ACID GAS INJECTION: PAST, PRESENT, AND FUTURE

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¹Acid 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 sweetening 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 requires 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 – twenty years ago. This was followed by 17 more in the next seven years. All of these projects injected less than 5 MMSCFD (140×10³ Sm³/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 (1.4×10⁶ Sm³/d) project at Sleipner West in the North Sea, 50 MMSCFD (1.4×10⁶ Sm³/d) at In Salah in Algeria, and the 65 MMSCFD (1.8×10⁶ Sm³/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 (2.8×10⁶ Sm³/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, and 3. Acid gas.

Comparison

To demonstrate some of the differences between the three types of 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.

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However from a corrosion point of view there is a different specification. These are outlined by such standards as NACE MR0175 or CSA Z662².

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.

	Sweet Gas	Sour Gas	Acid Gas		
Flammability	Very High	Very High	H ₂ S – High		
Fiaminability			CO ₂ – Non-flam.		
Toxicity	Low	High	H ₂ S – Very High		
			CO ₂ – Very Low		
Corrosivity (in the	CO ₂ -free – Low	High	High		
presence of water)	CO ₂ present – High	nigii	nigii		
Odor	None	Rotten Eggs	H ₂ S – Rotten Eggs		
			CO ₂ – None		
Color	Colorless	Colorless	Colorless		

Table 1 A Qualitative Comparison of Sweet, Sour, and Acid Gases

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.

In addition to the H₂S specification in sales gas there is also a total sulfur specification, which accounts for all of the other sulphur species.

Some have an additional term "highly sour" gas. Again there is no strict definition, but gas than contains more than about 10 mol% H₂S is considered highly sour.

The process of removing H_2S and/or CO_2 is called sweetening, again which leads to some confusion about gas that contains 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 on acidic solution.

Gas	mol%	mol/kg	рН
H_2S	2.04×10 ⁻³	0.11	4
CO ₂	6.95×10 ⁻⁴	0.039	4
Methane	2.66×10 ⁻⁵	0.0015	7

Table 2 Solubility of Gases in Water at 20°C

ACID GAS INECTION

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 Fig. 1.

² NACE is the National Association of Corrosion Engineers (www.nace.org) and CSA is the Canadian Standard Association (www.csa.ca).

The feed gas contains H_2S and CO_2 which is removed in the sweetening plant. The desired product for this process is the sweet gas which has the desired levels of H_2S , and CO_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.

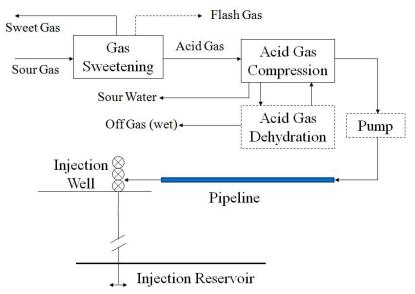


Fig.1 Block Diagram for Acid Gas Injection

- 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 jurisdiction illegal) to inject H₂S into an otherwise sweet zone.
 - a. 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_2S should probably only be used for EOR or for pressure maintenance in sour zones. Even then the producer should anticipate cycling of the H_2S (i.e. increase H_2S 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. and 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 compressin 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 bock 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 H₂S and CO₂. In many cases this can be added to the fuel gas system, even though it is sour. The overall H₂S 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).

Table 4 Economics of Wayne-Rosedale Injection Scheme					
	Size	Can (1995)	Can (2008)		
Compressor	300 hp	\$3,400,000	\$4,420,000		
Dehydration Unit	0.74 MMSCFD	\$1,300,000	\$1,690,000		
Pipeline 2-in,	100 m	\$100,000	\$130,000		
Injection Well	1900 m	\$1,300,000	\$1,690,000		

THE EARLY YEARS

The first injection scheme was the Chevron Acheson project near Edmonton, Canada. The data for this is project 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

These three injection projects listed in Table 3 are well described in the literature and the reader is directed to the original references for more of the details. One thing that these early projects shared and this can be seen for the three projects listed in Table 3, the required injection pressure was overestimated.

The early years of acid gas injection were reviewed by Longworth et al. (1996). That paper reviewed 17 injection schemes including the three noted above. To that date the maximum injection rate was 4.2 MMSCFD $(120\times10^3 \text{ Sm}^3/\text{d})$ and the maximum licensed injection pressure was 1740 psia (20 bar). It was not stated what the

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largest actual injection pressure was. The hydrogen sulphide concentration in the injected gas ranged from 5 to 68% with the balance being mostly carbon dioxide; however it is well-known that the acid gas off an amine striping plant contains more than 1% hydrocarbon.

A few other small injection schemes have been described in the literature. These include Dumas, Texas, USA (Whatley, 2000); Lisbon, Utah, USA, (Jones et al., 2004). Puskwaskau, North Normandville, West Culp, Rycroft, all in Alberta Canada (Maddocks and Whiteside, 2004); and Artesia, New Mexico, USA, (Root et al., 2007).

Most of the acid gas injection schemes designed today are still of the first generation type. These are typically small gas plants where neither sulfur production nor long-term combustion (flaring or incineration) is an option.

THE SECOND GENERATION

Several additional injection projects were constructed through the next few years; however a few were notable because of their size. These projects were in excess of 50 MMSCFD of gas injected. Three of these projects, Sleipner West, LaBarge, and In Salah, are described here. Sleipner West which is operated by StatoilHydro, LaBarge is operated by ExxonMobil, and In Salah is a joint project of BP, Sonatrach, and other minor partners.

The first of these larger projects was Sleipner West was started in 1996. A significant motivation for this project is the carbon tax imposed by the Norwegian government of some 350 Norwegian Kroner (roughly \$50 [US]) per tonne of carbon dioxide emitted to the atmosphere. The project injects about 1 million tonnes of CO₂ per year and thus the tax would amount to about \$50 million [US] per year.

The injection scheme at Labarge, Wyoming, USA started in 2005 and injects about 65 MMSCFD of a 65% H₂S and 35% CO₂ mixture. The injection well is quite deep, about 5000 m, and the injection pressure is quite high, greater than 17 MPa.

The In Salah project is in central Algeria. The produced gas contains significant amounts of CO₂ but is otherwise sweet. The CO₂ is removed from the raw gas and injected for disposal. The injection rate is approximately 50 MMSCFD.

The three projects discussed here are significantly larger than the first generation but all have a single injection well (although LaBarge has a spare well). They inject into relatively high permeability zones. At both LaBarge and In Salah the injection is into the same formation as the gas is produced from but it is into the water leg some distance from the producing wells. In this way it is hoped that there will be minimum communication between the producing fluid and the injected fluid for the duration of production.

Sleipner West has the additional unique feature of being the first offshore injection scheme. Other producing sour gas and gas rich in CO₂ are now considering acid gas injection as a means for dealing with their acid gas. Sleipner West has also conducted thorough seismic studies to determine the flow of the CO₂ through the reservoir.

The first of the larger projects in Canada was at the Westcoast (now Spectra Energy) Kwoen Gas Plant in northeast British Columbia, Canada, which started in 2003. This plant was licensed to inject about 30 MMSCFD, which makes it more than twice the volume of any other injection project in Canada. This project has a single compressor and a single injection well. This continues to be the largest injection project in Canada.

THE FUTURE

Most of the acid gas injection projects of the future will be like those of the past. The best application of AGI continues to be for the small producers who do not have sufficient H₂S to make elemental sulfur but have too much to continually flare it.

However the real future of AGI is in the mega projects – injecting more than 100 MMSCFD of acid gas.

There are two factors that have even larger producers considering acid gas injection. The first is the volatility in the sulfur market. The other is the desire not to have large sulfur stockpiles, which occupy a significant amount of space. These producers are considering injections scheme greater than 100 MMSCFD and in some case much greater. And to make this clear this is 100 MMSCFD of acid gas, not feed gas to the plant. For example, a plant with a raw feed 1 BSCFD and a combined acid gas concentration $(H_2S + CO_2)$ of 10% will produce an acid gas stream of up to 100 MMSCFD.

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Another possible large injection scheme would be associated with carbon capture and storage at a coal-fired electrical generation plant. For example a 750 MW coal-fired electrical generating plant could emit around 5 million tons (5.1 million tonnes) of CO₂ per year³. A city with a population of about 1,000,000 uses slightly more than 750 MW. This emission is equivalent to about 250 MMSCFD of carbon dioxide and does not include other gases (notably nitrogen) in that stream. The injection of this stream would make it a mega injection scheme similar to the one described in the previous paragraph.

Mega Injection Schemes

The basic components for these injection schemes are much the same as the smaller schemes with some important differences.

Since injection is plant critical, shutting down the injection means shutting in the plant. Therefore it is necessary to have redundant equipment available. Some examples are presented in the sections that follow.

Wells

The injection of such large volumes will require multiple injection wells. Injection of more than 100 MMSCFD into a single well; first because of the high resistance to flow in the reservoir and also because of the high pressure drop in the well, even with relatively large diameter wells. Furthermore, it may be wise to distribute the injected fluid throughout the reservoir rather than at a single point.

In addition it may be necessary to have spare wells in case one of the wells needs to be shut in or worked over.

Compression

The very large injection projects will require centrifugal compressors; the reciprocating compressors commonly used in the small injection projects are inadequate for this application.

Furthermore, it will be necessary to have redundant capacity. Typical arrangements are $3 \times 50\%$ or $4 \times 33\%$. Many factors enter into the decision of one method over the other, but they are based largely on reliability analysis.

The injection for these higher volume schemes will almost certainly require much higher pressures than in the low volume scheme. This dictates that pumping may be required beyond the pressures that can be achieved by compression alone. These would have to be special pumps that are completely sealed; even small leaks cannot be tolerated. They must be made from materials that are compatible with the acid gas. This is particularly true if polymer compounds are used to seal the pump. Again it will probably be necessary to have redundant pumps.

In the small injection schemes it is common to use electric motor drives. These offer some flow turn down using variable speed control. However the large centrifugal compressors will require gas turbine drives.

Pineline

Since it is likely that they will be several injection wells then a network of pipelines will be required to distribute the acid gas to all of the injection wells.

The diameter of the pipeline will be dictated by factors other than hydraulics. That is, pressure drop is not the only concern. Larger diameter pipe will lead to lower pressure drop but they will hold significantly more acid gas – more toxic fluid. Thus a release from a larger diameter pipe is more serious than from a smaller diameter one.

Offshore

Not only onshore producers will be faced with the problem of what to do with the acid gas, more and more offshore producers will have to examine this same option. Currently Sleipner West is the only offshore injection scheme, but EnCana at their Deep Panuke project off the east coast of Canada are committed to AGI. This will become the first offshore project to inject H_2S . Others will surely follow.

Alternate Processes

Another option for future projects is to process the raw gas at higher pressure in order to produce the acid gas at under pressure. His would greatly reduce the compression requirements for injection. Two such processes are: 1.

³ This comes from various pages on the Internet and represents a typical emission factor and is suitable for our purposes here.

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SPREX[®] from Total and 2. Controlled Freeze ZoneTM (CFZ), from ExxonMobil (Valencia et al, 2008). Although both have the potential to fill this niche, neither has progressed beyond the pilot stage to a commercial installation.

Another new process that may prove useful in the realm of AGI is Twister (Betting and Epsom, 2007). This may allow acid gas to be dehydrated without the problems of current dehydration methods. There have been Twisters installed in the industry but currently none for acid gas.

There will certainly other innovations that will help the injection process.

Software Tools

One of the challenges of designing acid gas injection is accurately predicting the complex phase equilibria involved, including: water content of the acid gas (in both gas and liquid phases), hydrate formation (particularly in dehydrated streams), phase envelope construction and the effect of small amounts of water on the phase envelope. Furthermore, the prediction of the physical properties of the acid gas: density, viscosity and thermal conductivity, are required for accurate design.

Software developers are meeting these challenges.

IN SUMARY...

Acid gas injection is a mature technology on the small and medium scale. It continues to be an option for producers of sour gas who do not want to produce elemental sulfur.

It also has the potential to be an environmentally friendly way for large producers to deal with unwanted acid gas; particularly in a volatile sulfur market.

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Table 3 Three Early Acid Gas Injection Projects

	Acheson	West Pembina	Wayne-Rosedale
Location	Alberta, Canada	Alberta, Canada	Alberta, Canada
Start up	1989	1994	1995
Injection well			
Bottom hole pressure (kPa)	2 300	30 000	$20~000^\dagger$
Bottom hole temperature (°C)	49	98	65
Injection pressure, design (kPa)	6 000	9 500	10 000
Injection pressure, actual (kPa)	3 500	7 500	6 000
Depth (m)	1 100	2 800	1 930
Acid Gas			
Composition, water-free (mol %)			
Hydrogen sulfide	10.2	77.17	17.4
Carbon dioxide	89.8	21.93	82.5
Methane	< 0.1	0.55	0.1
C_2 +	< 0.1	< 0.35	< 0.1
Flow rate (Sm³/d)	13 500	16 700	21 000
Flow rate (MMSCFD)	0.48	0.59	0.74
Pipeline			
Length (m)	2 200	480	100
Nominal diameter (in)	2	2	2
Material	carbon steel	stainless	carbon steel
Compressor Design			
Type	Ariel JG/4	Ariel JG/4	Knox West. TAP-445
Number of stages	four	four	five [‡]
Suction pressure (kPa)	157	143	132
Discharge pressure (kPa)	6 640	12 450	22 810
Compressor Actual			
Suction pressure (kPa)	124	136	140
Discharge pressure (kPa)	3 894	8 044	6 095
Reference	1, 2	1, 2	3

^{† –} sandface pressure based on injectivity tests, reservoir pressure is about 15 500 kPa

NS – not specified

References: 1. Lock (1997) 2. Bosch (2002) 3. Ho et al. (1996)

^{‡ –} in actual operation the fifth stage is not fully used