, it is essential to ensure that no chlorides are present in the hydrotest water. Distilled water should be used. There are recorded cases of chloride stress cracking of stainless steel vessels in which the root cause of the failure was traced back to using tap water for hydro test purposes.

Low stress stamps should always be used for identifying purposes on sour gas vessels and piping.

Threaded connections in the process system should be minimized. All lines 1.5" NPS and larger should be flanged and welded. 1" and smaller lines can utilize stainless steel tubing with stainless steel fittings in lieu of screwed piping. 1/2" and 3/4" threaded instrument connections are generally acceptable, although some customer specifications require all flanged connections on the pressure vessels.

All scrubbers should be equipped with bottom drains to allow complete draining of liquids during a shutdown. Drain valves should be installed on all discharge pulsation bottles and low points for the same reason. Most reputable compressor packagers design suction pulsation bottles to be self-draining to the cylinder nozzle as standard. This is especially important on an acid gas compressor where you want to be able to drain out all liquids after shutting the unit down.

Relief valve discharge headers are required. The compressor blowdown valve should be connected to this same header.

The purchaser should specify the number, size and type of corrosion coupons and/or corrosion monitoring points that are required, to ensure uniformity with the balance of plant. The compressor packager should select the locations where corrosion is likely to be the highest, such as a low point where liquid might collect, or a region of high velocity.

Proper handling of the fluids from the packing and distance piece vents and drains is essential. Figure 12 shows a typical set up, which includes a purge and vacuum

pump. This push–pull approach is the best solution, even though each manufacturer has a slightly different recommendation. The purge gas pushes any potential leak towards a vent where it can be safely handled. The vacuum pump on the drain tank helps pull leaking gas into the vent system and is essential any time there is more than 5 psig (0.3 barg) back pressure on the vent system, such as when it is connected to a flare that has other sources attached to it. Using a liquid seal in the drain tank prevents excess packing leakage blowing back into the distance piece.

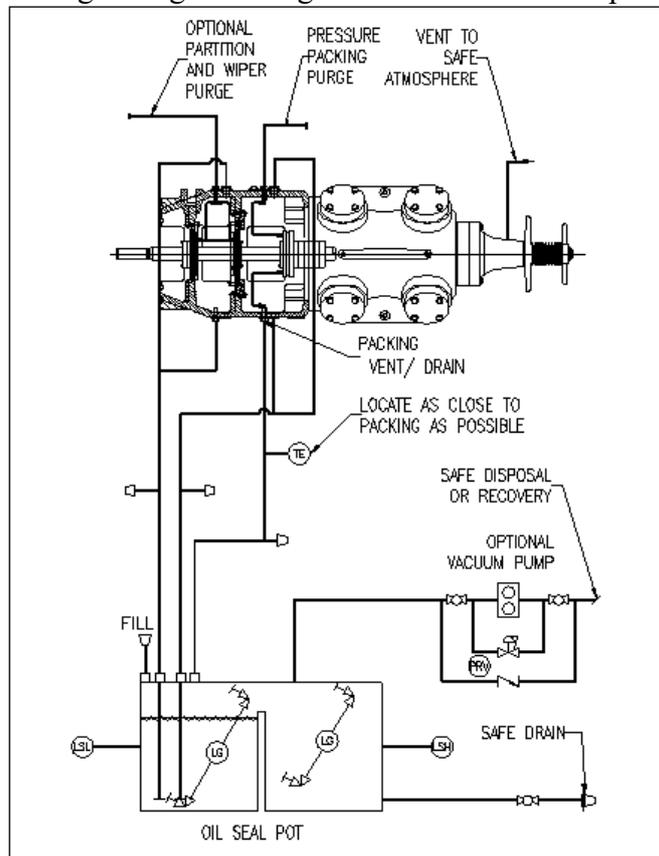


Figure 12. Diagram of Distance Piece Vent and Drain Handling System.

The compressor crankcase vent or breather should be piped away to a safe area to reduce acid gas fumes getting into the crankcase.

To provide maximum flexibility, drivers for acid gas compressors are typically variable speed. Some are gas engine drive, but the desire for reliability results in most being variable speed electric drive. To ensure the maximum operating speed range, it is often necessary to operate the compressor below its normal minimum speed. The minimum operating speed of a reciprocating compressor is set based on the crankshaft driven oil pump design. In order to operate below the minimum speed an external, electric motor driven, full capacity lube oil pump is added. Speed limitation is then only a matter of any torsional limitations. A detailed torsional analysis should be performed on all electric motor driven reciprocating compressors but it is even more critical with a variable speed application.

Compressor Controls

The controls around the acid gas compressor are similar to controls that might be found in other compressor applications, but there are some additional concerns that come with acid gas compression. The controls can broadly be broken into three different categories; start up and shut down control, capacity and pressure control, and temperature control.

Start Up and Shut Down Control

As discussed above, carbon steel is susceptible to corrosion when acid gas and liquid water are present on the steel surface. This corrosion may occur rapidly and lead to substantial wall loss in the affected area of the system so it is important to minimize the chances for corrosion to occur in carbon steel parts of the compressor system. This is commonly accomplished using automated valving around the compressor system. On shut down of the compressor system, the compressor is isolated by closing automated valves on the inlet and outlet of the compressor.

After isolation, the compressor should be blown down by a different automated valve that can route the venting acid gas to a safe location. The blown down acid gas will be extremely cold (potentially below -100 °F) at the start of the blow down operation and a safe location should be carefully vetted to be sure that there is no potential for the gas blowing down to freeze water unintentionally or vent in low-lying areas. After blow down is complete, the compressor should be purged with a dry gas, such as fuel gas or nitrogen, to further reduce the potential for a liquid water phase to form in an acid gas atmosphere.

Settle out pressure is also important in this application. The very high compression ratio across the entire compressor means that there is a large mass of compressed gas (or fluid in the case of the supercritical stage) that, if allowed to equalize across the entire compressor, can overpressure vessels and cause relief valves to lift on every shut down. The acid gas system designer needs to calculate the settle out pressure of the compressor and determine if it will be below the maximum allowed working pressure (MAWP) of all vessels in the entire compressor system. If the settle out pressure is above the MAWP of any of the vessels, the compressor should be blown down on a shut down before opening the recycle valves or start up bypass valves.

Capacity and Pressure Control

The amount of acid gas produced by the upstream acid gas removal unit will vary as the incoming gas flow rate changes, as the fraction of CO₂ and H₂S coming into the acid gas removal unit changes, and as the performance of the acid gas removal unit changes. The acid gas compressor system needs to be able to respond to all of these different scenarios by controlling the suction pressure to the compressor. Capacity control on reciprocating compressors can be done in a number of different ways; the compressor motor or engine can be slowed down to rotate the compressor more slowly, pockets can be opened on the compressor cylinders or entire cylinder head ends can be deactivated by unloaders that are actuated automatically or manually, or acid gas can be recycled around the compressor.

An engine will usually have a minimum speed of 70-80% of the design speed of the engine, while a variable frequency drive (VFD) will be able to operate the compressor

at a much slower speed, perhaps as low as 20-25%. It may be difficult for the compressor to operate at that low of a speed due to lubrication system limits of crankshaft driven oil pumps and there can also be natural frequencies at different speeds (critical speeds) that can cause very high vibrations in the compressor that need to be avoided. Pulsation studies also need to be completed across the entire speed range of the compressor. A common minimum limit on compressor speed is 50% of the rated speed of the compressor frame to be sure that the crankshaft driven oil pump can still operate correctly. Lower speeds may require the installation of an electric motor driven auxiliary oil pump.

Head end deactivation is accomplished by either opening a port on the compressor cylinder to return gas to the suction passage or suction pulsation bottle or by holding the compressor suction valves open during the compression stroke of the piston. Head end deactivation is most commonly done on the first stage cylinder(s) of the acid gas compressor and effectively reduces the cylinder capacity to 50%. Fixed volume head end pockets will open to increase the clearance volume of the head end of the compressor cylinder so that less gas is compressed per stroke of the compressor. On large compressor cylinders, more than one pocket can be installed and together the pockets can reduce the capacity of the head end of the compressor to less than 60% of design. Fixed volume pockets are normally actuated pneumatically. Variable volume clearance pockets (VVCs) are also installed on the head end of the cylinder and are turned manually by personnel to open or close the pockets as needed to adjust capacity. VVCs are only adjusted while the compressor is offline though, so the ability to make adjustments quickly is limited. All of these devices have packing that can leak to atmosphere, so there is some potential for an unwanted leak to atmosphere with these devices.

Recycle around the acid gas compressor is possible and done routinely, but it needs to be carefully engineered to avoid the formation of hydrates, liquid formation from condensed acid gas, or very cold and dense gas at the inlet of a compression stage. Acid gas from the discharge of a cooler expanding from a high pressure to a low pressure will result in cold temperatures (the Joule-Thompson Effect), which can lead to phase changes in the acid gas or the formation of hydrates. The Pressure Enthalpy (PH) diagram of the compression process in Figure 13 illustrates this phenomenon well when considering recycling gas from the discharge of the compressor to the inlet of the fourth stage of the compressor.

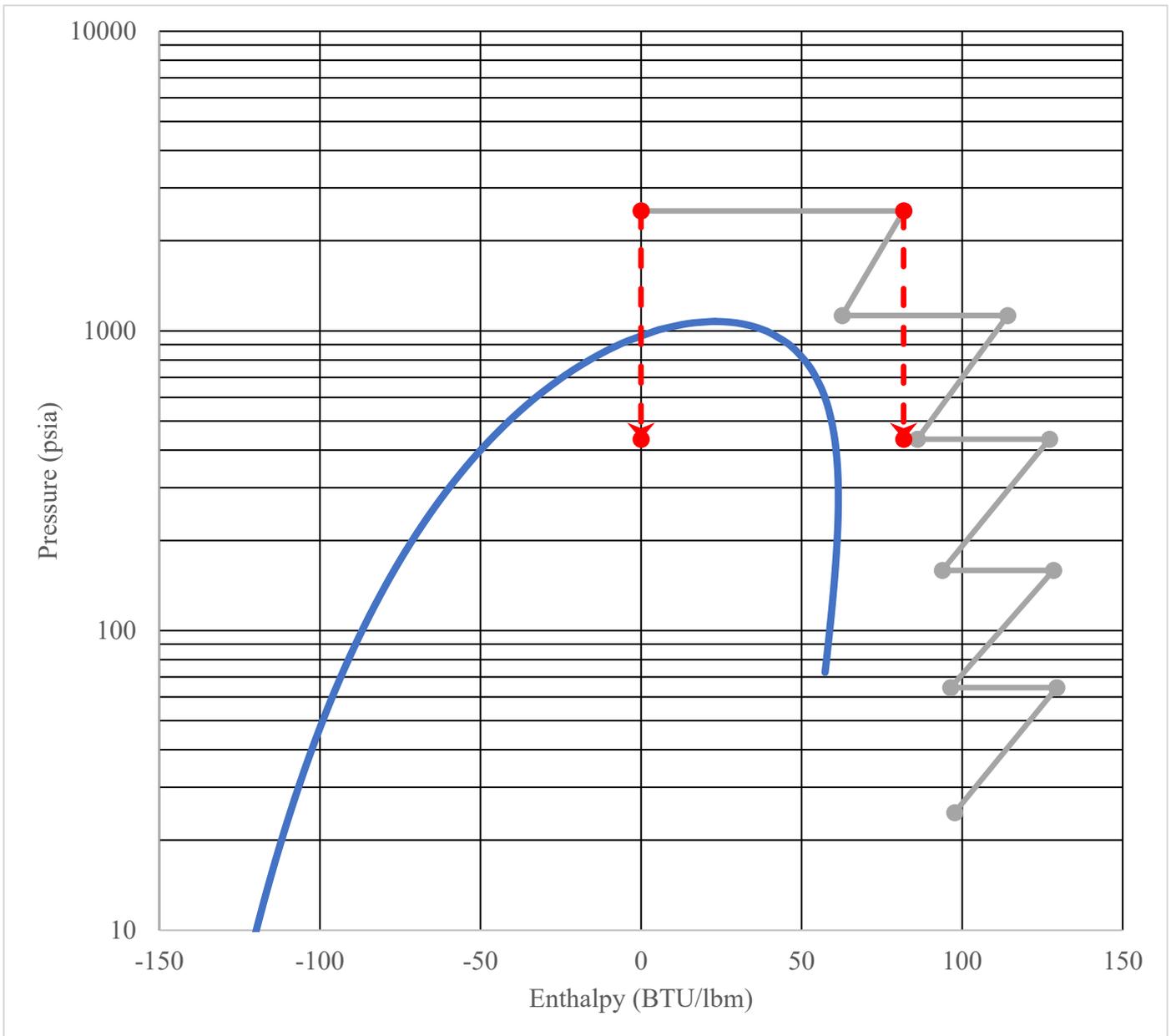


Figure 13. Pressure vs. Enthalpy (PH) Diagram of Recycle Around Acid Gas Compressor.

Recycling gas from the discharge of the Aftercooler down to the inlet of the fourth stage pressure results in a two-phase mixture of liquid and gas at 24 °F, which cannot flow through the compressor without risking damage to the machine. Recycling gas from the discharge of the fifth stage before the Aftercooler to the inlet of the fourth stage will result in a single phase gas stream at 105 °F, which is very near the design inlet temperature of the stage and is the appropriate source for recycle gas.

Recycle must be done across the entire compressor though, and recycling gas from the third stage discharge to the inlet of the compressor also needs to be checked to be sure that the recycled gas is at an appropriate temperature. Again, the PH diagram in Figure 14 shows this graphically.

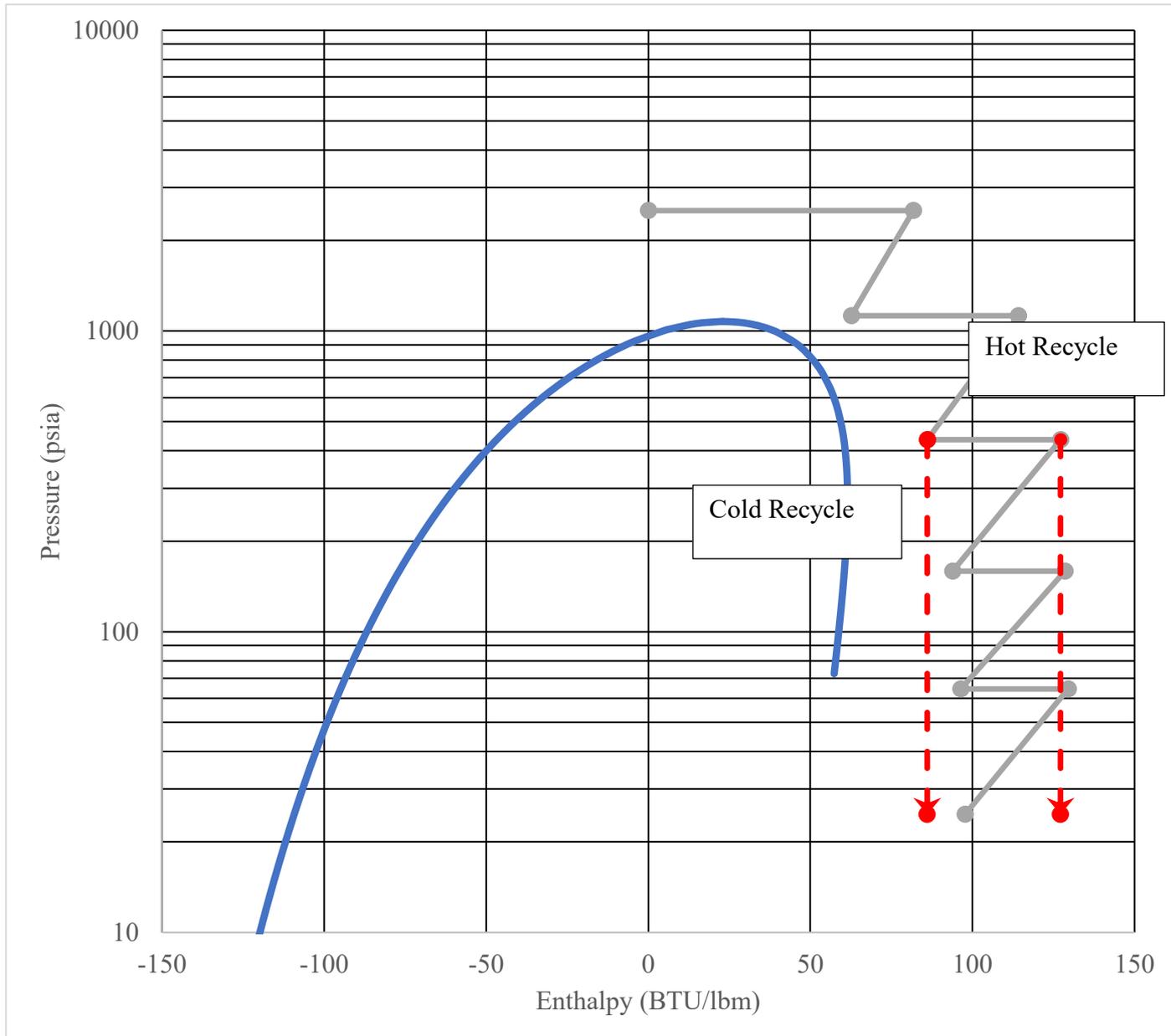


Figure 14. Pressure vs. Enthalpy (PH) Diagram of Recycle Around the Compressor.

Recycling from the fourth stage inlet of the compressor to the inlet of the compressor results in a gas flowing back to the compressor at 65 °F, which may or may not be acceptable for the compressor. Recycling gas from the discharge of the 3rd stage before the interstage cooler will result in a gas flowing back to the compressor at 259 °F, which is too hot for the compressor. If 65 °F is too cold for the compressor, some alternate methods may be utilized to achieve a more suitable recycle temperature.

1. Hot gas upstream of the compressor cooler may be blended with cold gas from downstream of the compressor cooler. This is usually accomplished with two control valves on either side of the compressor cooler blending gas together upstream of a final control valve. The temperature blending valves have a low differential pressure across them and the large pressure drop is taken across the final control valve.
2. Hot gas can be recycled through a control valve and then a cooler to get the gas closer to ambient temperature.

Either of the methods outlined above can work; the gas blending operation requires tight temperature control on the intercooler even in winter operation while the recycle cooling option requires extra capital investment. The system designer needs to weigh the benefits and drawbacks of each option.

Temperature Control

Reciprocating compressors in acid gas service are multiple stage compressors. Compression through each stage increases the temperature of the gas and it is necessary to cool the gas before it flows to the next stage to protect the soft parts of the compressor and to maximize the efficiency of the compression process. In acid gas compressors, it is possible to over-cool the gas in the interstage coolers, which can lead to the formation of hydrates or even partial liquefaction of the gas. Many acid gas compressors use air coolers as the interstage heat exchangers. The exchangers are normally mounted in the same air cooler bay and cooled by the same fans. Extensive controls are required in order to keep the acid gas warm enough, but not too warm, throughout the compression process. Temperature control is accomplished with variable speed fans, automated louvers over each gas cooler, and hot air recycle in colder climates. In addition to preventing hydrate formation and gas liquefaction, maintaining temperatures in the compressor system will provide for reliable recycle operation as noted above.

Operation and Maintenance Concerns

Generally, expected uptime for a reciprocating compressor is 98% or higher. The main culprit making this statistic not fully 100% is the driver of the equipment. Engines may be sensitive to their surrounding environment, such as encountering large temperature swings from day-to-night during seasonal changes, as well as other variables such as fuel gas, combustion/exhaust tuning, and others. Compressors used in AGI applications are mostly driven by electric motors. Motors tend to be sensitive to over-horsepower events due to off-design conditions. It is important to consider off design conditions during the initial stages of the project and to establish an expected operating envelope of suction/discharge pressures and temperatures for the compressor, so the motor can be sized properly. Best practice and industry standard is to apply a 10% margin over the greatest compressor power demand for the driver selection. For electric motor drivers, this 10% margin can be applied to the motor rated horsepower, or to the Service Factor. If applied to the Service Factor, a specific review is required with the motor and motor controller suppliers to ensure continuous operation within Service Factor can be allowed. This 10% margin is a selection criterion to account for the variables affecting power demand and power supply. This is not meant to limit the use of the available driver power.

Reciprocating compressors must undergo periodic maintenance just like any other piece of rotating machinery. The maintenance intervals will depend on if the compressor is intermittent duty or continuous duty, meaning if the compressor starts/stops frequently or if it runs without stopping for long periods of time. AGI applications are almost always continuous duty. Typical maintenance intervals for continuous duty are every 4,000 hours or 6 months. This is to change compressor frame lube oil. An engine will typically follow this same maintenance interval. At 8,000 hours piston rings, packing, and valves are suggested to be inspected and at 16,000 hours they are usually replaced. At 32,000 hours, inspection of the crosshead/conrod bushings and of the piston ring grooves is necessary. Lastly, the major maintenance interval to overhaul the compressor is 48,000 hours (24,000 hours for aluminum bearings/bushings depending on the compressor OEM). This is to replace main/connecting rod bearings, connecting rod/crosshead bushings, auxiliary end torsional damper (if applicable), and lubricator distributor blocks. There are many other important checks to perform at these maintenance intervals, such as frame oil sampling. The ones mentioned are just the highlights. Refer to OEM maintenance and repair manuals for frame specific guidelines.

Example Installation

For the example case followed throughout this paper the final installed AGI compressor system is capable of compressing 6 MMSCFD of acid gas from a suction pressure of 10 psig up to a discharge pressure of 2,500 psig. To accomplish this, the entire AGI compressor system will consist of:

- A six-cylinder, five stage reciprocating compressor.
 - The first stage will be two of the cylinders working in parallel and each subsequent stage will be a single cylinder.
 - Piston rod and valve materials will be upgraded metallurgy to reduce corrosion.
 - The compressor will have separate frame and cylinder oil systems and the cylinder oil will be compatible with the acid gas stream. It is likely that the cylinder oil will be a full synthetic oil.
 - The compressor will use long two-chamber distance pieces with purged seals to maintain separation between the frame the cylinders to minimize the potential for acid gas leakage into the non-pressurized parts of the compressor.
 - Yellow metals will be allowed in the frame.
 - The compressor will come with manual variable volume clearance pockets (VVCPs) on the stage 1 cylinders.
- An 8-pole electric motor driven by a VFD.
 - At full speed, the compressor will rotate at 891 RPM and be capable of compressing 7.77 MMSCFD of acid gas. This will be at a slightly higher piston speed (891 ft/min) than the specification of 850 ft/min, but for the initial design case, the compressor will rotate at a slower speed.
 - At a flow rate of 6 MMSCFD, the compressor will rotate at 689 RPM with a piston speed of 689 ft/min.

- At a minimum speed of 600 RPM with the stage 1 VVCPs open, the compressor will process 4.4 MMSCFD.
- An air-cooler bay with heat exchangers downstream of each stage of compression.
 - Fan motors powered by VFD.
 - Exchanger tubes and header boxes constructed of stainless steel or other alloy piping.
 - Automated louvers on each exchanger bundle.
 - Hot air recycle system.
- Recycle valve system with a single valve from the fifth stage discharge (hot side) to the fourth stage inlet and then a temperature blending system supplying hot gas from the third stage discharge and supplying cold gas from the 4th stage inlet to a final control valve that lets gas down to the first stage inlet of the compressor.
- Stainless steel or other alloy piping on all cold piping and vessels within the compressor system. Carbon steel piping and vessels on the hot side of the compressor system.

Fundamentals of Acid Gas Injection (AGI)

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SECTION 3: SUMMARY OF INDUSTRY EXPERIENCE WITH ACID GAS INJECTION

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INTRODUCTION

Historically, the sour gas conditioning and processing industry has utilized a number of process options to:

- Receive the acid gas (principally H₂S and CO₂) removed by the acid gas removal systems (e.g. amine treating unit);
- Convert the H₂S to molten sulfur (most often via the modified-Claus process); and
- Recover the sulfur for sales (principally for use in fertilizer manufacture);
- Before the so-called tail gas stream is fully oxidized and emitted to the atmosphere.

This process configuration can typically provide from 95% to about 99.8% recovery of the sulfur contained in the acid gas, depending on composition, quantity, environmental limitations and selected process options. These provide good environmental protection from emission of sulfur compounds to the atmosphere, but allow the CO₂ contained in the acid gas (and additional quantities of CO₂ generated from fuel gas requirements of the included process units) to vent to the atmosphere. Reduction of such emissions has received global attention in recent years.

Such process configurations:

- Are very sensitive to fluctuations in acid gas composition and flow variations
- Are capital intensive;
- Include about 60 pieces of primary process equipment that require close operations surveillance, control, and routine maintenance;
- Require periodic catalysts replacement (added cost);
- Generally provide about 98.5% reliability (on-stream time); and
- Require handling and marketing of the molten sulfur product.

In addition, in recent years the sales value of molten sulfur has experienced significant deterioration and many small-capacity facilities were forced to pay some considerable cost to have their sulfur hauled away.

The concept of acid gas injection was considered as a viable opportunity to avoid such issues, improve economics, and provide nearly “zero” emissions of sulfur compounds **AND** CO₂ to the atmosphere.

HISTORICAL OVERVIEW OF THE AGI INDUSTRY

DEVELOPMENT OF INFORMATION

The included table “Tabulation of AGI Industry Experience” is a compilation of most all of the reported AGI projects throughout the world. Special acknowledgement for this compilation is given to the following for sharing their own compilations of public and private information to support development of this Fundamentals Session for the LRGCC.

- Alberta Sulphur Research Ltd., principally Paul Davis, maintains an extensive living record of known AGI projects that summarizes most of the known acid gas injection projects from available public records and publications. Their compilation is readily available to ASRL membership companies.
- Ed Wichert is a renowned instructor in the AGI Industry and also maintains some records of AGI projects in support of his available course: “Acid Gas Compression and Injection”. Mr. Wichert conducts such courses periodically to the public, and for private audiences as requested.
- Duke Energy Field Services shared public information regarding their numerous projects.
- Gas Liquids Engineering Ltd. shared public information regarding their numerous projects. Gas Liquids Engineering also conduct a periodic course in various global locations.
- Washington Group International Inc. conducted further research of available public information from projects permitting documents, published literature, and conducted personal discussions with various AGI operators.

The detailed compilation of information was considered and reduced to provide the overview information in the table. Different sources of information often provided conflicting information for a given project. These differences likely reflect design basis or permit values versus actual experience, or changes in operation over time. Where such conflicts arose and could not be reconciled, ranges of the reported values are shown in the table below. In most cases, individual plants or companies have not been contacted to verify accuracy of the information. Limited data was available for 2003/2004 projects.

The reader should understand that the information provided in this table should only be considered as indicative and cannot be considered precise regarding current facilities installations or operation. The purpose of the effort was to assist those trying to gain an understanding of how acid gas injection has been applied to date, and to help identify installations and companies that have requirements and conditions very similar to those being considered for their specific project.

There are also numerous instances where the operating company name has either changed or the facility has been sold to another party. The information in the table reflects that history where possible but there has been no effort made to validate the accuracy of each project and company name.

HISTORICAL SUMMARY

The practice of Acid Gas Injection, or AGI, began in 1986 when a unit was installed in the U.S. to inject less than 0.5 MMSCFD of an acid gas containing about 85% H₂S. By the year 2000 there were about 60 AGI installations and the referenced table indicates now almost 90 operating AGI facilities worldwide. The projects are distributed worldwide as follows.

- | | | |
|--------------------------------|----------------------------|--------------------------------|
| • Canada | 60% of the projects | 50% of the total volume |
| • U.S.A. | 30% of the projects | 20% of the total volume |
| • Outside North America | 10% of the projects | 30% of the total volume |

CAPACITY: The capacity of most AGI installations ranges from < 1 Million SCFD to 5 Million SCFD, however many of the more recent projects (particularly the international projects) are in the range of 10-90 Million SCFD. The largest existing operating facility, reported to have started up in Canada in 2002, was designed to inject about 900 LT/D of sulfur equivalent as an acid gas mixture containing 80% H₂S. The most recent U.S. project will be injecting about 1250 LT/D sulfur equivalent.

The estimated total volume capacity of AGI projects is summarized below.

- | | |
|-------------------------|---|
| • Canada | 290 Million SCFD for 52 Projects |
| • U.S.A. | 105 Million SCFD for 26 Projects |
| • Outside North America | 180 Million SCFD for 6 Projects |
| • TOTAL GLOBAL | 575 Million SCFD for 84 Projects |

COMPOSITION: Acid gas composition has varied from 100% CO₂ to about 95% H₂S, with the remainder being principally CO₂. Typical impurities are small amounts of methane, other hydrocarbons and nitrogen. About one third of the facilities inject an acid gas containing more than 50% H₂S, and another one third inject acid gas in the range of 25-50% H₂S. The remaining one third handle 100% CO₂ or acid gases with less than 25% H₂S.

Note that this information does not include Enhanced Oil Recovery (EOR) projects that reinject CO₂ to improve oil recovery,

COMPRESSION: Most of the compressor drivers are electric motors. Variable Frequency Drive (VFD) has been used where strict capacity control is required and changing acid gas volumes and injection pressures are anticipated. A turndown of 5-to-1 can potentially be achieved with VFD.

A compression ratio of at least 50, often up to more than 100, is required for most AGI applications. Therefore, compression is most typically done in 4-stage and 5-stage compressor designs. Interstage conditions are designed to provide adequate interstage dehydration while avoiding hydrate formation, to avoid interstage liquid acid gas phase formation, and to avoid discharge temperatures higher than about 300°F maximum. To avoid formation of liquefied acid gas and hydrates, the compression curve and pipeline and wellstring profiles should be kept 10°F or more from the phase diagram and the hydrate phase boundary.

The system should be able to handle any acid gas rate between maximum and minimum, using a combination of number of compressor trains, speed control, variable volume pockets, and gas recycle.

DEHYDRATION: Most of the early AGI projects included dehydration of the acid gas, typically located at the third or fourth stage discharge of the compressor to take advantage of the acid gas water-holding characteristics. TEG was used almost exclusively for the dehydration, though a few facilities used refrigeration or solid desiccant.

More recently, engineers have gained a better understanding of the characteristics of acid gas mixtures regarding physical properties, phase boundary conditions, water holding capacity and hydrate formation conditions. In addition, predictive modeling tools and available data have improved regarding acid gas mixtures. Therefore, most recent projects are installed without a distinct dehydration system. They are designed to rely on the characteristics of acid gas to achieve self-dehydration in the compression sequence. Interstage dehydration is achieved by setting one of the interstage pressures (typically 3rd or 4th stage discharge) at a value as close as possible to the pressure at which acid gas can hold the minimum amount of water.

Most all facilities include the capability to inject methanol to handle startup, shutdown and upset operations when free water or unusually cold temperatures are experienced. Simultaneous injection of corrosion inhibitor is also utilized as the methanol/water mixture can be corrosive. Some early facilities required a small continuous methanol injection due to their unexpected operating conditions. Proper design can now generally mitigate the need for any continuous methanol injection.

PIPELINE: The size of the installed pipelines reflects the fact that most of the current acid gas disposal projects handle small acid gas flows. Most of the pipelines have a nominal 2-inch diameter, though a few range up to about 8-inch diameter. The line lengths in many instances are short, generally one mile or less. There are very few facilities with pipeline lengths up to 3 miles. Operators have typically chosen to drill the disposal well near the plant, or are using a prior existing well located close to the plant. Most lines are fabricated of carbon steel and are insulated to prevent acid gas sub-cooling, and possible water condensation and corrosion or hydrate formation. Many of the short pipelines are made of stainless steel and are left uninsulated. With the latter approach in short pipelines the capital cost penalty is relatively small. Most pipelines are above ground but some are buried. Emergency shutdown and depressuring valves are installed on the pipeline.

WELLS: The deepest Canadian injection well is reported as 12,400 feet deep, compared with the 25,000 feet deep wells to be used for the most recent U.S. injection project. Most wells are about 1,000 to 5,000 feet deep.

The wellhead is usually equipped with a pressure control valve that regulates pipeline backpressure. Regulations have required that all disposal wells be equipped with downhole packers, to protect the casing strings. Sub-surface safety valves have been installed in many tubing strings as a safety measure in the unlikely case of backflow of acid gas from the formation. Many tubing strings are internally coated and equipped with premium threads, to avoid potential tubing leaks. Overall, many precautions have been applied in well completions to ensure extended and continuous safe operations.

INJECTION PRESSURE: Generally, the compressed acid gas is injected in a pressure-temperature range where the acid gas is actually in a dense phase or even liquid phase state. This results in an appreciable static head pressure being available due to the height of this "fluid column" in the wellbore. This usually means that there is a substantial pressure rise down the wellstring, more than off-setting the frictional flow losses. Thus, the required compressor discharge pressure is usually much lower than the bottom-hole injection pressure. Most facilities have required a compressor discharge pressure in the range of 800 to 1300 psig to meet their specific reservoir injection pressure requirements.

About 20 of the facilities have a compressor discharge pressure exceeding 1500 psig. The maximum reported discharge pressure is about 3000 psig for a high-H₂S acid gas, and up to 15,000 psig for a low-H₂S, hydrocarbon gas re-injection stream (not yet reflected in the table).

One interesting observation is that most facilities report that the injection wellhead pressures have decreased over time on a per unit volume of acid gas injected. One theory attributes this effect to the continuous acidization of the wellbore perforations by the wet acid gas mixtures.

Just a few percent, say >3-5 volume percent of methane or other hydrocarbons and non-condensables, can have a significant impact on the acid gas physical properties, including density. Since the injection pressure is related to the density of the fluid, the presence of the methane increases the required injection pressure. Startup of AGI facilities may require a much higher compressor discharge pressure if hydrocarbons are not fully purged from the pipeline and wellstring. There are a few reports of hydrocarbons preferentially moving from the reservoir into the wellstring during a shutdown or low flow conditions, resulting in a higher required initial injection pressure.

SYSTEM RELIABILITY: Due to the significantly reduced number of equipment items and simplicity of the process, AGI is inherently more reliable than sulfur recovery processes. High levels of reliability (>99.2% on-line time) have been achieved in AGI facilities by developing proactive preventative maintenance programs, utilizing high reliability electrically-driven motors, stocking critical spare parts on-site, and having 24 hour access to maintenance specialists. This on-line time can perhaps be further improved using multiple and perhaps spare compressors, but with substantial added cost.

REPORTED COSTS OF AGI

Very limited data is available for AGI facilities but the following information is a summary of the reported figures.

- Capital Cost \$ 1.5 to \$3 / Thousand SCFD Injection Capacity
- Operating Cost \$ 200 to \$600 / Year per Thousand SCFD Injection Capacity

The reader is advised again that these values should only be taken as indicative. They will vary considerably depending on capacity, injection pressure requirements, how those capacity and pressure requirements fit given fixed compressor configurations, how many compressors are installed, cost of power, and geographic location of the facility.

REPORTED BENEFITS OF ACID GAS INJECTION

The principle benefits actually realized and reported by the projects that have implemented acid gas injection include the following.

- Near “Zero” continuous sulfur emissions
- CO₂ sequestration
- Elimination of sulfur transportation costs
- Reduced capital and operating costs for grass roots facilities
- Reduced capital and operating costs for sulfur recovery upgrade and revamp facilities
- Reduced plant complexity – about 50 fewer pieces of primary process equipment
- Reduced operations and maintenance support
- Smaller plot space requirements
- Higher on-line reliability (>99.2%)
- Greater ability to handle a wide range of H₂S and CO₂ composition ratios

RECOGNIZED DRAWBACKS AND LIMITATIONS OF ACID GAS INJECTION

The principle drawbacks or limitations actually experienced and reported by the projects that have implemented acid gas injection include the following.

- A nearby geologically isolated disposal or storage reservoir and a well(s) with sufficient injectivity are critical.
- Versus natural gas, extra safeguards and procedures are required to process and transport large volumes of high-pressure acid gas.
- A higher than normal amount of staff training and plant technical support is needed for initial projects to ensure understanding of the peculiar nature and dangers of handling acid gas mixtures at elevated pressure.
- Acid gas mixtures have physical properties and behavior much different than typical hydrocarbon natural gas streams. Engineers, operators and the public require considerable education and training to understand these differences and the risk/benefits of AGI projects.
- Energy liberated by the combustion of H₂S in the Sulfur Recovery Unit (SRU) is not realized.

SUMMARY OF DESIGN, COMMISSIONING AND OPERATING LESSONS LEARNED

The following represents a selective sampling and summation of “lessons learned” from reports in the literature regarding AGI facilities. Please reference the included comprehensive “AGI Reference List”. Several of the references include good detailed information about their design, commissioning, and continued operation. They are recommended reading for all anticipating involvement in an AGI project.

DESIGN

- Realize that acid gas mixtures have unusual physical properties and characteristics that make the acid gas injection process much different than typical natural gas processing. Involve operating personnel early in the project to improve their knowledge of the process and to gain their valuable insights.
- The downhole reservoir conditions dictate the AGI pressure requirements, which strongly influence selection of the AGI compression and pipeline system design configuration and operating conditions. Involve the reservoir staff early in the project to determine the downhole conditions and wellstring characteristics.
- Although important in natural gas processing systems design, it is very crucial for AGI projects that valid process simulation modeling tools be used to develop several aspects of the AGI process design.
 - Develop a phase envelope for the full range of anticipated acid gas compositions, including those expected during startup, shutdown, and during definable upsets.
 - Super-impose the actual compressor performance curve onto the phase diagram, plus the pipeline, wellhead and wellstring conditions profile down into the reservoir.
 - Develop water content charts for the design acid gas mixtures.
 - Develop hydrate formation curves for the design acid gas mixtures and for the water contents anticipated at each stage of the compression.
 - Develop a “Technical Reference Manual” that includes these “pictures of the process”, plus adequate descriptive information, to assist operations staff during startup, shutdown and continuous operations. Several facilities report the value of such a reference to allow process troubleshooting and optimization by engineers and operators.
- Continued technical support through the facility operating life may be needed due to the unusual characteristics of acid gas mixtures.
- Verify the process simulation against vendor-predicted compressor conditions.
- To ensure that no liquid acid gas or hydrates form, the acid-gas compressor temperatures are operated to remain above the hydrate and acid gas dew point curves. A minimum margin of about 10°F is recommended.
- Very detailed commissioning and start-up planning is required to ensure proper handling of the high-pressure acid gas.
- Turndown is a crucial characteristic for AGI systems and is especially important during startup. It is recommended to install speed control, possibly variable volume pockets, and a discharge-to-suction recycle valve (located upstream of the discharge cooler) to maximize the turndown capability of the compressor. When initiating a cold startup of the plant, bring in enough acid gas to start the injection compressor as soon as

possible and, if you have the option, start by introducing the raw gas streams with the highest CO₂/H₂S ratio first to minimize SO₂ flaring.

- Be careful to control the operating temperature and pressure of the compressor recycle source so that liquid acid gas is not formed due to the J-T effect on pressure letdown and recycle back to the compressor suction. The recycle is usually taken from upstream of the discharge cooler.
- Provide remote monitoring and ESD control of the acid gas injection well. This allows for remote shutdown capability as well as early diagnosis of hydrate and sulphur deposition problems.
- Install double block valves or break-out spools on all fuel gas connections to prevent leakage of non-condensables into the acid gas system and backflow of acid gas into the fuel gas system.
- Install independent temperature control capability for each stage of cooling. Tight temperature control of the interstage cooling is important to operate above the hydrate temperatures and acid gas dewpoint for each stage.
- Ensure you have a conservative design compressor discharge pressure to include pressure drop at the formation due to injectivity issues, the potential presence of non-condensables, and to allow for some uncertainty in density, pressure and temperature predictions in the injection tubing versus actual operation.
- Use stainless trim on all level control systems valves and floats (or use other methods such as radar to infer level). Some sites have experienced severe corrosion of carbon steel level floats and valves even though the primary vessel is carbon steel and does not experience such severe corrosion.
- Review compressor settle out pressure carefully. Because of the high discharge pressures and low suction pressures, you may have to go to a higher flange rating and/or vessel design pressure to prevent overpressure on a compressor shutdown.

COMMISSIONING AND STARTUP

- After completion of all hydrotesting, perform a low-pressure air test to identify sources of major leaks. This should be followed by a nitrogen or fuel gas leak test at maximum operating pressures to identify any remaining leak sources.
- Function-test the compressor and controls via an extended fuel-gas run test. Have all the bugs worked out of the system prior to introducing acid gas.
- Remove all hydrotesting water from the disposal pipeline for dry-based injection schemes. Any remaining water can result in the formation of hydrates or potential startup corrosion problems.
- Purge the AGI pipeline with N₂, CO₂ or fuel gas to remove oxygen from the system as it can result in sulphur deposition. If nitrogen or fuel gas is used the pipeline should be depressured to atmospheric conditions just prior to operation with acid gas to remove as much of the non-condensable purge gas as possible.

- Have a methanol injection connection downstream of the compressor and have an ample supply of methanol on-site for startup. If any significant amount of non-condensables are remaining in liquid based injection systems the disposal well may have to be primed with a liquid column of methanol to gain pressure and initiate injection. For Dehydration based systems, continuous methanol injection should be in operation until the water dewpoint of the acid gas downstream of the dehydrator can be confirmed.
- Confirm the operation of the acid gas flare and fuel gas blending ratio control for systems with low heating values. High-CO₂ acid gas can act as a fire extinguisher and therefore sufficient fuel must be added to prevent flare flame failure.
- Maintain communication with your local regulatory representatives. If your facility start-up does not go well, you may exceed permitted emissions. Keeping the regulator informed will give them the comfort that you are working diligently to resolve the problems.

OPERATION

- Manual and control valves can become inoperable or develop packing leaks. Typical operating conditions of AGI systems result in a “dry” acid gas in terms of water and hydrocarbons content that tends to dry out the valve packing. Initiate a preventative maintenance program on all valves in the AGI system.
- Maximize routine maintenance during planned outages. A proactive approach to oil changes, inspections and valve changes are critical when operating with no spare units.
- Minimize the time operations needs to spend inside enclosures, such as an acid gas compressor building, by fully automating the system and utilize a two-man response team for any H₂S alarms.
- Some operators have had problems handling the condensed water from the compressor interstage knockout drums. The lubricating oil forms an emulsion with the water as it is let down in pressure into the drain system. The emulsion is very difficult to break. One operator reports use of “calcium-free” oil as an improvement for such issues.
- Operators have reported incidents where the third stage compressor discharge cooler outlet temperature dropped into the two-phase region and began condensing acid gas along with the normal condensed water. This caused hydrate and emissions problems when these liquids were dumped to the water disposal system, and potentially could carry liquids into the next stage suction and damage the compressor.
- One operator reports high injection pressure during amine system foaming episodes when higher than normal hydrocarbons show up in the acid gas.
- Several operators indicate that the injection pressure on startup was higher than initially expected due to the amount of remaining non-condensables in the pipeline and wellstring. Several plant blowbacks to the flare system were necessary. One of the valuable lessons learned was that more frequent, short blowdowns during startup were more effective than fewer, long blowdowns.

- Oxygen present at even ppm levels can result in the formation of solid elemental sulphur that deposits in the pipeline and wellstring and restricts flow.
- Viton O-Rings were used in some cases to seal the valve cover plates on the compressors, and other Viton softgoods were used in some compressors and in manual and control valves. Bladders on water pumps also experienced failure. Some operators selected AFLAS as the most effective elastomer for handling acid gas streams.
- Some Dehydration Units reported accumulation of tar like deposits on the trays in both the absorber trays and in the regeneration section. These deposits became so bad that complete glycol change-outs and chemical washes of the system were required regularly to keep the system running. They found that lube oil from the acid gas compressor was carrying into the acid gas stream. A glycol-based synthetic lubricant has proven to remedy this problem. This lubricant would at least mix with the dehydration glycol and prevent the deposits from forming. Oil coalescers have been added to remove the lubricating oil from the acid gas prior to dehydration and prevent such dilution or degradation of the glycol.
- Liquid acid gas and hydrates can form in the interstage coolers, the gas recycle line, and in the interstage knockout drums water drain line. Ensure you have separate control of the louvers for each stage and control of the fan(s). VFD fans can be helpful. Some operators have included such features; yet still experience some of these problems on all the compression stages during turndown, especially in cold climate locations.
- Multiple sites had plugging issues on their interstage knockout drums water drain lines. Some installed tees with clean-out/wash-out connections to backflush the lines. Reported causes of the plugging were: freezing due to inadequate heat tracing, corrosion products (from CS trim), and amine salts that were found even in the AGI compressor interstage knockout drums. Some sites experienced apparent acid gas liquid formation in liquid dump lines leading to auto-refrigeration and plugging due to hydrates. Maintaining control of interstage temperature is important.
- If more than one compressor is installed and one compressor shuts down, you can slowly vent the gas to the suction of the compressor that is still running to help prevent acid gas flaring.

SUMMARY

Acid Gas Injection has proven to be a successful, long term, safe and economical process option for handling with acid gas. Residents, landowners, and operators have become comfortable with the technology and AGI can provide significant benefits with high reliability.

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2005 LAURANCE REID GAS CONDITIONING CONFERENCE - ACID GAS INJECTION FUNDAMENTALS - TABULATION OF INDUSTRY EXPERIENCE

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FIELD/PLANT	OPERATOR	START/UP (Approx.)	ACID GAS			COMPRESSION				DEHYDRATION			PIPELINE				WELLHEAD			WELLS			COMMENTS/OPERATING EXPERIENCE	
			COMPOSITION MOLE %		FLOW 1000's	Number	No. of Stages	Inlet P	Outlet P	HP	TYPE	Outlet H2O Content	Material	Insulated	Heat Traced	Length FEET	Pressure PSIG	Temp deg F	Depth FEET	Btm P PSIG	Temp deg F	Reliability		
			H ₂ S	CO ₂	SCFD			PSIG	PSIG	LB / MM SCF														
INTO DEPLETED HYDROCARBON RESERVOIR																								
1 Acheson	ChevronTexaco	June 1989	8-15	85-98	522	1	4	8.7	377	200	TEG	H2O Dewpoint -2 deg C	CS	No		7,200	334	40	4,000	384	120	99.2%		
2 Dunegan	Devon	Nov 1996	41-60	40-59	186	1		6.5	1,740	150	Mole Sieve		CS	No		14,100	1,015		4,500					
3 Gordondale East (into Water Depleted Zone)	ANG DEFS	Apr 1996	65	35	634-2,237	3	4		930-1,160	250 VFD	Refrig		CS	No		700	580-1,160		6400					
4 Paddle River	Keyspan Canadian Occidental	Apr 1996	5-10	90-95	1,044-1,491	1			551-1,088	300	TEG		CS	No		1,800	551-1,088		5,100					
5 Puskwaskua	Devon	Nov 1996	42-65	35-58	112-447	1	4	7	1,400-1,784	125	NO		SS	No		900	1,247-1,784	150	8,800	4,280	180			
6 Zama (2 wells)	Phillips Novagas/Gulf Apache	Apr 1995	20-38	62-80	4,473-11,928	2			1,118-1,740	600	TEG		CS	No		13,100	1,160-1,740		4,900					
7 Jedney I (B.C.)	DEGT	Dec 1996	50	43-49	4,250	2			926-1,600	1400	TEG		CS	Yes		3,900	870-1,126	150	4,900	2205	150			
8 Jedney II (B.C.)	PC/WCGS	July 1997	44	56	4,250	2			926-1,600	1400	TEG		CS	Yes		3,900	870-1,126	150	4,900	2205	150			
9 Normandville	Devon	Jan 1997	67-75	25-33	100	1			100	50	NO		SS	No		1,800	650		6,100	2,755	140			
10 Zama (Plant 2)	NGC / Apache	Feb 1998	30	70	4,300-7,828		4		1,130-1,740	960	TEG		CS				435-1,125						Dehy unit shutdown after 6 months. Compression suction lines are insulated and traced.	
11 Zama (Plant 3) (2 wells)	NGC / Apache	1999	65	35	4,300-7,828		4			600	TEG		CS				435-1,125						Dehy unit shutdown after 6 months. Compression suction lines are insulated and traced.	
12 Bellshill Lake (Sour Water Injection)	PC Viking	May 1998			v. small																			
13 Rainbow Lake	Husky Oil	1985	1.5-2		29,820	1			109	595	8595													
14 Innisfail	Samson Canada Ltd.																							
15 Eaglesham (West Culp)	Devon	2000	48-80	17-42	311-630	1	4		812-976	250 VFD	NO		SS	No		1,700	972-1,740		6,500	2,932	145			
16 Long Coulee	Conoco	2002	5	95	529-682																			
17 Kwoon (B.C.)	DEFS	2002	20		29,820																			
18 Brazeau River	Keyspan	2002	85	15	12,674					1,740														
19 Retlaw	Taylor	2004	5	95	3,168					1,247														
INTO WATER SATURATED ZONE																								
20 Clear Hills (Boundary Lake)	ANG / CNRL	June 1995	70	30	783					1,450														
21 Consort	PCP	Dec 1995	0.4	8.4						1,102														
22 Fourth Creek (Mulligan)	DEFS Canrock	May 1996	53	43	112-783	1	4		760-2,060	150 VFD	NO		SS	Yes	NO	500	760-2,060		5,500					
23 Galahad	Renaissance Husky	Feb 1994	20	80	1,118	1			1,305	350	TEG		SS	No		650	1,305		3,900					
24 West Pembina	ChevronTexaco Enerpro	Nov 1994	56-77	23-39	596-1,621	1	4	7.3	1,100-1,740	200	NO		SS, A312, Grade 170	Yes		1,600	1,015	100	9,400	3,915	210	99.4%	1. Methanol injection was discontinued in 1999 when hydrate formation was found not to be an issue. 2. Acid gas is liquified in the 4th stage discharge cooler.	
25 Provost (Cadogan)	Husky	Sept 1994	9-25	75-91	895	1			1,450	300			SS	No		250	1,450		4,700					
26 Watelet	ATCO Midstr	Jan 1997	11-25	70-80	895	1				350			SS	No		250	725-1,450		6,600					
27 Wayne-Rosedale	EnCana	Dec 1995	20	80	1,044	1				300	TEG		CS	No		300	943-1,450		6,600					
28 Beatty Lake (2 wells)	Paramount	Spring 1997	25	75	2,796-4,100																			
29 Caribou (B.C.)	NGC (Novagas) Coastal Field Services	Apr 1997	50-60	40-50	2,572-2,907	2			2.2	1,193-1,900	310		CS	No		1,000	1,123-1,900		12,100					
30 Ring (B.C.)	Canadian Hunter	Jan 1998	80	20	839																			
31 Redwater (Sour Water Disposal)	Redwater Disposal	Feb 1998	32	68	v. small																			
32 Leduc-Woodbend	Probe Enbridge	1997	56	43	2,162																			
33 W. Stoddart (B.C.)	TCM Previous Nova	Dec 1998	84	15	14,575-15,208	3				2225			CS	No		5,300	1,450		5,300					
34 Dizzy (Steen R.)	Gulf Penn West	Mar 1999	65	35	1,305-2,423	1				300			CS	No		3,000	914-1,015		3,200					
35 Golden Spike	Atco ATCO Midstr	1999	50	50	1,260-1,491					500														
36 Kelsey (Rosaland)	Thunder	1999	25	75	410																			
37 Cl. Hills	Blue Range	Nov 1995	33	67	559	1				300	Refrigeration		CS	Yes		1,000	754		5,500					
38 Bistcho L	Paramount	Apr 1997	25	75	3,765	1				1200	TEG		CS	No		1,600	1,897		3,000					
39 Rg Border	Canadian Hunter	Feb 1998	35	65	522	1				250			CS	No		650	914		3,100					
40 W Stoddart (B.C.)	CNRL	1998			14,910																			
41 Pouce Coupe	DEFS	1999	47-70	30-52	560-1,566	1	4		1,305	500 VFD			SS	No		400	1,160		7,000					
42 Pembina	Northrock	2000	35	65	596																			
43 Marlowe (Dizzy)	Bears paw	2000	64	36	980																			
44 Pembina	Burlington	2001	55	45	1,044																			
45 Bigoray	ChevronTexaco	July 2000	9-20	80-88	947-1,267		4	7.3	653-1,623		Refrigeration		CS			13,100	1,623	40	800	2,958	140	98.90%	Gas/liquid phase injection scheme, acid gas enters well and condenses into a liquid about 250m below grade.	
46 Rycroft	Devon	2001	64-70	26-30	830-913		4		1,200	250 VFD	NO		CS				522		5,800	2,368	145			
47 Wembley	ConocoPhillips	2002	85	15	3,951		4			250										5,800	2,368	145		
48 Zama	Apache	2003	65	35	7,828						NO													
MIXED AT SURFACE WITH WATER																								
49 Hansman Lake (David)	EnCana PCP	Feb 1995	25-34	68-75	27,808	1	4	6	1,110	150			CS + Liner	No		1,600	435-755		2,700			99.3%	Shut Down	
50 Mirage (Into Water Saturated Zone)	Summit	Dec 1995	68	24-28	4,734-5,740	1			1.3	1,784	75		CS	No		3,300	1827		4,600					Shut Down
51	EnCana	June 1995	20-25	75-79	48,645-62,511	1				800			CS	No		650	870-1,160		4,400					
52 Mitsue (Slave Lake)	ChevronTexaco EnerPro	1999	15	38-85	48-205	NONE		25			NO		CS	No		2,600	10		3,000			99.3%	Acid Gas is blended with produced water and injected.	
Approximate Total Canada			APPROXIMATELY 290 MILLION SCFD MAXIMUM PERMITTED OR REPORTED																					

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			COMPOSITION MOLE %		FLOW 1000's	Number	No. of Stages	Inlet P	Outlet P	HP	TYPE	Outlet H2O Content	Material	Insulated	Heat Traced	Length FEET	Pressure PSIG	Temp deg F	Depth FEET		Btm P PSIG	Temp deg F	Reliability
			H ₂ S	CO ₂	SCFD			PSIG	PSIG	---	LB / MM SCF												
TEXAS																							
53	Ozona	UPRC/Anadarko	Sept 1996		60			0.7	1,740												Shut Down		
54	Garza(Cedar Hill Plant)	Davis	Jan 1992																				
55	Sandhills	Dynegy	2000																				
56	North Fayette	DEFS	Feb 1999	10	90	2,250	2	5	8	2,000	400	TEG + REFRIG	CS	No	No	300	1,780	70	11,400	6,100	Compressor feeds Chiller to condense Acid Gas, then FMC M1212 Triplex, 30HP PUMP W/2500 PSIG discharge for warm restart, Dehydration normally not run		
57	Dumas	GPMDEFS	1999	27	72	450	1	4			250 VFD	NO	CS	NO	No	5,600	615		5,600	Shut Down			
58	Sneed	DEFS	2001	60	39	1,300	2	4	10	960	250 & 220 VFD	NO	CS	YES	No	600	700		4,350				
59	Tyler	James L. Smith & Associates				9,500																	
Note: 11 other wells in Texas referred to as "disposal into productive formation" with injectate permitted to contain H ₂ S.																							
WYOMING																							
60	Highland (prod. zone)	K&N Energy	Jan 1986	85	N ₂ C ₁₂ CO ₂	369																	
61	Muskat (depl't res.)	Wold Oil	1991	82	18	75																	
62	Big Sand Draw (depl't res.)	Wold Oil	Early 1993	78	20 (+C ₁)	52																	
63	Garland (w/H ₂ O @ surface)	Marathon Oil	1994	40	60	317																	
64	Salt Creek (non-prod zone)	Amoco	1995	10	90	104																	
65	Beaver Creek (depl't res.)	Amoco	Mar 1995	86	14	783																	
66	Brady (depl't res.)	UPRC	Mar 1998	15	85	11,593	2	5		2,800													
67	Manderson (depl't res.)	KCS Mountain Res	Jan 1996	95	5	746																	
68	Golden Eagle	KCS Mountain Res	1998																				
69	Grass Creek	Marathon Oil	1998																				
70	Labarge	ExxonMobil	2005	50	50	68,587															Not operating at time of writing.		
OTHER USA																							
71	Eddy Co., New Mexico	Marathon	1997	50	50																		
72	Traverse City, Michigan	Shell Northeast	1997	40	60																		
73	Oklahoma	Marathon	1998	25	5																		
74	Grasslands, N. Dakota	Bear Paw	2002	65	35	2,423																	
75	Indian Basin, New Mexico	Marathon	1997		50																		
76	Louisiana	Long Petroleum		6	6	1,500																	
77	Libson (Moab, Utah)	Encana Tom Brown Inc.	May 2003	32-38	62-68	1,500	2	5	10	1,500	250	NO	API X-42 CS			13,100	1,100-1,350	175	8,900	2,500	155		
78	Artesia, New Mexico	DEFS	2003	34-45	53-65	1,500	1	6	8.0	2200	600 VFD	NO	CS	Yes	No	400	2,000	120	11,500	6,000	105		
Approximate Total U.S.A.C70																							
APPROXIMATELY 105 MILLION SCFD MAXIMUM PERMITTED OR REPORTED																							
OUTSIDE NORTH AMERICA																							
79	Sleipner, North Sea (Norwa)	Statoil	Oct 1996	0	100	52,000											100		2,600-3,300				
80	Kharg Island, Iran		2005	33 - 64	29 - 57	85,800	3	4	10	2,600	15,420						2,400	105	300	6,048	250		
81	K12-B Platform	Gas de France	2002	0	95	48,098	1	4	0	508			duplex, well chromium 13	No	No	65	363	140	16,400	609	280	ORC Project (Offshore Re-Injection of CO ₂ on the K12-B platform).	
82	Tengiz	ChevronTexaco																				Limited information available.	
83	Blackstone	Husky Oil Operations																				Limited information available.	
84	El Porton, Argentina	Tecna, S.A.																				Limited information available.	
Approximate Total Outside North America																							
APPROXIMATELY 180 MILLION SCFD MAXIMUM PERMITTED OR REPORTED																							
Approximate Total Global AGI																							
APPROXIMATELY 575 MILLION SCFD MAXIMUM PERMITTED OR REPORTED																							
OTHER NOT DOCUMENTED																							
Kazakhstan	Chevron																					NOTE: THE INFORMATION INCLUDED IN THIS TABLE HAS BEEN ASSIMILATED FROM PUBLIC SOURCES AND BY AGREEMENT FROM CERTAIN OTHER PRIVATE SOURCES ACKNOWLEDGED IN THE TEXT. LIMITED DATA WAS AVAILABLE FOR 2003/2004 PROJECTS.	
Blackstone	Husky Oil Operations																					IN MOST CASES, INDIVIDUAL PLANTS OR COMPANIES HAVE NOT BEEN CONTACTED TO VERIFY ACCURACY OF THE INFORMATION.	
El Porton, Argentina	Tecna S.A.																					THERE WERE NUMEROUS INSTANCES WHERE THE OPERATING COMPANY NAME HAS EITHER CHANGED OR THE FACILITY HAS BEEN SOLD TO ANOTHER PARTY.	
																						THE INFORMATION BELOW REFLECTS THAT HISTORY WHERE POSSIBLE BUT THERE HAS BEEN NO EFFORT MADE TO VALIDATE THE ACCURACY OF EACH PROJECT AND COMPANY INFORMATION.	
																						DIFFERENT SOURCES OF INFORMATION OFTEN PROVIDED CONFLICTING INFORMATION FOR A GIVEN PROJECT, WHICH COULD REFLECT DESIGN BASIS OR PERMIT VALUES VERSUS ACTUAL EXPERIENCE AND CHANGES IN OPERATION OVER TIME.	
																						WHERE SUCH CONFLICTS AROSE AND COULD NOT BE RECONCILED, RANGES OF THE REPORTED VALUES ARE SHOWN IN THE TABLE BELOW.	
																						THE READER SHOULD UNDERSTAND THAT THIS INFORMATION SHOULD ONLY BE CONSIDERED AS INDICATIVE.	
																						THE PURPOSE IS TO ASSIST ONE IN UNDERSTANDING HOW ACID GAS INJECTION HAS BEEN APPLIED TO DATE, AND TO HELP IDENTIFY INSTALLATIONS AND COMPANIES THAT HAVE REQUIREMENTS AND CONDITIONS VERY SIMILAR TO THOSE BEING CONSIDERED.	