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Benefits Of A Mixed CO₂/CO/N₂ Gas For EOR

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Abstract

Benefits Of A Mixed CO₂/CO/N₂ Gas For EOR

Achieving maximum oil recovery utilizing CO₂ has limitations when operating at, or very close, to the Minimum Miscibility Pressure (MMP) of the CO₂ in the oil. A modular source of CO₂ would allow Enhanced Oil Recovery (EOR) flooding of “stranded” and shallow reservoirs. Unfortunately modular sources of CO₂ production often include CO and N₂ mixed with the CO₂. Thus, testing for EOR application of a mixed gas- containing CO₂, N₂ and CO was initiated.

Bench scale testing using Rising Bubble Apparatus (RBA), Slim Tubes, and linear core floods have been conducted on oils ranging from 16-42^o gravities and having viscosities of 0.5-250 cp. All tests were conducted at reservoir temperatures and pressures. CO, being a strong reducing agent, was further tested on reservoir rock containing swelling clays with hydrated ferric hydroxides. Due to the apparent reduction of the ferric hydroxide, and the liberation of its water of hydration, an increase in matrix permeability and clay stabilization, was observed.

For most oils tested, the CO₂/CO mixture increased rate of oil recovery by 2-3X, using approximately 60% as much gas/bo as compared to pure CO₂. Recovery factors of 80%, at immiscible pressures 30-40% below CO₂ MMP, were achieved. Addition of 15% N₂ (v/v) to the CO₂/CO mixture did not impair oil recovery. Interfacial testing (IFT) of oils, using pure CO, demonstrated a lowering of the IFT. RBA testing of asphaltine-rich heavy oils has shown that a mixture of CO₂/CO dissolves into the oil at a far faster rate than either CO₂ or CO individually and faster than the sum of both individual gases. A similar test using non-asphaltine type oils did not display this unique characteristic. Slim tube testing suggests that CO facilitates the mobilization of asphaltine-rich heavy oils and lowers viscosity. Linear corefloods of a reservoir containing 5% smectite + illite/smectite + and chlorite demonstrated a 275% increase in matrix permeability. Packed column tests, containing quartz sand and bentonite, demonstrated up to 900% increase in permeability in the presence of CO.

A method to recover oil faster, from stranded reservoirs, at pressures below MMP, using significantly less gas, appears possible. In addition the use of CO, either alone or in combination with CO₂ and/or N₂, has been shown to increase matrix permeability. Such a gas mixture may be beneficial to achieving low pressure EOR from shallow, “stranded” reservoirs, non-conventional shale oil reservoirs, and viscous, heavy oil reservoirs at low temperatures. Incorporation of CO, or CO₂/CO, in a frac fluid, or alternately as a post frac cleanup for shale oil and gas applications appears to warrant investigation.

Introduction

US DOE has estimated 34 billion BO exist in stranded reservoirs that are not located close to an existing CO₂ source. A modular source that produces CO₂ by burning essentially pure oxygen to minimize N₂ content was investigated. The modular source can utilize either coal, natural gas, or NGL; however, the cost to extract pure CO₂ from the produced gas was deemed prohibitively expensive. Common associated gases are CO, N₂, and H₂. Laboratory investigations for EOR applications utilizing this mixed gas of CO₂/CO/N₂/H₂ were compared to pure CO₂. Interestingly, the application of CO for aiding oil recovery appears to have generally been ignored. Thus, the chemistry of CO, as related to aiding oil recovery and as a component in a mixed gas, was investigated.

Laboratory studies were conducted to define basic CO-crude oil interactions such as Interfacial Tension (IFT) effects, thermodynamic evaluations of CO on ferric ion oxides and hydroxides, and rates of gas solubilization into a crude oil. Slim tube testing compared rate and volume of oil recovery under immiscible conditions for the mixed gas and pure CO₂. In addition, packed column and linear core flooding were used to evaluate the potential of CO to increase matrix permeability in a reservoir having swelling and/or water-damaged clays.

Critical temperature for CO is -222° F, thus achieving MMP for the mixed gas at normal reservoir conditions is unlikely. Immiscible, low pressure EOR, may demonstrate significant economic advantages.

Bench scale testing was conducted on oils ranging from 16.4-42° gravity having viscosities ranging from 1.0-280 cp. The heavier oils were asphaltine-rich, whereas the lighter oils were predominately paraffinic with minor aromatic components.

Purpose of all testing was to evaluate the potential technical feasibility of utilizing the mixed gas for EOR. Detailed follow-up testing is recommended on any future oil sample prior to conducting a field pilot test.

Chemical Characteristics of CO

CO is a unique, triple bonded, molecule. The triple bond allows shifting of the electron cloud between both the carbon and oxygen atoms. Thus, the electronegative dipole moment for the CO molecule can switch from the carbon atom to the oxygen atom, depending on CO's environment.

Compared to CO₂'s 44 g/mole, CO has a molecular weight of 28 g/mole. Molecular diameters for CO₂ and CO are 232 pm and 112 pm. CO's smaller molecular diameter may thus allow faster movement through a reservoir and greater access to clay-rich, lower permeability zones as compared to pure CO₂.

CO has been shown to help mitigate corrosion of steels in acidic conditions (Cabello, et al, 2013). Thus,

incorporation of CO in oilfield operations may be very beneficial, especially in the presence of CO₂. However, additional testing under oilfield conditions must be completed.

CO is far less soluble in water than is CO₂. Their ratio of solubilities is: CO₂/CO = 44/1. Thus CO may migrate from the aqueous zone into the tighter, low permeability, poorly swept zone, thereby recovering bypassed oil.

Of significant interest is the apparent higher solubility of CO in aromatic ring compounds as compared to paraffinic compounds (U.J. Jauregui-Haza, 2004, Luhring, 1989, and Koelliker, 1993). Tests were therefore conducted to investigate the potential for CO to mitigate asphaltine-related problems, and to recover heavy, asphaltine-rich crudes at low, reservoir temperatures.

Thermodynamics strongly favors CO as a reducing agent for ferric oxide/hydroxide molecules, thus liberating the attached water and shrinking their molecular diameter. Swelling clays (smectite, smectite/illite, montmorillonite, and bentonite) have significant amounts of ferric oxides/hydroxides both interlayer and especially on clay margins. Shrinkage of the ferric compounds would promote clay stabilization and increased reservoir matrix permeability. This could be a significant factor in increasing oil recovery from unconventional shale oil/gas reservoirs and glauconitic reservoirs. Due to the reducing capabilities of the CO, retardation of tubular corrosion in the presence of CO₂ and water warrants additional investigation. Thus, blending steam floods with a CO₂/CO mixture, below the MMP of pure CO₂, may be both economically and environmentally beneficial.

Description and Application of Equipment, Processes, and Crude Oils

Crude oils were obtained from a Kansas heavy oil field (22° API, 143 cp); the Schrader Bluff Milne Point Alaska heavy oil (16.1-18.0°API, 122-250 cp); the Grieve Field Muddy sandstone from Wyoming (33°API, 5 cp); the Morton Field Sussex formation light oil (38°API, 3.9 cp), and a light pinnacle reef Michigan oil. Purpose was to test the applicability of a mixed gas on a wide variety of oil types ranging from the viscous, highly asphaltic Kansas McClouth formation to the shallow, light paraffinic Wyoming Morton Field and Michigan crudes.

Two mixed gas compositions (on a volumetric basis) were used: Mixed Gas #1 contained 52% CO₂, 27% CO, 12% H₂, 7% N₂, 1% O₂, and 0.15% CH₄, whereas Mixed Gas #2 contained 66% CO₂ and 34% CO with no other gases.

Bench scale testing utilized Rising Bubble Apparatus (RBA); Slim Tube testing, Interfacial Tension (IFT) analysis, packed column testing, and linear core flooding.

Rising Bubble Apparatus (RBA)

Equipment for the RBA consisted of a glass tube 28 cm long, 0.5 cm wide, and 1 mm thick, equipped with cylindrical ends. Gas was injected in the water phase of the RBA tube and filmed throughout its ascent into the oil phase. Temperature and pressure were maintained within the enclosure to replicate reservoir conditions.

The RBA was employed to determine the rate of gas dissolution into the oil. Both individual gases and a mixture of gases were used to suggest the most efficacious ratios of CO₂:CO:N₂ to maximize oil recovery. To achieve reproducibility, tests were repeated a maximum of 3 times prior to replacing with fresh oil. Rates of dissolution (ROD) in a crude oil of individual gases were compared to the ROD of

the mixed gas.

Slim Tube Testing

Slim tube testing utilized a constant volume, constant pressure pump capable of injecting gas into the slim tube at reservoir temperature. A backpressure regulator controlled outlet pressure. Tests required 5-20 hours of constant monitoring. The slim tube consisted of a 60 ft. ¼" diameter, coiled, stainless steel tubing packed with varying mesh sands ranging from 140 to 230 mesh. The range in meshes allowed for achieving different slim tube permeabilities ranging from 0.8-2.5 Darcies. A 10 ft slim tube was also utilized to expedite testing of heavy, viscous oils. Produced fluids were directed to a graduated cylinder and both the rate and volume of produced fluids were recorded.

Slim tube procedures involved injection of 1.25 PV of as-received crude at reservoir pressures and temperatures under immiscible conditions. Mixed gas was then injected at 0.1 ml/min into the oil filled slim tube. Following the completion of the slim tube test, 2-4 PV of hexane was injected to displace any residual oil. Oil content in the produced hexane was determined after a low temperature evaporation of the hexane. Following hexane injection, a vacuum was applied for a period of 48-72 hours to remove all residual hexane from the slim tube. If formation water had also been injected as part of a slim tube test, a hexane flush, followed by a methanol flush, and then a second hexane flush was conducted. Analysis of the produced gases as a function of PV injected was also measured as deemed required.

Interfacial Tension (IFT) Measurements

IFT's of a crude oil and formation water after CO introduction were determined by Surtek, Inc., a third party laboratory, using the duNois ring apparatus. Viscosity and API gravity of both the as-received oil and the produced oil were also determined.

Packed Column Experiments

Packed column experiments were conducted by a CSM graduate student in fulfillment of the MS requirements. The column was 17 cm X 2.5 cm. Columns were filled with a mixture of 95% sand (typically 140-150 mesh Brea sand) and 5% (v/v) bentonite having a porosity of 35%. Injected brines, having 50,000 ppm sodium chloride content, were found to induce formation damage by reducing permeability to ~4.5 md from the initial 110 md. Following brine injection, gravity and vacuum-aided drainage occurred, followed by injection 2-4 PV of CO. The system was shut in for a soak time of 48-96 hours. A second slug of 50,000 ppm NaCl was then injected and the permeability measured to compare pre and post CO injection effects. Injection pressures varied from 1000-1500 psi and backpressures ranged from 500-750 psi. To determine the effects of CO permeability on a 3 phase condition (50,000 ppm brine, residual oil, and CO) a fresh column was prepared. The sequence of injection consisted of brine injection followed by injection of a 36° API oil having a viscosity of 3.90 cp. The packed column was placed under a vacuum to assist drainage, then flushed with 3+ PV of the 50,000 ppm brine solution to achieve residual oil saturation. Next the column was injected with 2-3 PV of CO and allowed to soak for 96 hours. A vacuum was then applied to remove any residual free CO. Finally 3 PV of the brine was again injected and the relative permeability measured to compare pre- and post- CO treatment effects.

Linear Core Flooding

Surtek, Inc. conducted the linear core flood testing. Equipment consisted of a Ruska pump injecting

fluids into a 12.5 X 2.5 cm core plug held in a stainless steel core holder equipped with numerous pressure monitoring positioned along the length of the core holder. Depth of the preserved Cretaceous Muddy Formation core was 9359 ft. The core had spotty oil shows, contained 1.4% smectite/illite, 1.6% chlorite, 1.1% illite/mica, and 4.2% kaolinite, along with 89.2% quartz and 2.2% siderite. The core was saturated with synthetic formation water having 18,143 TDS, and placed in the core holder under 2000 psig confining pressure. Injection pressure of the water was ~ 1000 psig. Back pressure was set at 400 psig. Additional synthetic formation water was then injected to determine effective permeability to water at reservoir temperature of 120° F. Next 1.5 PV of CO was injected and effective permeability to CO determined. The system was shut in for 48 hours to allow reaction with the core. CO injection was then resumed and the post CO permeability determined. Finally, synthetic formation water was injected and produced to determine any permeability changes due to the CO treatment.

Results for the IFT, Packed Column Permeability Remediation, Linear Core Flood, RBA, and Slim Tube Testing are Shown Below

The above equipment and test procedures were thus designed to determine the following factors:

- 1) Change in the produced oil viscosities and API gravities due to mixed gas flooding;
- 2) CO remediation of an oil reservoir containing swelling clays that has suffered formation damage due to fresh water flooding;
- 3) Recovery of residual oil after ~50% of a PV of mixed gas was injected followed by a Water Alternating Gas (WAG) injection;
- 4) Compare the rates and volumes of oil recovery of mixed gas compared to pure CO₂ at pressures below CO₂ MMP;
- 5) Compare the rates and volumes of oil recovery by a mixed gas versus pure CO₂ under residual oil conditions;
- 6) Effect of a Huff-n-Puff recovery of a heavy oil using a 10' slim tube;

Interfacial Tension Data

The potential effects of pure CO on the IFT of the 32° Grieve crude oil, was determined by a third party lab using the duNoy Ring IFT testing apparatus. Sample preparation consisted of bubbling pure CO through a 12 inch tall by 1 inch wide column containing both formation water and crude oil for 15 minutes at atmospheric pressures. IFT testing was completed by Surtek, Inc. on the non-treated, and the CO treated, sample.

Even at atmospheric conditions, the CO achieved a lowering of the IFT by approximately 15% from 18.8 to 15.9. Solubility of CO in at atmospheric pressure was < 1600 ppm whereas calculated solubility at 2000 psi reservoir condition would be approximately 52,000 ppm. Solubility at atmospheric pressure is 28 ppm CO versus ~3000 ppm at 2000 psi. Thus the lowering of IFT, at reservoir conditions in the presence of CO, would be expected to significantly increase.

Figure 1 shows the water leg in the glass RBA tube having small droplets of Kansas asphaltine-rich paraffinic, heavy oil clinging to the glass sidewall at 1000 psi and 135°F. A rising bubble of pure CO encounters these droplets and results in decrease in the IFT as evidenced by the smearing out of the oil droplets along the silica glass sidewalls. MMP of the Kansas oil, as determined by RBA testing was 2045 psi. Smearing of the oil droplets occurred at <60% of pure CO₂ MMP.

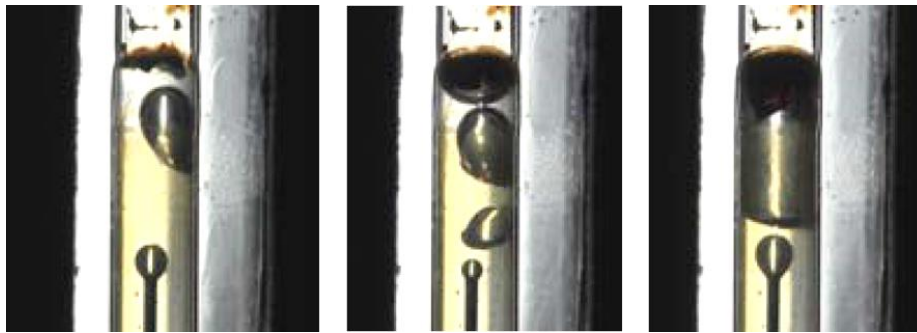


Figure 1-IFT lowering by CO (20° gravity, viscous oil, 700 psi, 95°F, ~50% asphaltenes, formation ater)

Packed Column Tests to Remediate Water-Damaged Oil Reservoirs and Increase Matrix Permeability

Markey, CSM, 2015, 1234567) investigated the use of CO to: 1) facilitate 4D seismic evaluations of a steam reservoir at an early stage of flooding, and 2) to reverse the induced formation damage caused by swelling clays in contact with condensed steam.

Original permeability for 100,000 ppm NaCl salinity showed 108 md. Lowering the salinity to 50,000 ppm decreased permeability to 4-22 md. Fresh water addition effectively resulted in <0.1 md of permeability. Injection of pure CO into the water-damaged packed column was conducted to determine if formation damage and loss of permeability could be reversed.

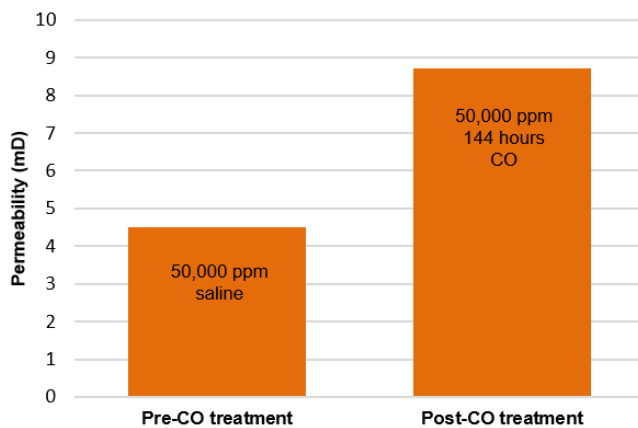


Figure 2-CO remediation of water damaged packed column (2 phase)

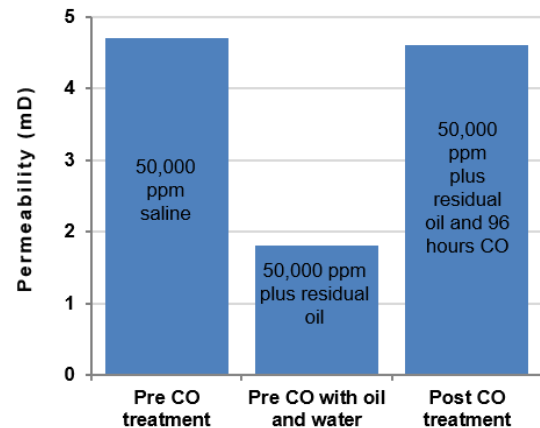


Figure 3-CO remediation of water damaged packed column (3 phase)

As shown in Figure 2, the original permeability of a freshly prepared packed column, after injection of 50,000 ppm NaCl brine, was 4.5 md. After injection of CO, and then re-injection of the brine, permeability had increase to 8.7 md or almost a doubling in permeability. The experiment was repeated to determine the effect of CO on a brine-residual oil packed column. Results in Figure 3 demonstrate permeability post CO treatment for 3 phase conditions. Permabilities were 4.7 md post brine injection, 1.8 md post oil injection and 4.5 md post CO injection/treatment. Thus the relative permeability for the brine-oil test was 1.8 md, whereas after CO treatment the relative permeability for the brine-oil increased from 1.8 md to 4.5 md or almost the same as the absolute permeability of the brine. Testing was repeated 3 times to insure reproducibility of the results.

Linear Core Flood Testing to Determine CO Effect on Increasing Matrix Permeability

A linear core flood using preserved core from an oil producing zone of the Muddy SS (Wyoming) was conducted. The core contained 8.3 % total clays and 2.2% siderite. The 8.3% total clays consisted of 1.4% smectite/illite, 1.08% illite, 1.6% chlorite, and 4.2% kaolinite. The concept tested was the ability of CO to shrink the strongly hydrated ferric hydroxides associated with smectite/illite and possibly the chlorite. Since the reservoir pore throats could be lined by such clays, shrinkage would increase matrix permeability. A secondary goal was to determine if any clay mobilization occurred.

Increasing matrix permeability of any reservoir rock will significantly aid oil/gas recovery. However it is especially important for unconventional reservoirs having extremely low permabilities but possessing high swelling clay contents.

<u>CONDITIONS</u>	<u>mD</u>
Initial Gas Perm	0.0004
After CO Treatment (275%)	0.0011
Initial Water Perm	0.0091
After CO Treatment (168%)	0.0153

Note: all perms are relative permeable

Table 1-Increase in matrix permeability of a preserved core

As seen in Table 1 the matrix permeability for the preserved Muddy sandstone core, obtained from the Denver Basin in southern Wyoming, demonstrated 168% increase in relative permeability for synthetic formation water after CO treatment, whereas the gas permeability increased by 275%.

Rising Bubble Test Results

Crude oils were tested by the RBA method to determine the rate of dissolution (ROD) of the gas into crude oil. The ROD compared the relative solubility of the mixed gas versus the pure gases of CO₂, CO, and N₂. In addition, the rate of dissolution (ROD) allowed a method of comparison between different oils for their EOR potential using a mixed gas versus a single gas.

Volume reduction and calculated ROD of a rising bubble, as it traversed the 25 cm RBA tube, were determined. However, due to differing initial bubble sizes, API gravity differences, and experimental temperatures, volume reduction was deemed not a reliable indicator of the potential solubility of the mixed gas into the tested oil. Instead, the dissolution rate was considered to be an appropriate means for categorizing the different oils and determining ratios of CO₂:CO for future slim tube testing. Not all oils were subjected to RBA testing due to the unavailability of RBA equipment early in the program.

Results of three crude oils having significantly different API, viscosities, and compositions were evaluated. A heavy oil was obtained from Kansas, a medium crude from the Wyoming Grieve field, and a lighter oil from the Morton Field in Wyoming.

RBA tests with pressures up to 5000 psi, the equipment limits, showed Mixed Gas #2 did not obtain miscibility for the Grieve oil, whereas for pure CO₂ the MMP was 2035 psi.

Dissolution of Gases in Heavy Crude Oils				
Asphaltene > 20%			Asphaltene > -10%	
Kentucky Heavy Oil			Schrader Bluff	
Psi	N ₂	CO	CO ₂	Mixed Gas
450		0.82	0.23	2.30
500				
530	0.83			
600				
1200				
1800			0.23	0.39
				0.56

Table 2-Rate of Dissolution (ROD) of heavy asphaltene-rich crude

Dissolution of Gases in Light Crude Oils		
Morton Oil		Grieve Oil
(Paraffinic)		(Paraffinic)
Psi	Mixed Gas	Mixed Gas
250	27	
500	31.4	25.0
750		25.0

Table 3-Rate of Dissolution (ROD) of light paraffinic crude

The difference in ROD is significant between heavy asphaltene-rich oils and lighter paraffinic oils (Tables 2 and 3). Heavy oils showed an order of magnitude less ROD as compared to the lighter oils. The ROD for the CO exceeded the ROD for CO₂ in the asphaltene-rich crudes, whereas, for paraffinic crudes the reverse was observed. Interestingly, the combined ROD for the CO and CO₂ was only 1.05 mm³/min as compared to the Mixed Gas #2 (66% CO₂ and 34% CO) showing a 2.30 mm³/min ROD. This rapid dissolution of the mixed gas, compared to each individual gas, may suggest the chemistry of the CO is not only interacting with the asphaltene electron cloud but the CO could be “pulling” or catalytically aiding the inclusion of CO₂ into the oil phase. Slim tube testing of the Schrader Bluff heavy oil also suggests an interaction is present and aids the mobilization of asphaltines (please refer to following Slim Tube Results section). Thus the presence of CO may be beneficial to heavy oil recovery.

Table 3 lists the ROD for a medium (Grieve Oil 32°API) and a Wyoming light oil (Morton 38° API). As expected, the Morton ROD results demonstrated an increased ROD as the pressure increased, whereas the Grieve oil did not increase. Additional testing verified the initial results.

Based upon the data presented in Tables 2 and 3, the following preliminary observations should be subject to additional investigations:

1. Presence of CO appears to interact with asphaltines;
2. CO dissolves into an asphaltene-rich oil at a faster rate than does CO₂;
3. The combined CO₂/CO mixed gas has a ROD 2.2 X faster than the sum of its component gases;
4. Based upon the heavy oil ROD the CO₂:CO ratio should be increased to closer to 50:50 as opposed to 66:34.
5. RBA has shown pressures up to 5000 psi do not achieve miscible conditions for the Grieve oil which has a CO₂ MMP of 2045 psi.

Slim Tube Test Results

Slim tube testing under immiscible conditions was conducted on various crude oils to evaluate the following:

1. comparison of mixed gas vs. pure CO₂ for the rate and volume of oil recovered;
2. comparison of mixed gas vs. pure CO₂ under residual oil conditions;
3. comparison of oil recovery using pure CO, followed by pure CO₂ vs pure CO₂ to determine if pretreatment with pure CO, as a preflush would adversely affect total oil recovery for the Mixed Gas #1;

4. use of slim tube to evaluate heavy, asphaltine-rich oil recoveries by both Huff-n-Puff and Line Drive methods.

Comparison of Rates and Volumes of Oil Recovery

Using the 60 ft slim tube and 43° API Michigan oil, four immiscible tests at 75.3% and 93.7% of CO₂ MMP were completed using Mixed Gas #1. Results of all four tests are shown in Figures 4 & 5.

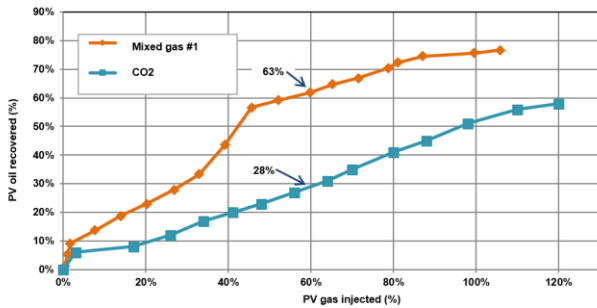


Figure 4-Slim tube rate and volume of MI oil recovery at 900 psi

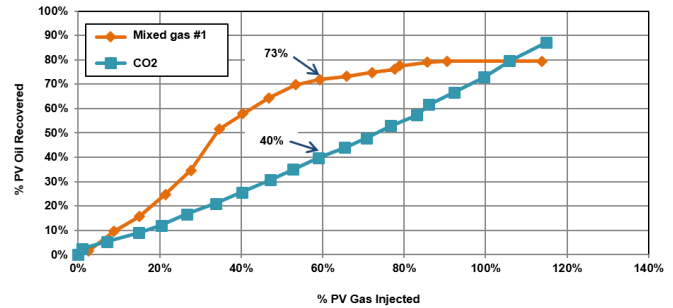


Figure 5-Slim tube rate and volume of MI oil recovery at 1120 psi

Based on the above test results, the rate of oil recovery for Mixed Gas # 1 was 1.7-2.2 X faster than pure CO₂. In addition at 900 psi, 60% of a PV of mixed gas injected recovered 63% of the oil PV whereas the pure CO₂ recovered only 28% of the oil PV. Similarly at 1120 psi (or 94% of CO₂ MMP) and 57% PV of mixed gas injected, the Mixed Gas #1 recovered 73% of the oil PV compared to only 42% of the oil PV recovery by pure CO₂.

A potentially significant economic advantage is thus indicated based on BO recovered/ mcf gas injected. Thus the Mixed Gas #1 demonstrated both a faster rate of oil recovery and a higher total volume of oil recovery under immiscible conditions as compared to pure CO₂.

A similar test was conducted on the 33° API Grieve crude oil. The test was run at 71% of the Grieve oil CO₂ MMP. Results were similar to those above. Mixed Gas #1 recovered 82% of the oil in place after 1.2 PV injected, whereas the CO₂ only recovered 43% of the oil in place after 1.2 PV injected. Thus a different oil also showed the beneficial effects of a mixed gas to achieve both faster rates and increased volumes of oil recovery as compared to pure CO₂.

Effects of a Mixed Gas vs CO₂ on a Residual Oil Saturation Condition

Slim tube testing of the Grieve oil was conducted to compare EOR post-water flood oil recoveries using Mixed Gas #1 and pure CO₂ at pressures approximately 88% of CO₂ MMP. The sequence of the flood involved: (1) injection of Grieve oil into the 60' slim tube, (2) injection of formation water to a point of 1% oil cut, i.e. residual oil saturation, (3) injection of the mixed gas into the slim tube, (4) production of the fluids, and (5) repeat of steps 1-4 with pure CO₂. Thus a 3 phase situation was present, similar to most field conditions. Past experiences of using pure CO₂ in conjunction with a water flood at < CO₂ MMP has shown marginal success. This test was designed to provide preliminary information on the potential for Enhanced Water Flooding, using a mixed gas, for certain reservoirs to achieve early oil recovery below CO₂ MMP.

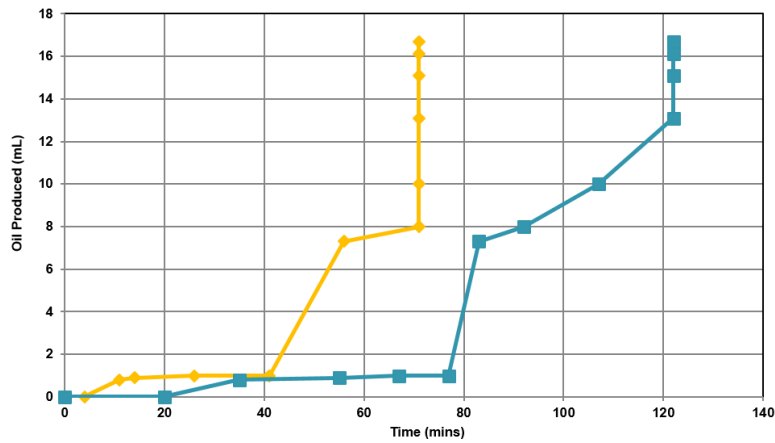


Figure 6-Slim tube three phase (oil, water, gas) test results

Results were very encouraging. The Mixed Gas #1 recovered similar amounts of total oil as pure CO₂ but 1.7X faster than pure CO₂. This test also provided initial information that the mixed gas was compatible with 3 phase reservoir conditions. Additional investigations should therefore be conducted to determine the technical feasibility of a mixed gas, low pressure enhanced water flood for marginally economic water floods.

Pure CO vs Pure CO₂ Oil Recovery

The pervious slim tube testing has demonstrated the mixed gas’ capability of achieving faster rates of oil recovery as compared to pure CO₂. This slim tube test sequence evaluated the rate and volume of oil recovery using only pure CO. Secondly, the test evaluated CO as a preflush to expedite oil recovery and cash flow, but followed by pure CO₂ to maximize ultimate oil recovery. Such a situation may be very beneficial even if minor amounts of swelling clays are present in the reservoir, or alternately if the reservoir was previously flooded with a fresh water source causing formation damage and loss of permeability.

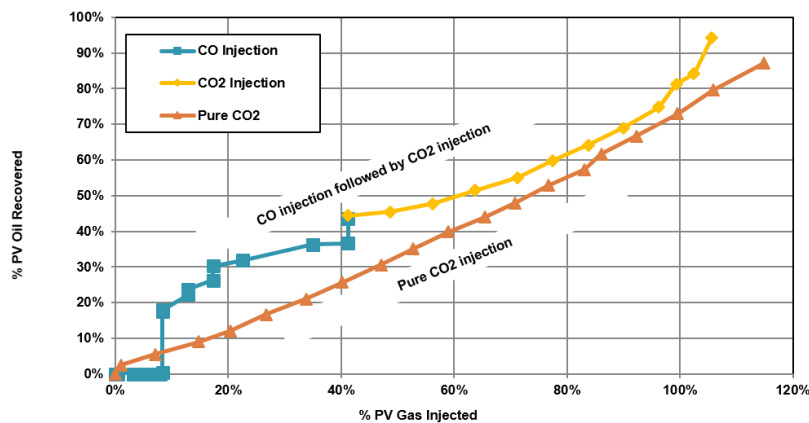


Figure 7-Slim tube CO oil recovery plus CO2 oil recovery

CO, by itself, is therefore initially capable of achieving oil recovery at a faster rate than pure CO₂. However pure CO results in rapid gas breakthrough, thus limiting the total volume of oil recovery as compared to either pure CO₂. However, after CO breakthrough, the addition of pure CO₂ was successful in recovering more oil and at a faster rate, than did a pure CO₂ flood from the inception.

Slim Tube Results for Heavy Oils

Two heavy oils were tested using the 10 ft. slim tube. The North Slope Alaska, Schrader Bluff Fm., 16.1-18° API gravity, 122- 281 cp oil, and a Kansas McClouth Fm., 22° API gravity, 143 cp oil. Although both oils contained asphaltines, the Kansas oil contained a higher concentration of asphaltines.

The Schrader Bluff oil was subjected to 0.87 PV Mixed Gas #2 injection as a line drive, followed by a 0.45 PV WAG injection at the reservoir temperature of 80°F. As seen in Table 4, the mixed gas appears to have stripped the lighter ends of the crude increasing the oil gravity by 8% and decreasing the viscosity by 25% at reservoir pressures and temperatures. Surprisingly the WAG flood mobilized the heavier oil fractions, as evidenced by the produced oil having an 11% lower oil gravity. Furthermore, the WAG recovered oil demonstrated a drop in viscosity of 8% as compared to the original crude oil and after having the lighter ends previously stripped by the line drive.

Total oil recovery of 85% was observed by the Schrader Bluff line drive/WAG injection are shown in Table 4.

A Huff-n-Puff test was also conducted on the Schrader Bluff crude oil using the 10' slim tube. This test used oil from a different well than that used for the line drive/WAG test. API gravity was 16.1° and viscosity was 281 cp for this second Schrader Bluff crude. After injection of the crude oil, 3 PV of Mixed Gas #2 were injected and allowed to soak for 48 hours prior to flowback. After flowback a total of 85% of the oil PV was recovered. Recovered oil had API gravity of 20.1° and 119 cp. Drops in viscosity and increases in API gravity were thus observed for both the Schrader Bluff line drive/WAG and the Huff-n-Puff tests conducted at reservoir temperatures and pressures.

The Kansas heavy oil Huff-n-Puff test also used the 10' slim tube. After injection of the heavy crude, 3 PV of Mixed Gas #2 were injected at 92° F and 500 psi and allowed to soak 80 hours prior to flowback. After dropping the outlet pressure to 0 psi, and waiting 18 hours, a total of 81.5% of the PV of oil was recovered. Recovered oil showed a 7% increase in gravity and a 6% drop in viscosity as compared to the original crude oil. This consistent increase in oil gravity and decrease in viscosity for both the Kansas and the North Slope recovered oils by the Mixed Gas #2 supports the positive effect of CO on heavy oil recovery at low temperatures.

Mixed Gas #2 SLIMTUBE TEST
Schrader Bluff Line Drive WAG/Flood

Oil Analysis % Recovery

	<u>AS RECD</u>	<u>Mixed Gas #2 Recovery</u>	<u>WAG Recovery</u>	<u>Total Recovery %PV</u>
API° Gravity	18.5	20.0	16.4	
VISC.@ 80° F	122 cp	91 cp	112 cp	
PV Injected		0.87	0.45	
% Recovery		42.0%	43.0%	85%

Table 4-Schrader Bluff slimtube test results with Mixed Gas #2

CONCLUSIONS

Based on laboratory test results, EOR using a mixed gas, at immiscible conditions, has very beneficial results for EOR of both light and heavy crude oils. The mixed gases recovered oil faster using significantly less gas/BO recovered as compared to pure CO₂. Typically, the mixed gas recovered approximately 80-85% as much oil as did pure CO₂; however, since the recovery occurs early in the flood, project economics could be greatly enhanced.

These positive results were obtained both in the presence and absence of significant amounts of N₂ and H₂ present in the mixed gas. Such similar positive results strongly suggest the presence of CO is the major contributing positive factor, even in the presence of both N₂ and H₂.

Medium to light API gravity oil testing with Mixed Gas #1 containing N₂ and H₂, showed a ~2X faster recovery with a mixed gas containing CO as compared to pure CO₂. Preliminary testing has also shown approximately 2X more oil recovered per PV of mixed gas injected as compared to pure CO₂.

Thermodynamics, packed column testing and a linear core floods all demonstrated the ability of CO to achieve an increase in matrix permeability when swelling clays (or glauconite) are present. Packed column testing showed remediation of a water damaged swelling clays is achievable. For residual oil situations, the relative permeability increased by almost 300%. Linear corefloods of a preserved core reservoir rock, containing, 5% or less of swelling clays, demonstrated a 168-275% increase in matrix permeability. Thus introduction of CO into formation damaged reservoirs containing swelling clays appears feasible. Also low pressure enhanced water floods containing a mixture of CO₂/CO should also be investigated. Since shale oil/gas reservoirs typically contain 10-60% swelling clays, the use of either CO alone, or mixed with CO₂, or N₂, may be beneficial for EOR from unconventional reservoirs at low pressures. Use of CO or a mixed gas, could also be useful in stimulation and frac applications, especially since CO has been shown to decrease IFT.

For heavy oil recovery at reservoir temperatures < 100°F, and using both Huff-n-Puff and line drive/WAG processes in a 10 ft. slim tube, recovery factors varied from 81.5-85% of PV oil present with Mixed Gas #2. Interestingly the mixed gas produced oil showed a decrease in viscosity of 20-200% coupled with a 20-30% increase in API gravity. Also the WAG produced oil showed a decrease in viscosity but a decrease of API gravity. This may suggest the presence of CO assists in mobilization of asphaltenes. The similarities of electron cloud distribution for both CO and aromatic asphaltines may help explain this observation.

Recovery of two different heavy oils by the mixed gas, at reservoir temperatures and pressures, is encouraging for low temperature heavy oil recovery if CO is present in the mixed gas.

Due to the positive effects of CO on corrosion inhibition for oilfield tubulars, injection of a mixed gas, or only CO may also be beneficial for aiding the economics of steam floods. This may be especially true if swelling clays or siderite are present in the heavy oil reservoir that may have suffered formation damage.

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