

Coreflooding Studies to Investigate the Potential of Carbonated Water Injection as an Injection Strategy for Improved Oil Recovery and CO₂ Storage

Mehran Sohrabi · Nor Idah Kechut ·
Masoud Riazi · Mahmoud Jamiolahmady ·
Shaun Ireland · Graeme Robertson

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Abstract Carbonated water injection (CWI) is a CO₂-augmented water injection strategy that leads to increased oil recovery with added advantage of safe storage of CO₂ in oil reservoirs. In CWI, CO₂ is used efficiently (compared to conventional CO₂ injection) and hence it is particularly attractive for reservoirs with limited access to large quantities of CO₂, e.g. offshore reservoirs or reservoirs far from large sources of CO₂. We present the results of a series of CWI coreflood experiments using water-wet and mixed-wet Clashach sandstone cores and a reservoir core with light oil (*n*-decane), refined viscous oil and a stock-tank crude oil. The experiments were carried out to assess the performance of CWI and to quantify the level of additional oil recovery and CO₂ storage under various experimental conditions. We show that the ultimate oil recovery by CWI is higher than the conventional water flooding in both secondary and tertiary recovery methods. Oil swelling as a result of CO₂ diffusion into the oil and the subsequent oil viscosity reduction and coalescence of the isolated oil ganglia are amongst the main mechanisms of oil recovery by CWI that were observed through the visualisation experiments in high-pressure glass micromodels. There was also evidence of a change in the rock wettability that could also influence the oil recovery. The coreflood test results also reveal that the CWI performance is influenced by oil viscosity, core wettability and the brine salinity. Higher oil recovery was obtained with the mixed-wet core than the water-wet core, with light oil than with the viscous oil and low salinity carbonated brine than high-salinity carbonated brine. At the end of the flooding period, an encouraging amount of the injected CO₂ was stored in the brine and the remaining oil in the form of stable dissolved CO₂. The experimental results clearly demonstrate the potential of CWI for improving oil recovery as compared with the conventional water flooding (secondary recovery) or as a water-based EOR (enhanced oil recovery) method for watered out reservoirs.

Keywords Carbonated water injection · Enhanced oil recovery · CO₂ storage · Coreflooding

M. Sohrabi (✉) · N. I. Kechut · M. Riazi · M. Jamiolahmady · S. Ireland · G. Robertson
Institute of Petroleum Engineering, Heriot Watt University, Riccarton, Edinburgh, EH14 4AS, UK
e-mail: mehran.sohrabi@pet.hw.ac.uk

1 Introduction

Currently around 86% of the world primary energy use is supplied by oil, gas and coal ([International Energy Annual 2006](#)). The demand of these fossil fuels is anticipated to increase in tandem with the projected 40 to 45% increase of the global energy consumption between now and 2030. The world oil reserves are however diminishing and exploration for new discoveries are becoming increasingly more difficult and costly. We will therefore have to make better use of our current position and resources by increasing the recovery factor from the existing oilfields.

An inevitable undesired side effect of burning the fossil fuels is CO₂ emission which is believed to have contributed to the problem of global warming. With the increased atmospheric concentrations from pre-industrial levels of 280 to 380 ppm in 1994 ([IPCC Report 2007](#)), CO₂ produced by the burning of fossil fuels becomes the main greenhouse gas that contributes around 60% of the total global radiative forcing of all the anthropogenic gases. The capture of this CO₂ and its subsequent storage in geological formations such as deep saline aquifers, depleted oil and gas reservoirs and un-mineable coal beds is an important strategy for achieving substantial reductions in anthropogenic CO₂ emissions levels while enabling continued use of existing energy supply ([IPCC Report 2007](#)). Saline aquifers represent much larger storage as compared to hydrocarbon reservoirs. However, there are many advantages of injecting CO₂ in the oil reservoirs such as the existence of infrastructure, wealth of data, the presence of proven structural trap to hold the injected CO₂ and the revenue from the incremental oil that may partly offset the CO₂ storage cost. It was estimated that at \$20/t of CO₂ stored, ~930 Gt of CO₂ could be stored in depleted oil and gas fields worldwide ([International Energy Annual 2006](#)). Dissolving this anthropogenic CO₂ into the injected water for otherwise plain waterflooding would contribute in reducing the CO₂ emission to the environment.

The conventional CO₂ flooding normally requires large quantities of CO₂, thus secured and low cost source of CO₂ is essential. However, natural CO₂ resources are often located too far from oil fields to be used. The high cost of capturing large quantities of CO₂ from coal-fired power stations is also likely to make conventional CO₂ flooding uneconomical in many oil reservoirs around the world which would otherwise be suitable candidates for improved oil recovery and CO₂ storage. An alternative injection strategy in which much less CO₂ is used as compared to conventional CO₂ injection is carbonated water injection (CWI). This process is particularly attractive for offshore oil reservoirs or other reservoirs with limited access to CO₂. It could also serve as water-based enhanced oil recovery (EOR) method for watered-out oil reservoirs in which high water saturations adversely affects the conventional CO₂ injections. For CO₂ storage, CWI eliminates the risk of buoyancy-driven leakage as in the case of bulk phase injection ([Burton and Bryant 2007](#)) since carbonated water is denser than the native brine ([Hebach et al. 2004](#)), thus securing storage and reducing the cost of monitoring the stored CO₂.

In CWI, CO₂ is dissolved in and transported through the reservoir by the flood water. At typical pressure and temperature of oil reservoirs, CO₂ solubility could be as high as 30 Sm³/m³ (168 Scf/bw), much higher than hydrocarbon gases, which is favourable for oil recovery and beneficial for CO₂ storage. As a single phase, carbonated water mobility contrast with oil is more favourable than in the CO₂ gas-oil system. CO₂ is more evenly distributed within the reservoir thus retards CO₂ breakthrough and improves sweep efficiency.

Field applications of secondary CWI in Texas and Oklahoma in the 1960s reported more than 40% incremental oil recovery above the original estimates of conventional waterflood potential ([Hickok et al. 1962](#)) and improved water injectivity ([Ramsay and Small 1964](#);

Hickok et al. 1962). The process unfortunately lost its way as the then high CO₂ cost from the liquefaction plant rendered it uneconomic. In the current situation with the legislation drives in reducing CO₂ emission and with development of more efficient CO₂ capture process, the cost of CO₂ might no longer be the limiting factor and its CO₂ storage advantage would favour this process more than ever before.

Despite the concerns that carbonic acid, which is formed when CO₂ dissolved in water, may cause localized corrosion of steel (Browning 1984). Hickok et al. (1962) reported no evidences of further corrosion apart from the normal waterflood corrosion in the K&S carbonated waterflood project. The CO₂ injection lines were even re-used several times during the staging of the CO₂ injection. It was hypothesized that the limited proportion of CO₂ formed sufficient amounts of alkali and alkali earth carbonates and bicarbonates and these salts act as buffers which prevent the corrosion of the steel (Martin 1951).

There is limited information on the effectiveness of CWI for oil recovery particularly in tertiary recovery mode. Tertiary CWI in the cores was reported to have reduced the oil saturations after plain water injection by almost 50% (Holm 1963; Hickok et al. 1960). Based on the results of high pressure direct flow visualization (micromodel) experiments on decane and refined viscous oil, Sohrabi et al. (2008) deduce that oil swelling and viscosity reduction due to CO₂ diffusion from the water into the oil phase were one of the main oil recovery mechanisms in CWI. Further micromodels work by Riazi et al. (2009) also on decane at 13.789 MPa (2000 psig), 38°C (100°F) shows that the incremental oil recovery from the tertiary CWI could be as high as 16% at the pore scale.

In this study, CWI is primarily examined as a method to increase the oil recovery (CO₂-augmented waterflooding) with an added benefit of storing CO₂. The coreflood experiments were carried out to quantify the recovery benefits of CWI as compared to plain waterflood, both in secondary and tertiary oil recovery modes. The tests were to determine whether carbonated water can bring favourable effects to oil recovery in a porous media as does the gaseous CO₂ in the conventional CO₂ flooding. The experiments were also to investigate the influence of oil viscosity, rock wettability and brine salinity on the CWI process performance. The potential of this injection scheme for CO₂ storage which, to the best of the authors' knowledge, has never been experimentally investigated before was also looked into.

2 Experimental Setup and Procedures

2.1 Coreflood Rig

A high-pressure high-temperature coreflooding rig was used in the tests. The core holder was mounted horizontally. Two setups of the equipment were employed; the difference being the conditions of the effluent collection and the size of the core holder.

The first equipment setup is schematically shown in Fig. 1a. It consists of a dual-cylinder pump system connected to a transfer vessel, which was used to deliver the fluids into the core. The core effluent would be carried through a backpressure regulator where the pressure would drop to atmospheric pressure, and hence any dissolved gas would be liberated. The separated liquid would then be collected in a graduated cylinder while the gas would be collected in a gasometer. The standard conditions at which the effluent volumes were measured in these tests were 15.5°C (60°F) and ambient pressure. The results reported in this paper are mainly using this setup unless otherwise stated.

In another setup (Fig. 1b), four high-pressure positive displacement pumps (piston pumps) are connected to a transfer vessel each. Two pumps are for injecting brine and oil at the desired

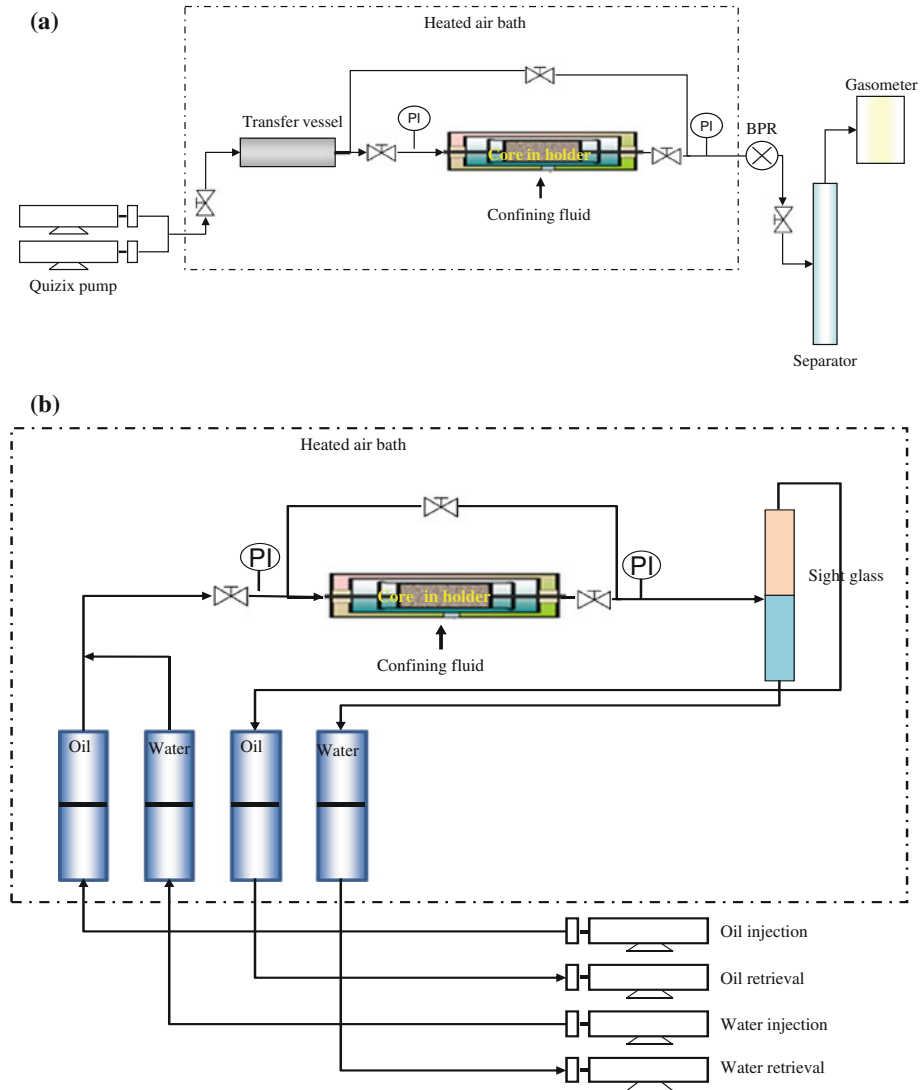


Fig. 1 **a** Schematic of the coreflood rig with effluents measured at the ambient conditions. **b** Schematic of the coreflood rig with effluents measured at the test conditions

flow rate and pressure to the entry side of the core holder. The other two pumps; one for the brine and the other for the oil, are for retrieving the fluid through a sight glass with calibrated viewing lens. The retrieving pump rate was held constant similar to the injection rate to ensure constant average pressure throughout the test. The viewing lens is easy to read when the interface of the oil and brine are within certain positions with respect to its total height. The fluid withdrawn (either oil or brine) was thus dependent on the main fluid being produced so as to ensure the fluid interface is within the required viewing range. The interface level of the fluids in the calibrated sight glass was monitored and recorded throughout the test which was later used to calculate the amount of each fluid produced at the test conditions.

Both rigs are capable of operating at pressures up to 41.368 MPa (6000 psia) and temperatures as high as 149°C (300°F). Pressure and temperature at the inlet and outlet end of the core holder are displayed continuously on the computer which has a built-in data acquisition system. Temperature is maintained by keeping the apparatus inside a temperature-controlled enclosure.

2.2 Core Samples

Three types of cores were used in the study, i.e. a reservoir core and two Clashach sandstone cores; one with its natural water-wettability (water wet) whereas the other was made mixed-wet by ageing it in a crude oil. The Clashach core is a pale yellow buff, non-calcareous, medium grained sandstone from the Permian age. The environmental scanning electron microscope (ESEM) analysis shows that it composed of 75% quartz, calcium carbonate, feldspar and traces of clay mineral (illite) contents. The reservoir core is a relatively unconsolidated core taken from a North Sea sandstone oil reservoir. The sand particles on the surface of the core disintegrated rather easily upon friction but the core was able to withstand the test flow and pressure without collapse. No measurement of the core compressive strength was however made.

Porosity of the core was determined by helium porosity test and the pore volume of the core was determined as the total volume of fluid used to saturate the system minus the dead volumes of tubing connecting the core to the rest of the system. Permeability of the core was first measured using methane at the test pressure and temperature followed by measurement using brine or oil sample at the same conditions. Measurements were repeated at least three times to ensure reliability. For the Clashach core, permeability measured using methane was very rate-dependent while those measurements using the oil sample (decane) were very stable and repeatable, thus we used the effective permeability to oil to represent the Clashach core permeability. For the reservoir core, the average measured base permeability to brine was $4.58\text{E}-12\text{ m}^2$ (4580 mD) while that to methane was 16% lower. Instability of differential pressure readings at high flow rates when using methane introduced some uncertainties in the calculated permeability values. We therefore take the base permeability to brine to represent the permeability of the reservoir core. During these repeated permeability measurements using brine, no fines were observed in the effluent. The dimensions and properties of the cores used are given in Table 1.

2.3 Fluid Samples

For the tests reported here, three oil samples and two brines were used. The oil samples were high purity *n*-decane (C₁₀H₂₂), refined mineral oil and a reservoir stock-tank crude oil sample. Decane is miscible with CO₂ at the test temperature and pressure of 38°C (100°F)

Table 1 Dimension and properties of the cores used in the study

Core name	Length (cm)	Diameter (cm)	Porosity (fraction)	Absolute <i>k</i> (mD)	Injection rate (cc/h)	Wettability
Clashach 1	33.20	4.99	0.185	1300	20	W-wet
Clashach 2	61.30	4.99	0.165	850	20	M-wet
Reservoir core	8.14	3.72	0.350	4580	1	W-wet

Table 2 Compositions and properties of the oil samples used at 13.789 MPa (2000 psig), 38°C(100°F)

Component	Mole%		
	Decane	Refined viscous oil	Crude oil
C3–C9	–	–	8.15
C10	100.00	–	2.95
C11–C19	–	–	37.88
C20–25	–	9.90	15.77
C26+	–	90.10	35.25
Total	100.00	100.00	100.00
Viscosity (cP)	0.82	81	145
Density (g/cm ³)	0.73	0.91	0.93

Table 3 Ionic content of the higher salinity brine (Brine 2) used

Ion	Content (ppm)	Ion	Content (ppm)
Na	11700	Li	2.2
Ca	1170	Cl	18200
Mg	326	SO ₄	3180
K	123	Br	34
Sr	31		

and 13.789 MPa (2000 psig), respectively. The relatively heavy refined and crude oil contain mainly C20+ components (Table 2) and are immiscible with CO₂ at the test conditions.

The first brine used was synthetic brine made of degassed distilled water with 10,000 ppm salinity containing 0.8 wt% sodium chloride (NaCl) and 0.2 wt% calcium chloride hexahydrate (CaCl₂ · 6H₂O). The second brine used is of higher salinity representing seawater. It contains 2.6 wt% of sodium chloride (NaCl) and 0.6 wt% of calcium chloride hexahydrate (CaCl₂ · 6H₂O) with a total dissolved solid (TDS) of 35,380 ppm. The ionic contents of the second brine are given in Table 3. The low and high salinity brine is referred to as Brine 1 and Brine 2 with the corresponding carbonated brine as Carbonated Brine 1 and Carbonated Brine 2, respectively. The terms carbonated water and carbonated brine is used interchangeably throughout this article.

To make up the carbonated brine, CO₂ was mixed with brine in a pressure cell until saturation at carbonation pressure and at 38°C (100°F). The mixture was agitated to facilitate mixing and stabilized at the test pressure and temperature. Properties of the brine samples are presented in Table 4. The viscosity of Brine 2 and Carbonated Brine 2 at 2000 psig and 38°C (100°F) were measured values. Brine 1 viscosity was assumed as that of fresh water viscosity and taken from National Institute of Standard database while viscosity of Carbonated Brine 1 was estimated using correlation by Bando et al. (2004). The densities of carbonated brines were extrapolated from the data measured by Garcia (2001).

Chang et al. (1998) proposed correlations based on published experimental data to estimate the CO₂ solubility in water (R_{sw}) and brine. The solubility of CO₂ in Carbonated Brine 1 at 13.789 MPa (2000 psi), 38°C (100°F) was estimated to be 31 sm³/m³. The effect of brine salinity on the CO₂ solubility was estimated by Eq. 1. For Carbonated Brine 2, at 2500 psig and 38°C (100°F), R_{sw} was calculated to be 45.1 sm³/m³ (184.3 scf/stb), which was reduced to 29.3 sm³/m³ (165 scf/stb) after correction due to brine salinity.

Table 4 Properties of the brine samples used

Fluid	Viscosity (cp)	Density (g/cm ³)
Brine 1	0.67	0.99
Carbonated Brine 1	0.68	1.01
Brine 2	0.65	0.99
Carbonated Brine 2	0.85	1.02

$$\log \left(\frac{R_{sb}}{R_{sw}} \right) = -0.028S \cdot T^{-0.12} \quad (1)$$

where R_{sb} is the CO₂ solubility in brine of salinity S in scf/stb, R_{sw} is the CO₂ solubility of water in scf/stb, S is the salinity in weight% of solid, and T is temperature (°F). Good agreement was observed between the calculated values and the measured values, which are on average 29.9 and 28.2 sm³/m³ for Brine 1 and Brine 2, respectively.

2.4 Test Preparation and Procedure

The core was first cleaned and then wrapped in an aluminium foil. For the relatively friable reservoir core, a heat shrink was applied after wrapping the core to ensure the core did not disintegrate under the test flow and pressure, before putting it into a sleeve and mounting it horizontally in a high-pressure core holder. Brine was placed in the annular space between the core and the core holder and pressurized to provide a confining pressure. Different displacement rate was used for different core size; 20 cc/hr for the Clashach cores and 1 cc/hr for the much shorter reservoir core to ensure the linear displacement rates were within the range of 0.1 to 1 m/day; the typical displacement rates at the reservoir scale.

Two sets of coreflood test were carried out. The first set was secondary carbonated waterflood (without preceding water injection) at 38°C (100°F) and 13.789 MPa (2000 psig) using Clashach cores with no initial water saturation, S_{wi} . The reason of not having S_{wi} was to exclude any pre-existing water in the core thus enabling us to accurately monitor the flow of the injected carbonated water and the manner in which the dissolved CO₂ is transported within the porous medium. Decane, refined viscous oil, Brine 1 and Carbonated Brine 1 were used in this set of tests, which were performed in the core rig with effluent volumes measured at the test conditions (Fig. 1b). The core was first saturated with oil. Plain water injection (WI) was then carried out to quantify the oil recovery from the core by WI. Water injection continued until the rate of oil production reduced from 1 PV of oil produced per pore volume injected (PVI) to about 0.02 PV oil/PVI or much lower. The example of oil produced versus PVI plot for the secondary CWI of decane is shown in Fig. 2. No measureable oil produced was visually indicated by no change in the level of the collected oil in the measuring cylinders as the injection continued. Prior to the subsequent secondary CWI, the core was first flushed with many pore volumes of acetone and then methanol in order to remove any residual water or oil from the preceding waterflood test. The core was then fully saturated with the oil under the same conditions followed by carbonated waterflood.

The second set of coreflood tests were performed in the reservoir core with crude oil using the core rig shown in Fig. 1a. All the coreflood tests in the reservoir core were at S_{wi} in order to closely mimic the presence of irreducible water in the reservoir. The coreflood displacements with Carbonated Brine 1 and Carbonated Brine 2 were carried out at 13.789 and 17.237 MPa (2000 and 2500 psig), respectively.

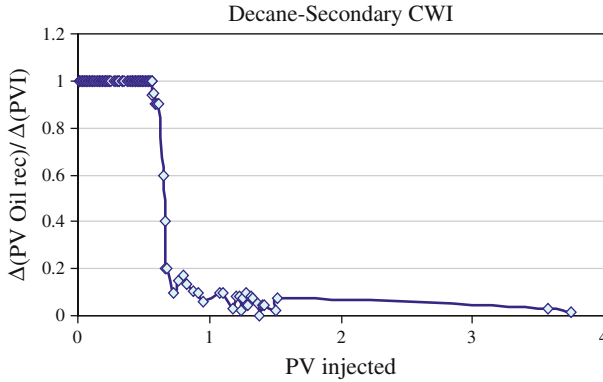
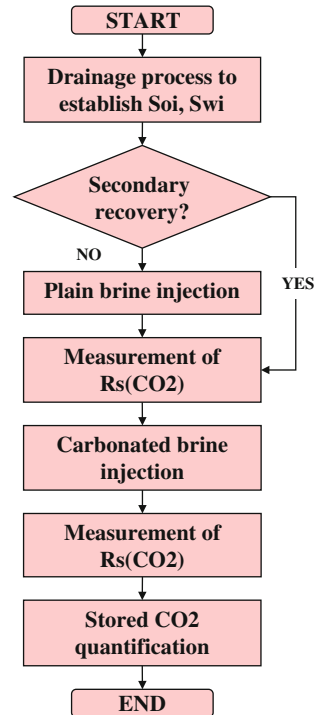


Fig. 2 Variation of the rate of change of decane production with PV injected in the secondary CWI, 13.789 MPa (2000 psig), 38°C (100°F)

Fig. 3 General work flow of the coreflood test with initial water saturation, S_{wi}



The general workflow of the tests is shown in Fig. 3. The initial oil and water saturations were first established in the core through a drainage process of the brine-saturated core with the oil. For the secondary carbonated water displacement, the CO₂ content of the injected carbonated water was then measured followed by the carbonated waterflood. For the tertiary (post-waterflood) CWI process, plain water was injected after establishing S_{wi} until no measurable amount of oil was produced. This was afterwards followed by CWI.

The recovery of oil, gas and water, and the differential pressure (DP) across the core as well as the ratio of CO₂ gas produced to carbonated water injected were recorded throughout

the tests. This ratio was compared with the initial CO₂ content in the carbonated water. This is to check whether the fluid inside the core was still taking up the CO₂ from the injected carbonated water. If it is, then the ratio is showing increasing trend. On the other hand, if the ratio started to level off it indicates the fluid inside the core was almost saturated with CO₂. Although it is desirable to stop the test when the residual oil in the core is almost saturated with CO₂, practically this would take many more pore volumes of CWIs. We stopped our tests when the Rs(CO₂) has at least started to stabilize. When the coreflood test ended, plain water was flushed through the core and the produced CO₂ was measured to quantify the amount of the CO₂ stored in the core at the end of the coreflood test.

3 Experimental Results and Discussion

The displacement tests carried in the study are listed in Fig. 4.

3.1 Secondary Versus Tertiary CWI

The comparison is made between the coreflood test results in the reservoir core using crude oil and Carbonated Brine 2 (Test 2 and 3). Since CWI could alter the permeability in sandstone cores due to dissolution of rock minerals by the carbonic acid (Ross et al. 1982; Sayegh et al. 1990; Tang and Morrow 1999), the CWI performance was compared with that of WI coreflood test carried out chronologically closest to it to ensure that comparison is made at reasonably similar core properties.

The crude oil was first injected into the brine-saturated core whereby Swi of 10.6 %PV was established. Plain Brine 2 was then injected (Test 1) at 1 cc/h and stopped at 0.8 PVI

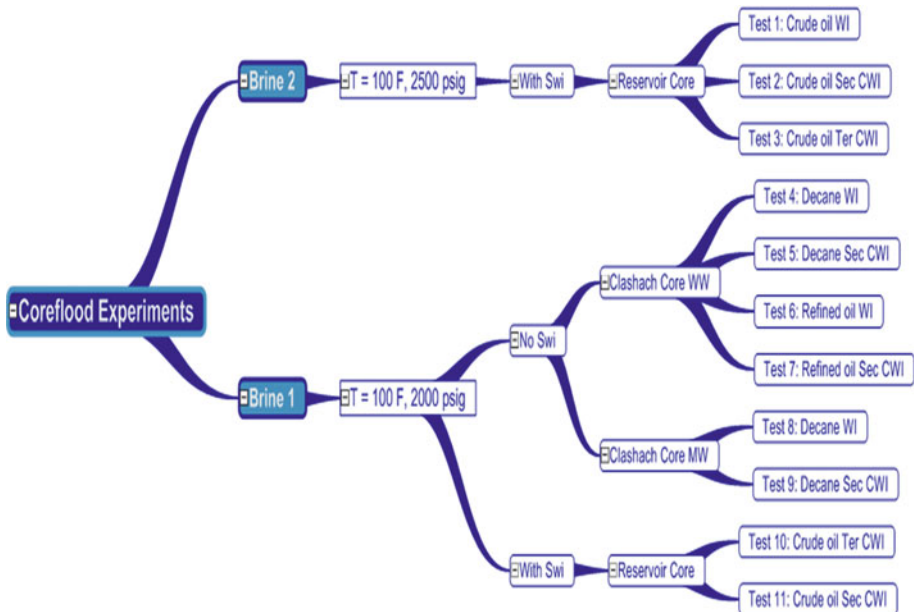


Fig. 4 List of experiments reported in this article

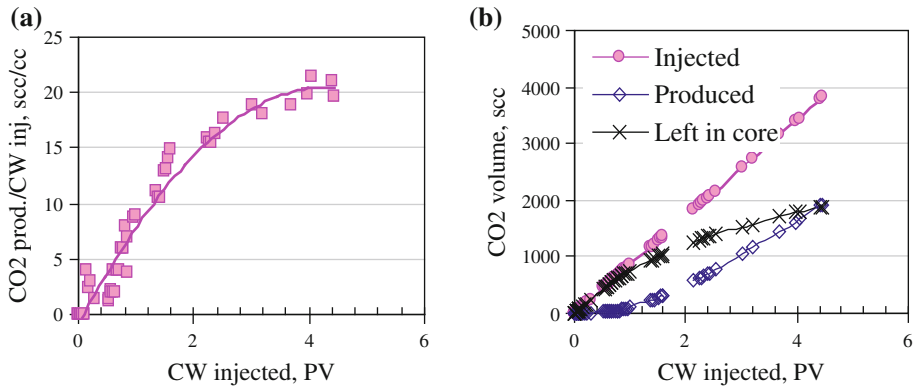


Fig. 5 **a** The ratio of the CO₂ produced to the carbonated water injected. **b** Cumulative CO₂ injected, produced and instantaneously left in the core during secondary CWI, crude oil in reservoir core at 38°C (100°F), 17.237 MPa (2500 psig) (Test 2)

(pore volume injections) where the rate of the oil production dropped to a very small value (0.013 PV or 0.4 cc of oil produced per pore volume of water injected). With this very low amount of oil produced, it was taken that continuing the plain brine injection would produce no measurable amount of oil. 41.6 %PV (46.5 %Soi) was recorded as the ultimate oil recovery from this WI.

The core was next thoroughly cleaned by two cycles of toluene and methanol to prepare for the secondary CWI (Test 2). The initial oil and water saturation in the core were again established and this time S_{wi} of 7.2 %PV was obtained. The carbonated water was then injected through the core at 1 cc/h. At certain stage during the CWI, the water and oil effluent appeared emulsified. A sediment layer was also observed to sit directly under the oil level and in some cylinders there were spidery oil webs on cylinder walls. Such emulsion and sediments were not observed during the preceding brine injection. In order to confirm the effluent volume, the cylinders containing core effluent were settled in an oven at 50°C to allow separation of phases; corrections to the recorded effluent volume were accordingly made. 60.6 %PV (65.3 %Soi) of oil was recovered at the end of this secondary carbonated waterflood. No analysis was done on the sediment, however the analysis of the water effluent using Inductively Coupled Plasma (ICP) spectrometer showed the presence of Fe, Al and Si which was not present in the initial brine. This confirms rock dissolution to give fines. Measurement of the core permeability after the test also reveals that the permeability has increased by 17% to $5.36E-12$ m² (5360 mD).

Figure 5a shows the ratio of CO₂ produced to the carbonated water injected recorded during Test 2. After the CO₂ breakthrough, the ratio increased gradually until it slowly levelled off at about 77% of the initial value, which was 27.7 sm³/m³ in this case. At this point, the fluid in the core was minimally taking up the CO₂ in the injected carbonated water. The amount of CO₂ injected (through carbonated water), produced and left in the core at any particular time during the displacement is plotted in Fig. 5b.

The tertiary CWI (Test 3) was carried out to quantify the level of increase in the oil recovery by CWI after a plain water injection. S_{wi} of 12.7 %PV was first established in the core. Then, in order to simulate conventional water flooding, plain brine was injected up to 2.86 PVI by which time no further oil recovery was observed. 58.4 %PV (66.9 %Soi) of oil was recovered leaving 28.9 %PV of residual oil after the waterflood. This much higher oil recovery from

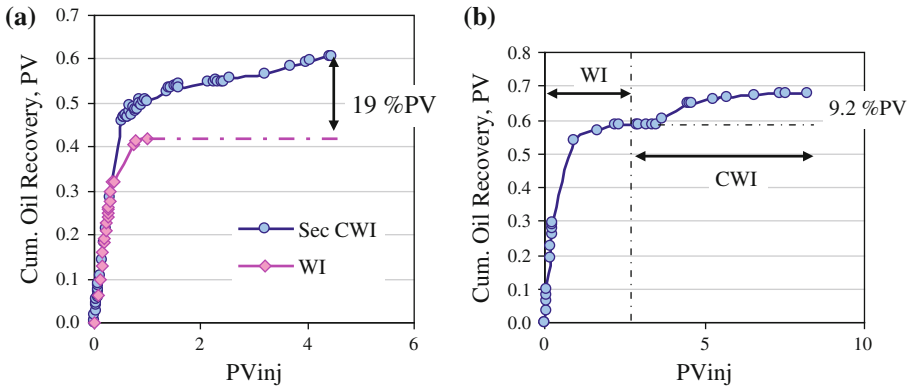


Fig. 6 Measured cumulative crude oil recovery in **a** secondary and **b** tertiary carbonated seawater flooding in the reservoir core, at 38°C (100°F) 17.237 MPa (2500 psig) (Test 2 and 3)

WI as compared to that from Test 1 is consistent with the increase in permeability of the core after Test 2. The carbonated water, which for this test contained 28.7 sm^3 of CO_2 per m^3 of brine, was then injected into the core at 1 cc/h. The CO_2 produced was monitored throughout the test and after 5.36 PVI, the ratio of CO_2 produced to carbonated water injected reached 82% of the original value. At this point, no measurable amount of oil was produced and the CWI was stopped with 67.6 %PV (77.4 %Soi) of oil recovered.

The oil recovery profiles of the secondary and tertiary CWI are shown in Fig. 6. The secondary CWI (Test 2) recovered 19 %PV (18.8 %Soi) oil more than the plain WI (Test 1) while 9.2 % PV (10.5 %Soi) incremental oil was produced from the tertiary CWI (Test 3). These results clearly show that CWI has a decent potential as an EOR process in both secondary and tertiary recovery modes with higher recovery in the former than the latter. The tertiary CWI can re-mobilize part of the oil that had been trapped in the preceding water injection period.

CO_2 solubility in crude oils is typically five to six times higher than water and hence, during CWI, as the injected carbonated water comes in contact with the oil, its CO_2 content partitioned into the oil phase. This transfer of CO_2 from the carbonated water to oil is desirable for oil recovery and CO_2 storage objectives. Part of the CO_2 -diluted oil will be recovered which contributes to the additional oil recovery by the process. However, a large part of the transferred CO_2 will remain dissolved in the remaining oil which is important from CO_2 storage perspective.

These coreflooding results also demonstrate the CO_2 storage potential of CWI. Based on volume of CO_2 collected and material balance, about 45 and 51% of the total CO_2 injected (in the carbonated water) after about 4.5 PVI was stored at the end of the secondary and tertiary CWI, respectively. The presence of plain water and higher residual oil after the preceding waterflooding could contribute to the slightly higher CO_2 left behind in the tertiary process. In the conventional CO_2 flooding, the injection strategy aims to reduce the retention factor but in CO_2 storage high retention factor is favourable. Retention factor in this case is defined as the ratio of the amount of CO_2 left in the reservoir per barrel of the oil produced. In the secondary CWI, the retention factor was measured at 93 sm^3/m^3 ; much higher than 32 sm^3 of CO_2 retained per m^3 of produced oil (ca. 181.6 scf/barrel) reported by [Klins and Farouq Ali \(1981\)](#) for an immiscible CO_2 flooding on 100 cP viscous oil at 100°F. Much higher retention factor of 742 sm^3/m^3 was obtained for the tertiary CWI process.

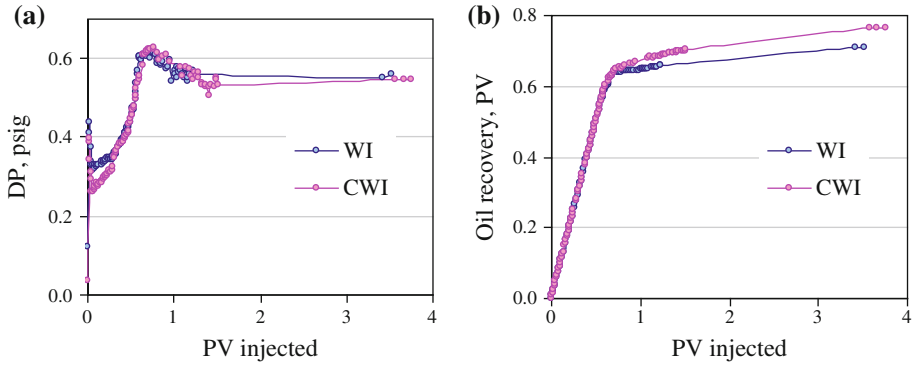


Fig. 7 Comparison between measured differential pressure across the core and cumulative oil recovery for WI and CWI, decane, water-wet core at 38°C (100°F) 13.789 MPa (2000 psig) (Test 4 and 5)

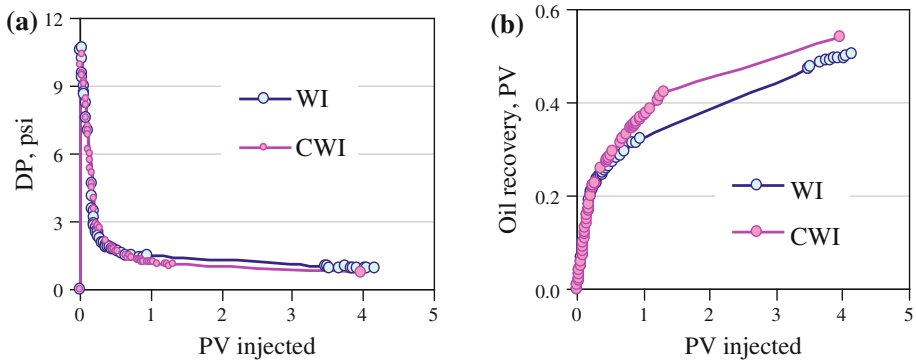


Fig. 8 Comparison of measured differential pressure across the core and cumulative oil recovery between WI and CWI, refined viscous oil, water-wet core at 38°C (100°F) 13.789 MPa (2000 psig) (Test 6 and 7)

3.2 Effect of Oil Viscosity

In order to investigate the effect of oil viscosity on the CWI performance, the secondary CWI in the water wet Clashach core using decane (Test 4 and 5) was compared with those of the refined viscous oil (Test 6 and 7). The refined oil viscosity (81 cP) is about two orders of magnitude higher than that of decane (0.82 cP).

The cumulative oil recovery and differential pressure across the core for decane and the refined viscous oil are shown in Figs. 7 and 8, respectively. Prior to water breakthrough, the rate of oil recovery equalled the rate of the fluid injection. Both WI and CWI broke through at about the same time after which the oil production rate slowed down significantly.

Carbonated water injection gives higher additional oil recovery with decane than with viscous oil. With a favourable viscosity ratio of 1.2, closer to piston-like displacement with sharper breakthrough was observed for decane. The oil production took place mainly before the water breakthrough during which 64 %PV of oil was produced. A total of 71 %PV of decane was recovered by WI while CWI produced 7.6% (5.4 %PV) more at the end of injections.

In addition to a very favourable mobility ratio, the oil recovery in CWI of decane was also enhanced by the miscibility of decane with CO₂. Although carbonated water is immiscible

with decane but the fact that decane and CO₂ are miscible at the pressure and temperature of the experiment causes decane to exhibit unlimited swelling with CO₂ which enhances the oil production. As observed by [Sohrabi et al. \(2009\)](#) in their micro-model experiments on tertiary CWI using decane and viscous oil at the same temperature and pressure as used in this study, significant oil swelling took place during CWI; up to 105% for decane as compared to only 23% for 16.5 cP viscous oil.

On the contrary, the high viscosity ratio of 119 between carbonated water and the viscous refined oil might have caused unstable front displacement that lead to fingering thus early water breakthrough. This is evident by a much lower oil recovery from waterflooding of only 50.2 %PV as compared to 71 %PV for decane. Unlike decane displacement where most of the oil was recovered prior to breakthrough, for the viscous oil, a significant amount of oil was produced after breakthrough; 21.8 %PV in the plain waterflooding and 25.8 %PV in the CWI. After 4 PV of total injections, 50.2 and 54.1 %PV of oil was recovered from WI and CWI, respectively. This is equivalent to 7.8 % higher oil recovery than from the plain WI.

Despite having disadvantage of viscous fingering and much lower CO₂ solubility (lesser oil swelling) than decane, the additional oil recovery of viscous oil above that of WI from CWI is more or less the same with that of decane. This shows that apart from the oil swelling due to CO₂ diffusion from carbonated water into the oil, other mechanisms are also playing their roles that the viscous oil could be more influenced by. One of those mechanisms is oil viscosity reduction due to CO₂ diffusion into the oil. CWI of the viscous oil benefits more from the viscosity reduction than the oil expansion. As reported by [Miller and Jones \(1981\)](#), larger percentage reduction occurs in the viscosity of more viscous crudes. Higher viscosity of carbonated water as compared to the viscosity of plain water ([Hebach et al. \(2004\)](#)) could have also benefited the recovery process.

[McFarlane et al. \(1952\)](#) demonstrated that CWI could result in more oil recovery than that theoretically possible by an oil volume expansion (oil swelling) alone. They also reported similar observation of negligible difference in oil recovery when the viscosity of the Bradford oil used in their CWI coreflood tests was reduced from 2.86 to 1.42 cP by mixing with heptane, at 5.17 MPa (750 psig) and 23.9°C (75°F). They reported up to 50% of oil viscosity reductions.

The trend in DP between CWI of the light and viscous oil is also very different. For decane, differential pressure across the core was just a fraction of 1 psi, which increased gradually to a peak value at breakthrough before gradually stabilizing as more carbonated water was injected. However, the higher oil viscosity requires much higher differential pressure to displace the oil (Fig. 8) with sharply declining trend. The slightly lower differential pressure in CWI than those of WI after the breakthrough, despite more oil was produced in the former, indicates a more efficient displacement.

3.3 Effect of Wettability

Reservoir wetting state or wettability has been widely reported to affect the pore displacement mechanism and the fluid distribution. Among the factors that affect wettability are oil and water composition, the mineralogy of the rock, the initial water saturation, and the temperature ([Buckley et al. 1989](#); [Buckley and Liu 1998](#)).

The impact of core wettability on CWI performance was assessed by comparing the oil recovery and differential pressure of the WI and CWI for decane in the water-wet (Fig. 7) and mixed-wet (Fig. 9) core. For the mixed wet core, the additional oil recovery from CWI took place at breakthrough, i.e. much sooner than in the water wet core in which the additional oil recovery took place gradually after the breakthrough. A much more efficient displacement in

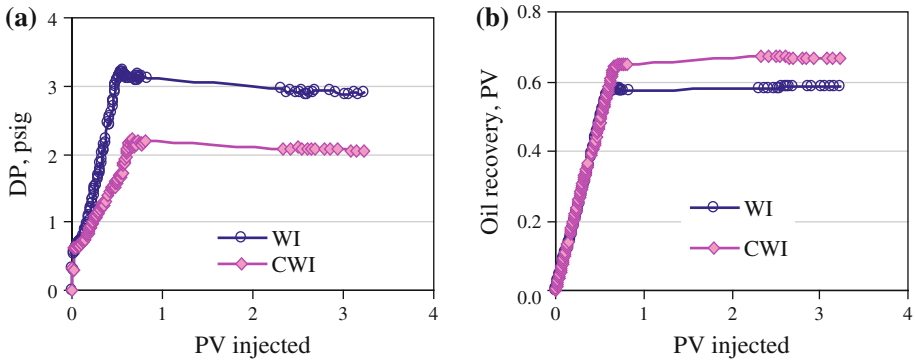


Fig. 9 Comparison of measured differential pressure across the core and cumulative oil recovery between WI and CWI, decane, mixed-wet core at 38°C(100°F) 13.789 MPa (2000 psig) (Test 8 and 9)

CWI is apparent in Fig. 9 by much lower pressure drops across the core as compared to WI despite more oil was produced. The difference in the differential pressure of WI and CWI is also much larger in the mixed wet core.

For more or less the same pore volume injected, oil recovery from WI is lower in the mixed wet core (58.5 %PV) than in the water wet core (71.0 %PV). In the water wet system, water occupies the small pores and forms a thin film over the rock surfaces while oil occupies the centres of the larger pores (Donaldson and Thomas 1971). During waterflooding, water will tend to imbibe into small-sized pores and displaces the oil into the centre of the large pores. This results in efficient oil recovery.

The improvement of oil recovery by CWI (relative to that of WI) is however higher in the mixed wet core i.e. by 11.8%, as opposed to only 7.6% in the water wet core. It was postulated that there is formation of continuous oil-wet paths of appreciable length through the mixed wet rock that give rise to better connectivity and film flow of oil along the wetting phase even at low oil saturation (Salathiel 1973). This connectivity is further enhanced by oil swelling thus contributing to better oil recovery.

These observations are significant for CWI potential application since it is now generally accepted that many oil reservoirs are mixed wet (Morrow 1990; Jerauld and Rathmell 1997). This encouraging observation was verified by another secondary carbonated water coreflood test with recovery measured at standard conditions (not reported here).

3.4 Effect of Brine Salinity

CO₂ solubility in brine is a function of pressure, temperature and the brine salinity (Klins 1984). It increases with pressure but decreases with temperature and water salinity. In order to examine the impact of brine salinity on CWI recovery, we compare the results of the secondary and tertiary carbonated Seawater (Carbonated Brine 2) flooding of the crude oil in the reservoir core with those using low salinity carbonated brine (Carbonated Brine 1). It should however be noted that the latter was performed at 2000 psig, 38°C(100°F) with estimated CO₂ solubility of 31 sm³/m³. The CO₂ solubility in the Seawater (Carbonated Brine 2) at 17.237 MPa (2500 psig), 38°C(100°F) is around 29.3 sm³/m³. Only relative comparison in the oil recovery trend could be made due to this difference in the test pressure. As can be seen in Fig. 10, the oil recovery from the secondary CWI with the low salinity Carbonated Brine 1 is slightly higher than that of Carbonated Brine 2. The results indicate that, where possible,

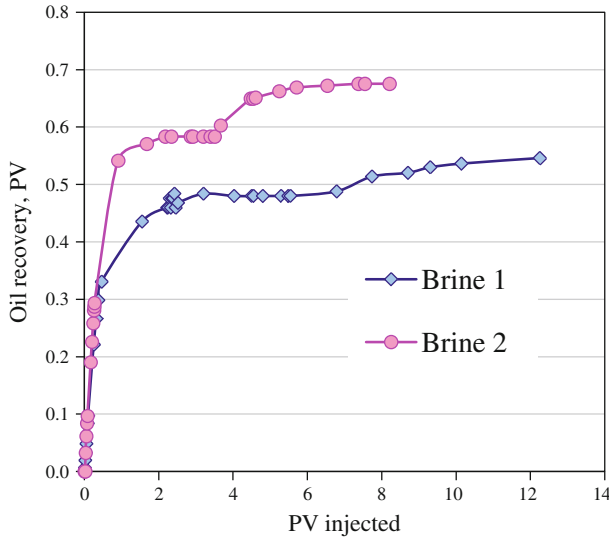


Fig. 10 Cumulative oil recovery for secondary CWI using Carbonated Brine 1 (1% salinity) and Carbonated Brine 2 (3% salinity), crude oil in reservoir core (Test 2 and 11)

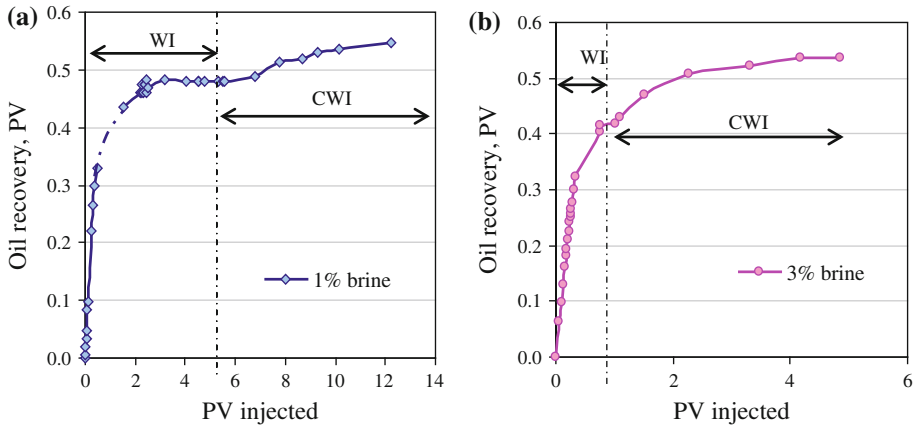


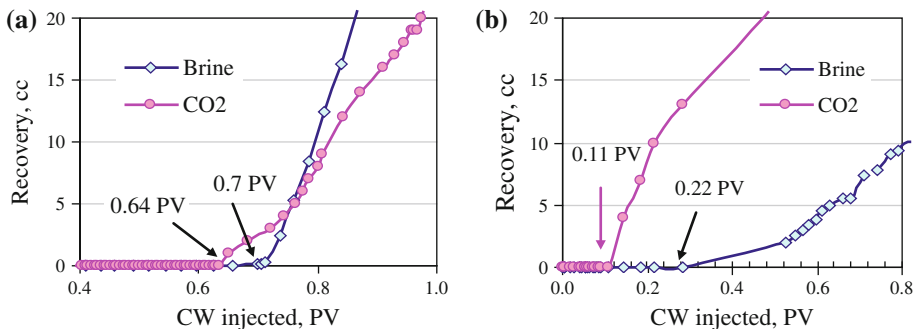
Fig. 11 Comparison of oil recovery from tertiary CWI using **a** Carbonated Brine 1 (1% salinity) (Test 10) and **b** Carbonated Brine 2 (3% salinity) (Test 1), crude oil in reservoir core

injection of low salinity carbonated brine may lead to recovering more oil compared to the higher salinity one.

A similar trend was observed with the plain WI whereby Brine 1 flooding (Test 10) yields higher oil recovery (48 %PV) than that obtained from Brine 2 injection (41.6 %PV) (Test 1). On the contrary, the incremental oil recovery was higher in the high salinity Carbonated Brine 2 for the tertiary CWI (Fig. 11). The incremental oil recoveries are summarized in Table 5.

Table 5 Comparison of incremental oil recovery from the secondary and tertiary CWI between Carbonated Brine 1 (1% salinity) and Carbonated Brine 2 (3% salinity)

Process	Carbonated Brine	Swi (% PV)	PVI	Incremental oil recovery	
				% PV	% Soi
Secondary CWI	1	14.5	6.3	18.8	22.0
Secondary CWI	2	7.2	4.5	19.0	20.5
Tertiary CWI	1	15.4	6.7	6.6	7.8
Tertiary CWI	2	10.6	4.1	11.9	13.3

**Fig. 12** Early production of CO₂ and brine recovery during secondary CWI of **a** decane in mixed wet core and **b** crude oil in the reservoir core (Test 2)

3.5 Displacement Front Propagation

Carbonated water injection as an EOR method relies on delivering the dissolved CO₂ to the oil and the subsequent favourable changes that happens to the oil physical and flow properties. If the carbonated water front is completely deprived of its CO₂ early and moves forward as plain water, its performance would be adversely affected and would approach that of plain WI. It is therefore important to investigate the CO₂ front propagation from the injected point towards the production point.

The brine and CO₂ breakthrough times were thus closely observed and compared during the coreflood experiments. Figure 12a shows the early time production of water and CO₂ in the secondary CWI experiment with decane in the mixed wet core with recovery measured at the standard conditions. CO₂ broke through after 0.64 PVI whereas water broke through at 0.7 PVI. The same behaviour was also observed during the secondary Carbonated Brine 2 injection of the crude oil in the reservoir core (Test 2), with even larger gap between CO₂ and brine breakthrough time. The CO₂ from the injected carbonated water had departed from the carbonated water, dissolved into the oil and produced together with the oil and ahead of the water as shown in Fig. 12b.

This small yet noticeable difference shows that carbonated water front had not been depleted from its CO₂ content and the CO₂ has moved ahead of the carbonated water front. This serves as an evidence of the diffusion of CO₂ from the carbonated water into the oil i.e. as a result of the CO₂ transfer from carbonated water into the oil.

This process is somewhat analogous to the process of mass transfer and mixing that can lead to multiple-contact miscibility during some gas injections. As the injected carbonated

water contacts the resident oil, a mixing zone is formed. This mixing zone, which is made of a mixture of oil and CO₂, moves ahead of the carbonated water front and its size increases with time as it moves forward into the reservoir. This important observation helps us to understand the behaviour of the dissolved CO₂ and its interactions with the oil and water inside the reservoir as the CWI progresses, which impacts the effectiveness of CWI as an oil recovery method.

4 Overall Discussions

In this article, the results of a series of coreflood experiments were presented and discussed. Three different cores with different states of wettability, three different oil samples and two different brines were used in the experiments with the main aim of investigating the performance of CWI for improved oil recovery and CO₂ storage.

The results clearly show that both secondary and tertiary CWI could improve oil recovery above that of plain waterflooding. Secondary CWI gives higher and earlier incremental oil recovery than the tertiary CWI process. In the coreflood tests presented here (Test 2 and 3), the residual oil saturation from the plain waterflood was 53.5 %Soi while the residual oil saturation after secondary CWI was 34.7 %Soi; giving 35% reduction of the waterflood oil saturation by secondary CWI. This falls within the range of 33–48% reduction of residual oil saturation due to waterflooding reported by [McFarlane et al. \(1952\)](#) from their carbonated water coreflood experiments on much lighter Bradford oil of 2.86 cP. This represents 40% improvement in oil recovery above the original estimates of conventional waterflood potential, which again is in good agreement with 43% increase of oil recovery in the K&S secondary CWI project in Oklahoma ([Hickok et al. 1962](#)). For the tertiary CWI process, the waterflooding residual oil saturations reduced by 31%, falls within 14–47% improvement in the tertiary carbonated coreflood also on Bradford crude reported by [McFarlane et al. \(1952\)](#).

Several mechanisms could have contributed to the additional oil recovery in this process. Once in the reservoir, carbonated water gradually loses its CO₂ by transferring the CO₂ to the oil. CO₂ solubility in oil is higher than water and can be infinity as in a miscible case. Oil viscosity will reduce as CO₂ diffuses into it, which will improve the mobility of the oil.

[Sohrabi et al. \(2008\)](#) studied the dominant mechanisms in secondary and tertiary CWI using decane as the oil phase through a series of two phase fluid flow experiments in high pressure two dimensional glass micromodel. They monitored the oil saturation in the micromodel versus time during CWI. As depicted in [Fig. 13](#), prior to the breakthrough, oil recovery is mainly by displacement. As more carbonated water is injected, CO₂ from the injected carbonated water diffuses into the trapped oil left behind in the main displacement and results in swelling. Over time, the isolated, swelled oil ganglia would coalesce with each other and produced. Similar observation was reported in the tertiary carbonated displacement in the micromodel ([Riazi et al. 2009](#)) except that the level of swelling is less due to the presence of mobile water from the preceding waterflooding.

Oil swelling could cause fluid flow in some of the pores become partially or completely restricted as demonstrated in [Fig. 14](#). Again, through micromodel experiments using decane at 38°C and 13.789 MPa (2000 psi), [Riazi et al. \(2009\)](#) observed as in [Fig. 14a](#), that before CO₂ dissolution in the oil droplets (shown as white blob surrounded by the blue carbonated water), the carbonated water can flow through the sides of the pores but as the oil blobs swell ([Fig. 14b](#)), some of the paths become partially or totally blocked. This gives rise to fluid redistribution or flow diversion; carbonated water will flow and contact oil droplets in other area that otherwise could have been bypassed, thus improve oil recovery.

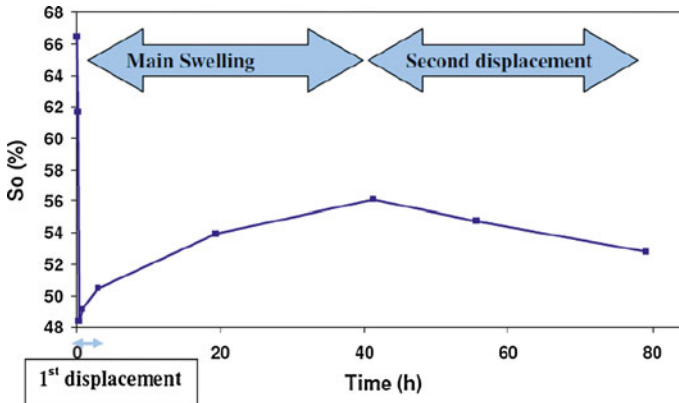


Fig. 13 Oil saturation versus time during CWI as a secondary recovery method in a micromodel (Sohrabi et al. 2008)

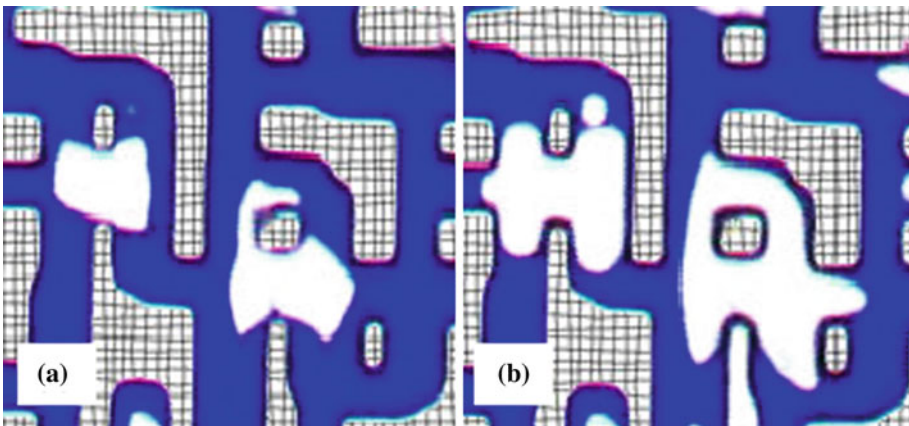


Fig. 14 **a** Free oil droplets (white) surrounded by carbonated water (blue). **b** Swelled oil droplets as a result of dissolved CO_2 that block some of the fluid paths (Riazi et al. 2009)

We have shown in the earlier section that the native state of wettability of the rock is influential to the performance of CWI. CWI has also found to change the rock wettability that could also play a role in the oil recovery. In this study, we carried out CWI in micromodel with 16.5 cP mineral oil 13.789 MPa (2000 psig) and 38°C (100°F) following the procedure as described elsewhere (Sohrabi et al. 2009; Riazi et al. 2009). We observed the shape of the fluid interface to investigate as to whether there was a change in the wettability of the micromodel surface. There was evidence as shown in Fig. 15, of micromodel surface becoming even more water wet after CWI. After several hours of plain water injection, the oil phase snapped off as the water films around the oil ganglia thickened, Fig. 15a. As can be seen, the oil/water interfaces show a more rounded shape after CWI than after WI (Fig. 15b). The capillary forces change the shape of the fluids' interfaces in the porous medium conditions. As the dimensions of pores are the same in both images, the shape of the fluid interfaces is determined, in this case, by wettability and interfacial tension (IFT) between the oil and the aqueous phase. Since the IFT between oil/water decreases in presence of CO_2 , the most likely reason for the change in the balance of capillary forces is wettability alteration. These

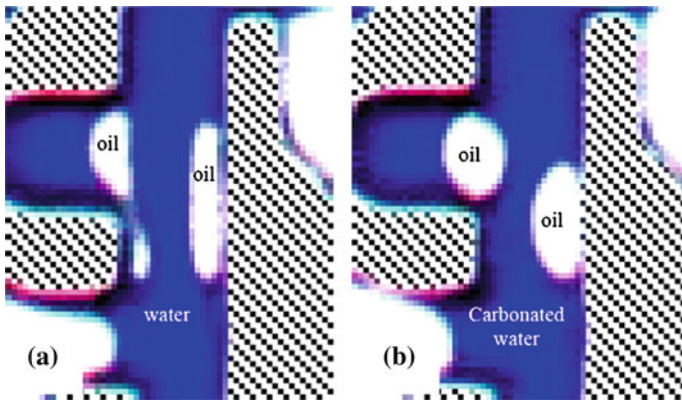


Fig. 15 A magnified image of a section of the micromodel demonstrating different micromodel wettability: **a** more oil wet after WI, **b** less oil wet after 15.8 h of CWI

visual data of the shape of the fluid interfaces reveal that the micromodel has become more water wet in the presence of carbonated water than in the presence of plain water.

Our study emphasizes CWI as a CO₂-augmented waterflooding process with the main objective of increasing the oil recovery. But there is a potential to use this injection strategy for safe storage of CO₂. Many oil reservoirs in the world particularly offshore reservoirs are under waterflooding. In the North Sea area, for instance, waterflooding is the standard method of oil recovery with almost every reservoir under waterflooding. According to the data published by DECC (UK Department of Energy and Climate Change), in 2010 around 227 million cubic meters of water was injected in the North Sea offshore reservoirs (<https://www.og.decc.gov.uk/pprs/pprsindex.htm>). Assuming a CO₂ solubility of 5.7 lb CO₂/100 lb water (equivalent to what we obtained in the laboratory at 2000 psi and 100°F), 11.6 million tonnes of CO₂ could have been stored in 2010 alone in the North Sea offshore reservoirs, had carbonated water been injected instead of water. This is equivalent to around 10 medium size CCS projects. Therefore, although, in our article, we put forward CWI as an alternative CO₂ injection strategy for improving oil recovery from reservoirs too far from natural sources of CO₂, we believe that CWI projects can also collectively contribute to storing significant quantities of anthropogenic CO₂ separated from activities around oilfield, e.g. natural gas or associated gas or downstream activities, e.g. refineries and petrochemicals plants.

5 Conclusions

Based on the results of the experiments presented in this article, the following conclusions are drawn:

- For all the rocks and fluids samples used in this study, the ultimate oil recovery by CWI was consistently more than (plain) water injection in both secondary and tertiary recovery mode. This demonstrates the potential of CWI for increasing oil recovery from both virgin and water flooded reservoirs.
- Secondary CWI resulted in higher and earlier incremental oil recovery than the tertiary CWI process, as one would usually obtained for other oil recovery methods as well. This is expected given that in tertiary recovery, the remaining oil is more likely to be

disconnected and exists in the form of isolated or by-passed patches which are more difficult to remobilise.

- For miscible systems, as with decane and CO₂ at pressure and temperature of our experiments, CWI presents great advantage in terms of improved sweep since carbonated water results in very large oil swelling (infinite) as in the direct CO₂ injection despite only a fraction of the injected fluid is CO₂.
- The core wettability appears to affect the oil recovery by CWI considerably. While incremental oil recovery in the water wet cores mainly occurred after breakthrough (behind the displacement front), the additional oil recovery in the mixed wet core occurred at breakthrough (at the displacement front).
- The oil viscosity was also observed to affect the amount of oil recovery by CWI. In terms of %PV, higher oil recovery was obtained by CWI in light oil than in viscous oil as the more piston-like displacement pattern in the light oil is more favourable for the oil recovery. Nevertheless, the oil improvement above that oil waterflooding due to CWI was more or less similar in both oils, indicating other recovery mechanism such as oil viscosity reduction is more dominant than the adverse effect of viscous fingering in the CWI of the viscous oil.
- Close examination of the CO₂ and water production graphs revealed that the carbonated water front was not depleted of its CO₂ content and that the CO₂ was moving ahead of the carbonated water front. This proves good delivery of CO₂ by carbonated water front.
- Carbonated water injection is a potential injection strategy for combining oil recovery and CO₂ storage. Relatively high percentage of the total volume of CO₂ injected (ca. 40-50%) was stored at the end of the secondary and tertiary CWI experiments.

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