

# **CO<sub>2</sub> Retention and Injectivity Changes: Laboratory Tests [Paper 145]**

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## Abstract

The apparent consequences of increased greenhouse gas emissions will encourage increased carbon dioxide (CO<sub>2</sub>) injection into oil reservoirs for enhanced oil recovery (EOR) and encourage injection into other geological formations for sequestration.<sup>1</sup> The development of CO<sub>2</sub> plumes and their subsequent dissolution into formation brine are essential mechanisms in most sequestration scenarios and could aid in understanding long-term injectivity reduction in EOR WAG (water alternating with gas injection) projects. This paper describes laboratory tests on sandstone and carbonate core samples. Two types of displacement tests were performed; gas injection to a residual brine saturation with respect to gas, followed by brine injection to a residual gas with respect to brine. The level of CO<sub>2</sub> saturation in the injected brine at reservoir pressure and temperature was varied from zero to over 90% saturation. Sandstone and carbonate rock samples were tested. This variation in CO<sub>2</sub> saturation in the injected brine determined the effect on the CO<sub>2</sub> saturation or plume size in the core. This information can be used in CO<sub>2</sub>-EOR-WAG projects and for carbon sequestration into geological formations.

Injecting CO<sub>2</sub> into brine-saturated sandstone and carbonate core results in brine saturation reduction of 62 to 82% in the various tests. In each test, over 90% of the reduction occurred with less than 0.5 PV of CO<sub>2</sub> injected, with very little additional brine production after 0.5 PV of CO<sub>2</sub> injected. During brine injection, CO<sub>2</sub> production was equivalent to the rate expected from brine saturated with CO<sub>2</sub> at reservoir conditions, except for the first ~0.1 PV of the Queen Sandstone CO<sub>2</sub> production. This indicates that in each core at high end-point brine saturation at the tested flow rate (~2 m/day); the CO<sub>2</sub> plume was reduced through dissolution, not displacement. With increasing CO<sub>2</sub> saturation in the injected brine, the brine volume required to remove (dissolve) the CO<sub>2</sub> plume increased proportionally. Results will be used to aid in predicting injectivity in CO<sub>2</sub>-EOR-WAG operations and CO<sub>2</sub> plume migration and CO<sub>2</sub> dissolution in EOR and sequestration.

## Introduction

Residual CO<sub>2</sub> saturation is suspected to be a significant factor for reducing injectivity during many water alternating with gas (WAG) processes for CO<sub>2</sub> EOR projects.<sup>1</sup> Also, there is increasing interest in minimizing CO<sub>2</sub> (greenhouse gas) emissions by sequestering CO<sub>2</sub> in depleted oil and gas reservoirs or in saline aquifers.<sup>2</sup> The interest in increasing CO<sub>2</sub> injection into geological formations requires a better understanding of mechanisms and extent of CO<sub>2</sub> plume development and subsequent dissolution into formation brine. This paper describes laboratory tests on Frio and Queen Sandstones, Indiana limestone, and Lockport dolomite. Several types of displacement tests were performed; gas injection into a core until no additional free brine was produced, thus to a pseudo-residual brine saturation with respect to gas injection, followed by brine injection into a core partially saturated with gas. The level of CO<sub>2</sub> saturation in the injected brine at reservoir pressure and temperature was varied from zero to over 90%. This variation of CO<sub>2</sub> saturation in the injected brine was to determine the effect on the CO<sub>2</sub> saturation or plume size in the core.

Determination of CO<sub>2</sub> saturation in a core was sought after injection of CO<sub>2</sub> into a core that was originally saturated with brine. This was then followed by the injection of brine into the core while differentiating brine displaced of free-phase CO<sub>2</sub> versus producing CO<sub>2</sub> dissolved in brine. Currently in the field, CO<sub>2</sub> is being injected into reservoirs nearing their waterflood economic limit and into aquifers; thus CO<sub>2</sub> is being injected into geological formations containing high brine saturation. To aid in conformance control and reduce the amount of CO<sub>2</sub> required for injection, CO<sub>2</sub> and water are alternately injected into oil reservoirs. Also, it is being proposed to inject CO<sub>2</sub> into innumerable aquifers for carbon sequestration. Thus tests are required for both the understanding of how brine and CO<sub>2</sub> streams flow through porous media and how their mutual solubilities change their saturations with time.

## Experimental

### Material

Frio cores used in these tests were obtained from depths of 2493, 2496.6, and 2497.8 m in the Felix Jackson # 62 Well, located south of the S. Liberty DOE CO<sub>2</sub> pilot site in Chambers County, Texas. These cores were selected because they were consolidated sandstone (see Frio Core Parameters listed in Table 1). The DOE carbon sequestration test site south of Houston is at a shallower depth and the test horizon is in poorly consolidated rock. These tests were performed in the consolidated core to simplify the development of test procedures. Table 2 lists the composition of the synthetic brine used in these tests, which is intended to represent the Frio reservoir brine. Indiana limestone is from a quarry near Victor, Indiana. The parameters for this core are also listed in Table 1. More details

of the Frio sandstone and Indiana Limestone are found in an earlier publication.<sup>3</sup> The Queen sandstone core used in these tests was obtained from the West Pearl Queen Field, southeast New Mexico, Stevison Federal well #1 at 1375.0 m. The permeability was measured at 21.61 md by mini-permeameter estimation (+/- 5.86). The whole core permeability was then determined by brine injection to be 15 md before the first test and 17 before the second test. Both compare well with mini-permeameter tests performed using air; one on the whole core and the other at the end of the core and the other on the whole core. Other parameters are found in Table 1 with the brine used listed in Table 2. The dolomite core is Lockport dolomite. The core parameters and brine are listed in Table 2.

### Core Flooding Apparatus

The core flooding apparatus is located in a temperature-controlled air bath, with a syringe pump and separator system outside the air bath (see Fig. 1). The dead volume of this system (non-flow path volume) and non-core volume (determined to be 4.3 cc) was minimized by reducing the number of pressure control devices, pressure transducers and valves in the system. All the cores were prepared by wrapping them longitudinally in a lead (Pb) foil which functioned as a diffusion barrier between the core and the overburden sleeve. In this way the diffusion of the CO<sub>2</sub> from the core into the overburden fluid is minimized and the mass balance is optimized. During the analysis care was taken to capture all the water using an ambient condition separator (liquid trap) to catch the brine/water and a salt breaker (vapor trap) to capture water vapor. For a volume check the liquid and vapor traps were weighed before and after each test and in a couple of cases at an intermediate point. The wet-test meter was used to determine gas production at ambient conditions. Included in the gas calculations were corrections for gas displaced by brine/water in the separator.

### Test Procedures

Frio sandstone tests were performed at the reservoir conditions of about 62.8°C (145°F) and 15.3 MPa (2200 psig), except for a couple of comparison tests at 37.8°C (100°F) that will be indicated. The overburden pressure was maintained at 27.7 MPa (4000 psig). The brine was prepared with the composition indicated in Table 2. In some cases the brine had CO<sub>2</sub> dissolved in it to represent brine that had been in contact with CO<sub>2</sub>. The brine will be indicated as dead brine (no dissolved CO<sub>2</sub>), 50% CO<sub>2</sub>-brine (brine saturated to about 50% CO<sub>2</sub>), and 90% CO<sub>2</sub>-brine (brine saturated to about 90% CO<sub>2</sub>). Brine saturated to 100% CO<sub>2</sub> was not used to ensure no new free CO<sub>2</sub> occurred from CO<sub>2</sub> evolving from the brine. Pressure drop across the core and/or dissolved solid changes in the brine due to dissolution of core material or water vaporizing into the CO<sub>2</sub> phase could perturb brine 100% saturated with CO<sub>2</sub> and result in small but undesirable amounts of free CO<sub>2</sub> forming from the injected fully saturated brine.

In all but one case the coreflood was initiated in core 100% saturated with dead brine. Dehydrated CO<sub>2</sub> was then injected into the core until no free brine was produced for several PV. The CO<sub>2</sub> was stored outside the air bath at ambient temperature and injected at rates from 10 to 200 cc/hr (20 cc/hr was used unless otherwise indicated) at ambient temperature and about 15.3 MPa. The CO<sub>2</sub> injection volume at 63°C was about 65% higher than at ambient temperature; both at 15.3 MPa. The temperature of the air bath, core, and injection pump were recorded. The head plus end volume of the core system is 4.3 cc; thus in Figs. 2, 3, 5, 6, and 8 the volumes are shown starting at -4.3 cc.

All Indiana limestone tests were performed at about 37.8°C (100°F) and pore pressure of about 15.2 MPa (2200 psig). In the first four tests the core was initially saturated with dead brine and displaced with CO<sub>2</sub> until no free water was being produced; usually requiring 2–3 PV after the last production of free water was detected. In all but the third tests, the CO<sub>2</sub> injection rate was 20 cc/hr at room temperature or about 21.7 cc/hr at core conditions. In series three the injection rate was initially 21.7 cc/hr and then increased incrementally to 43.4, 86.8, and 130.2 cc/hr.

All Queen tests were performed at the reservoir conditions of about 35°C (95°F) and 14.5 MPa (2100 psig). The overburden pressure was maintained at 21.5 MPa (3100 psig). The brine was prepared with 220,000 ppm NaCl with no dissolved CO<sub>2</sub> before injection into the core. In each test the core was initially 100% saturated with dead brine. Dehydrated CO<sub>2</sub> was then injected into the core until no free brine was produced for several pore volumes (PV). The CO<sub>2</sub> was stored outside the air bath at ambient temperature and injected at 20 cc/hr at ambient temperature and about 14.5 MPa. The CO<sub>2</sub> unit volume at 35°C was about 8% higher than at ambient temperature or a lower density; both at 14.5 MPa. There is a slight reduction in permeability indicated from 17 to 15 md before and after the first test series.

The Lockport dolomite tests were performed at room temperature which varied from 18° to 23°C (65° to 73°F) and elevated pressures from 24.2 to 28.7 MPa (3500 to 4142 psia), see Table 2. The overburden pressure was maintained at about 34.6 MPa (5000 psig). The core was initially 100% saturated with dead-water (degassed, distilled water). CO<sub>2</sub> was injected at 20 cc/hr into the core until free brine production had essentially stopped. Though water production does continue as water vapor in the produced CO<sub>2</sub>, it is at a slow rate.

## Discussion of Results

### Results – Frio Sandstone

Figure 2 compares two tests of CO<sub>2</sub> displacing brine in Frio Core A. In both about 7 cc of brine was produced before CO<sub>2</sub> breakthrough. After CO<sub>2</sub> breakthrough there was a small quantity of brine produced and then brine production stopped except for water dissolved in the CO<sub>2</sub>. Usually over 95% of the brine production occurred before 1 PV of CO<sub>2</sub> had been injected. Any continued production after less than 1 PV of CO<sub>2</sub> had been injected was from vaporized water. The salt vapor trap (Fig. 1) was weighed only at the end of the test and this value was added evenly over the duration of the test scaled to the injection rate in the brine/water production plots. The time when the vapor was actually produced is not known. In Fig. 2 the first system had an injection rate increase from 20 to 100 cc/hr after 200 cc of CO<sub>2</sub> had been injected. There was additional free brine produced following the injection rate increase. During the second test, injection was continued overnight at a reduced injection rate of 10 cc/hr and then increased to 100 cc/hr for a short time at the end of the test.

In each case the saturations reached what might be considered stable pseudo-end point saturation. However this stable saturation changed by increasing the flow rate, decreasing pressure, and by evaporating water. What is the definition of an end point or residual water saturation? For this paper it will be referred to as a pseudo-end point. After completion of CO<sub>2</sub> injection, brine was injected into the core to displace the CO<sub>2</sub>. Figure 3 compares the first two brine injection tests which used dead-brine in Frio Core A after CO<sub>2</sub> injection in each test (see Fig. 2). In each about 4.3 cc of reservoir condition CO<sub>2</sub> was produced (the same as the end plate dead volume), then the CO<sub>2</sub> production rate decreased significantly. After this change in production rate, approximately 4 to 5 cc of additional CO<sub>2</sub> at reservoir condition were produced at a fairly constant rate. Using values from Wiebe and Gaddy<sup>4</sup> adjusted for dissolved solids,<sup>5</sup> these rates are what would be expected from CO<sub>2</sub> dissolved in Frio brine fully saturated with CO<sub>2</sub> at the test conditions. The CO<sub>2</sub> produced after the dead volume was produced was not a free phase. The final value of produced CO<sub>2</sub> from the system, including blowdown to ambient pressure, was equal to the brine produced during CO<sub>2</sub> injection; thus a good material balance was obtained throughout the experiments.

The second set of experiments was performed on Frio Core B. In this set the tests used the same procedure as for Frio Core A, except that CO<sub>2</sub> dissolved in the injected brine varied from 0 to 90% of CO<sub>2</sub> saturation. In each case the production rate of CO<sub>2</sub> in cc/cc of brine produced was around 24. This was what would be expected from saturated brine. Figure 4 compares the production rate of CO<sub>2</sub> during the injection of brine into Frio Core B during three different tests. Excluded in Fig. 4 was the first PV of brine injection where the production of free CO<sub>2</sub> was occurring, which exceeded 150 cc/min during free-phase CO<sub>2</sub> production. Each of the three tests shown in Fig. 4 followed the injection of CO<sub>2</sub> into the core saturated with dead brine. The three tests differ in the concentration of CO<sub>2</sub> in the injected brine. During the early time period the production rates are essentially equal for all three scenarios. The brine produced from this 6.1 cm core was saturated with CO<sub>2</sub> and did not depend on the CO<sub>2</sub> concentration of the injected brine. Thus the brine was saturated with CO<sub>2</sub> over a relatively short flow path.

The injection test using 90% CO<sub>2</sub>-brine was not continued until free CO<sub>2</sub> was depleted in the core as in the other two cases. Injection and production continued long enough to verify the production rate of CO<sub>2</sub> during the first part of the injection. From Fig. 4, CO<sub>2</sub> depletion in the core during the dead brine injection shows a rapid decline in the CO<sub>2</sub> production rate after most of the CO<sub>2</sub> had been produced. In the 50% CO<sub>2</sub>-brine the drop is slower and as might be expected the system stabilizes at a rate of about 3 cc/min, which is the same as the content of the brine being injected. When the pressure was released on the 50% CO<sub>2</sub>-brine system the produced CO<sub>2</sub> was equal to about that which would be evolved from 1 PV of brine saturated to 50% CO<sub>2</sub>, indicating that all the free-phase CO<sub>2</sub> had been removed.

The production of CO<sub>2</sub> during the injection of 50% CO<sub>2</sub>-brine at 37.8 and 62.8°C were similar, but the lower temperature appeared to be about 10-15% higher. This compares well with the higher solubility of CO<sub>2</sub> in brine at lower temperatures. The final set of Frio tests was in core C. Figure 5 has an expanded production rate scale to demonstrate the rate comparison during free-phase CO<sub>2</sub> production and production evolving from CO<sub>2</sub> dissolved in brine at reservoir conditions. In these tests the first step was started with a dry core. This was then saturated with 100% dehydrated CO<sub>2</sub>; then dead brine was injected into the core. In this test about 9 cc of CO<sub>2</sub> at reservoir conditions were produced before production stabilized. This rate was equal to that of CO<sub>2</sub> evolved from brine saturated with CO<sub>2</sub> at 37.8°C and 15.2 MPa and 20 cc/hr flow rate. Then an additional 11 cc (reservoir conditions) of CO<sub>2</sub> were produced at a rate of about 8 cc/min at ambient conditions. This totals 20 cc of produced CO<sub>2</sub>. Subtracting the 4.3 cc dead volume yields 16 cc or almost 90% of the 18.1 cc core PV. Another 2 cc were produced during the remaining injection period and subsequent blowdown. This test required about 4 cc of brine or 0.22 PV to establish a brine flow path. Shortly after brine breakthrough, it appears that only CO<sub>2</sub> dissolved in the brine was produced.

## Results – Limestone

Several tests on Indiana limestone were conducted using the same procedure used for the Frio sandstone. All tests were performed at about 37.8°C and pore pressure of about 15.2 MPa. In the first four tests the core was initially saturated with dead brine and displaced with CO<sub>2</sub> until no free-phase water was being produced; usually requiring 2–3 PV after the last production of free-phase water was detected. In all but the third tests, the CO<sub>2</sub> injection rate was 20 cc/hr at room temperature and core pressure or about 21.7 cc/hr at core conditions. In series three the injection rate was initially 21.7 cc/hr and then increased incrementally to 43.4, 86.8, and 130.2 cc/hr while the incremental produced water was 7.8, 0.3, 0.1, and 0.1 cc, respectively. Again, the first 4.3 cc produced was from the line volume resulting in brine production from the core of about 4.0 cc and vapor production caught in the salt trap of 1.4 for a total of about 5.4 cc of brine from the core. The brine/water production in the third test is compared to the other three tests in Fig. 6. There is a contrast of the production at similar injection rates between the first two and last two tests of almost 1 cc (Fig. 6). This is believed to be due to the formation of a solution channel in the limestone core.

Figure 7 compares flow tests at three different times during these tests that indicates a permeability change (increase). As the number of tests and PV of fluid injected into the core increased, the pressure drop versus flow rate increased. This is an indication that the core permeability was decreasing with time or PV of fluid injected. Tests performed after the last test indicated almost no pressure drop at all tested flow rates (20–200 cc/hr), indicating a very high permeability. In earlier tests with limestone, total core permeability increased over time until a solution channel through the core had been formed, and then the permeability drastically increased.<sup>6,7</sup> In each case there had been plugging or deposits advancing ahead of the solution channel.

Figure 8 compares the reservoir volumes of CO<sub>2</sub> produced for each test during the injection of brine. For Tests 1 and 2 dead brine was injected and for both there was a good material balance. For Tests 3 and 4, a 50% CO<sub>2</sub> saturated brine was injected. Again in both cases there was a good material balance, but a decrease in CO<sub>2</sub> production. This is also shown in Fig. 9 where the production rate in the later tests dropped before the free CO<sub>2</sub> was dissolved and produced. Indicating the brine was not being saturated when a channel formed. In Tests 1 and 2 the core had very little CO<sub>2</sub> remaining at blowdown. For Tests 3 and 4 the production dropped much more quickly to the baseline for the 50% CO<sub>2</sub>-brine and at blowdown both had significant amount of CO<sub>2</sub> remaining. Test 4 had almost 3 cc compared to about 1 cc remaining in Test 3 (Fig. 8). It is believed that the difference is due to the formation of the solution channel, where most of the flow bypassed the bulk of the core.

## Results - Queen

Figure 10 compares two tests of CO<sub>2</sub> displacing brine in the West Pearl Queen Core. In both just over 9 cc of brine was produced before CO<sub>2</sub> breakthrough (9.02 and 9.15 cc, respectively). Subtracting the 4.3 cc dead space leaves 4.72 and 4.85 cc or 0.373 and 0.383 PV, respectively (PV = 12.65 cc). After CO<sub>2</sub> breakthrough there was a small quantity of brine produced and then brine production stopped except for water dissolved in the CO<sub>2</sub>. About 90% of the brine production occurred before one PV of CO<sub>2</sub> had been injected. Much of the production after one PV of CO<sub>2</sub> was injected was from vaporized water. The salt vapor trap was weighed only at the end of the test and this value was added evenly over the duration of the test scaled by injection rate to the brine/water production plots. There were 0.6 and 0.2 grams of water captured in the vapor trap during the two tests, respectively. The time when the vapor was actually produced is not known. The flow rate was not changed in any of the tests as was done in some of the earlier tests. Figure 11 compares the pressure drop across the core during the injection of CO<sub>2</sub>.

After completion of CO<sub>2</sub> injection, brine was injected into the core to displace the CO<sub>2</sub>. Figure 12 compares the two brine injection tests, which both used dead brine after the CO<sub>2</sub> injection in each test (see Fig. 10). In each, about 4.3 cc of reservoir condition CO<sub>2</sub> was produced (the same as the end plate dead volume), then another 0.94 to 1.14 cc of the free-phase CO<sub>2</sub> was produced before the rate decreased; this seemed to indicate a residual CO<sub>2</sub>. After this break, additional CO<sub>2</sub> was produced at a fairly constant rate. Using the values of Wiebe and Gaddy<sup>4</sup> adjusted for dissolved solids,<sup>5</sup> these rates are as expected from CO<sub>2</sub> dissolved in the brine fully saturated with CO<sub>2</sub> at test conditions. The final reservoir volume of produced CO<sub>2</sub> from the system, including blowdown to ambient pressure, was within 5% of the brine produced during CO<sub>2</sub> injection; thus a fair material balance.

Figure 13 compares the production of CO<sub>2</sub> during the injection of brine for the two tests. The production rates are essentially identical until the blowdown in the first test. The rate of about 170 cc/min at ambient is equivalent to the production of CO<sub>2</sub> at ambient conditions from a core at 14.5 MPa and 35°C. Then as the free CO<sub>2</sub> production ends the rate settles at about 8cc/min, which is about the solubility of CO<sub>2</sub> in brine.<sup>4</sup> At 58 minutes into Queen Test #1, blowdown started. During Queen Test #2 injection was stopped at 62 minutes and restarted at 73 minutes and continued until stopping injection at 140 minutes. Blowdown started at 153 minutes. For both tests the total CO<sub>2</sub> produced was equivalent and about equal to the reservoir volume of brine displaced. The 0.94 and 1.14 cc of free-phase CO<sub>2</sub> produced represent 0.074 and 0.090 PV in Queen Tests #1 and #2, respectively. This is compared to no free-phase CO<sub>2</sub> from the core seen in the Frio sandstone and Indiana limestone tests. This leaves a CO<sub>2</sub> residual

saturation of 0.309 and 0.283 PV respectively, where any additional CO<sub>2</sub> production was from CO<sub>2</sub> dissolved in the brine.

The laboratory finding from the corefloods is what was found in the West Pearl Queen Reservoir Huff-n-Puff pilot. In this scenario, after injection of CO<sub>2</sub> the subsequent production would be relatively rapid for the first 20 to 25% of the injected CO<sub>2</sub> and much slower thereafter. A prolonged, slow, consistent production is derived from CO<sub>2</sub> dissolved in the brine and/or oil with a short production burst early in the Puff cycle after the soak period in the Huff-n-Puff schedule.<sup>8,9</sup> In the reservoir this would be a production rate of about 24 m<sup>3</sup> of CO<sub>2</sub> per m<sup>3</sup> of produced brine (135 scf of CO<sub>2</sub> per barrel of produced brine). The potential for produced CO<sub>2</sub> that is dissolved in the oil can be at least an order of magnitude greater. This compares to about 500 m<sup>3</sup> of produced CO<sub>2</sub> at ambient condition from a m<sup>3</sup> of CO<sub>2</sub> at reservoir conditions (35°C and 14.5 MPa). Thus, CO<sub>2</sub> production from the reservoir comes from free CO<sub>2</sub>, CO<sub>2</sub> that was dissolved in brine, and CO<sub>2</sub> that was dissolved in produced oil. The production rate for the CO<sub>2</sub> will depend on the production rate of each. After CO<sub>2</sub> in the reservoir is reduced to residual CO<sub>2</sub> the later production rates of CO<sub>2</sub> will be from CO<sub>2</sub> dissolved in the produced brine and oil. Since there are a number of zones, and between and within zones a range of permeabilities and porosities, production from free and dissolved CO<sub>2</sub> may be occurring simultaneously.

### Results - Dolomite

As with the other rock types, the core was first saturated with water and water permeability was determined. Also, during CO<sub>2</sub> flooding of carbonate rock, dissolution and subsequent precipitation can occur. Both fines movement and precipitation results in permeability decreasing while dissolution increases permeability. From experience we have found that decreases in permeability in the early times dominates over dissolution increases in permeability and later dissolution dominates.<sup>6,7</sup> In these tests the permeability decreased during the series of test.

Figure 14 shows a plot of data from Flood 1. In this test the core saturated with water had CO<sub>2</sub> injected at 20 cc/hr at the indicated conditions (Table 3). Plotted versus time are the differential pressures (left y-axis) and produced water, produced CO<sub>2</sub> at reservoir conditions, and injected CO<sub>2</sub> at reservoir conditions (right y-axis). The fluid production volumes were only recorded until gas breakthrough. At this point the separator top blew off several times and lost fluid, thus the results were not considered accurate from that point. In Fig. 14 it is shown that this is a pressure increase as CO<sub>2</sub> displaces water and there is two-phase flow. After CO<sub>2</sub> breakthrough the average pressure drops is similar to the starting differential pressure across the core, except less stable. The initial condition is single-phase flow of brine at 100% brine saturation; post-breakthrough, it is single-phase flow of gas, but with two-phase saturation. Thus, under these conditions the relative permeability of the core to the less viscous CO<sub>2</sub> after breakthrough is similar to the permeability of the more viscous single-phase water before gas injection.

Dolomite Flood 2 is shown in Fig. 15. The pressure differential, cumulative CO<sub>2</sub> injection, cumulative water production, and cumulative CO<sub>2</sub> production plots all look similar to Flood 1 (Fig. 14), except some post-gas breakthrough data was obtained. No difference can be distinguished between the two.

### Summary and Conclusions

These were relatively short cores (5.71 to 8.17 cm), about 3.8 cm in diameter, and therefore care must be taken when extrapolating results to reservoir scale. Figure 16 compares the end-point saturation of each core with the comparison of end-point versus flow rate for Frio, 20 cc/hr (1.6 m/D) with 100 cc/hr "h" (8 m/D) and Frio B2h at 200 cc/hr (16 m/D). As stated earlier only in the Queen core was there free CO<sub>2</sub> produced from the core during displacement of CO<sub>2</sub> by brine injection with end-point brine saturation. These findings of end-point saturation are significant parameters in determining flow patterns, retention rates, and injectivity changes and their longevity that will enable improved predictions of CO<sub>2</sub> behavior in reservoirs for EOR and/or sequestration considerations.

Conclusions of the work include:

1. In the range of 0.2 to 0.3 PV fraction of free-phase CO<sub>2</sub> saturation was required to establish a CO<sub>2</sub> flow path, after which there was little brine production except through evaporation, which is a slow process. The CO<sub>2</sub> saturation can be increased by increasing flow rate, reducing pressure, and water evaporation.
2. At the end of CO<sub>2</sub> injection there is a relatively low CO<sub>2</sub> saturation and high brine saturation in the core, thus no reduction in CO<sub>2</sub> saturation was required to return to brine flow. Only in the Queen sand was free CO<sub>2</sub> produced during brine injection.
3. Brine is equilibrated with CO<sub>2</sub> in a short time frame over a relatively short distance. Only when a channel was formed was brine produced that was not saturated with CO<sub>2</sub> while a significant residual CO<sub>2</sub> remained in the core.
4. The injection of brine into a 100% CO<sub>2</sub> phase required 0.2 to 0.3 PV fraction saturation to establish a brine flow path.

- The sandstone and carbonate systems initially performed similarly. This was changed when through dissolution of the rock matrix a solution channel was formed in the limestone, creating a dominant flow path that significantly altered the flow behavior of the core.

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**Table 1. Core Parameters**

	Frio Sandstone			Queen Sandstone	Indiana Limestone	Lockport Dolomite
	Frio A	Frio B	Frio C			
Depth [m]	2493.0	2496.6	2497.8	1375.0	Quarried	Quarried
Diam [cm]	3.73	3.66	3.73	3.81	3.84	3.78
Length [cm]	6.08	6.10	5.71	7.21	7.95	8.17
Bulk vol [cc]	66.44	64.18	62.39	82.20	92.07	91.68
Pore vol [cc]	18.51	18.01	18.29	12.65	16.28	15.72
Por [%]	27.9	28.1	29.3	15.4	17.7	17.1

**Table 2. Synthetic Brine Composition**

Component (mg/L)	Frio and Limestone	Queen	Dolomite
NaCl	82,753	220,000	-
CaCl <sub>2</sub>	8,584	-	-
MgCl <sub>2</sub>	2,152	-	-
KCl	362	-	-
NaHCO <sub>3</sub>	186	-	-
			-
Total Dissolved Solids	94,037	220,000	0

Table 3. Flooding Parameters				
	Frio Sandstone	Queen Sandstone	Indiana Limestone	Lockport Dolomite
Pressures (MPa)	15.17	14.45	15.17	24.14 – 28.62
Temperatures (°C)	37.8 & 62.8	35.0	37.8	18.3 – 22.5
Flow Rates (cc/hr)	10 - 200	20	20 – 120	20
Brine (% CO <sub>2</sub> saturated)	0, 50, & 90	0	0 & 50	0
System Dead Vol. (cc)	4.3	4.3	4.3	4.3

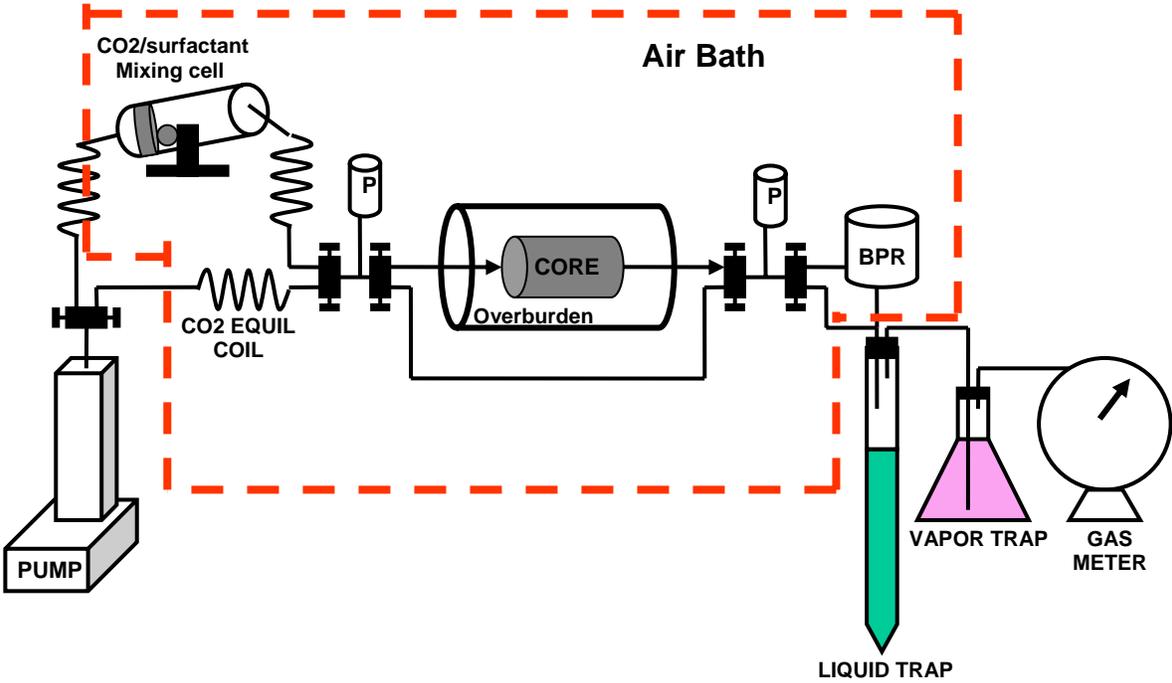


Fig. 1. Coreflooding apparatus.

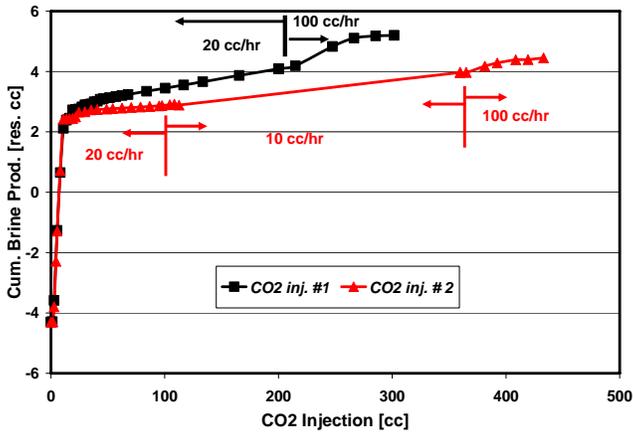


Fig. 2. Comparison of brine production during CO<sub>2</sub> injection of two tests in Frio Core A.

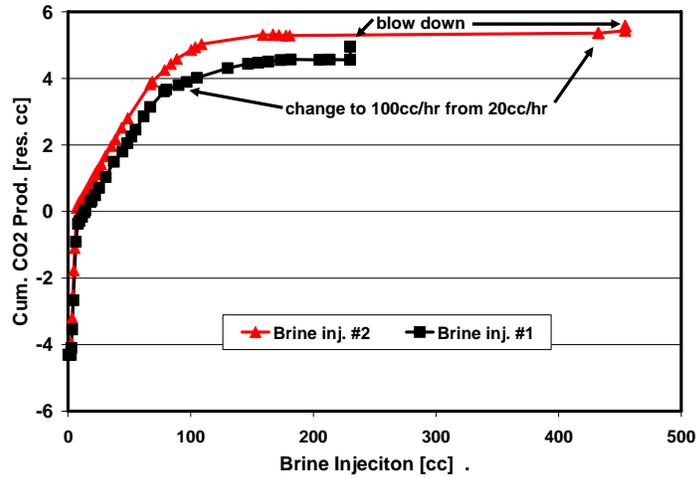


Fig. 3. Comparison of CO<sub>2</sub> production during brine injection for two tests in Frio Core A.

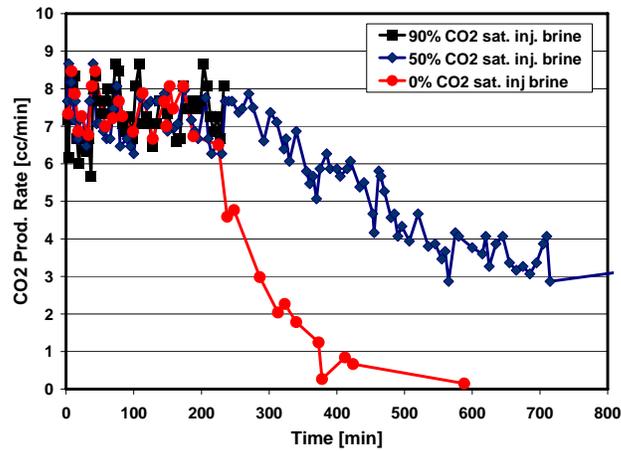


Fig. 4. Production rate of CO<sub>2</sub> during the injection of brine into Frio Core B for three different tests, each at different concentrations of CO<sub>2</sub> in the injected brine.

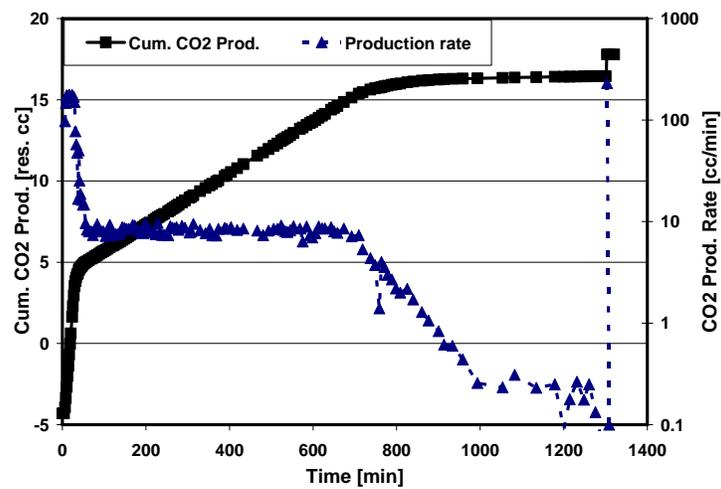


Fig. 5. Comparison of total CO<sub>2</sub> production rate at reservoir and ambient conditions at 37.8°C for Frio Core C.

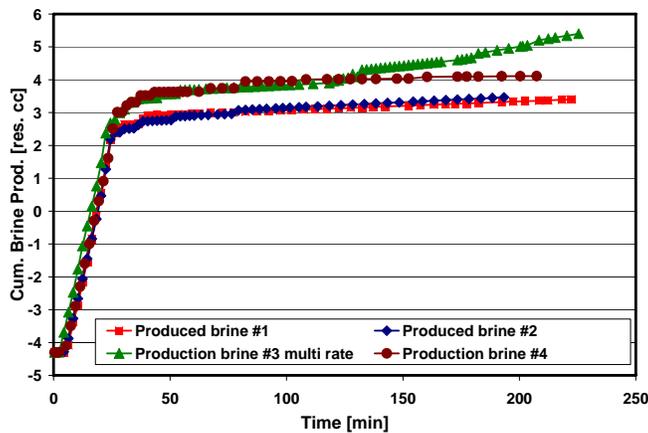


Fig. 6. Comparison of brine production during CO<sub>2</sub> injection of four tests in Indiana limestone.

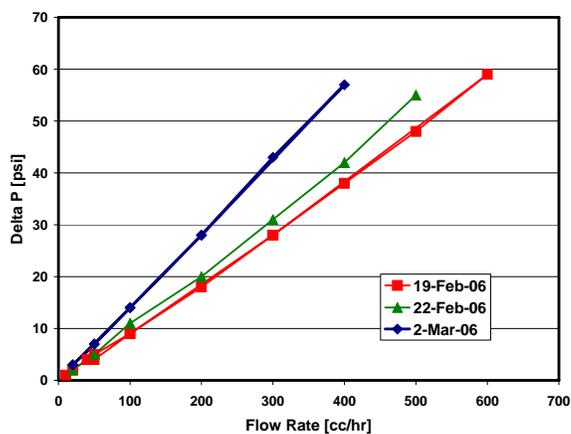


Fig. 7. Pressure drop versus flow rate for Indiana limestone on three different days. The indication was an decrease in permeability with time.

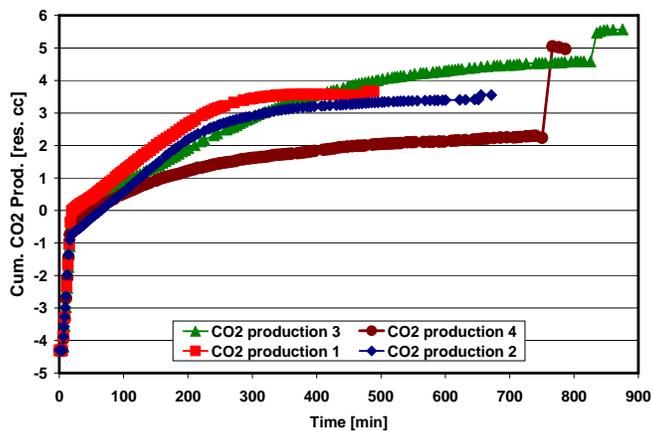


Fig. 8. Comparison of CO<sub>2</sub> production during brine injection for four tests in Indiana limestone.

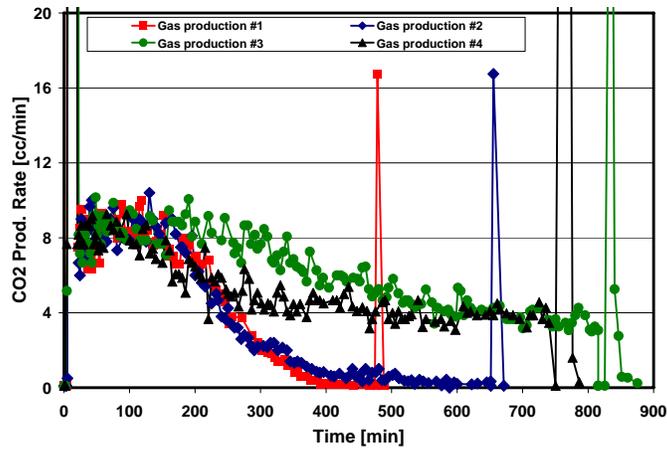


Fig. 9. Production rates for CO<sub>2</sub> at ambient conditions at a brine injection rate of 20 cc/hr in Indiana limestone.

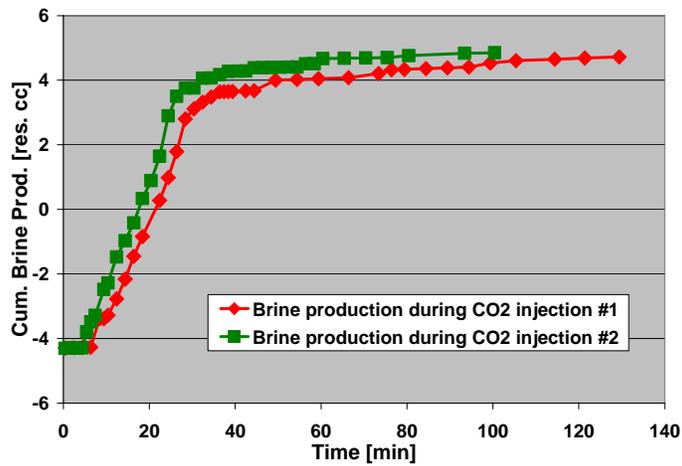


Fig. 10. Comparison of brine production versus time for both CO<sub>2</sub> injection Queen tests. One PV of injection is equal to about 38 minutes of injection.

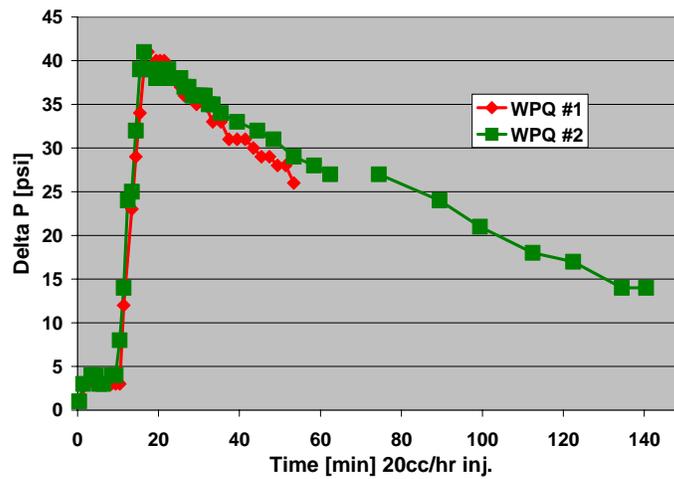


Fig. 11. Comparison of pressure drop across the core during CO<sub>2</sub> injection versus time during brine injection for both Queen tests. One PV of injection is equal to about 38 minutes of injection.

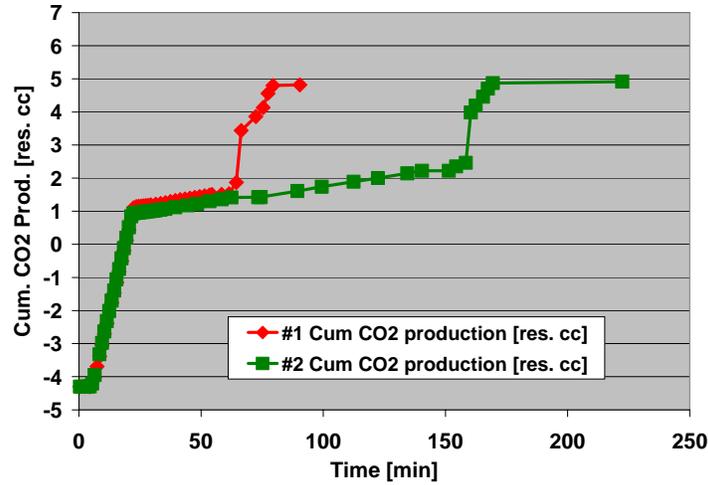


Fig. 12. Comparison of CO<sub>2</sub> cumulative production versus time during brine injection for both Queen tests. One PV of injection is equal to about 38 minutes of injection.

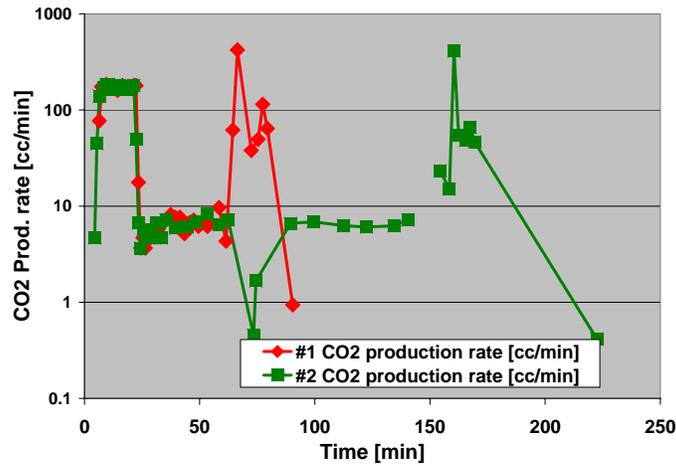


Fig. 13. Comparison of CO<sub>2</sub> production rate versus time during brine injection for both Queen tests. One PV of injection is equal to about 38 minutes of injection.

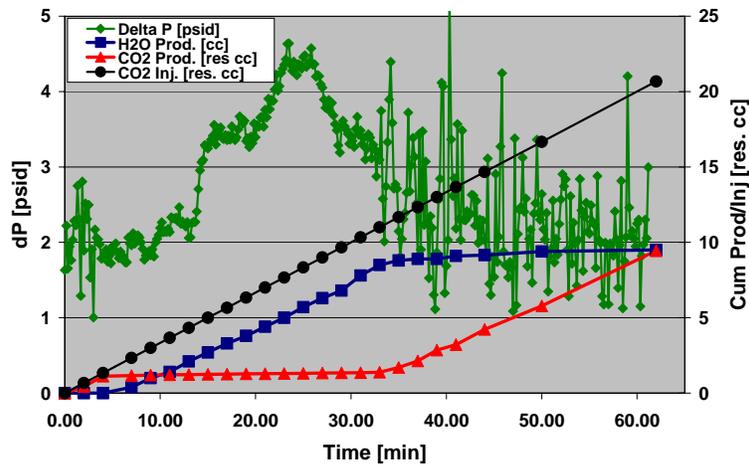


Fig. 14. Dolomite Flood 1 showing the injection and production of CO<sub>2</sub>, production of water, and differential pressure until CO<sub>2</sub> breakthrough.

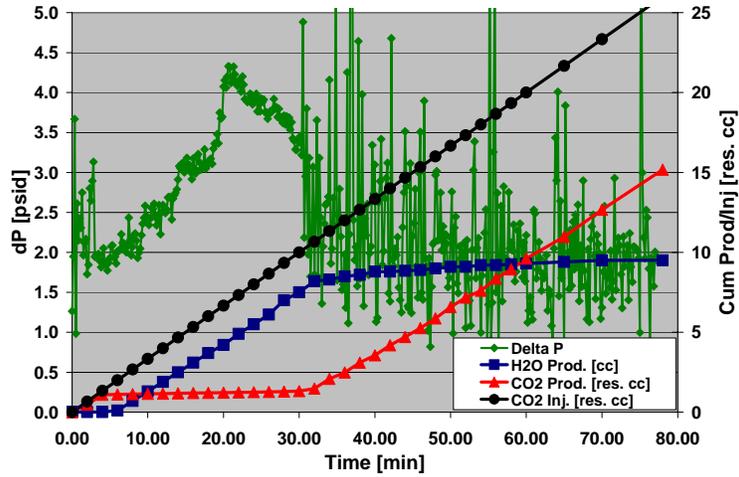


Fig. 15. Dolomite Flood 2 is similar to Flood 1 except production of CO<sub>2</sub> and water were recorded after CO<sub>2</sub> breakthrough.

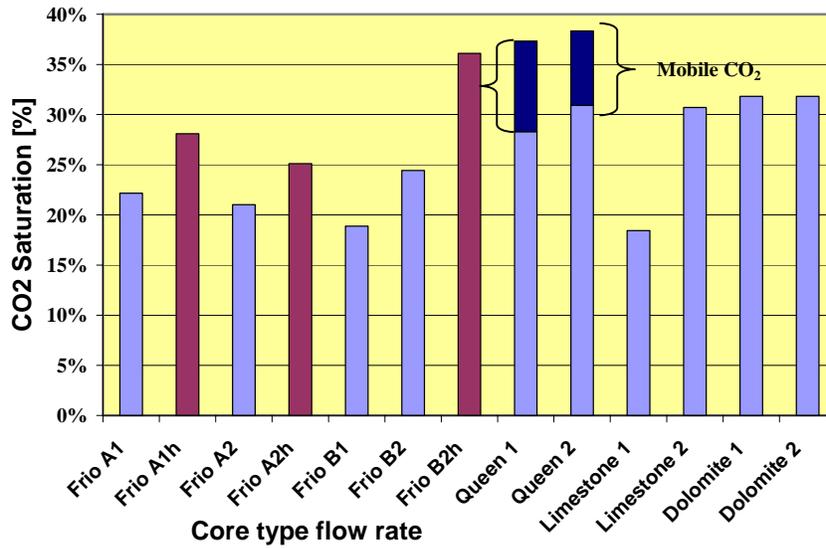


Fig. 16. CO<sub>2</sub> saturation in several core types. For all systems, the original injection rate was about 20 cc/hr; for each Frio system it was then increased to 100 cc/hr (200 cc/hr for Frio B2h) with the indicated increase in saturation indicated by the “h”. Only for Queen was there mobile CO<sub>2</sub>.