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Abstract

A single cycle Huff-n-Puff wellbore remediation of a formation-damaged shallow turbidite sandstone, containing 4-5% illite/montmorillonite, was conducted to 1) chemically shrink the water-damaged swelling clays to increase matrix permeability, and 2) increase production. Chemical reduction of ferric oxides/hydroxides to ferrous oxide in, and on, the surface of swelling clays by a gaseous reducing agent (carbon monoxide-CO) was utilized. Extensive bench-scale and core flood testing have previously demonstrated CO's ability to chemically increase matrix permeability. Slim tube studies have also demonstrated a mixture of CO2/CO can recover 80-90% of OOIP under immiscible conditions and at less cost than CO2.

Treating depth of the well was 700-820', having a 146 psi SIP, and a production rate of 0.4 BOPD. Treatment consisted of 1) injecting 70 mcf of CO over 3 day period at an average of 380 psi; 2) shut-in 4 days to allow the CO to react with the ferric ions; 3) injection of 18 Mcf of gaseous CO2 at 400 psi, 4) switch to liquid CO2 injection. After a 48-day shut-in, reservoir pressures again were 146 psi. Pressure transient analysis (PTA) was conducted on the data collected during the injection and falloff of CO and the injection of CO2 gases. During the flowback period, with both gases present, the oil rate was monitored and compared to pre-treatment rates.

PTA showed a 400% increase in gaseous CO2 injectivity compared to the CO rates. Oil production increased 10-fold from 0.4 up to an average of 4 BOPD during the production cycle when CO2/CO was

flowing back. After all the CO2/CO was recovered, production dropped to a sustained 1.2 BOPD versus the original 0.4 BOPD for a 300% increase in oil with minor volumes of gas.

Permitting was not an issue. Operational safety was ensured safety meetings and training of personnel combined with CO monitors, flare lines for the CO2/CO, and self-rescuer gas masks. A leak of CO at the wellhead occurred, was safely mitigated, and no safety problems were encountered during subsequent injection and flowback periods.

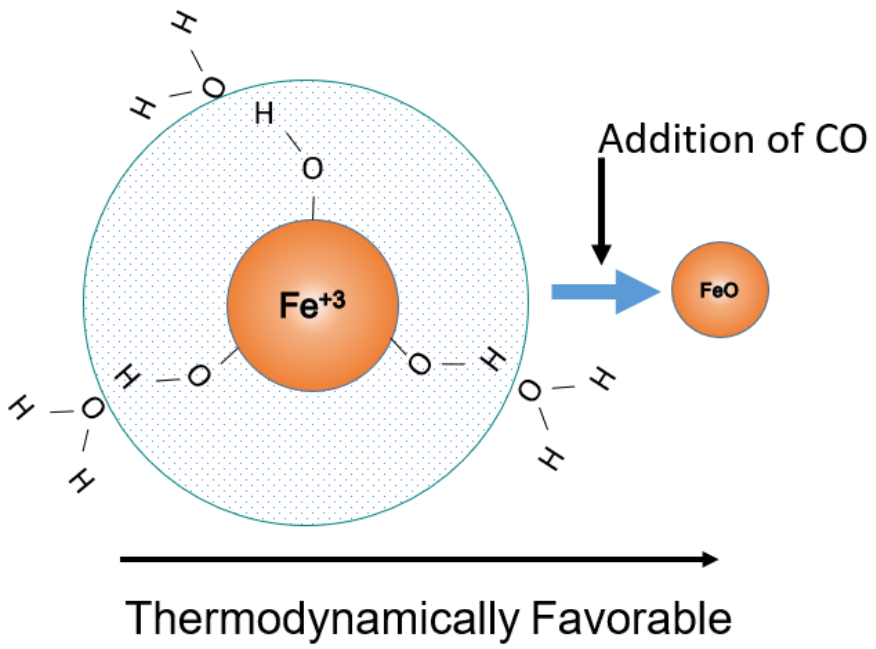
INTRODUCTION

Swelling clays are subject to formation damage in the presence of low salinity water introduced by freshwater drilling, fracing, or completion techniques. Once formation damage occurs, it is very difficult to reverse/shrink the swelling clays. Over the past few years, a new technology has been extensively bench-scale tested and shown to increase matrix permeability by shrinking the swelling clays. Effective permeability increases have ranged from 130-800% after treatment with a strong reducing gas. This paper reports on a successful wellbore remediation field operation employing this new gaseous technology, which has been awarded two patents with a third pending. The field test verified the results of previous bench-scale tests.

Under USA 45Q, both CO2 and CO have been decreed as eligible for sequestration credits. Like CO2, the non-sequestered CO produced with the oil is recycled. Both CO2 and CO can be produced by burning flared gas, natural gas, ethane, NGL's, and even coal under a low oxygen content in a reformer.

STATEMENT OF THEORY AND DEFINITIONS

Swelling clays contain both ferric and ferrous ions. The ferric ions may be oxides or hydroxides- both strongly hydrated. Clays may occur as discrete mineral grains and also act as cementing agents by coating mineral grains. Additionally, they may form a significant portion of pore throat walls, with the hydrated ferric oxides/hydroxides protruding into the pore throats, effectively decreasing its effective diameter. Injection of a small diameter, gaseous molecule (CO-carbon monoxide) could then access these small pore throats, react with the strongly hydrated ferric oxides/hydroxides to chemically reduce them to a non-hydrated ferrous oxide. **Fig. 1** is a cartoon of a hydrated ferric hydroxide molecule compared to ferrous oxide after reduction by CO. The cartoon only shows a single layer of water molecules attached to the ferric hydroxide while in the reservoir there are multiple layers of bound water. Ferrous oxide occurs in nature as the mineral "wustite" and is thermodynamically stable in the reducing environment of an oil and gas reservoir. **Fig. 2** shows how the pore throats are opened by the reduction of ferric oxide to ferrous oxide with the resultant release of the bound water.



$$Fe(OH)_3 \bullet nH_2O + CO \longrightarrow FeO^* + CO_2 + 2H_2O + H^+$$

*mineralogically known as "Wustite"

Figure 1 Reduction of Hydrated Ferric Hydroxide to Non-hydrated Ferrous Oxide by CO

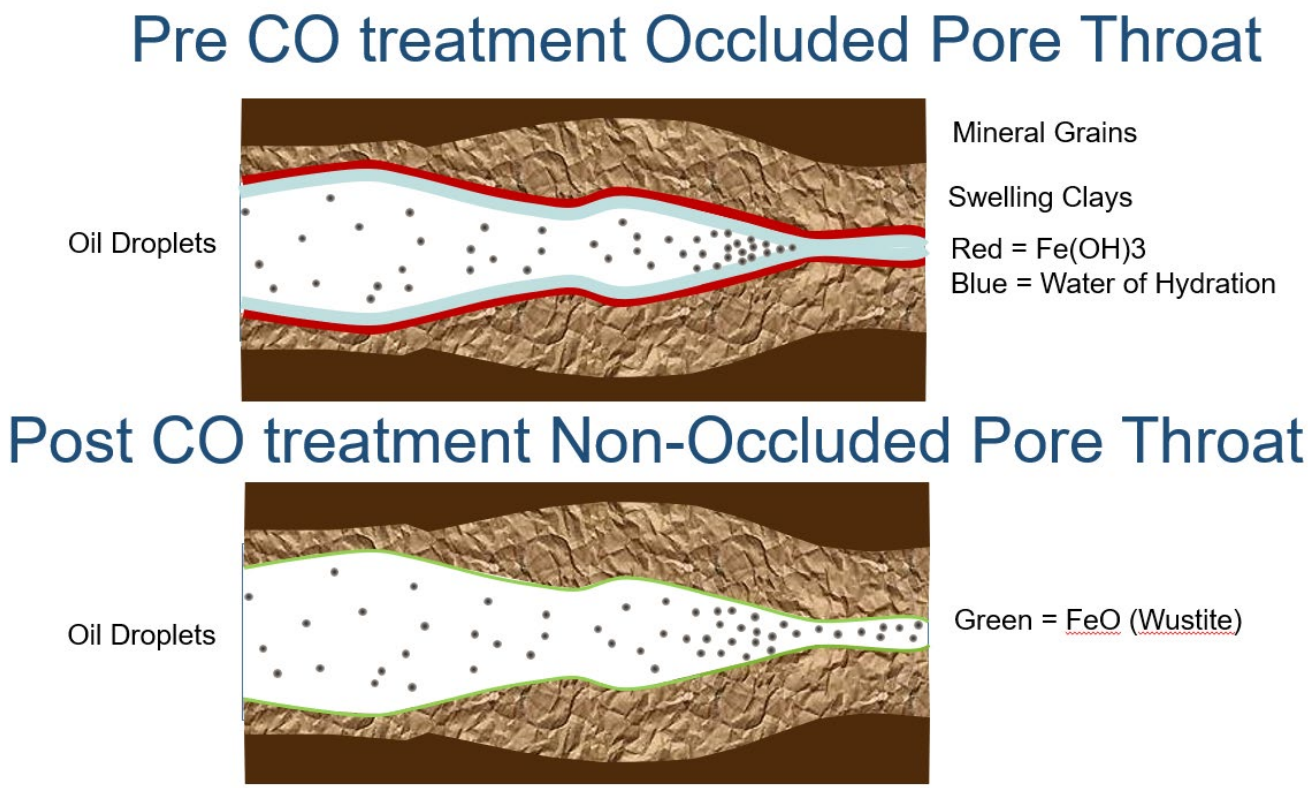


Figure 2 Opening Pore Throats Using CO

Core flood and packed column tests were run to determine the effect of CO on damaged formations. The core flood was performed on a preserved core of Muddy sandstone with water and less than 2% spotty oil shows in the pores. The core had relatively small amounts of swelling clays and was extremely tight. The initial effective permeability to gas of the 1" x 3" core was determined by injecting CO. After injecting CO, the core was allowed to soak for 96 hours. At the end of the soak period, CO was again injected to measure the final effective permeability to gas. Packed column testing was done on a 1" diameter by 14" long column packed with medium-grained Berea sand and 5% montmorillonite. The column was flooded with 50,000 ppm total dissolved solids (TDS) sodium chloride water. The absolute permeability to water was 4.5 md. The column was then flooded with 40 °API oil, followed by a flood of 50,000 TDS water to get the column to residual oil saturation. The effective permeability to water after "waterflooding" the "oil reservoir" was 1.8 md. CO was then injected and allowed to soak for 72 hours. After the soak, 50,000 TDS water was again injected and the effective permeability to water was 8.8 md. Significant oil recovery was observed, but unfortunately not quantified. **Table 1** summarizes the results of the two tests.

Test Type	Material	Initial Permeability	Final Permeability	% Increase in Permeability
Core Flood	Sandstone 1.4% Smectite Illite 7% Kaolinite	0.4 nd	1.1 nd	275%
Packed Column	Berea sand 5% Montmorillonite 40 °API Oil	1.8 md	8.8 md	488%

Table 1- Permeability Increase by Application of CO

Bench-scale testing has also shown CO capable of lowering interfacial tension (IFT) and favoring a change from oil-wet to water-wet conditions. Additionally, CO is well known to form cobalt (Co), nickel (Ni), vanadium (V), and iron (Fe) carbonyls. Asphaltenes generally contain Co, Ni, V, and Fe. Slim tube studies have shown mobilization and recovery of heavy oils containing asphaltenes in range of 5-15% by weight, is feasible at reservoir temperatures and pressures. No added heat is required. It has been postulated that the asphaltene recovery at low temperatures and reservoir pressures is due to the presence of the CO, which forms a weak bond to the asphaltene through the Co, Ni, V, and/or Fe ions.

A total of 48 slim tube tests on five oil samples with API gravities of 18-42° were conducted under immiscible conditions. Recovery rates and total oil recovery were compared for both pure CO2 and the mixture of CO2/CO. In all tests, the rate of oil recovery, per pore volume injected of CO2/CO, was 2.5-3X faster than just pure CO2. Even under immiscible conditions, total oil recovery was essentially the same as pure CO2. **Fig. 3** is one example of several tests that were run. Additionally, slim tube testing was conducted having post-waterflood, residual oil conditions. **Fig. 4** shows the results of the post-waterflood test. Under immiscible conditions, the gaseous mixture of CO2/CO recovered more oil than pure CO2. Bench-scale testing has demonstrated an average of only 4-5 mcf/bo produced is required for the CO2/CO mixed gas versus the 10-12 mcf/bo for pure CO2. Rising bubble testing of CO2/CO, at pressures up to 6200 psi, could not achieve miscibility with an oil that had 2200 psi miscibility with pure CO2.

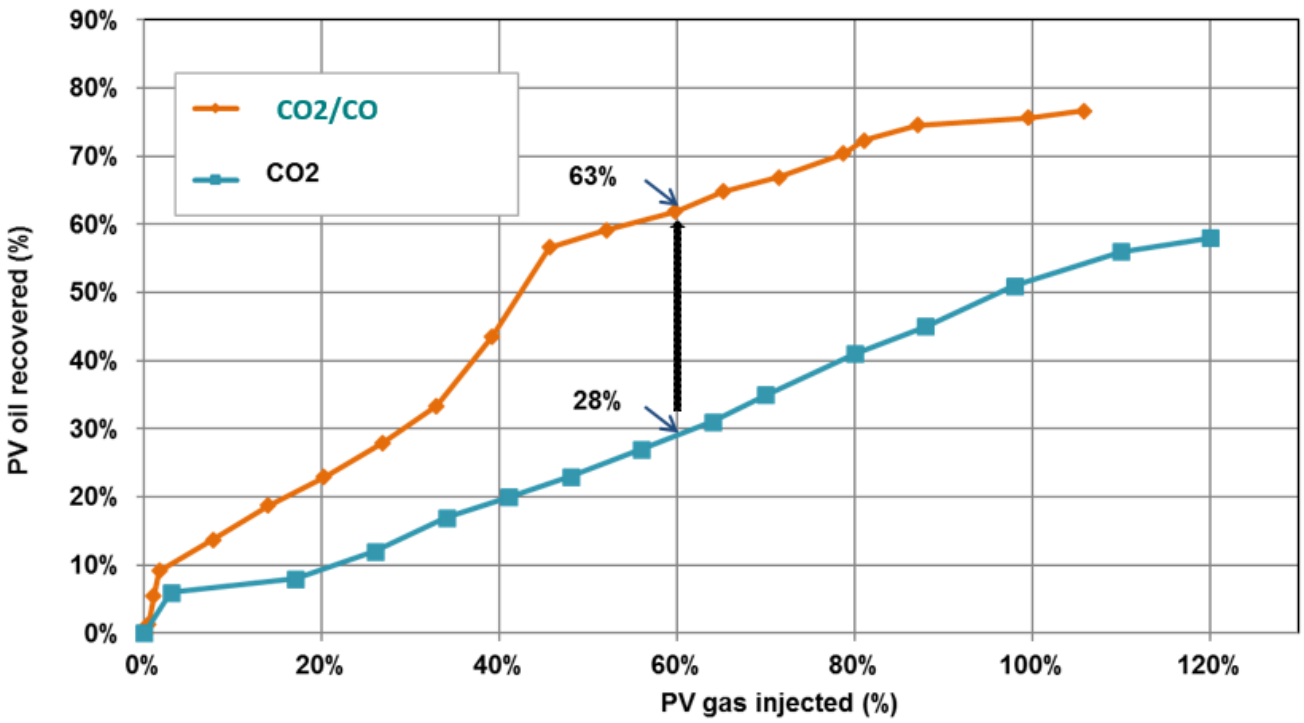


Figure 3 Slim Tube Rate and Volume of CO2/CO versus Pure CO2

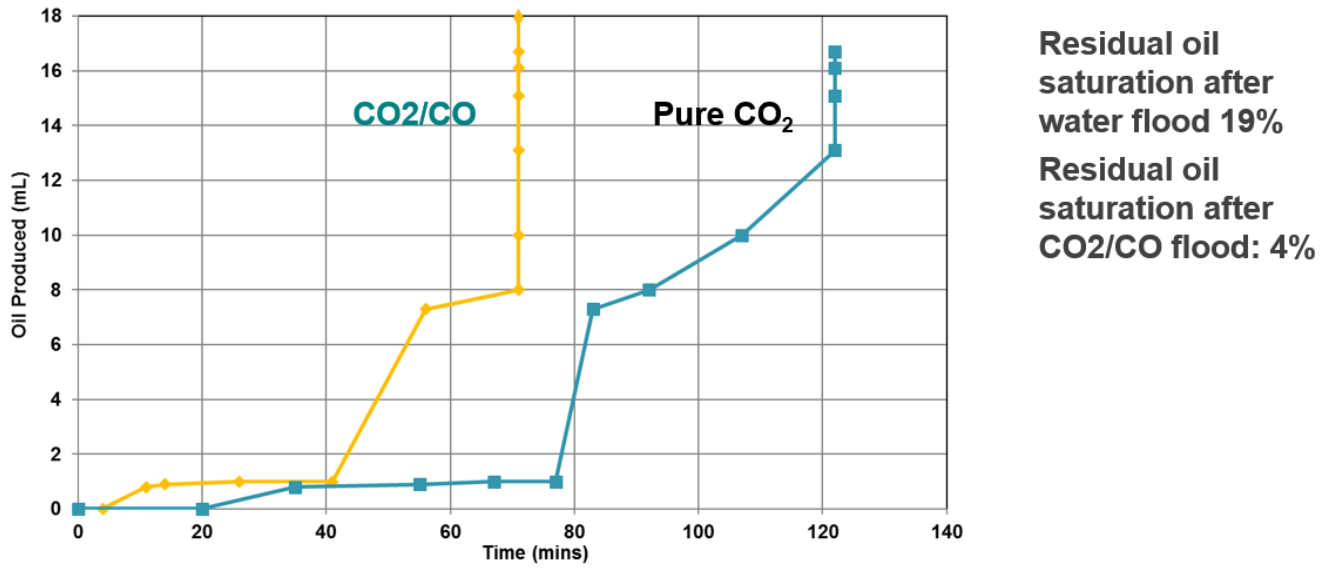


Figure 4 - 3-Phase Slim Tube Test Post Waterflood

The cost of CAPEX and OPEX for producing the mixed gas by a syngas-type modular unit is highly dependent on the cost of the fuel feedstock. For example, if flared gas is available, the cost per MCF of the CO2/CO mixture would be less than $1.00. The cost to burn natural gas, selling at $2.40/ mcf, would be about $3/mcf. However, the CO2/CO mixture is tolerant of up to 15% N2. Thus, dilution with N2 is economically and technically feasible, which results in a further lowering of the cost of the mixed gas.

CO PRODUCTION, SAFETY, AND SAFE OPERATING CONSIDERATIONS

The chemical industry produces CO and H2 under a syngas process. Over 240 CO/H2 syngas producing plants are present worldwide to meet market demand. Syngas is a common fuel for power plants. Large volumes of CO and/or syngas are required during the manufacture of steel, hardening of steel (knives), certain soaps, plastics, petroleum products, and other chemical agents. In fact, CO has commonly been injected into packaged meat at grocery stores to maintain the vivid red coloration of the meat by preventing a reaction with oxygen (air). This widespread usage is related to the strong reducing nature of CO in chemical reactions. One new syngas-type plant in Texas currently under construction is designed to produce 125,000 Mcfd of syngas (CO/H2). Common syngas-derived products are ammonia, hydrogen, refinery products, clean diesel, naphtha, methanol, acetic acid, and fuel additives.

A modified, modular, small syngas plant, capable of 500 Mcfd, is currently in the engineering design process for completion and field application on a CO2/CO flood scheduled to begin in 2020. The plant will be located on the project site.

Carbon monoxide is significantly less toxic than H2S, with a danger level 1500% safer than H2S. More importantly, it is slightly less dense than air and thus readily disperses rather than collecting in low spots. Well-known CO home exposure situations are frequently encountered in a restricted, enclosed environment allowing slow buildup to toxic levels. Alternately, field application of the CO occurs in an open, dispersive environment.

The human body produces its own CO used to regulate our immune system and acts as an anti-inflammatory and antioxidant agent. Recent medical research has also shown CO increases the

effectiveness of cancer chemotherapy by 1000%. Additionally, CO is being investigated to aid blood flow to the heart.

Early detection of CO is simple and effective, as evidenced by the low-cost home CO detectors and personal safety monitors. Safe field application of the CO for this wellbore remediation involved the development of a detailed safety plan, training of personnel, and use of personnel monitors, monitors around both the CO source and the wellbore, wind direction indicators, and self-rescue masks. In addition, the wellhead was equipped with a flare to divert and burn any injected CO if required. Carbon monoxide (CO) burns with a pale blue flame.

During the injection of the CO into the wellbore, a leak of CO was observed at the wellhead. Alarms went off, the well was shut-in, personnel evacuated upwind, and the CO supply line was shut-in. The injected CO from the leaking well bore was safely and easily diverted to a flare for combustion. After a 10-hour bleed down, the wellhead was removed, packing refurbished and resealed. No alarms, concerns, nor safety issues occurred during this repair period. After wellhead repairs, CO injection was re-initiated, no leaks were present, and injection completed.

During the Huff-n-Puff blowdown cycle, the off-gases (CO2/CO) were collected at the production tank outlet and recycled/injected into a nearby well to achieve treatment of that well.

FIELD OPERATING CONDITIONS

The damaged formation is a Paleozoic turbidite, containing 4% illite/montmorillonite, 1-2% kaolinite, and a mixture of quartz, feldspars, micas, and lithic fragments. The porosity was 12-15% with a permeability of less than 1-2 md. The depth of the treated zone was 700-820', with a perforated interval of 100', and a reservoir pressure of 146 psi. The pre-treatment production rate was 0.4 BOPD of 35 °API oil with minor amounts of gas and no water. The well has been producing sporadically for the past 30 years and is just one of many damaged wells in this field. Because of the volume of illite/montmorillonite, this formation appeared to be an excellent candidate for this novel technology.

Both the CO and CO2 were obtained from commercial sources and trucked to the well site to minimize the initial capital cost. The CO tube trailer shown in **Fig. 5** contained 200 mcf at a pressure of 2000 psi. The CO2 truck had 20 tons of liquid CO2 at a temperature of -35°F and a pressure of 217 psig. Because the well location was wet and muddy, a 1500 ft., 2-7/8" pipeline was laid to the well from the gas supply trucks located at the tank battery. A tee was installed in the injection line near the wellhead along with three valves so the injection line and/or the well could be isolated and gas from either could be sent to a flare line.

Figure 5-CO Tube Trailer on Location

Plunger lift pressure recording equipment was installed at the well to monitor the casinghead and tubing head pressures. These data were telemetered to the "control van" near the tube trailer so the pressures could be monitored in real time. The CO injection rate was measured using a sonic flowmeter attached to the outside of the injection line with a remote readout in the "van." Both the pressure measurement and flow measurement equipment performed flawlessly during the CO injection.

The test was designed to inject CO to reduce the ferric oxides to ferrous oxides, thereby shrinking the swelling clays. Carbon dioxide (CO2) was then injected to push the CO further into the formation and to mix with the CO to achieve the desired CO2/CO mixture to aid oil recovery. Due to the 2000 psi in the CO tube trailer, no injection pump was required. Flow control valves were used to stay below frac pressure in the well. The small volume of the CO was dictated by the high cost of the CO and transportation. The first injection period only lasted about 20 minutes, with about 6 Mscf injected before a significant leak at the wellhead was visually observed and sensed by the CO monitors both around the well site and on the personnel. Although personnel were equipped with self-rescue masks, they were not required. A strong wind rapidly dispersed the CO. After shutting the well in and ceasing CO injection, personnel rapidly moved upwind away from the wellhead. Within 10 minutes, all monitors showed background concentrations of CO, allowing the well to be reopened and the injected CO to be directed to the flare line. The next morning the well was again opened, and a minor volume of gas was directed to the flare until the flare showed only methane as indicated by both the monitors and the color of the flame at the flare (CO burns with a powder blue flame). After the wellhead was removed, the packing was reset, and new

seals emplaced, the well was placed back on injection. No safety issues were encountered during any of the wellhead repair activities. The flowline joints were also tightened.

On day two, CO injection resumed at an initial rate of about 200 Mscfd. As the casing pressure built, the rate was decreased to about 100 Mscfd to keep the casinghead pressure below 400 psi. Operations were shut down for the night after about 36 Mscf of CO had been injected. On day three, the initial injection rate was about 550 Mscfd. The rate was again decreased throughout the injection period to keep the casinghead pressure below 400 psi. After 27 Mscf of CO had been injected on day three, the pressure in the trailer had decreased to the point that the injection rate was only about 60 Mscfd at a casinghead pressure of 380 psi. The well was shut-in, and the pressure was continuously monitored.

After a 4-day shut-in, gaseous CO2 injection was initiated. The gaseous injection rate of 1.3 MMscfd was estimated by counting the pump strokes on the CO2 injection pump. Gaseous CO2 injection continued for 20 minutes to allow PTA data collection. Liquid CO2 injection was then initiated until the equivalent of 300 Mscf were injected. Pressure data were continuously recorded during both the gaseous and liquid CO2 injection. Both rate and pressure data from the entire CO injection/falloff time and the first 20 minutes of the CO2 injection period were analyzed to estimate permeability and apparent fracture length. The best fit during the CO2 injection resulted in an estimate of an 11 ft. effective fracture length and a permeability-thickness of 6 md-ft. The data for the CO2 injection period were analyzed keeping the fracture length at 11ft. to be able to determine the injectivity rate as compared to the CO injection/falloff period. The permeability-thickness during the CO2 injection period was 25 md-ft, a 400% increase in injectivity.

CONCLUSIONS

The following conclusions have been made.

1. Handling and injection of CO, although a hazardous substance, was readily achieved under safe operating conditions.

2. After a 4-day shut-in to allow reaction of the CO with the swelling clays, injection rates of the twice-as-large CO2 molecule showed a 400% injectivity increase as compared to the initial rate of the CO injection.

3. Injection of the CO2 was used to displace the CO further into the reservoir and also to mix with the CO and aid oil recovery under a single huff-n-puff operation.

4. After a 48-day shut-in period, primarily due to access problems and inclement weather, the well was flowed back under a normal, single-cycle Huff-n-Puff method. During the five-day flowback, when the CO2/CO mixture was present, oil recovery increased to 4 BOPD (average). When all CO2/CO was recovered, oil production dropped to 1.2 BOPD which has been sustained for the past 10 months at the original reservoir pressure of 146 psi.

5. Field application of this new, novel sequestration technology verified the prior bench-scale research.

6. A full-field EOR displacement flood on a sandstone with CO2/CO as the injectant is currently being developed.