PROBLEMS ASSOCIATED WITH CHEMICAL DEHYDRATION OF NATURALLY PRODUCED CO_2

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ABSTRACT

Enchanced oil recovery (EOR), by gas flood, has been a successful practice since the 1930's. One of the more recent gases to be used in these operations has been CO_2. Large natural CO_2 production from fields in New Mexico, Wyoming, Mississippi, and Colorado have begun to supply EOR projects.

Naturally produced CO_2 gas undergoes three major process steps before being transported, via pipeline, to the end users: production, purification, and compression. The purification step is performed to remove other gas and liquid contaminants from the CO_2. Although other methods have been considered, dehydration by glycol absorption has been most widely employed.

Early in 1984 an invitation was issued, by a major producer of CO_2 gas, to test the efficiency of different separation equipment on problems associated with the purification of naturally produced CO_2 and process by-products. This article presents the results of one series of tests which includes: liquid gas separation pre and post contactor, produced water purification, and unexpected hydrocarbon in glycol entrainment.

INTRODUCTION

It has been suggested that one of the greatest limiting factors for enhanced oil recovery, (EOR) via CO_2 injection would be product availability. (1) Several major oil companies have begun large scale CO_2 production facilities in Colorado, New Mexico, Wyoming, and Mississippi. Naturally produced high purity CO_2 from Colorado and New Mexico are already being supplied to EOR operations in West Texas.

Producing CO_2 from natural reservoirs has not proven unchallenging. The CO_2 from Colorado and New Mexico is considered high purity, the main contaminant in the gas being water. On the other hand, the CO_2 produced in Wyoming is a constituent of the gas being produced. It has to be separated and purified before being transported to the end user (see figure 1). (2)

CO_2 production is similar in many respects to natural gas production. The gas is produced from subsurface reservoirs. After production the gas is purified or treated to remove unwanted contaminants. The pure gas is then compressed into the liquid form and transported to the end user, via pipeline. It is the pipeline and end user specifications that dictate the

level of CO_2 purification. (2)

In March 1984, Arco Oil and Gas Company issued an invitation to test coalescing equipment in an effort to solve process problems in the Sheep Mountain CO_2 production facility. As can be seen in figure 2, tests one and two were liquid gas separation trials. Tests three and four were liquid/liquid coalescing trials. This communication presents and discusses the results of the filtration trials performed at the Arco Sheep Mountain CO_2 production facility, in southern Colorado.

Testing Background (refer to figure 2)

It was established prior to testing that as the CO_2 passed through the contactors a significant volume of triethylene glycol (TEG), 0.5gal/MMSCF, was being lost. Attempts to detect the liquid entrained in the dry gas had previously failed.

Experience with amine treatment and glycol dehydration of natural gas indicated that if the hydrocarbon level in the gas entering the contactor were high enough, foaming and subsequent carry over might take place. (3-6) This was considered unlikely because of the low hydrocarbon levels encountered in the free water removed by the pre-contactor demister. However, it was a possibility and was to be examined.

The water produced with the CO_2 was removed at the demister level as free water, and at the condenser level from glycol regeneration. Water from both sources was mixed in the produced water storage tank. The produced water had to be injected into a disposal well, as opposed to surface disposal, because of the contaminants present. It contained liquid hydrocarbon, was white in color, and had an alcohol smell.

Filtration Testing

The liquid from gas coalescing tests (no. 1 and 2), were carried out utilizing the same apparatus. The difference was in the quality of CO_2 accessed from the facility. In test number one, the gas was post contactor and considered dry. The fluid filtered in the second test was pre-contactor and considered wet.

The filters used in the first two tests were U78Y4-2 and TSM 600 disposable filter elements (AMF Cuno, Meriden, CT). The U78Y4-2 elements were gradient density depth cartridges manufactured of acrylic fibers and melamine resin. They were rated in liquid service as 1 micrometer nominal porosity. No gas rating existed for this element. It was naturally hydrophobic, but not considered by the manufacturer as a coalescing filter. The TSM 600 filter was a charge modified (+) pleated element manufactured of cellulose and inorganic

filter aid. The filter was rated at 0.75 micrometers nominal porosity in liquid service, and were naturally hydrophilic.

In both tests, the filter vessel was loaded with six filter elements. The filtration surface area was 6 square feet with the U78Y4-2 and 72 square feet with the TSM 600 elements. In each case, the vessel was placed on line and allowed to operate for approximately 15 hours prior to inspection. After this time, the vessel was opened and inspected for liquid accumulation. If no liquid was present the filters had failed and the test was terminated. If there was liquid accumulation, the amount that would drain from the housing was collected and measured. This data was considered a baseline zero point. The vessel was then closed and allowed to run four hours, after which the liquid accumulation was drained and measured.

The results of test one are given in table 1. As can be seen in this table, both the U78Y4-2 (hydrophobic) and TSM 600 (hydrophilic) filters removed liquid from the dry CO_2. After the baseline 15 hour run, the U78Y4-2 elements removed 0.14 gal/MMSCF of dry CO_2. Curiously, after the next four hour run the elements had removed 0.15 gal/SCF of gas. Arco personnel confirmed that the gas quality was constant during the test. Upon inspection, the material drained from the housing was a mixture of free liquid and foam. Per the four hour accumulation rate, the 15 hour test should have rendered 0.6 gal/MMSCF of CO_2. It was agreed that the foamy liquid accumulation above the 0.15gal level had filled the available sump area and escaped through the bottom of the filter cartridges.

The TSM 600 filter elements also removed foamy liquid from the dry CO_2. Here again, in the 15 hour test, the accumulation volume was 0.14 gal/MMSCF. To test the liquid loss through the cartridge hypothesis, after the next four hour run not only was the accumulated liquid drained from the cartridge side of the vessel, but also drained was the clean side sump. If the gas entrained liquid had in fact been coalesced by the filter and drained through the bottom of the element when that level was reached, there should be little reentrainment of the large droplets which should have dropped into the bowl shaped area below the filter diaphragm. After draining both sides of the vessel, a total volume of 0.38 gal/MMSCF was collected.

The conclusions from test number one were positive. Liquid TEG was in fact being carried over in the form of foam, and it was recoverable by filtration. Also suggested was that liquid/gas coalescers did not have to be hydrophobic or pleated to efficiently remove liquid from gas.

Test number two results are also given in table 1. The U78Y4-2 and TSM 600 filter elements removed 18.4 - 10.2 gal/MMSCF and 13.92 gal/MMSCF of gas. The suggested water content of

the pre-contactor gas was 20 gal/MMSCF. The water removed by the filter elements contained only a very slight indication of hydrocarbon. The 3.78 gal/MMSCF reading for the TSM 600 second trial was disregarded. Arco explained that the gas source to the vessel had been changed, nullifying the results from the four hour test.

The conclusion for test number two was considered positive. The water and trace hydrocarbon could be removed from the CO_2 gas by filtration prior to glycol contactor treatment.

Two different test apparatuses were utilized for the produced water tests, number 3 and 4. The first unit tested was the U78Y4-2 and filter vessel used in tests number 1 and 2. This unit was tested on the produced water because of its efficiency with gas/liquid separation. The second apparatus used in the produced water tests was a test kit (AMF Cuno, Meriden, CT) that required 90mm disc filters as opposed to cartridge filters. The test kit was self contained, including pump, and was calibrated to simulate flow conditions through full scale cartridge systems. The results of test number 2 and 3 are given in table 2.

To be acceptable, the produced water filtration system had to render the water surface disposable. The raw water was milky white with some settleable hydrocarbon and a strong alcohol odor. It was suspected that the white color was caused by an oil in water emulsion, and the odor by dissolved triethylene glycol from the contactor. A filtration trial performed by Arco Oil and Gas personnel, using AMF Cuno APll7/AC46285-1 filter cartridges, produced optically clear and odor free effluent. The subsequent analysis showed a significant variation between the raw water and the filtrate, only in the hydrocarbon content. Before filtration the oil content was 690ppm while after was reported as less than 2ppm.

In general, the test approach was to break the suspected emulsion and remove the free oil. If the emulsion were to be broken, the filter porosity had to be tight enough to capture and hold the deformable oil in water droplets (micelles), and allow them to accumulate on the filter surface. The force of the water flow and surface cohesion between like particles had to cause the micelles to pop and form a larger deformable oil particle on the surface of the filter element.

The AMF Cuno Micro-Klean #U78Y4-2 filter was the first to be tested. After approximately 15 hours of operation a 0.5gpm/ft^2 of lateral surface area, only a small amount of oil had accumulated at the top of the filter housing (approx. lqt.) and the emulsion was unbroken. The flow rate was then reduced to 0.13gpm/ft^2 and the unit allowed to operate for approximately 1.5 hours. The effluent was unchanged and the decision to try the tighter porosity Zeta Plus was made.

The AMF Cuno Zeta Plus filters were charge modified (+) cellulose matrix based filters containing other materials; i.e. glass micro-fibers and filteraids. They were considered a medium depth filter with a 5/32 inch average thickness. The first Zeta Plus filter tested was the 05U grade.

As can be seen in table 2, the 05U material had no observable effect on the emulsion. There was no detectable differential pressure, nor did any appear after approximately ten minutes of operation. According to a water analysis performed by AMF Cuno, 68% of the contaminant load (by weight) should have been in the 5-25 micrometer range. (Particle analysis rarely distinguishes deformable from solid particulates). What should have been stopped by the barrier actually deformed and passed directly through the filter.

In order to finalize the emulsion breaking capability of the Zeta Plus filter media, the tightest grade available, 90S, was used in the next trial. After the flow was initiated, the differential pressure steadily rose to 25 psig and the filter effluent was optically clear. The flow-rate was reduced from 0.8 to 0.4gpm/ft^2 of surface area after ten minutes of operation. The differential pressure dropped accordingly to 15psig. The surface of the pooled effluent had a rainbow sheen indicating a hydrocarbon film, but the vast majority of the hydrocarbon had been removed.

Knowing that the contaminant was in fact an emulsion and breakable by filtration, it was necessary to identify what porosity would allow the removal of the oil and odor, and not be plugged by existing solid particulates, if present.

Zeta Plus 60C grade was the next filter to be tested. The flow rate varied from 0.3 to 1.0gpm/ft^2 of surface area. The filter broke the emulsion, but also unloaded proportionally with throughput of water. It appeared as though the media would break the emulsion and accumulate surface bound oil up to a point where it would pass through the media and enter the flow stream as variable sized droplets of separated oil. The faster the flow rate, the more frequently the filter would unload and the smaller the droplets would be. At 0.3gpm/ft^2 the filter would unload one very large slug of accumulated oil into the flow stream. Once in the collection bottle, the oil rapidly rose to the surface of the clean water. (A total of 4.5 gallons were filtered with the 90mm 60C disc. This simulated a throughput of 77.50 gal/ft^2 without a $\triangle p$ increase observed.) The ZP 60C failed to remove the odor from the water.

The MRM Zeta Plus was tested for its ability to remove the odor by the same method soluble iron is commonly removed, i.e. oxidation. Samples showed that the element did break the emulsion, but only removed part of the smell. MRM was not judged to be a viable candidate for removing this odor.

Each grade was tested for its ability to remove the smell from the 60C effluent, break the emulsion from the raw produced water, and hold the raw separated oil coming out of the 60C filtrate. With both the R11S and the R52S filters, the odor was removed or reduced proving that carbon will work, break the emulsion from the raw water and hold the 60C effluent raw oil slugs.

As previously mentioned, Arco personnel found that by filtering the produced water through an activated carbon element (AMF Cuno, Meriden, CT) the odor could be removed. Samples of the raw produced water and the pilot system filtrate went to an independent laboratory for analysis. The results of the analysis are given in table 3. As can be seen in the table, the filtration system alone removed the bulk contaminant in each category. The results of the carbon filtration confirmed Arco's field test. The COD had been reduced from 9700ppm to less than 5.0ppm. The O&G had been reduced from 770 to undetectable. Figure 3 shows the proposed filtration system that rendered the produced water hydrocarbon and odor free and potentially surface disposable.

Oil in Glycol Problem

Samples of the liquid being sent to the produced water storage tank were examined. The analysis indicated a serious and apparently unusual problem. The water sample from the demister located at the bottom of the contactor showed a water to liquid hydrocarbon ratio of 98:2 percent by volume. This was considered a high concentration of hydrocarbon (s.g. 0.90). The sample from the condenser was milky and had to be filtered with the Zeta Plus 60C to break the emulsion. After filtration, the ratio was found to be 96% liquid hydrocarbon to 4% water. The specific gravity of the hydrocarbon was again 0.9. The liquid exiting the condenser was almost 100% by volume liquid hydrocarbon.

It was suggested that the TEG storage tank be inspected for liquid hydrocarbon. After inspection, the tank showed no floating hydrocarbon. A method could not be found that would separate non settleable liquid hydrocarbon from TEG. It was decided to take a sample of TEG from the storage tank, add an equal volume of water and mix slightly. After allowing the mixture to settle, the liquid hydrocarbon, if present, should float to the top of the container. The TEG scrubbing test revealed a 25:75 percent by volume liquid hydrocarbon to TEG ratio.

This finding reinforced the TEG carryover due to hydrocarbon theory, but the hydrocarbon causing the problem was not being introduced directly by the gas entrained water/hydrocarbon mixture from the demister. It was apparent that the hydrocarbon was being introduced into the contactor with the

recycled glycol.

Summary and Conclusion

As summary and conclusion, figure 4 illustrates a general depiction of the CO_2 dehydration flow pattern. Indicated by number on the diagram are the problem areas tested and the recommended solutions.

1. Testing indicated that 0.5gal/MMSCF of TEG could be recovered from dry CO_2 with hydrophobic depth, or hydrophilic pleated filtration media.

2. Of the estimated 20gal/MMSCF of water and hydrocarbon entering the contactor with the gas, as much as 18.4gal/MMSCF could be removed with a hydrophobic depth filter element. The hydrophilic pleated element would also coalesce the liquid from the gas.

3. The milky produced oil in water emulsion could be broken with Zeta Plus 60C filter media. The oil and water fractions could be separated with the filtration system.

4. The odor remaining in the produced water could be removed with activated carbon. The organic's level could be reduced to extremely low levels for possible surface disposal of the produced water.

5. Unexpectedly, a liquid hydrocarbon in TEG entrainment existed in the surge tank supplying the dehydration contactor. A water scrubbing method for the separation of entrained liquid hydrocarbon in TEG was developed and used to detect the problem.

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Table 1
CO_2 Filtration Test Results - ARCO Sheep Mountain Project

FILTER ELEMENT	MATERIAL[a] REMOVED	AMOUNT RECOVERED ACTUAL (L)	L/FT^2	AMOUNT FROM 1X10^6 SCF (GAL)	FLOW RATE(SCFM) HSG(X10^2)	/IN^3	TOTAL GAS THROUGHPUT	RUNNING TIME (HRS)
U78Y4	TEG	0.187L	0.03	0.14	4.01X10^2	1.21	3.52X10^{5}SCF	14.5
U78Y4	TEG	0.100L	0.014	0.15	7.13X10^2	2.12	1.71X10^{5}SCF	4
U78Y4	H_2O	1.685L	0.23	18.4	4.05X10^2	1.21	2.43X10^{4}SCF	1
U78Y4	H_2O	1.590L	0.22	10.2	6.83X10^2	2.04	4.1X10^{4}SCF	1
ZP TSM 600	TEG	0.190L	0.038	0.14	4.01X10^2	U/A	3.6X10^{5}SCF	15
ZP TSM 600	TEG	0.150L	0.03	0.38	4.4X10^2	U/A	1.05X10^{5}SCF	4
ZP TSM 600	H_2O	1.375L	0.03	13.92	4.35X10^2	U/A	2.61X10^{4}SCF	1
ZP TSM 600	H_2O	0.685L	0.14	3.78	7.98X10^2	U/A	4.79X10^{4}SCF	1

a. TEG = TRIETHYLENE GLYCOL, H_2O = WATER

Table 2
Produced Water Filtration Test

FILTER ELEMENT	FLOW RATE (GPM/FT^2)	P (PSIG)	EFFLUENT DESCRIPTION
U78Y4(1.0)	0.5	2	NO EMULSION BROKEN, SOME ACCUMULATED OIL
U78Y4(1.0)	0.13	0	NO EMULSION BROKEN
ZP90S(0.2)	0.8	25	OPTICALLY CLEAR EFFLUENT, NO APPARENT OIL FILM ON SURFACE
ZP90S(0.2)	0.4	15	" " " , SLIGHT OIL FILM
ZP60C(0.8)	0.9	17	" " " , FILTER UNLOADING AFTER 0.5 GAL AS DROPLETS IN FLOW STREAM
ZP60C(0.8	0.3	11	" " " , FILTER UNLOADING IN LARGE SLUGS LESS FREQUENTLY
ZP60C(0.8)	1.0	10	" " " , SLIGHT OIL FILM ON SURFACE
ZP60C(0.8)	0.5	10	" " " , FILTER UNLOADING LESS FREQUENTLY, SLIGHT SURFACE FILM
ZPR11S(4.0)	0.7	1	" " " , EMULSION BROKEN, AFTER 60C NO SMELL APPARENT
ZPR52S(1.0)	0.6	4	" " " , HELD RAW OIL SLUG TEST, NO SURFACE FILM
ZP MRM(5.0)	1.0	4	" " " , EMULSION BROKEN, SLIGHT SURFACE FILM, SMELL SLIGHTLY
ZP05U(7.0)	0.8	0	NO EMULSION BROKEN

Table 3
Produced Water Analysis

TEST	RAW(PPM)	FILTRATE(SYS)	CARBON
BOD	800	375	--
COD	9700	2100	0-5.0
TOC	3980	1930	--
O&G	770	10	0

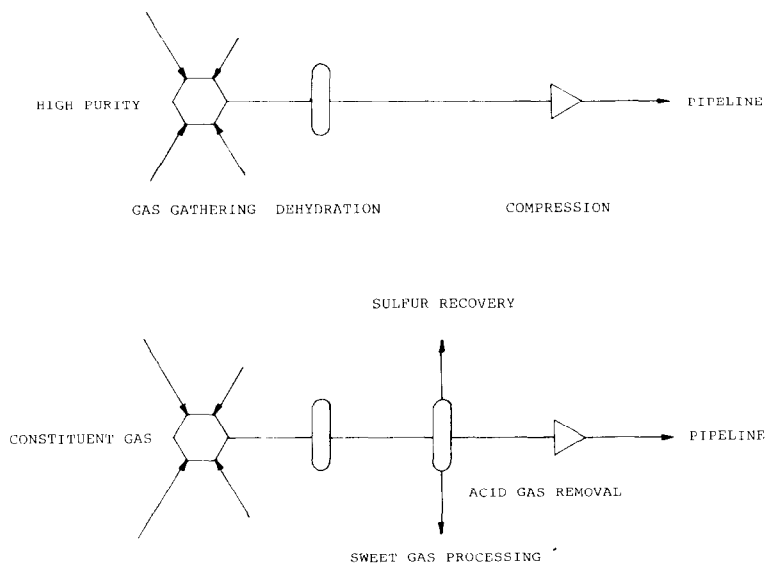


Figure 1 - High purity and constituent CO_2 processing

Test #1. Objective - glycol recovery from dry gas

1. pressure 880psig
2. temperature 90 F
3. gas density 8.3#/ft³
4. flow rate 80MMSCF
5. line size 11.5"
6. TEG loss 0.5gal/MMSCF

Test #2. Objective - water and trace hydrocarbon removal from wet gas

1. pressure 880psig
2. temperature 90 F
3. flow rate 80MMSCF
4. water content 20gal/MMSCF

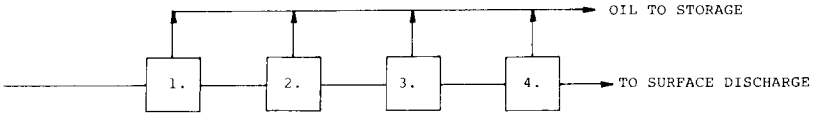
Test #3. Objective - oil removal from produced water

1. produce and maintain 8ppm oil in water
2. 80bpd production
3. oil present 40-2000ppm

Test #4. Objective - odor removal from produced water

1. installed downstream of coalescing unit
2. 80bpd production

Figure 2 - Test condition outline



1. FILTER VESSEL WITH ZETA PLUS 60C FILTER MEDIA TO COALESCE EMULSIFIED OIL.
2. FREE OIL ACCUMULATION TANK.
3. ACTIVATED CARBON VESSEL FOR TRACE OIL AND ODOR REMOVAL.
4. FILTER VESSEL WITH ZETA PLUS 60C FILTER MEDIA TO POLISH WATER AND GUARD AGAINST OIL LEAKAGE FROM THE SYSTEM.

Figure 3 - Produced water filtration system

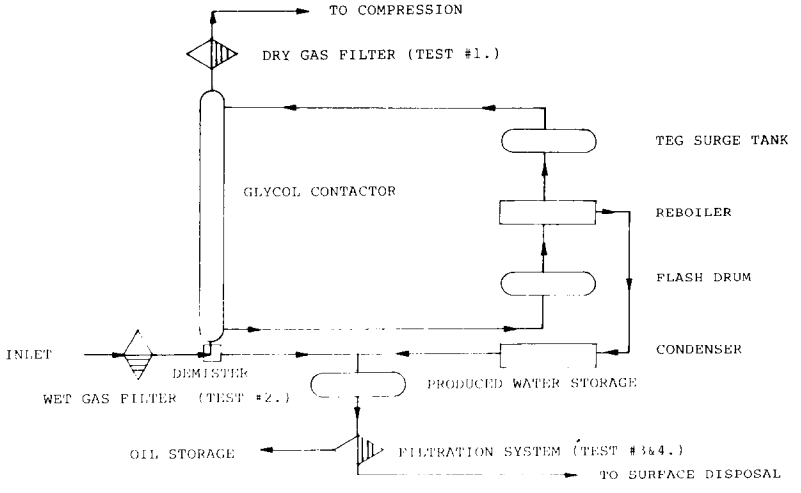


Figure 4 - Glycol system summary