Designing an Optimized Injection Strategy for Acid Gas Disposal without Dehydration

By

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Abstract

The economics of recovering sulfur from sour natural gas have become unfavorable for small fields. Hydrocarbon producing companies require a cost effective yet environmentally sound alternative to deal with acid gas. Compressed acid gas re-injection into producing, depleted or non-producing formations has emerged as a viable alternative to traditional sulfur recovery. Most injection schemes include dehydration facilities to remove the saturated water from the gas, preventing corrosion and hydrate formation. An alternative, less costly approach is to keep the water in the vapor phase throughout the injection circuit, eliminating the need to dehydrate.

To design an optimized injection strategy, determination of thermodynamic and physical properties such as water content, dewpoint, bubble point, hydrate conditions and density of the acid gas is necessary. Experiments were conducted to determine properties of an acid gas containing a nominal 10% H$_2$S with remaining 90% CO$_2$ and a minor amount of methane. Results indicate that the acid gas can be cooled between compression stages to 40°C (104°F) without entering the two phase region. For an injection pressure of 17700 kPa (2567 psia), dehydration is not required to cool the compressed gas to 8°C (46°F) without hydrate formation or corrosion problems. At 9000 kPa (1305 psia) the gas can be safely cooled to -2°C (28°F).

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Introduction

The unfavorable economics of constructing small Claus sulfur recovery plants, due to their inherent operating difficulties when the H₂S feed concentration is low and the decreased demand and oversupply of elemental sulfur, necessitate an alternative technology. Air emission standards and regulations are increasingly stringent, compounding the need for an environmentally-friendly, cost-effective method to deal with acid gas. Acid gas compression and re-injection into depleted reservoirs or disposal zones, similar to produced water disposal, is a viable alternative to traditional sulfur recovery processes with the added advantages of reducing greenhouse gas emissions and providing pressure support for producing reservoirs.¹,²,³

Acid gas mixtures, separated from hydrocarbons in a sweetening plant, are compressed through several stages, dehydrated and pumped into a reservoir. Phase behavior, water content and physical properties of the acid gas are required for facility design. Phase behavior data is used to avoid the two-phase region during multi-stage compression to ensure equipment is not damaged by the appearance of a liquid phase. The injection pressure required is dependent on several factors including the formation pressure and the density of the acid gas mixture.¹,⁴ The hydrostatic head of the acid gas column in the wellbore aids injection, particularly if the fluid is injected above its critical point as a dense phase. Information regarding hydrate formation conditions of the undersaturated acid gas is required to ensure that the system never cools enough to form hydrates, avoiding pipeline plugging. Water content data determines the need for and aids in the design of dehydration facilities.

Although experimental data is available for pure hydrogen sulfide and pure carbon dioxide, little work has been done determining the water content, density, phase behavior and hydrate formation conditions of acid gas mixtures.⁵,⁶,⁷,⁸,⁹ This paper reports the results of a study in which water content, dew point, bubble point and hydrate formation conditions were measured for an acid gas mixture containing 10% H₂S/90% CO₂ and a minor amount of methane. The mixture was saturated with water at 2800 kPa and 24°C (400 psia and 75°F).

Background

Hydrogen sulphide and carbon dioxide are removed from sour gas by absorption with a regenerative solvent in an amine plant. The acid gas mixture of H₂S, CO₂ and a small amount of light hydrocarbons leaves the sweetening unit saturated with water at the amine still conditions of low pressure and high temperature, represented by point A in Figure 1. The gas mixture is then
compressed from points A to F in 3 or 4 stages. After each stage, the gas mixture is cooled, without entering the two-phase region. Condensed water is removed after each stage. After the last stage, the mixture travels down a pipeline into the disposal well. Ideally, at the final compressor discharge pressure the mixture will be supercritical. Further cooling in the pipeline will increase the density without a phase change, increasing the hydrostatic head of fluid in the well and reducing the required injection pressure. The operator must ensure that the mixture does not cool below its water saturation temperature, especially in the hydrate region, to avoid corrosion and hydrate plugging of the pipeline and wellbore.

Corrosion and hydrates may occur when the gas is saturated with water. Due to the safety hazard associated with acid gas equipment failure, most injection schemes currently include dehydration facilities to ensure the acid gas is undersaturated throughout the system. Unfortunately, dehydration facilities and stainless steel comprise a major portion of the capital cost of re-injection facilities. Methanol injection is an option to combat corrosion and hydrate formation, but can significantly increase operating expenses.

Although there is little experimental data on acid gas mixtures, the solubility of water in pure hydrogen sulfide and pure carbon dioxide lead to some interesting hypotheses. The ability of the pure compounds to hold water in the vapor phase decreases as the pressure increases up to about 3000 kPa (400 psi) for H₂S and 6000 kPa (900 psi) for CO₂. At higher pressures the water holding capacity of the gases increases, corresponding to a higher water absorption capacity in the liquid phase or dense phase compared to the vapor phase. In both cases, increasing the temperature allows more water to be absorbed in the gas phase. Small amounts of methane substantially reduce the water absorption ability of both components.

If it is assumed that solubility of water in the gas mixtures mimics the trend of the individual components, then a minimum water holding capacity exists at some pressure. Figure 2 demonstrates how this information could eliminate the need for dehydration facilities. Points A through G in Figures 1 and 2 correspond to the same stages in a re-injection facility. Over each compression stage, the pressure and temperature increase and after each compression stage the gas is cooled. Initially the water holding capability of the gas decreases from stage to stage, until the minimum water holding capacity is reached. If the condensed water is removed at this point, the gas will be undersaturated with water throughout the rest of compression. Stainless steel will not be required in the compressors or coolers after point E. If the temperature of the compressed gas does not drop to the new water saturation temperature, point G, in the pipeline or wellbore, dehydration can be eliminated and stainless steel materials and methanol injection will not be necessary.
Figure 1 – Acid Gas Compression in Relation to Phase Behavior and Hydrate Formation

Figure 2 – Water Content and Solubility in Acid Gas During Compression vs Pressure and Temperature
If it is concluded that dehydration cannot be completely eliminated due to a particular set of conditions, for example in an extremely cold climate, the experimental data will still be beneficial. The operator will know the inlet water content of point A and the conditions of the lowest water solubility of the system. The glycol contactor tower, regenerator and circulation system can then be designed appropriately.

Currently, estimates of the density, water content and phase behavior of acid gas mixtures are being predicted with equation of state models, as experimental data is unavailable. The equations can produce considerable error and result in over or underdesigned facilities. Experimental data results in proper decisions on the equipment and materials required for each particular set of conditions, which can lead to considerable cost-savings.

Apparatus and Experimental Procedure

The apparatus consists of a temperature controlled air bath, a high-pressure cell with a sight glass, a positive displacement pump, a gas volume meter, a cooled water trap, a mass balance and a Hewlett Packard 5890 gas chromatograph (GC). The sight cell has an internal volume of approximately 80 cm$^3$ (5 in$^3$) and a maximum working pressure of 70 MPa at 150°C (10000 psi at 300°F). The 2.5 cm (1 in) thick sight glass located on the front and back of the cell allows visual observation of the cell contents throughout experimentation. As shown in Figure 3, the high-pressure sight cell is mounted in the center of the oven as are the cylinders containing gas mixtures and distilled water. The oven can be heated up to 150°C (300°F) and the temperature is measured and controlled to within ±1°C (2°F).

The sight cell volume and pressure are controlled by the addition and withdrawal of mercury through a port at the bottom of the sight cell. Sample fluids are pumped in and out of a port at the top of the cell. The pump measures volume displacement with a precision of ± 0.02 cm$^3$ (0.001 in$^3$). A dead-weight calibrated digital pressure gauge is connected to the pump outlet. The oven is connected to a motor via a steel arm. The motor rotates the arm, rocking the oven and its contents in a 180° arc. The mercury in the sight cell agitates the fluids and enhances mixing when the oven and cell are rocked.
The apparatus is contained in a sour gas laboratory. The lab is continuously flushed with fresh air pumped in from the ceiling and drawn out of vents located in the bottom four corners of the room to an incinerator stack. A permanent H$_2$S monitor is located close to the floor, below the apparatus. If the monitor detects 10 ppm H$_2$S, an alarm sounds outside the sour gas lab and the incinerator fires up. At 20 ppm the main lights in the lab shut off and emergency lights flash. Personnel working in the lab with supplied air breathing apparatus (SABA) may not hear the alarm and the flashing lights ensure their evacuation. The lab is equipped with a video camera for continuous remote monitoring of personnel performing dangerous work. An "H$_2$S Panic
A gas mixture is synthesized from pure components in the laboratory using partial pressures. Concentrations are verified using the GC. The system is purged and gas is transferred to the sight cell. The gas in the cell is saturated with water at the desired temperature and pressure and allowed to equilibrate while rocking. At equilibrium, usually reached within a few hours, a stable free water phase should be visible in the cell, ensuring the gas is fully saturated.

Water content analysis is performed by flashing a sample of gas through a valve to a cooled water trap while maintaining constant cell temperature and pressure. The trapped, condensed water is weighed and the dried gas volume is measured. The average water content is obtained over several samples. This crude method of water content analysis has not proved reliable due to the very small quantities of condensed water being measured. The water content data obtained for this report can be regarded as accurate only within an order of magnitude. A control with pure CO₂ was within 20% of accepted values and the average difference between samples was ± 20%. An online, repeatable and precise method of water content analysis using gas chromatography has been designed and successfully tested for future experiments.

Experiments

The objective was to establish the phase behavior, water content and hydrate conditions of an acid gas mixture saturated at the compression inlet conditions of 2.8 MPa (400 psi) and 24°C (75°F). A mixture of 10% H₂S and 90% CO₂ was prepared. A small amount of and CH₄ was added and the exact composition verified with the GC. The mixture was saturated with water at 2.8 MPa (400 psi) and 24°C (75°F). After several hours of rocking, the average water content was determined.

Several isotherms were obtained to establish the phase envelope. The cell temperature was set and allowed several hours to equilibrate. The cell mercury volume was increased incrementally, resulting in 15-30 psi pressure steps. Transient and stabilized phase behavior was observed and recorded. The change in mercury volume was recorded as a function of pressure. At pressures close to the dew and bubble points, the volume/pressure increment was reduced. By taking a series of data points immediately above and below the appearance and disappearance of the two-phase region, the dew and bubble points were established.
Isobaric cooling experiments were performed to establish the hydrate formation conditions for this acid gas/water mixture. The oven temperature was raised to 50°C (122°F) and the gas was pressurized to between 9000 kPa (1305 psia) and 17700 kPa (2567 psia) and allowed to stabilize. Since the gas was saturated with water at 2800 kPa (400 psia) and 24°C (75°F) and the water content was not changed as the temperature and pressure were raised, the gas was undersaturated at the conditions of high temperature and pressure. The temperature was then reduced in 1.6°C (3°F) steps every 30 to 45 minutes until a hydrate was visually observed in the cell.

The hydrate formation temperature measured in this manner differs from the traditional hydrate temperature obtained by cooling gas in contact with a liquid water phase. When liquid water is present, hydrate formation is predicted to occur at elevated temperatures in the order of 20°C (68°F) at 9000 kPa (1305 psia). When the gas is not in contact with a water phase and is undersaturated, hydrates cannot form until the temperature drops sufficiently that the gas can no longer hold all the water in solution and "free" water is available for the formation of hydrates. Hydrates form preferentially to a liquid water phase, since the gas is already below its saturated hydrate temperature at these conditions.

Results, Observations and Discussion

As recorded in Table 1, dew points were observed at 7°C/4100 kPa, 9°C/4342 kPa, 15°C/5045 kPa, 26°C/6355 kPa, 34°C/7479 kPa and 37°C/7955 kPa. Bubble points were observed at 7°C/4528 kPa, 9°C/4755 kPa, 16°C/5510 kPa, 27°C/6900 kPa and 34°C/7844 kPa. Volume of mercury in the cell is plotted in Figure 4 vs. pressure for each isotherm. As seen in the figure, two distinct slope changes occurred for each isotherm. The slope changes correspond to the dew and bubble points, verifying the visual observations.
Above 37.5°C (99.5°F), a stable two-phase region was not observed. Some droplets, and elongated bubbles appeared during a volume/pressure change and while the system was stabilizing, but upon reaching equilibrium, the system was single phase at all pressures.
At 37.5°C (99.5°F) and 8253 kPa (1197 psia) the critical point was observed. At all other temperatures the contents of the cell were clear and colorless in the vapor, liquid and two-phase regions. In the critical region, a small change in pressure (3-5 psi) resulted in the entire cell contents becoming a murky, grey cloud and then stabilizing out into a variety of shades of yellow. Above 8303 kPa (1205 psia) the contents were single phase, clear and colorless. At about 8274 kPa (1200 psia), the see-through single phase took on a slightly yellow tint. At the critical point of 8253 kPa (1197 psia), two phases appeared with an indistinct thick yellow interface, a darker yellow color at the bottom of the cell and a lighter yellow color on top. At 8212 kPa (1191 psia) the bottom half of the cell was a distinct dark orange liquid and the top half a colorless vapor. At 8198 kPa (1189 psia) the liquid phase faded to yellow and below 7957 kPa (1154 psia) the cell contents were again a colorless single phase.

In Figure 5, the calculated equation of state phase envelope is plotted along with the experimental data. The widths of the two phase envelopes are similar, but the calculated envelope falls below and to the left of the experimental data. The calculated critical point occurs at 34.9°C and 7633 kPa (94.8°F, 1107 psia), 2.6°C and 620 kPa below the experimentally determined critical point of 37.5°C and 8253 kPa (99.5°F, 1197 psia). The deviations between actual and calculated phase behavior emphasize the importance of obtaining an experimental data set for acid gas mixtures. The equation of state was regressed to fit the phase behaviour data obtained experimentally. The regressed curves and critical point match the measured data within the experimental error. The modified equation of state allows some extrapolation to different conditions, but experimental verification will be necessary until more data becomes available and a general regression is completed.
The saturated water content of the gas mixture at 2860 kPa and 24°C (415 psia and 75°F) over four samples was measured to be 0.6 mole percent or 270 lb water/MMSCF. This value is over three times the value that analysis of accepted pure component data and equation of state calculations predict. The difference is attributed to experimental error and reflects on inaccuracies inherent in the gravimetric water content measurement.

Due to the apparent errors, the apparatus has since been modified by the addition of an online gas chromatograph to accurately measure the water content. The new method has been calibrated and tested with CO₂. The average standard deviation between runs is 3% of the water content measured. Data obtained with the new procedure matches published CO₂ data with an average standard deviation of 5% of the water content measurement.

Figure 6 summarizes the phase behavior and hydrate formation data obtained for this acid gas mixture. The two-phase region can be avoided during compression by cooling the gas to a minimum of 37.5°C between compression stages. The fluid is in the supercritical, dense phase above 8253 kPa and above 37.5°C.
The hydrate formation temperature is below the traditional hydrate temperature since the gas is not in contact with a liquid water phase. With undersaturated gas, hydrate formation is expected to coincide with the water saturation temperature. In this study, hydrates were observed at temperatures above the expected water saturation temperature of the gas. At 9000 kPa (1305 psia) and 17700 kPa (2567 psia) predictions based on pure component water saturation data indicate the gas will be saturated at approximately -9°C (15°F) and -18°C (0°F), while hydrates were observed at -2°C (28°F) and 8°C (46°F). The difference can be attributed either to experimental error or the inaccuracies inherent in predicting mixture saturation temperatures from pure component data. In either case, since the observed hydrates occurred at higher temperatures than expected, a conservative design would not require dehydration of the gas unless the temperature in the pipeline or wellbore dropped below the observed hydrate formation temperature.

Conclusions & Future Plans

Acid gas re-injection may be the optimum solution for producing small sour gas fields. As the issue of greenhouse gases heats up, re-injection will become viable for even moderate to large operations. The operating company must avoid the two-phase region during compression.
Water condensation and hydrate formation in the post-compression equipment must be prevented to ensure safe, cost-effective operation. Experimental data on the water content, density, hydrate and phase behavior of acid gas mixtures is therefore necessary. In the case of the studied acid gas mixture of 9.9% H₂S, 89.5% CO₂ and 0.6% CH₄ dehydration is not required unless the temperature drops below 8°C at 17700 kPa. The two phase region will be avoided during compression by maintaining the gas temperature above 37.5°C between stages.

A comprehensive joint interest project is underway to obtain data for several different acid gas compositions over a range of operating temperatures and pressures. Several improvements to the apparatus used in this study have been made, as shown in Figure 7. An online, repeatable and precise method of water content analysis using gas chromatography has been designed and tested. Temperature control and measurement has been improved and a density meter installed and tested. Currently, mixture data is being generated and should be completed in six months. Until this or other experimental data becomes available, operating companies will be forced to rely on equation of state predictions and over-design accordingly.
Figure 7 – New Experimental Apparatus for Acid Gas Study
References


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