Limitations and Challenges Associated with the Disposal of Mercaptan-Rich Acid Gas Streams by Injection – A Case Study

Felise Man, Gas Liquids Engineering Ltd., Calgary, AB, Canada
John J. Carroll, Gas Liquids Engineering, Ltd., Calgary, AB, Canada

1.0 Introduction

As oil and gas reserves become depleted, producers are increasingly driven to process difficult or unconventional petrochemical fuel sources to sell to the market in order to meet rising demand. One such source is the production of sour gas wells that contain high levels of mercaptan (thiol) species.

In sour gas processing applications, a waste acid gas stream (ie. a stream containing high concentrations of hydrogen sulphide and carbon dioxide) is produced as an effluent stream in the gas sweetening unit. Generally speaking, when these volumes are relatively low (less than 5 MMSCFD or less than 20 t/d sulphur equivalent), a suitable method of waste handling of the stream is by injection to a wellbore formation. Acid gas injection is a mature technology with over 50 applications in Western Canada and another 20 around the world.

In the application where mercaptan-rich sour gas wells are produced, the resultant effluent stream from a gas sweetening process will be one that contains high levels of H_2S, CO_2, mercaptans and hydrocarbons. While investigating the ability to dispose this stream in a similar manner to that of a typical acid gas injection scheme, a number of challenges have been identified. These challenges stem from three main sources. First, little experimental data is available with regards to phase equilibrium, water content, hydrate formation conditions, and transport properties of both pure mercaptan species and mercaptan mixtures. Second, current simulation programs used for process design can employ poor assumptions or contradictory data in generating the models. And third, even when these programs are used to generate results around the injection scheme, several additional issues are revealed which requires attention. These issues are investigated in a hypothetical case study, comparing the injection of a mercaptan-rich acid gas stream to a conventional acid gas stream.

2.0 Properties of Mercaptans

Mercaptans are sulfur-containing organic compounds with the general R-SH formula. They are relatively common in natural gas and petroleum systems as naturally occurring species in low concentrations. Mercaptans are also routinely added to gas products as an odourant for leak detection. As these species are generally encountered only in small quantities, much of the experimental research has been conducted in concentrations of the hundreds of parts per million ranges. In order the predict the behaviour and processing capabilities of streams containing mercaptans, studies including those that investigate the pure component properties, phase equilibrium with other natural gas components (hydrocarbons and non-hydrocarbons), water properties (solubility and water content), and hydrate formation are of particular importance.

2.1 Pure Component Properties

A cursory review of the literature available on pure mercaptan components yields some data on boiling points, critical temperature and pressures, acentric factors and molar mass. Sources include studies by Poling et al. (2001), Tsonopoulos and Amborse (2001), Linstrom (2005), or estimation using equation 1. Of importance to note is that reported critical constant values were measured at or before the turn of the 20th century, and have not been verified by modern methods.

$$\omega = \frac{3T_{boilR}}{7(-T_{boilR})} log(P_C) - 1$$

(Eqn. 1)

2.2 Phase Equilibrium

Experimental data for vapour liquid equilibrium results are necessary in order to develop accurate and reliable process designs. In the case of mercaptan systems, little data exists for binary systems composed of two mercaptans, mercaptans and carbon dioxide, mercaptans and hydrogen sulphide, or mercaptan and hydrocarbons.

Of significant importance is the research conducted is that of Lee et al. (1978). This study is the only one found in the literature survey conducted that explores VLE data for H_2S and light mercaptan binary systems, at relatively high H_2S concentrations. Another interesting study was that of Denyer et al. (1949) where azeotropes in mercaptan + hydrocarbon mixtures were studied. No data on systems containing two mercaptans, nor mercaptan and CO_2 mixtures were found.

2.3 Water Content and Solubility

There are only a few data points available for the equilibrium between light mercaptans and water. A thorough review of the literature revealed only the six studies investigating experimental measurements for phase equilibria involving water and mercaptans. From the point of view of this study, the most important findings would be those of Gillespie and Wilson (1984) findings, where water content data for methyl and ethyl mercaptan only were reported. No data are available for the water content of n-propyl and n-butyl mercaptan and none for mixtures of acid gas with mercaptans nor for hydrocarbons with mercaptans.

Figure 1 shows the water content of methyl mercaptan at 311K as determined by Gillespie and Wilson (1984). The curves were fit through the data points determined in the study and do not represent a rigorous thermodynamic model. For comparison, also shown on this plot is the water content for H_2S. These data points shown are from Gillespie and Wilson (1982), however the curves are calculations from *AQUAlibrium*. *AQUAlibrium* is a thermodynamic model and thus there is some error between the experimental data and the calculations from the model.

2.4 Hydrates

A review of the literature found that there is some discussion of the formation of gas hydrates from methyl mercaptan, but very few specific details (such as a temperature-pressure locus). Having said that, Stackelberg and Müller (1954) report that the hydrate of methyl mercaptan dissociates at the relatively high temperatures of 273K and 34 kPa and 283K at
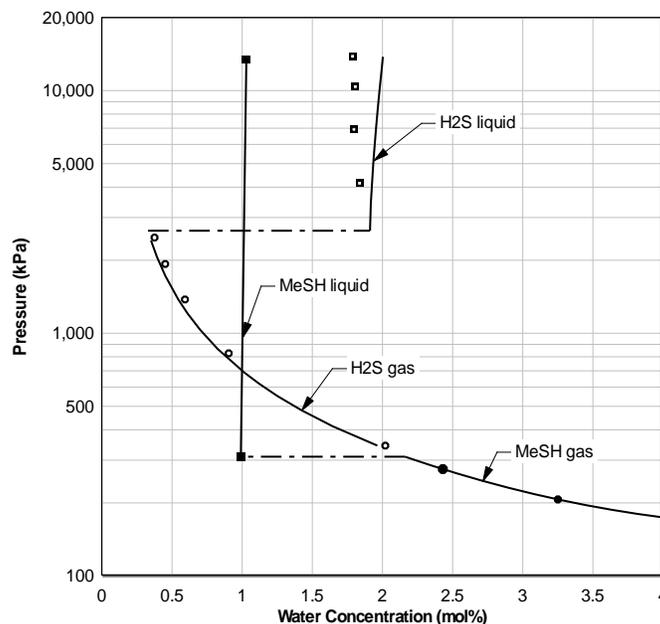
Fig. 1 Water Content of Hydrogen Sulphide (open points) and Methyl
Mercaptan [MeSH] (solid points) at 311K

atmospheric pressure (101 kPa). In comparison, the hydrate of H_2S dissociates at 273K, 98.6 kPa and at 283K, 275 kPa (Carroll and Mather, 1991).

There is no specific mention of the hydrates of other mercaptans in the literature, but based upon their size and chemical similarity to methyl mercaptan, ethyl, n-propyl, and i-propyl mercaptans are surely all hydrate formers. No experimental data were found to verify this.

3.0 Limitations of Process Simulation Tools and Process Design

Almost all of the simulation work presented in this paper was completed using *VMGSim* with the Advanced Peng-Robinson (APR) property set, as recommended by *Virtual Materials Group* (*VMG*). Some phase equilibria were calculated using *AQUAlibrium*, but these were for systems that did not contain any mercaptans. The injection pressure for the acid gas case was calculated using *GLEWPro*. Since *GLEWPro* uses the *AQUAlibrium* calculation engine it also could not be used for systems that contain mercaptans.

An interesting paper by Twu et al. (2004) demonstrates some of the difficulties in modeling the vapor-liquid equilibrium in systems containing mercaptans and light hydrocarbons. Although their model is not used in this work, the reader should review the paper in order to understand some of the complexities involved in the systems investigated by the study.

3.1 *Vapour-Liquid Equilibria and Hydrate Formation*

As described earlier, the lack of experimental data available around VLE of binary component mercaptan systems greatly impacts the accuracy of simulation tools used. In situations where data do not exist, simulation models may rely on assuming ideal behaviour of the component. As azeotropy is known to occur in many mercaptan-hydrocarbon systems, this is

clearly a poor assumption and may lead to erroneous process models that do not reflect plant behaviour.

The lack of even basic data makes it impossible to build models to predict both the hydrate formation in the pure mercaptan systems and in multicomponent mixtures that contain mercaptans. In fact, many programs either do not include mercaptans in their database or treat them like non-formers. *VMGSim* treats mercaptans as non-formers. Thus, the predictions of hydrate formation in mixtures containing mercaptans are approximate at best. In cases where the mercaptan concentration is low, its effect may be assumed to be negligible. In cases where the concentrations are sufficiently high, such as the one described in the case study that follows, ignoring the effect of mercaptans may result in highly flawed simulation results.

3.2 Water Content and Dehydration Processes

Dehydration in acid gas injection design is critical to ensure corrosion protection of the injection pipeline. In situations where the design model is questionable, a thorough review of the methods available to mitigate against potential design or equipment failures is required. As witnessed in Table 1, the values used by *VMGSim* are sufficiently variable compared to the interpolated value from data determined by Gillespie and Wilson (1984).

Furthermore, when Figure 1 is reviewed it can be noted that there is a clear difference between the water holding capacity of methyl mercaptan to that of H_2S. H_2S systems hold more water in its liquid phase than in its gas, while the opposite is true for mercaptan systems. Conventional H_2S-rich injection schemes generally take advantage of this ability to dehydrate the acid gas prior to injection through compression and cooling alone. Given that the mercaptan systems do not follow the same behaviour, along with the lack of experimental data and poor model predictions, the process decision is made to add an additional dehydration operation beyond the typical compression and cooling schemes normally encountered. The three options available include triethylene glycol (TEG) absorption, refrigeration, and molecular sieves. These options are investigated in the following case study.

Table 1. Water Content of Methyl and Ethyl Mercaptan at 311K

	Water Content (mol%)	
Methyl Mercaptan	Gillespie and Wilson (1984)	From *VMGSim*
689 kPa	0.99	21.1
6890 kPa	1.01	21.4
10 340 kPa	1.02	21.5
13 780 kPa	1.03	21.6
Ethyl Mercaptan	Gillespie and Wilson (1984)	From *VMGSim*
689 kPa	0.360	23.8
6890 kPa	0.365	23.8
10 340 kPa	0.368	24.0
13 780 kPa	0.371	24.1

4.0   Case Study

　　With these modelling inaccuracies already described in mind, a case study has been prepared to provide an idea of the mercaptan rich stream's potential behaviour when processed for acid gas injection. While the information may have severe errors built-in from using a simulation program, the exercise does serve to reveal further issues that may arise while preparing the waste stream for disposal, including difficulties during compression and dehydration.

　　The input data are based on a current injection project in northwestern Alberta. The process conditions and compositions of the two streams used in this study are given in Table 2. The acid gas stream is hypothetical but is typical for an acid gas mixture. The mercaptan-rich stream is similar to the first but contains mercaptans and a higher concentration of hydrocarbons. The high hydrocarbon content was included as it is anticipated that the sweetening of a mercaptan-rich stream would be completed using a mixed solvent or a physical solvent, both of which are notorious for absorbing more hydrocarbons than the more common aqueous alkanolamine solvents.

Table 2. Process Conditions and Compositions of Two Cases

	Acid Gas	Plus Mercaptan
Flowrate (Sm^3/d)	14.16×10^3	14.16×10^3
Pressure (kPa)	152	152
Temperature (K)	322	322
Composition (mol%)		
Hydrogen Sulfide	62.55	52.92
Carbon Dioxide	34.48	26.18
Methane	2.39	3.80
Ethane	0.47	1.81
Propane	0.11	0.40
Methyl Mercaptan	–	8.03
Ethyl Mercaptan	–	4.14
n-Propyl Mercaptan	–	1.93
n-Butyl Mercaptan	–	0.79

4.1   Injection Pressures

　　The injection pressure for the acid gas stream was calculated using *GLEWPro*, a software package designed specifically for acid gas wells (Wang and Carroll, 2006). For the acid gas mixture given in Table 2, the fluid remained in a single phase down the length of the reservoir, where a wellhead injection pressure of 9.1 MPa was calculated.

　　Since the mercaptans are not library components in *GLEWPro*, a different approach was required to estimate the injection pressure. The calculation involved the integration of the original flow equations using Euler's method. The physical properties of the stream were calculated using *VMGSim* and the pressure drop due to friction was estimated using their pipe model. The frictional pressure drop is quite small relatively to the hydrostatic contribution, common to this type of injection. The resultant injection pressure was estimated to be 9.17 MPa.

In spite of the differences in the calculation methods, the injection profiles for the two mixtures are essentially the same. Based on these calculations, the acid gas compressor is designed to a discharge of 12.4 MPa to meet injection pressure following frictional and head losses through the discharge and transport piping.

4.2 Phase Envelopes and Compression

VMGSim was used to generate the phase envelopes for the two mixtures given in Table 3. The acid gas mixture has the typical banana-shaped phase envelope, whereas the plus mercaptans mixture has a much broader phase envelope that extends to higher temperatures and pressures. This broader shape is not due to the addition of hydrocarbons as the increase in methane in the mercaptan-rich stream should produce a more volatile mixture (ie. lower dew point temperatures), while propane and ethane should have a negligible effect. Thus the differences observed between the two phase envelopes are largely due to the addition of the mercaptans.

Figure 2 shows the side-by-side plots of compression of the conventional acid gas stream versus the mercaptan-rich gas stream, plotted along with their respective phase envelopes. Both streams were saturated with water. For both cases, the same fixed discharge cooler temperatures and pressure drops, compressor ratios and compressor efficiencies were used. In addition, condensation of non-aqueous fluids was avoided for both streams, despite the fact that the accuracy of mercaptan-rich data used in the model is suspect. The conventional acid gas stream reaches the desired discharge pressure following five stage of compression and cooling, at a total power requirement of 101 kW.
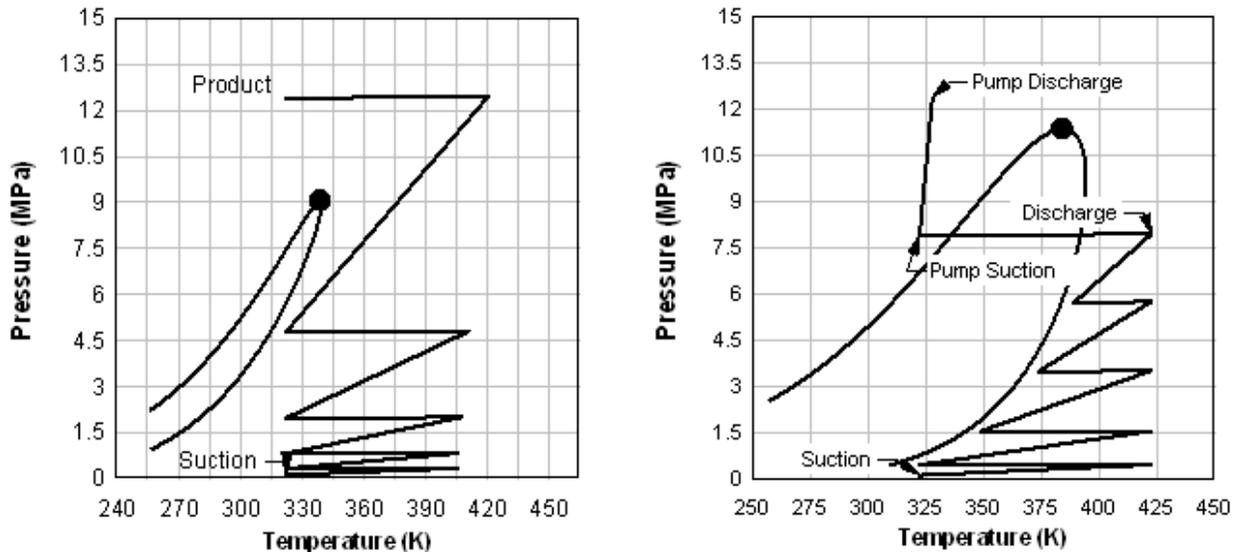

Figure 2. Compression Curves with Phase Envelopes for a Conventional Acid Gas Stream (L) and for a Mercaptan-rich Acid Gas Stream (R)

The increase in interstage cooling temperatures used to avoid condensation of non-aqueous fluids had a notable effect on the mercaptan-rich stream, wherein 5-stages of compression is not sufficient to attain injection pressure. Instead, an acid gas pump had to be installed to boost the liquefied product to pressure. Total power requirements for the mercaptan-rich system is 97 kW (compression) with a 2.5 kW pump. Other options for compression of the

mercaptan-rich system were investigated however found to be not as suitable as the 5-stage compressor + pump option, based on cost or operability.

4.3 Dehydration

Dehydration for the conventional acid gas stream can be completed through compression and cooling alone, by strategically fixing an interstage pressure where cooling can occur to knockout an optimal volume of water from the vapour phase. This results in the compressed and cooled acid gas to be undersaturated in its liquefied form, which in turn prevents corrosion and hydrate issues in the stream for disposal.

Dehydration of the mercaptan-rich blended stream cannot be completed in a similar manner due to the lack of understanding of the water holding capacity of this stream as described earlier, and because of the relatively high temperatures required on the interstage. Therefore even if it were possible to achieve near-optimal water knock out, the water content may still be too high for pipeline transport. Three types of processes are available for dehydration, including glycol, mole sieve, and refrigeration units.

All three processes have specific issues associated with dehydrating mercaptan-rich streams. First, refrigeration units cannot be used as the process would result in the formation of a non-aqueous liquid. Second, the suitability of mole sieve units for this application is poor due to the low pressure, high water content nature of the stream. Furthermore mercaptan species are readily adsorbed on most mole sieve materials. Finally, the operation of glycol dehydration units is also limited due to the high interstage pressures, along with the glycol's affinity to both acid gases and mercaptans.

Despite the limitations, a TEG dehydration unit was modelled to gain an understanding of TEG dehydration capabilities, TEG circulation rate requirements, potential impurity loadings, and rough equipment sizing. The model was designed to include a contactor column, lean-rich heat exchanger, stripper column with reboiler and condenser, and a gas-glycol heat exchanger. Two cases were generated, one to process the stream exiting the first stage of compression and another case to process the output from the second stage of compression. Based on the findings, the system would have better operability with the first processing case.

An outlet water content of 0.8 g/Sm³ (50 lb/MMSCF) gas was specified for the dehydrated stream. This relatively lenient specification allowed for a low TEG circulation rate, approximately 13.4 L/kg (1.6 gal/lb) water removed, and a low lean glycol concentration. This circulation rate, in fact, represented the lowest volume that could be simulated within the capabilities of *VMGSim*. The overhead stream exiting the regenerator column was quite sour (11 mol% H_2S and 1 mol% CO_2), and contained a total of 32 mol% of mercaptans, indicating the high absorption levels of these compounds within the TEG solution. However, as with other aspects of this project, there was no experimental data for the solubility of mercaptans in glycol that could be used to verify this observation. The model predicted that the overhead stream contained only 57% of water.

5.0 Conclusions

An approach for handling naturally occurring mercaptan species in natural gas production is the disposal of the stream via injection, similar to acid gas injection schemes common to

Western Canada. Under further investigation, several design issues and processing challenges have been identified under this approach.

Through a literature review, it was determined that very little data exist on mercaptans that were generated by experimental studies, either as a pure compound or in binary mixtures. These include phase behaviour, water content, and hydrate formation conditions. Information that does exist is either dated, or represents only a few data points over the range of conditions of interest. This lack of experimental data can be carried through to the process design of these systems, as many of the deficiencies have not been captured in the process simulation programs; rather assumptions are made or conflicting data have been designed into the program.

As a result, those designing processes around mercaptan-rich systems must be skeptical and discerning when reviewing the data and models simulated. A case study wherein a compression scheme was generated, however phase behaviour, water content and hydrate data were questioned highly. While some information was gathered using the model involving compression and cooling of the mercaptan-rich stream, the decision was made to ignore data generated by the model on dehydration of the stream. To err on the conservative side, additional dehydration was determined to be necessary to prevent corrosion and hydrates from occurring.

6.0   REFERENCES

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