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Acid Gas Injection and Related Technologies

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Gas Liquids Engineering

Scrivener

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Preface

The First International Acid Gas Injection Symposium (AGIS 2009) was held in Calgary, Canada in September 2009. This volume is a compilation of select papers from the conference.

In the natural gas industry the common acid gases are hydrogen sulfide and carbon dioxide, so-called because when they are dissolved in water they form weak acids. However, there are many aspects to the injection of acid gases. In the sense used here, acid gas injection is a broad topic covering:

1. the injection of streams rich in hydrogen sulfide and carbon dioxide for disposal purposes
2. the injection of carbon dioxide (and possibly acid gas) for enhanced oil recovery (EOR)
3. carbon capture and storage from plants producing flue gas which would otherwise be emitted to the atmosphere

The most obvious form of acid gas injection is the injection of a stream composed mostly of H_2S and CO_2, which is compressed, transported via pipeline to an injection well where it travels downward to a subsurface formation usually for disposal. Many of the papers in this volume are directly related to this subject. This includes papers on the required physical properties, thermodynamics and phase equilibria required to design such processes.

However, the injection of carbon dioxide is not always for disposal purposes. The injection of CO_2 for enhanced oil recovery is an important aspect of the petroleum industry and as oil supplies become reduced this may become even more important. Thus, several of the papers included in this volume are related more closely to this subject.

YW & JJC
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Acid gas injection has become an effective way to deal with the acid gas stream that is the by-product of the process for sweetening natural gas. The acid gas stream is composed mostly of hydrogen sulfide and/or carbon dioxide. If an aqueous solvent is used to sweeten the gas, which is usually the case, then the acid gas is saturated with water. If a non-aqueous solvent is used then there may be only a minimal amount of water in the stream.

Water is a component of concern in the mixture. Excess amounts of water can lead to either an aqueous liquid phase or hydrates. The aqueous liquid phase is corrosive and thus either should be avoided or it will require special metallurgy. The hydrates may cause plugging of lines or even the injection well.

The injection process is quite simple. The gas from the sweetening unit is at low pressure and must be compressed to sufficient pressure in order to achieve injection into a subsurface reservoir. The basic unit operations are therefore a compressor, a pipeline, and an injection well. Depending upon the composition and the specifications of the operating company, it may also be necessary to dehydrate the acid gas.

The first injection scheme started in 1989 – 20 years ago. This was followed by 17 more in the next seven years. All of these projects injected less than 5 MMSCFD (140 × 10^3 Sm^3/d) of acid gas and represent the first generation of injection schemes. Many lessons were learned from these projects and they were carried forward to future schemes.

Larger schemes were to follow such as the 50 MMSCFD (1.4 × 10^6 Sm^3/d) project at Sleipner West in the North Sea, 50 MMSCFD
Acid Gas Injection and Related Technologies

(1.4x10^6 Sm^3/d) at In Salah in Algeria, and the 65 MMSCFD (1.8 x 10^6 Sm^3/d) scheme at LaBarge in Wyoming. These are amongst the largest injection schemes currently in operation. In spite of their large injection volumes they share much in common with the first generation projects.

Uncertainty in the sulfur market combined with the problems associated with stockpiling large quantities of elemental sulfur have large producers considering acid gas injection as well. These projects will dwarf the first generation ones – injection volumes greater than 100 MMSCFD (2.8 x 10^6 Sm^3/d). And note this is the flow of the acid gas and not the feed rate to the plant.

Natural Gases

In the natural gas business there are many terms to describe the composition of the gas. Here we will focus on three:

1. Sweet
2. Sour
3. Acid gas.

Comparison

To demonstrate some of the differences between the three types of gas, first consider the information in Table 1 which provides a quick comparison of the properties of the three types of gases.

The three types of gases are described in some detail in the following sections.

Sweet Gas

Sweet gas is natural gas that contains only a small amount of sulfur compounds. More about these sulphur compounds in the next section.

Unfortunately there is no strict definition as to what constitutes a "small amount". For sales gas, the hydrogen sulfide concentration could range from 4 to 16 ppm (¼ to 1 grain/100 SCF) depending upon the sales contract. However, from a corrosion point of
Table 1. A qualitative comparison of sweet, sour, and acid gases.

<table>
<thead>
<tr>
<th></th>
<th>Sweet Gas</th>
<th>Sour Gas</th>
<th>Acid Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flammability</td>
<td>Very High</td>
<td>Very High</td>
<td>$H_2S$ - High</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CO_2$ - Non-flam.</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Low</td>
<td>High</td>
<td>$H_2S$ - Very High</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CO_2$ - Very Low</td>
</tr>
<tr>
<td>Corrosivity</td>
<td>$CO_2$-free - Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>(in the presence of water)</td>
<td>$CO_2$ present - High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odor</td>
<td>None</td>
<td>Rotten Eggs</td>
<td>$H_2S$ - Rotten Eggs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CO_2$ - None</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless</td>
<td>Colorless</td>
<td>Colorless</td>
</tr>
</tbody>
</table>

view there is a different specification. These are outlined by such standards as NACE MR0175 or CSA Z662\(^1\).

By the definition above, a natural gas that contains carbon dioxide but no sulfur compounds is classified as being sweet. To my knowledge there is no specific name for gas that is rich in $CO_2$ but free of sulfur compounds. However, there is a specification for $CO_2$, typically around 2 or 3 mol%, and thus often it must be removed from the raw gas. The processes for removing the $CO_2$ are the same as those for removing $H_2S$. Thus, gas rich in $CO_2$ but free of sulfur is often also called sour, but this is not strictly the case.

### Sour Gas

In contrast to sweet gas, sour gas is natural gas that contains sulfur compounds. The most important of these sulfur compounds is hydrogen sulfide. There are other sulfur compounds found in natural gas, but usually in small concentrations. These include the mercaptans (or thiols) which are organic chemicals similar to alcohols where the oxygen atom has been substituted with a sulfur atom. These compounds also have a foul odor.

\(^1\) NACE is the National Association of Corrosion Engineers (www.nace.org) and CSA is the Canadian Standard Association (www.csa.ca).
In addition to the $\text{H}_2\text{S}$ specification in sales gas there is also a total sulfur specification, which accounts for all of the other sulfur species. Some have an additional term: "highly sour" gas. Again there is no strict definition, but gas than contains more than about 10 mol% $\text{H}_2\text{S}$ is considered highly sour.

The process of removing $\text{H}_2\text{S}$ and/or $\text{CO}_2$ is called sweetening, again which leads to some confusion about gas that contains $\text{CO}_2$ but no sulfur compounds.

### Acid Gas

Acid gas is very different from sweet or sour gas and is composed almost entirely of hydrogen sulfide and carbon dioxide, with a small amount of hydrocarbon (typically less than 5 mole percent).

Both hydrogen sulfide and carbon dioxide form weak acids when dissolved in water and it is for this reason that they are called acid gases. Table 2 shows the solubility and the pH of the resulting solution of three gases in water. A pH of 7 is a neutral solution – neither basic nor acidic. A pH less than 7 is indicative of an acidic solution.

### Acid Gas Injection

Acid gas injection involves compressing the acid gas from the sweetening plant, transportation via pipeline to an injection well. The gas travels down the well and into a subsurface formation. The block diagram for an injection scheme, including the sweetening plant, is shown in Figure 1.

The feed gas contains $\text{H}_2\text{S}$ and $\text{CO}_2$ which is removed in the sweetening plant. The desired product for this process is the sweet

<table>
<thead>
<tr>
<th>Gas</th>
<th>mol%</th>
<th>mol/kg</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>$2.04 \times 10^{-3}$</td>
<td>0.11</td>
<td>4</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>$6.95 \times 10^{-4}$</td>
<td>0.039</td>
<td>4</td>
</tr>
<tr>
<td>Methane</td>
<td>$2.66 \times 10^{-5}$</td>
<td>0.0015</td>
<td>7</td>
</tr>
</tbody>
</table>
gas which has the desired levels of H\textsubscript{2}S and CO\textsubscript{2}. The undesired by-product is the acid gas mixture. Typically the acid gas is at low pressure (less than 2 bar, 30 psia), at about 50°C (about 120F), and is saturated with water.

The design of the injection scheme begins with the section of a reservoir. This may be a reservoir for disposal or for enhance recovery or for pressure maintenance. Most of the injection schemes are simply for disposal. Regardless of the purpose of the injection the reservoir should have the following characteristics:

1. The reservoir must contain the acid gas. And there are several aspects to this containment:
   a. Sufficient volume to hold the injected fluid.
   b. No leakage through the cap rock. The cap rock should have an extremely low permeability.
   c. No leakage through any other wells penetrating the injection zone. Thus you should verify the integrity of all wells (including abandoned wells) to ensure they will not leak the injected fluid to other zone or, even worse, to the surface.
2. Minimum interactions with the reservoir rocks or native fluids. Chemical reaction between the injected fluid and the reservoir may impede injection as time goes on and may ultimately prevent it.
3. Sufficient permeability that it does not pervert injection. For the low flow schemes this is usually not a problem, but may be a significant consideration for the larger projects.

4. It is probably unwise (and in some jurisdictions illegal) to inject H$_2$S into an otherwise sweet zone.

   e. It is not uncommon to use CO$_2$ for enhanced recovery (even in sweet zones). Another reason for injecting gas into a producing zone is for pressure maintenance. However, H$_2$S should probably only be used for EOR or for pressure maintenance in sour zones. Even then the producer should anticipate cycling of the H$_2$S (i.e. increase H$_2$S concentration in the produced fluids).

The next step is the design is to consider the surface facilities. In many injection schemes compression and cooling alone is sufficient to dehydrate the gas to a point where neither free water nor hydrates are a problem. This will be examined in more detail later in this paper. However, in some cases additional dehydration may be required. When dehydration is necessary, some compression is required because the gas cannot be dehydrated at pressures less than 2.5 bar. There are at least two reasons for this:

1. The water content of a low pressure stream is very high.
2. The actual flow rates are quite large and thus large diameter equipment would be required to process a relatively small stream.

Since dehydration is not always required, the lines connecting it to the block diagram are dashed.

For most injection schemes compression alone can achieve the pressure required to achieve injection. Typically compression can raise the pressure of the acid gas stream to 2000 psia (138 bar), but this should be examined on a case-by-case basis. However if the injection pressure is high, then a pump might be necessary beyond compression. After compressing the acid gas to about 1000 psia (69 bar) the fluid is in the liquid phase or in a dense fluid state and thus can be pumped to higher pressure. Again, for this reason the pump is connected to the block diagram using dashed lines.

Another dashed line on the block diagram is the flash gas. In many amine plants the rich amine from the absorber is sent to a flash tank
where the pressure is dropped from the absorber pressure to about 3.5 bar (50 psia). The gas that is released from this pressure reduction is largely hydrocarbon that was co-absorbed. This stream also contains some H$_2$S and CO$_2$. In many cases this can be added to the fuel gas system, even though it is sour. The overall H$_2$S in the fuel gas may be sufficiently low that it can be used as fuel in internal combustion engines or indirect heaters. The question is, can it be added to the acid gas stream and be disposed as a single stream?

**Sour Gas Injection**

In the earlier sections of this paper the differences between sour gas and acid gas were given. There are several large sour gas injection schemes in the world. However, these have little in common with the acid gas injection projects described in this paper.

These projects are typically for pressure maintenance and the gas is injected back into the original formation. The sour gas is compressible and thus requires high injection pressures and very large compressor.

Currently the largest compressors in the world are to handle sour gas reinjection in the Caspian region (Chellini, 2005).

**The Early Years**

The first injection scheme was the Chevron Acheson project near Edmonton, Canada. The data for this project is summarized in Table 3. The acid gas at this location was relatively high in carbon dioxide (approximately 90 mol%).

The next project was also from Chevron, but this was at West Pembina. It too is described in Table 3.

A third of the early injection projects that is also listed in Table 3 is the project at Wayne-Rosedale, near Drumheller, Alberta. Again, like the other early projects, this is a low volume injection scheme. The paper of Ho et al. (1996) also gives the costs associated with this project which are given in the Table 4. The original dollar values are converted to 2008 dollars using inflation factors alone (Bank of Canada, 2009).

The cost of the TEG dehydration units seems a little large, even when compared to sour gas dehydration units. However, this unit is completely made from 316 stainless steel and includes a condenser on the regenerator overhead and these may be the reasons for the additional cost.
### Table 3. Three early acid gas injection projects.

<table>
<thead>
<tr>
<th>Location</th>
<th>Acheson</th>
<th>West Pembina</th>
<th>Wayne-Rosedale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alberta, Canada</td>
<td>Alberta, Canada</td>
<td>Alberta, Canada</td>
</tr>
<tr>
<td>Start up</td>
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<td>1994</td>
<td>1995</td>
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<td>Injection well</td>
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<tr>
<td>Bottom hole pressure (kPa)</td>
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<td>30 000</td>
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</tr>
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<td>Bottom hole temperature (°C)</td>
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<td>98</td>
<td>65</td>
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<td>9 500</td>
<td>10 000</td>
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<tr>
<td>Injection pressure, actual (kPa)</td>
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<td>7 500</td>
<td>6 000</td>
</tr>
<tr>
<td>Depth (m)</td>
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<td>2 800</td>
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<tr>
<td>Acid Gas</td>
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<td>Composition, water-free (mol %)</td>
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<tr>
<td>Hydrogen sulfide</td>
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<td>77.17</td>
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<td>21.93</td>
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<td>C₂+</td>
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<td>&lt;0.35</td>
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<tr>
<td>Flow rate (Sm³/d)</td>
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<td>16 700</td>
<td>21 000</td>
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<tr>
<td>Flow rate (MMSCFD)</td>
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<tr>
<td>Type</td>
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<td>Ariel JG/4</td>
<td>Knox West. TAP-445</td>
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<td>four</td>
<td>five‡</td>
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<tr>
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<td>132</td>
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<tr>
<td>Discharge pressure (kPa)</td>
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<td>3</td>
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</table>

+ sandface pressure based on injectivity tests, reservoir pressure is about 15 500 kPa
‡ in actual operation the fifth stage is not fully used
NS - not specified