Laboratory Assessment of CO2 Storage in Oil Reservoirs through Converting Waterfloods to Carbonated Waterfloods

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Abstract. As we embark on our journey to net zero, there is an urgent need for strategies that can remove large quantities of CO2 from the atmosphere efficiently and cost-effectively. Geologic formations such as those found in oil and gas reservoirs have an unrivalled capacity to permanently store CO2 in a similar manner that they held oil and gas for millions of years. Globally, oil reservoirs are flooded with millions of barrels of water every day. If carbonated, this flood water can carry and store massive amounts of CO2 inside these reservoirs. This would significantly reduce the carbon footprint associated with oil and gas production using a well-established existing technology. In this paper, we investigate the performance of carbonated water injection by performing various experiments including coreflood experiments and direct visualization experiments. Compared to free CO2 injection, injection of carbonated water requires much less CO2 compression and re-injection and hence, it costs much less. Our coreflood results show that most of the CO2 injected in the form of carbonated water, is retained by the fluid inside the reservoir and will never be produced. Coreflood results also clearly show that carbonation of water increases the performance of waterflood in all types of oil reservoirs including light oil, heavy oil, sandstone as well as carbonate reservoirs. The additional oil recovered by carbonated water injection may offset the cost of retrofitting existing waterfloods and converting them to carbonated waterfloods. Storage of CO2 in oil reservoirs as carbonated water, as opposed to free CO2, eliminates the risk of CO2 leakage from caprock, which is a major concern in conventional CO2 injection and storage projects. Carbonation of water increases the water density and hence, carbonated water sinks in the reservoir rather than rising up by buoyancy and pressuring against the caprock and minimises the risk of leaks through undetected fractures or wells. This study demonstrates, by presenting laboratory data, that the oil and gas industry can help reduce the volume of CO2 in the atmosphere by converting conventional waterfloods to carbonated waterfloods.

1 Introduction

CO2 emissions must be reduced significantly in order to meet governments targets. While this would need cleaner sources of energy, that alone would not be enough. Large quantities of CO2 must also be removed from the atmosphere if we are going to achieve net zero emissions. As can be seen in Figure 1, achieving net zero by 2050 depends on our ability to not only significantly reduce our CO2 emissions but also remove giga tons of CO2 from the atmosphere each year [1]. Few options currently exist to allow us to remove such huge quantities of CO2 in the desired timescale. Injection and storage of CO2 in geological formations is one such option, but the uptake of the technology has been slow. There are concerns about leakage of CO2 from storage reservoirs. The cost of CO2 capture and compression is also often excessive. An alternative strategy to conventional CO2 injection and water flooding is carbonated water injection (CWI) [2-12]. Globally, millions of barrels of water are injected in oil reservoirs every day. Figure 2 shows the UK production/extraction to October 2011. As can be seen, by October 2011, nearly 47 billion barrels of water had been injected in the UK oil reservoirs (and billions more barrels of water have been injected since then). This very large volume of water would have removed billions tons of CO2 from the atmosphere had the water been carbonated before injection. Figure 3 shows the CO2 solubility in water as a function of pressure and temperature. Under the conditions of a typical oil reservoir, around 35 volumes of CO2 can be dissolved in each volume of injected water. Therefore, the 47 billion of barrels of water that were injected in the UK North Sea reservoirs by October 2011 could have removed nearly 9 TCF (Trillion Cubic Feet) or 250 gigatons of CO2, which is equal to 80 years of total CO2 emissions of the European Union countries.

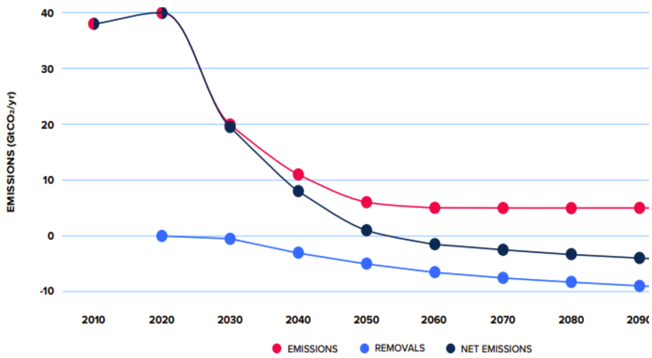

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Fig. 1. Emissions trajectory for 1.5 C warming. Adapted from Friedmonn et al, 2020. Intergovernmental panel on climate change (IPCC) 2018.

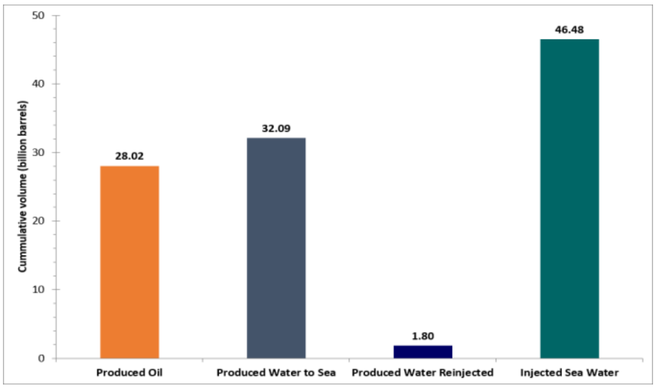

Fig. 2. UK production and extraction to October 2011.

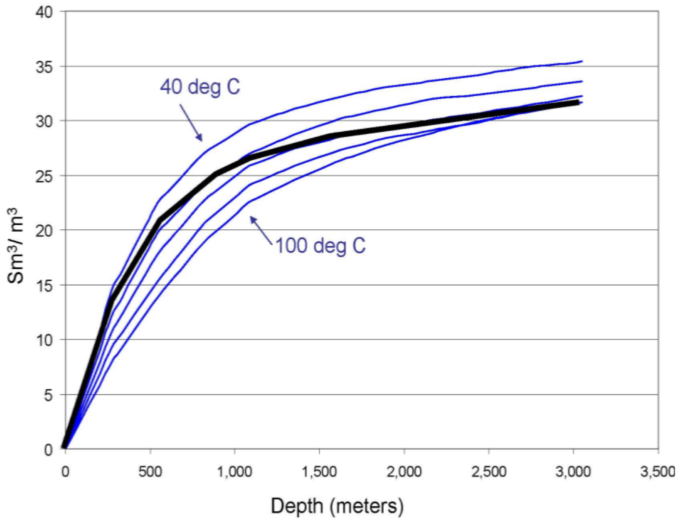

Fig. 3. CO_2 Solubility in water versus temperature and depth (pressure).

2 Results and Discussions

In this study, we have investigated the performance of CWI as a method for improving oil recovery factor and at the same time safe storage of CO_2. We have performed direct flow visualisation experiments as well as coreflood experiments. Visualisation experiments revealed the mechanisms of interactions between carbonated water and crude oil and allowed us to study the process of CWI qualitatively. Coreflood experiments were performed under reservoir conditions using rock and oil samples taken from a carbonate oil reservoir. The experiments were performed using live crude oil (oil plus dissolved hydrocarbon gas) in order to quantify the performance of CWI in the lab under simulated reservoir conditions.

2.1 Advantages of carbonated water injection

In CWI, CO_2 is dissolved in water and this has a number of advantages compared to conventional CO_2 injection where CO_2 is injected as a free phase. Some of the main advantages of CWI are as follows:

- There will be no buoyancy challenge in CWI. Gravity segregation is a major challenge during conventional CO_2 injection for both CO_2-EOR or for CO_2 storage. Buoyancy effects adversely affect the performance of CO_2 EOR as well as significantly increasing the risk of CO_2 leakage from storage sites.
- Viscous fingering too is a major challenge in conventional CO_2 injection, much like gravity segregation. There will be no viscous fingering in CWI compared to conventional CO_2 injection because the fluid that is injected is essentially water.
- CWI can be implemented in fields with on-going or planned waterfloods with small modifications on waterflood facilities.
- Much less gas handling (compression, separation, and recycling) is required in CWI injection.
- At the end of CWI injection, it is still possible to implement tertiary oil recovery techniques as in the case of conventional waterflood.
- There is much less risk of CO_2 leakage through any undetected fractures in the caprock or around the wellbore, if CO_2 is injected as carbonated water. Dissolving CO_2 in water increases the density of water and hence the resultant carbonated water sinks in the reservoir rather than pressing against the caprock.
- There are potential disadvantages associated with CWI as well that must be considered carefully in our design and planning. Dissolution of CO_2 in water reduces the pH of water and makes the injection water mildly acidic. That may cause more corrosion compared to conventional waterfloods. Rock dissolution around the wells and hydrate formation in wellbore in cold environments could happen as well. Also, for CWI to have a role in the reductions of atmospheric CO_2, CO_2 capture technologies must be available too.

2.2 Mechanisms of oil recovery by carbonated water injection.

In addition to providing a long-term safe mechanism for CO_2 storage, CWI can also significantly improve oil recovery.

Solubility of CO_2 in crude oil is more than that in water and hence, when carbonated water comes in contact with crude oil in the reservoir, CO_2 will spontaneously move from water into the oil. Dissolution of CO_2 in crude oil brings about a few changes that leads to the improvement of oil recovery. These include oil swelling and hence oil relative permeability improvement, oil viscosity reduction, as well as a favourable change in the wettability of the reservoir rock due to a reduction in the water pH.

The extent of the reduction in oil viscosity by CO_2 dissolution is a function of the initial viscosity of the oil. Normally, the higher the initial oil viscosity, the higher the reduction in its viscosity by CO_2 dissolution. Figure 4 shows the reduction in viscosity of a heavy crude oil as CO_2 dissolves in it. The oil initial viscosity was 600 cp and the graph shows how the oil viscosity changed as CO_2 was dissolved in the oil. As can be seen, a significant reduction in the oil viscosity was observed when the oil was only 20% saturated by CO_2, and when the oil was fully (100%) saturated with CO_2, the oil viscosity dropped from 600 cp to only 15 cp. This represents a massive reduction in the oil viscosity. From the oil recovery point of view, while a 600 cp viscosity would hardly be moved by water, a 15 cp oil is water floodable.

Another very important and effective mechanisms of oil recovery by CWI is a spontaneous hydrocarbon gas evolution within the oil phase. During CWI, as CO_2 is transferred into the oil phase, there will be competition between the CO_2 and the hydrocarbon gas which is dissolved in crude oil. Since oil has a higher tendency to keep CO_2 in solution rather than hydrocarbon gas, hydrocarbon gas (mainly methane) starts coming out of solution. This leads to a spontaneous formation of a gas phase within the oil. The formation of this gas phase improves the flow and recovery of oil. To observe this mechanism, it is important to perform any CWI experiments in the lab using live oil (oil with dissolve hydrocarbon gas) not dead oil.

Figure 5 demonstrates the mechanism of oil recovery by in situ hydrocarbon gas formation during CWI. In this Figure we are using two images taken from the same spot at different times during a direct flow visualisation (micromodel) experiment. The top image in Figure 5 shows the residual oil phase (the brown colour) remaining after seawater injection. This oil is referred to as residual oil to waterflood and cannot be produced by continuation of waterflooding. At the end of waterflooding, the injection water was carbonated and the micromodel was flooded with carbonated water. During CWI, the trapped oil was observed to swell gradually which was an indication of the transfer of CO_2 from carbonated water into the oil. As the oil volume increased, gas bubbles were seen to nucleate within the oil phase and as CWI continued further the gas bubbles increased in size and became gas ganglia, as can be seen in the bottom image in Figure 5. The evolving gas is mainly hydrocarbon gas that is dissolved in oil. What happens is that oil takes CO_2 from carbonated water and it gives off hydrocarbon gas. This process resembles a WAG (water alternating gas) injection process with the exception that the gas is formed in situ and spontaneously rather than being injected externally. This process, which favours light oil reservoirs where the oil has significant amount of gas dissolved in it, leads to significant additional oil recovery. Formation of the new gas phase within the oil creates a three-phase fluid system which causes a reduction in the saturation of the oil compared to residual oil saturation to waterflood.

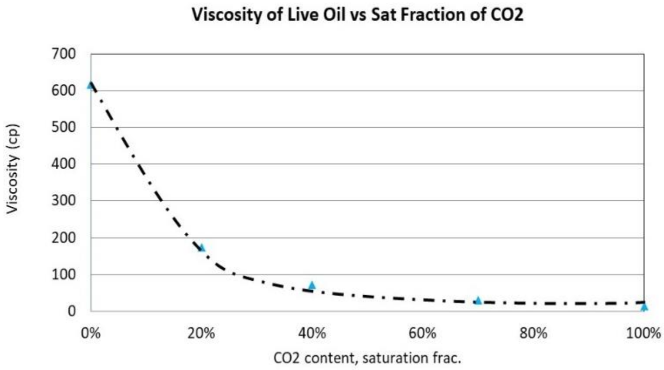

Fig. 4. CO_2 Solubility in crude oil and oil viscosity reduction.

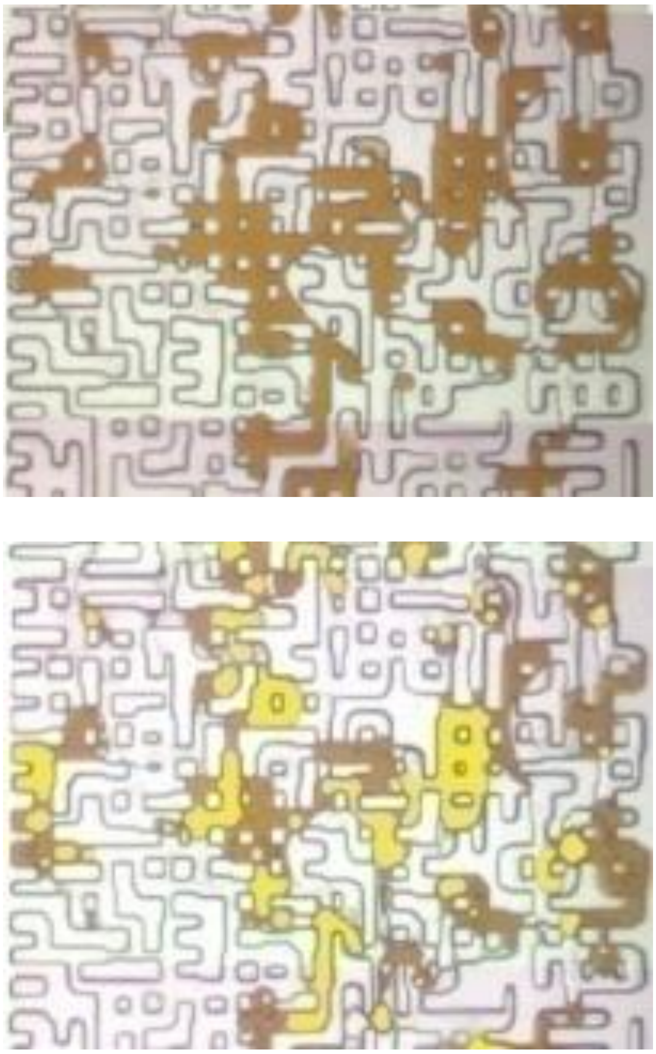

Fig. 5. CO_2 dissolves in the oil phase, a new gas phase is formed spontaneously within the oil phase during CWI.

2.3 Coreflood Experiments

A series of coreflood experiments were performed to quantify the performance of CWI. The experiments presented here were performed on a composite carbonate reservoir core formed using four core plugs, which is shown in Figure 6. The total length of the core was 23 cm, with a diameter of 3.8 cm, and a brine permeability of 10 mD. Darcy's equation for linear and laminar flow was used to measure the permeability of the core. The porosity and pore volume (PV) of the composite core were 25.17% and 66.29 cc, respectively. The porosity of the core was measured with a helium porosimeter set-up. The reservoir core samples, crude oil, formation and seawater brines were from the same reservoir source to conduct the core flooding experiments at reservoir conditions.

Fig 6: Core plugs were put together to make the composite core for the experiments

The crude oil used in the experiments had an API gravity of 40.8 and a density of 0.82 g/cm^3 measured at 60 C. Table 1 presents the composition of the brine used in the xperiments.

Table 1: Compositions of the brines used in the experiments.

Ions	Sea Water (ppm)	Formation Water (ppm)
Na^+	18,300	59,491
Ca^{+2}	650	19,040
Mg^{+2}	2,439	2,439
SO_4^{-2}	4,290	350
Cl^-	32,200	132,060
HCO_3^-	120	354
TDS	**59,046**	**213,749**

The following different iterations of Brine (SW) were used in the performed experiments:

- Low Salinity Sea Water (LSSW): which is a 10 times diluted version of Brine #1 (SW);
- Carbonated Sea Water (CSW): a fully CO2 saturated version of Brine #1 (SW);
- Low Salinity Carbonated Sea Water (LSCSW): a CO2 enriched version of LSSW, with a fixed amount of CO2 that is similar to CSW;
- Fully CO2 Saturated Low Salinity Carbonated Sea Water (LSCSW*): A LSSW mixture that is fully saturated with CO2.

A multi component mixture of recombined gas was dissolved for making ''Live Oil'', with its composition shown in Table .

Table 2: Live oil multi-component gas mixture

Component	Mole %
CO_2	9.18%
C1 (Methane)	47.49%
C2 (Butane)	22.53%
C3 (Propane)	13.25%
iC4 (Iso Butane)	1.16%
nC4 (Normal Butane)	3.74%
C5 (Pentane)	1.78%
C6 (Hexane)	0.56%
C7 (Heptane)	0.19%
C8 (Octane)	0.09%
C9 (Nonane)	0.03%
C10 (Decane)	0.01%
Total	**100**

Figure 7 shows the coreflood rig used in these tests schematically. Fluid saturations in the core at every stage of the experiments were determined by material balance. The rig was equipped with a separator, a gasometer and a CO2 analyser, which allowed the amount of the hydrocarbon gas and CO2 produced from the core to be collected and measured. The gasometer would measure the volume of the total produced gas (hydrocarbon + CO2) and the CO2 analyser would measure the amount of CO2 in the gas.
The main components of the rig are as follows::

- a custom-built high pressure/temperature chamber oven that stored all the fluids (gas, oil and brine) and core holder set at 100ºC;
- oven temperature controllers;
- pressure transducers;
- back pressure regulator BPR set at 3100 psig;
- multiple dual injection pumps;
- gasometer;
- separator;
- core holders;
- multiple fluid holding cells.

The core was first saturated by formation water with a total salinity of 214,000 ppm. The crude oil was then injected in the rock until the water saturation was reduced to 22%. The core was then aged for three weeks at 100 °C and 3100 psi. After the three weeks ageing, live oil was injected through the core to replace the dead oil.

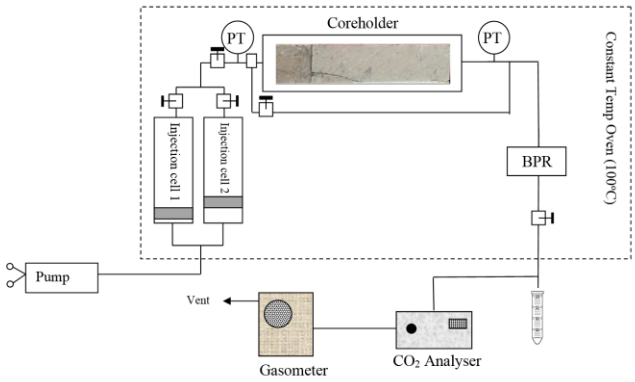

Fig. 7. *Simplified schematic of the experimental setup used for the core flood experiments*The core was then flooded with seawater, which resulted in around 60% oil recovery. At the end of seawater flooding, there were a series of higher rate (bump) floods to minimise any capillary end effects. Bumped floods resulted in some additional oil recovery. In a separate coreflood experiment, performed in the same core, instead of injecting seawater, carbonated seawater was injected in the core, keeping every other test parameter the same as before. Figure 8 compares the amount of oil recovered by seawater and carbonated seawater. As can be seen, significant additional oil recovery was obtained when seawater was carbonated before being injected in the core, with carbonated water producing 20% more oil compared to seawater.

To compare the additional oil recovery obtained by CWI with other comparable water-based oil recovery methods, the core was cleaned and primed again and a new experiment was performed using the same core. This time instead of flooding the core with seawater (SW) or carbonated seawater (CSW), it was flooded by low salinity seawater (LSSW). To produce LSSW, the seawater used in previous tests was diluted 10 times by adding fresh water to it. Figure 9 compares the performance of seawater injection with that of low salinity water injection. As can be see, low salinity seawater injection has resulted in around 5% additional oil recovery compared to seawater injection.

As shown in Figure 8 and 9, CSW injection resulted in much more oil recovery that LSSW injection. These two oil recovery methods work by completely different mechanisms. CWI works based on the transfer of CO2 into the oil whereas low salinity water injection works by changing the wettability of the rock [13]. However, combining CWI with LSWI can further boost the performance of these augmented waterflood methods. In a new coreflood experiment, which was performed in the same core, we reduced the salinity of seawater and carbonated it and then injected low salinity carbonated seawater (LSCSW) in the core. To be able to have a sound comparison, the solubility of CO2 in seawater and in low salinity seawater was kept the same which was 27 ccGas/ccinj. Figure 10 compares the performance of the low salinity carbonated seawater (LSCSW) injection experiment with all the previous different water injection scenarios. As can be seen, combining low salinity mechanisms of oil recovery with those of CWI has significantly boosted oil recovery with almost 30% additional oil recovery compared to conventional seawater injection. Under the conditions of our experiments, each cubic centimetre of LSCSW contained 27 cubic centimetres of CO2 dissolved in it (when flashed to atmospheric conditions), which represent a significant CO2 injection and storage potential by CWI.

In all the above coreflood experiments, water had been injected in secondary mode. Many reservoirs are mature and have already been under waterflood for a long time. Would CWI in tertiary mode lead to additional oil recovery if we convert the ongoing seawater floods to CWI? To answer this question, a number of new coreflood experiments were performed in tertiary mode. Figure 11 shows the performance of CWI in tertiary mode. The core had already been waterflooded using seawater. The injection of the secondary seawater continued until oil production ceased. Then seawater was carbonated and carbonated seawater was injected in the core with the same injection rate as the proceeding seawater. As can be seen in Figure 11, after nearly 1 pore volume (PV) of carbonated seawater injection, oil recovery began again. The additional oil recovery by tertiary carbonated seawater injection continued for as long as the injection continued and ultimately after 13 PV CSW injection, 24% additional oil was obtained.

A new Coreflood experiment was performed to evaluate the performance of CWI in quaternary mode where the rock was first flooded by seawater, and then low salinity seawater, followed by low salinity carbonated seawater. Tests were also performed in tertiary mode by combining carbonated water and low salinity. The results of this series of corefloods are summarised in Figure 12. As was the case in secondary injection, in tertiary injection too, the performance of carbonated water injection was boosted when it was combined with low salinity water injection. The ultimate oil recovery was the same whether carbonated water was injected in secondary mode or in tertiary mode after an initial waterflood period. For the conditions of our experiments, the ultimate oil recovery by CWI was 82% of the initial oil in place irrespective of the injection mode being secondary or tertiary. However, the additional oil recovery took place faster in secondary mode compared to tertiary. In one experiment, carbonated water was injected in quaternary mode. This test began by a secondary seawater injection period which was then followed by tertiary low salinity water injection followed by quaternary low salinity carbonated seawater injection. The ultimate oil recovery by tertiary and quaternary low salinity carbonated water injection was almost the same (82%-84%), which indicates that the history of the reservoir prior to CWI would not adversely affect the ultimate oil recovery by CWI. This indicates that most oil reservoirs can be considered for CWI whether the reservoir is already under waterflood or is a new reservoir and has not been waterflooded before.

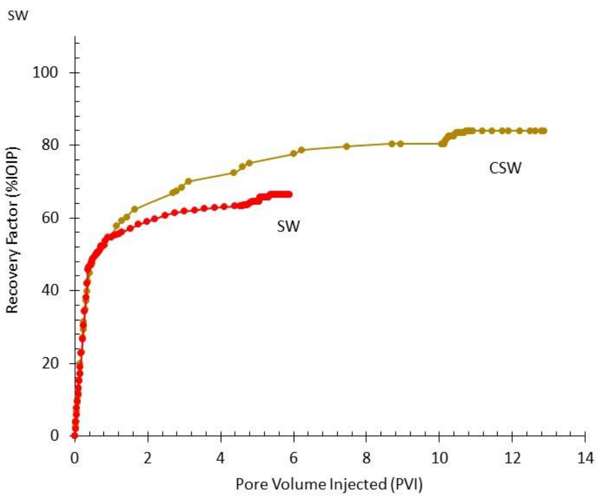

Fig. 8. Comparison of oil recovery by seawater injection and by carbonated seawater injection.

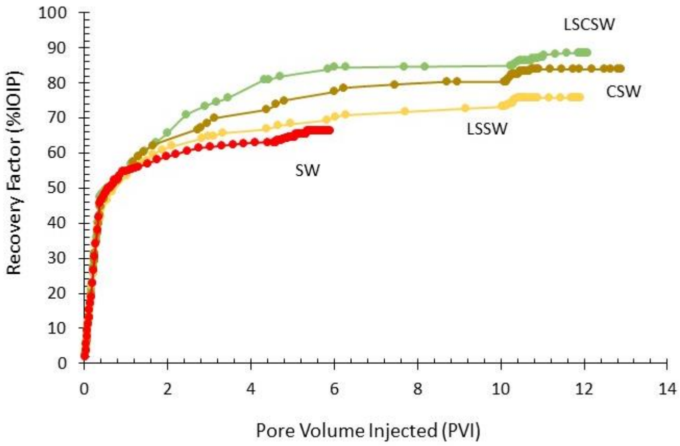

Fig. 10. Comparison of oil recovery by seawater, carbonated seawater, low salinity seawater, and low salinity carbonated seawater injection.

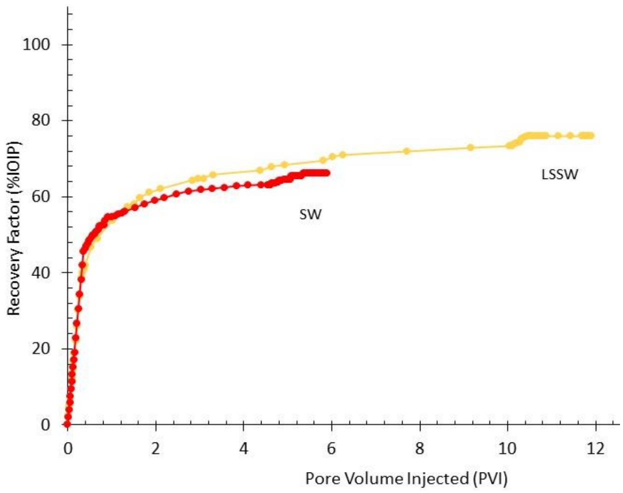

Fig. 9. Comparison of oil recovery by seawater injection and by low salinity seawater injection.

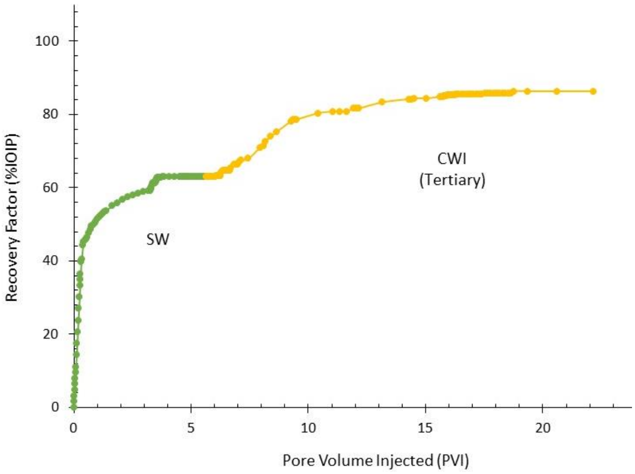

Fig. 11. Oil recovery by seawater injection followed by tertiary CWI.

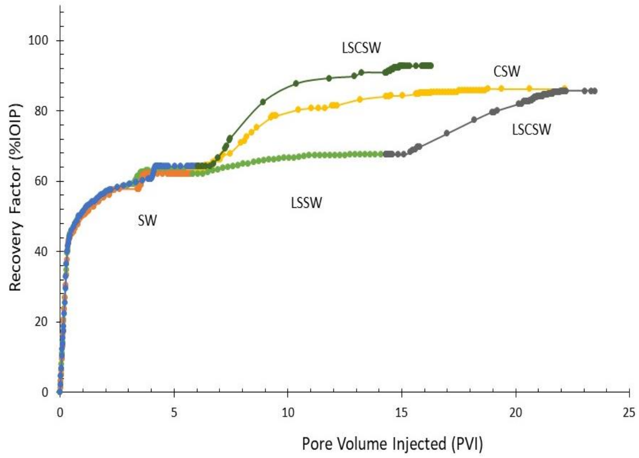

Fig. 12. Comparison of oil recovery by tertiary carbonated seawater, tertiary low salinity carbonated seawater injection, and quaternary low salinity carbonated seawater injection.

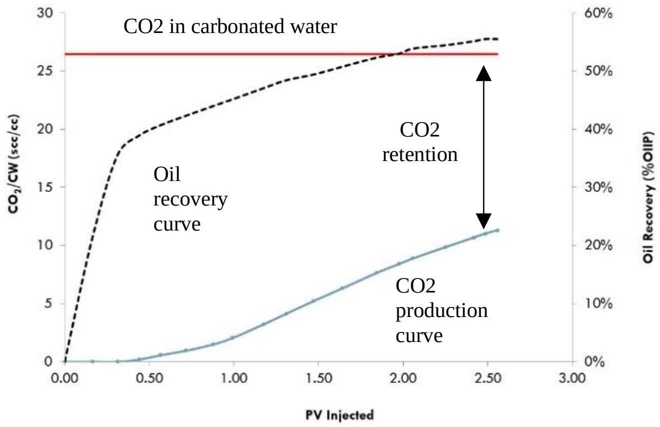

Fig. 13. CO2 retention in the rock during CWI.

2.4 CO2 Retention

As mentioned above, one of the advantages of CWI compared to conventional CO2 flood is that CWI needs much less CO2 compression in injection wells, much less CO2 handling in the production wells, and much less recirculation and recompression of CO2. Figure 13 demonstrates the retention of CO2 in a typical coreflood experiment. The horizontal red line in Figure 13 shows the amount of CO2 dissolved in the carbonated water that was injected in this test (27 cc/cc). This is the amount of CO2 delivered to the rock though water. The blue curve in this graph shows the amount of CO2 that was produced together with the produced oil and water in this test. The arrow shows the difference between the amount of CO2 delivered and the amount of CO2 produced, or the CO2 retention in the core. The dashed curve represents the amount of oil recovered at different times in this test. As can be seen the CO2 production curve has a very gentle slope after the breakthrough of carbonated water. This is in contrast with conventional CO2 floods in which after the breakthrough the CO2 production rises very rapidly which typically results in the production and recirculation of 2/3 of the injected CO2. The other point worth mentioning about Figure 13 is the fact that after injecting 2.5 PV of carbonated water, the CO2 content of the produced fluids is still much less that the CO2 content of the injection carbonated water. This reveals that unlike conventional CO2 flooding, in carbonated water injection, a large fraction of CO2 is taken by the fluids in the reservoir instead of moving rapidly towards the production well.

2.5 Conclusions

- Carbonating the flood water before injecting it into oil reservoirs can result in significant additional oil recovery in both secondary and tertiary injection modes. For the conditions of our experiments the additional oil recovery was around 20% above seawater injection.
- The ultimate additional oil recovery was the same in both secondary and tertiary CWI, but the additional oil recovery was observed to happen faster if carbonated water was injected as a secondary oil recovery method.
- Reducing the salinity of water used in CWI significantly increased the performance of CWI. Water salinity reduction increases CO2 solubility (although in our experiments the amount of CO2 dissolved in water was kept constant) and may favourably modify the rock wettability.
- A significant percentage of the CO2 delivered to the core through CWI was retained in the rock and when CO2 finally reached the production end of the rock, its rate of increase was very gentle. In our experiments, even after 2.5 pore volume of CWI, nearly 2/3 of the CO2 content of the injection carbonated water was still being retained in the rock.

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