UNDERSTANDING CO_2 DEHYDRATION WITH CONVENTIONAL TEG SYSTEMS IN CO_2 EOR PROJECTS

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ABSTRACT

As CO_2 miscible flooding becomes commonplace in our industry, more and more emphasis is given to gas dehydration and corrosion control in CO_2 handling systems. This paper deals with the design of CO_2/methane dehydration facilities, related metallurgical considerations, and the sizing of contact towers and reboilers to meet the varying CO_2 concentration expectancies.

INTRODUCTION

Since the early 1970's, CO_2 injection has been utilized as an Enhance Oil Recovery (EOR) method. These Enhanced Oil Recovery projects require gas processing plants that remove water, methane gases, and natural gas liquids to produce purified dry CO_2 for reinjection. Since the purchase of CO_2 is the largest single cost component of a CO_2 flood project, the CO_2 produced after break through is typically processed and recycled to limit additional outside purchases. Because of the economic impact of recycling the increasing importance of CO_2 treatment and processing is apparent. Relatively pure CO_2 of more than 95% by volume is generally required for injection. When free water is present, carbonic acid forms causing rapid corrosion of all mild steel pipelines and equipment. Thus dehydration of the CO_2 is required for corrosion control throughout the processing facilities. CO_2 can form solid ice-type crystal (hydrates) when liquid water is present. This condition can occur at temperatures as high as 60° F. Therefore, the dehydration of CO_2 is also necessary to prevent solids blockage problems in the pipelines, valves, compression and processing equipment.

GLYCOL DEHYDRATION EQUIPMENT

Triethylene glycol (TEG) has been commonly used as a water absorbent for natural gas streams and CO_2 for decades. Figure 1 is a typical flow diagram for TEG dehydration systems in CO_2 service.

In this typical system the wet gas enters the bottom of the absorber (contactor) column and exits the top as dried gas. The glycol flows countercurrent to the gas stream. Dry (lean) glycol enters the top of the contactor column containing 0.2-1.5 wt % water and leaves the bottom of the column containing 3-8 wt % water. Bubble-cap or valve trays are used to maximize the gas/liquid contact. It is generally conceeded that bubble caps offer the highest contact efficiency along with operating "flexibility". The absorber may operate at up to 800 psi and 130° F for efficient CO_2 dehydration service.

The wet glycol exiting the absorber column is thermally regenerated in the reboiler and its reflux column. The reboiler temperature is set to operate at between 380° and 400° F when TEG is used as the absorbent. The reflux column is generally mounted atop the reboiler vessel. Heat exchange between the (water) rich and the regenerated lean glycol reduces the energy consumption of the reboiler and minimizes glycol losses to the gas stream in the contactor. The injection of a stripping gas and/or application of vacuum to the reboiler may be used to decrease the concentration of water in the lean glycol. Without a vacuum and/or stripping gas, lean TEG will exit the reboiler at 99.0 wt % TEG or less. Glycol purity approaching 99.9 wt % may be necessary for adequate dehydration. Although the dehydration system for CO_2 is similar to that for natural gas, several new factors need consideration when designing a system for CO_2. These factors are as follows:

1) Equilibrium data for CO_2 and liquid water and/or hydrates.

2) Vapor-liquid equilibrium between CO_2 and desiccant solutions.

3) Corrosion/metallurgy.

The equilibrium data relevant to the CO_2 dehydrator inlet gas has been studied by several investigators (1,2,3,4) who measured the water content of carbon-dioxide rich phases in equilibrium with liquid water. Recent data by Song and Kobayashi (5,6) has extended the data base to more temperature and pressure regions. Figure 2 illustrates some of the available data and compares it to the saturated water content of sweet natural gas. CO_2 contains more water vapor at saturation than natural gas. Therefore, the dehydrator design must reflect the larger volume of water to be removed, with emphasis on the reboiler heat duty requirement.

At sufficiently low temperatures CO_2 exhibits hydrate formation behavior similar to natural gas. For example, a solid phase hydrate containing water and CO_2 appears at about 40-50° F at 700 psia. Several studies (7,8,9) have evaluated the temperature and pressure conditions where hydrates initially form in CO_2/H_2O systems. Work by Sond and Kobayashi (5,6) provides data on the water content of the CO_2-rich phase in equilibrium with the solid hydrate phase.

Equilibrium data is necessary to define the dehydration equipment water load and the treatment level required for corrosion control and/or hydrate permeation. For the process design of the dehydration equipment, vapor-liquid equilibrium data between CO_2 and the desiccant solvent is required. Triethylene glycol (TEG) has been the most common desiccant in this service to date. However, Takahasi and Kobayashi (10) have studied and compared both CO_2/diethylene glycol (DEG)/H_2O and CO_2/TEG/H_2O systems. The water content of CO_2 gas in equilibrium with these desiccants was reported as a function of temperature, pressure, and water content of the desiccants. The equilibrium solubility of CO_2 in the desiccants was also measured as a function of these same variables. Figure 3 illustrates this data for TEG at 765 psia. Figure 3 also shows data for sweet methane gas and illustrates that its behavior is quite similar. This information is used primarily to determine the absorber tower design parameters. The number of absorption trays, the desiccant circulation rate and the glycol purity required to produce a given gas treatment level depends on this information.

In their studies, Takahashi and Kobayashi (10) also found that CO_2 is quite soluble in the glycol-water solutions. Figure 4 illustrates their data for TEG with 7 wt % H_2O as a function of temperature and pressure. This behavior data impacts the glycol still and reboiler design. The design of the glycol regeneration still column must reflect the increased vapor traffic due to liberated CO_2. And, the reboiler design must account for the heat input required to desorb CO_2 from the glycol. Another researcher, J.J. Sekerka, (11) discusses problems encountered with the reboiler at the SACROC project, in Snyder, Texas, due to lack of extra design duty for liberation of dissolved CO_2. Glaves et al (12) in associated studies, suggest a gas stripping tower to remove dissolved CO_2 from the rich glycol before it flows to the reboiler. Most units, however, use a flash tank operated at an intermediate temperature and pressure (as shown in Figure 1) to remove the majority of the dissolved CO_2 from the rich glycol before it enters the thermal regenerator.

The concentration of glycol in the CO_2 phase at the absorber exit conditions is also of economic and operating importance. Sekerka (11) reports that the glycol losses at the SACROC facility are higher than expected. Unfortunately, no data has been reported at the time of this writing that would allow prediction of glycol losses. Because of this, Gas Processors Association project Number 856 has been proposed for 1985 to obtain this data.

CORROSION/METALLURGY

The phenomenon of corrosion due to the presence of CO_2 and organic acids has received much attention. Gas condensate wells often contain significant amounts of CO_2 and water. In the early 1940's corrosion problems in high pressure condensate wells were observed. The Natural Gasoline Association of America (NGAA) formed a committee to study these corrosion problems early in 1944. The NGAA Condensate Well Corrosion Committee's work culminated in the 1953 publication of a text (13) detailing the mechanisms of corrosion and inhibition in gas condensate wells.

Although we are dealing with essentially pure CO_2, the work done on condensate well corrosion is helpful for understanding the corrosion mechanism that will be active in the CO_2 dehydration system. Carbon dioxide is not corrosive to mild steel unless free water is present. The overall corrosion reactions are simple:

$$CO_2(g) + H_2O \rightarrow H_2CO_3$$

$$Fe + H_2CO_3 \rightarrow H_2\uparrow + Fe^{++} + CO_3^{=}$$

Carbon dioxide dissolves in the water phase forming carbonic acid which dissolves iron while liberating hydrogen. A film of solid $FeCO_3$ forms on the steel surface and exists in a state of equilibrium. The outer layer of $FeCO_3$ continuously dissolves in the low pH aqueous phase while the precipitate is deposited adjacent to the metal surface. The morphology, or structure, of the surface layer deposited on the steel governs the nature of the corrosion. Three types of layers have been observed on mild steel in condensate well service. They are:

1) A porous and relatively adherent layer which promotes deep pitting of the metal.

2) A porous and relatively easily removed layer which results in fairly uniform corrosion of the metal.

3) A thin and relatively adherent and non-porous layer which affords some protection against corrosion.

The first type of deposit is generally observed when the partial pressure of CO_2 is greater than 1 atmosphere. The second type of film is observed at lower than 1 atmosphere CO_2 partial pressure. The third type of film is observed to contain significant amounts of organic compounds, generally naphthenic acids that were naturally present in the gas stream. After the initial attack on the metal surface, the diffusion of corrosive compounds through the surface layer controls the rate of corrosion. Other naturally occuring acidic components in the condensate like acetic acid and formic acid contribute to corrosion, but carbonic acid is the primary corrodent.

Although a great deal of work has been done by C-E Natco and others investigating the corrosion of carbon steel in CO_2/free water systems, the prediction of corrosion rate is not generally possible. Since severe corrosion of metal by CO_2 requires the presence of free water, concern arises about the agressiveness of CO_2 in the presence of wet rich glycol. This concern has often resulted in a conservative approach to materials of construction selection, as shown on Table 1, favoring stainless steel.

Although very little published information is available in the literature, Montrone and Long (14) do report the results of a corrosion study of materials for use in CO_2 absorption systems. They found that carbon steel can be suitable for vessel and exchanger shells where the dessicant was aqueous MEA or concentrated TEG in dehydration units for CO_2. From this work the following general observations can be made:

1) Absorption of CO_2 into the glycol-water phase will markedly depress its pH and may make it corrosive to mild steel.

2) The tendency will be towards pitting corrosion on the high pressure sections of equipment.

3) Corrosion will be more uniform in the reboiler section where the condition of lower CO_2 partial pressure exists, but it may be serious.

4) Film-forming liquid and vapor phase corrosion inhibitors will afford some protection to mild steel.

5) Buffering the aqueous phase with alkaline agents (borax, $NaHCO_3$, NaOH, etc.) will reduce corrosion.

The depression of the pH of the glycol-H_2O absorbent by CO_2 can also have adverse effects on the glycol. Below a pH of 5.5 the thermal degradation and autoxidation of glycols is accellerated, and peroxides, aldehydes and organic acids are formed (15,16). The resulting contamination of the glycol can aggravate any corrosion problems. Researchers Grosso and Hall (17,18) outline analytical techniques useful for troubleshooting problems with glycol systems due to contamination in their recent papers.

Thus control of the glycol pH in CO_2 dehydration systems is especially critical and necessary. The pH should be maintained between 7 and 8.5 to limit the corrosion and degration potential of the glycol.

Corrosion in CO_2 water systems has been studied extensively, but no specific information has been reported on corrosion behavior in CO_2-glycol dehydration process equipment. A study was initiated by C-E Natco (19) to generate the data required for the development of rational material specifications for construction of CO_2 dehydration systems. Table 1 shows details on the materials used in some CO_2 dehydration process systems. One finds stainless steel components on most systems. Our study resulted in laboratory and field data demonstrating that carbon steel components can be acceptable for most of the components in a CO_2 dehydration system. Also, our study discovered a potential problem with intergranular attack in the weld heat affected zones of austenitic stainless 304 and 316 steels normally used for this application. The CO_2 environment in the absorber was studied at 300 and 700 psig and the reboiler was evaluated at 400° F. The following metals were tested:

1) 304L - welded specimen
2) 316L - welded specimen
3) 410 - not welded
4) A-516-70 - stick welded (stress required and not stress relieved)
5) A-516-70 - sub-arc welded (not stress relieved)

Table 2 shows the results tabulated from our studies in the order of relating corrosion resistance of various alloys in a CO_2-water environment. The mpy corrosion rates represent the range observed for all coupons exposed in the autoclave for each material.

The effect of a corrosion inhibitor (3 wt % sodium mercaptobenzothiazole, 1 wt % borax) added to the TEG was evaluated. The test results are as follows:

1) A-516-70 fine grain carbon steel is a suitable material of construction for both the reboiler and absorber vessels if 1-2 mpy corrosion is acceptable.

2) While 304L and 316L showed very low overall corrosion (less than .2 mpy), intergranular attack was observed in the weld heat-affected zones.

3) Reboiler corrosion rates were slightly higher in the corrosion-inhibited glycol tests. A possible cause is the likely decomposition of the NACAP to H_2S or COS. Borax may be the preferred additive to TEG for this application.

4) Minor pitting corrosion was observed on all coupons.

5) Grade 410 stainless is suitable for vessel internals (trays) fabrication.

6) Results of limited field testing on units in CO_2 service corroborate the first conclusion above.

CONCLUSIONS

For CO_2 dehydration with TEG where the absorber operates between 300-700 psig and where the reboiler operates at up to 400° F, the following conclusions can be made, assuming H_2S is <u>not</u> present in the gas.

1) CO_2 contains more water vapor at saturation than natural gas. Therefore the equipment must reflect a larger design due to the larger volume of water to be removed.

2) CO_2 is more soluble in glycol and glycol-water solutions than methane. Therefore the design of the glycol reboiler and the glycol still column must reflect a larger design due to the increased heat required to desorb CO_2 from the glycol and the increased CO_2 and water vapor traffic.

3) A flash tank operated at an intermediate pressure and temperature should be added to the dehydration system. This can remove most of the dissolved CO_2 from the rich glycol stream before it is exposed to the reboiler.

4) Higher system glycol losses can be expected than with sweet natural gas dehydration systems. The high solubility of CO_2 in glycol in the absorber makes higher glycol losses to the CO_2 gas stream possible. The high CO_2 vapor rates in the glycol reboiler at temperatures approaching 400° F, makes higher glycol losses possible. A still column, or reflux, overhead temperature control system, optional on typical methane drying systems, should be considered a must to minimize glycol losses from the still column.

5) A-516-70 is a suitable material of construction for both the absorber and reboiler vessels if 1-2 mpy corrosion can be tolerated.

6) In laboratory and field tests 304L and 316L showed very low overall corrosion rates (less than .2 mpy) but intergranular corrosion attack (IGA) was observed in the welded heat affected zone.

7) Minor general pitting corrosion will likely occur for all materials considered.

8) 410 stainless is suitable for vessel internal components fabrication.

The occurrence of IGA in the heat affected zone of austenitic stainless samples (304L, 316L) is disconcerting. Since the low carbon grade of these materials was used, one would not expect to see this behavior. However, the Chevron SACROC plant has been dehydrating CO_2 in a 316 stainless dehydrator using TEG since 1972. No problems with IGA have been reported for this unit. This leads one to wonder if IGA is a real or significant long-term concern.

Small amounts of H_2S in the gas will certainly accelerate the corrosion of carbon steel. Further tests are needed to quantify this effect. The previous conclusions provide sufficient information to design a CO_2 dehydration system where the pressure is less than 800 psia. When higher operating pressures are contemplated, the situation becomes complicated due to the unusual behavior of CO_2 near its critical pressure. But regardless of the conditions it is suggested that the assistance of an experienced CO_2 dehydration equipment supplier be sought.

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Table 1
Some Glycol Units in Carbon Dioxide Service

SIZE/SCFD	CARBON DIOXIDE %	MATERIALS
3 MM	81	Carbon Steel
14 MM	99	Bottom half tower 304L SS, skimmer 304 SS
33.4 MM	95+	Tower 304L clad, still column 304L
16 MM	90+	Tower 304L
12 MM	85+	Tower C.S. with 304 trays, still column 304L
19.3 MM	99	Tower up to 2nd tray 304, top of tower C.S. with 1/8" C.A., SS trays, still column, skimmer
3 MM	98	Carbon Steel
60 MM	90+	Bottom of tower 304 clad, top coated
35 MM	95+	2.3 MM Btu/hr reconcentrator skid assembly, 316 SS material on reboiler, still column flash tank and all piping in rich TEG service

Table 2
Summary of Relative Corrosion Resistance* of Tested Materials

		OPERATION WITH INHIBITOR			
		ABSORBER		REBOILER	
MATERIAL		CORROSION RATE-MPY	OTHER	CORROSION RATE-MPY	OTHER
	304L	(-).00 - .08	IGA	.01 - .04	IGA
	316L	.00 - .13	IGA	(-).00 - .01	IGA
No Weld	410	.02 - .13		.06 - 24	
Stick Weld Not SR	516	.16 - .39		.95 -2.19	
Stick Weld SR	516	.04 - .49		.96 -2.22	Not Recommended
Sub Arc Not SR	516	.16 - .53		1.39 -2.22	
		OPERATION WITHOUT INHIBITOR			
	304L	(-).00 - .13	IGA	.00 - .01	IGA
	3156L	(-).04 - .15	IGA	.00 - .01	IGA
No Weld	410	.01 - .17		.00 - .03	
Sub Arc Not SR	516	.15 - .70		.12 - .17	
Stick Weld SR	516	.09 - .79		.15 - .18	
Stick Weld Not SR	516	.04 -2.32		.15 - .49	

* Materials listed in relative (best to worst) order of corrosion resistance. No significant difference was noted among materials grouped together. Corrosion rates (MPY) represent a range of values for the combined vapor, surface, and liquid phases.

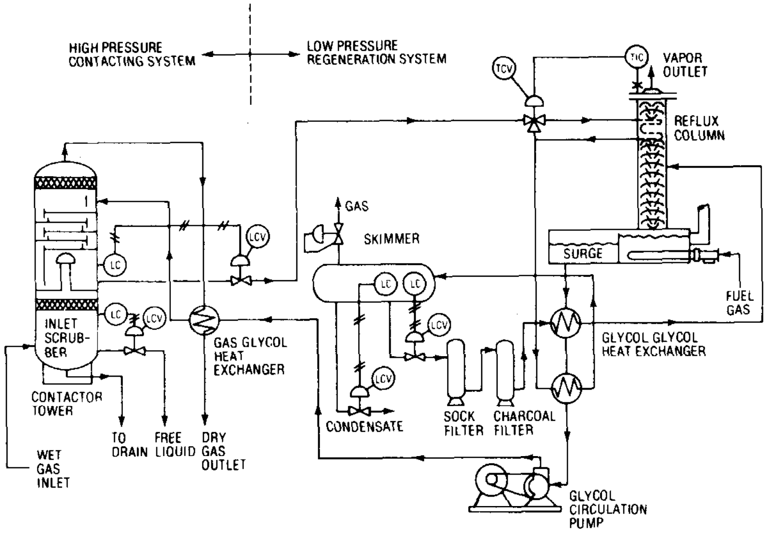

Figure 1 - Glycol dehydration equipment for CO_2

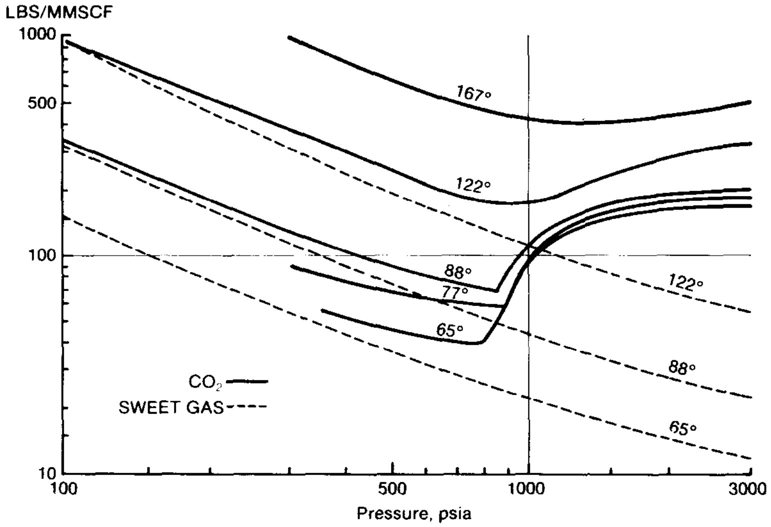

Figure 2 - Water content of CO_2

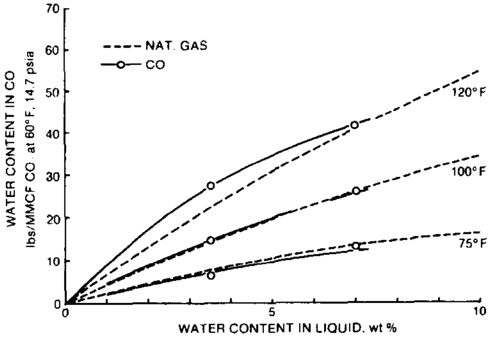

Figure 3 - CO_2 - H_2O equilibrium for TEG-water solution at 765 psia (11)

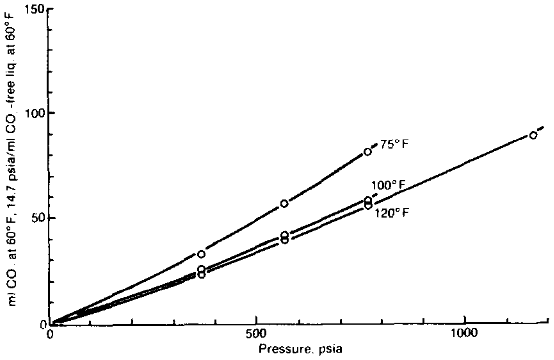

Figure 4 - CO_2 solubility in TEG 7.0 wt% H_2O (11)