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Carbonated water injection under reservoir conditions; in-situ WAG-type EOR

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Abstract

Enriching injection water with CO_2 has demonstrated promising results as a method for improving the oil recovery and securely storing CO2 in oil reservoirs. However, mutual interactions taking place between carbonated water and reservoir oil at elevated reservoir conditions are not fully understood. Herein, we present the results of a thorough and direct investigation of the interactions between live-oil/CO2/aqueous-phase leading to additional oil recovery and enhanced CO2 storage in pore-scale and core-scale.

CO2 transfer from carbonated water to live oils can trigger liberation of light components in form of a new gaseous phase. This unique phenomenon would bring about higher degrees of oil swelling, and it can also create a three phase flow regime, which leads to effective reduction of residual oil saturation. The observations confirm that the performance of carbonated water injection (CWI) should be investigated under reservoir conditions using multi-components live oil and reservoir cores. From the core displacement tests, it was observed that secondary CWI could recover a significant amount of additional oil, which was 26% compared to conventional seawater injection. When CO2 content of injected CW (carbonated water) was halved, the oil recovery dropped by $1/3$. Using live oils, it was found out that CO2 would be trapped in the new phase, which brings about an enhanced CO2 trapping mechanism. Under realistic reservoir conditions where complex mass transfer of CO2 from aqueous phase to oil and gas phases takes place, an "in-situ WAG-type" three-phase flow is generated with more effective sweep efficiency and pore-scale advantages.

1. Introduction

Enrichment of injection water with CO2 has been recognised as a feasible method to improve the oil recovery [(de Nevers, 1964) (Blackford, 1987) (Christensen, 1961) (Dong , et al., 2011) (Sohrabi, et al., 2015), (Mosavat & Torabi, 2014), (Riazi, et al., 2011)]. Field trials and laboratory experiments (Sohrabi, et al., 2011) have demonstrated that the CO2 transfer from the aqueous phase to the resident oil can bring about favourable swellings and viscosity reductions, which leads to the additional oil recovery (Alizadeh, et al., 2014). However, when the systems under study were oversimplified to dead conditions (i.e. no solution gas in oil or reduced pressure and temperature), the conclusions would not adequately address the controlling mechanisms behind carbonated water injection or as it is called CWI [(Riazi, et al., 2011) and (Zuo, et al., 2013), (Foroozesh, et al., 2016)]. Recently, it has been visually demonstrated that the presence of associated gas in live systems can trigger formation of a gaseous new phase within the oil ganglia, which in turn would make a three-phase system for the system under CWI (Sohrabi, et al., 2015). In line with this new finding, other studies (Seyyedi, et al., 2017) has attempted to characterize the process of CO2 partitioning into the resident oil, which elaborated the sequences behind the gaseous phase formation where CO2 transfer to live oils would liberate the methane content of the oil. It was reported that in the early stages, the new phase would be composed of methane and towards the later stages, CO2 would be the prevailing component in the gas phase. As the new phase would have a very low mobility due to high critical gas saturation (this would be discussed here in this work), an additional CO2 trapping can take place due to transfer of CO2 into the new phase, which enhances CO2 storage in oil reservoirs. These previous works were performed on crude oil saturated with methane and additional oil recoveries were obtained using sandstone rocks (Sohrabi, et al., 2015). Carbonated water has relatively lower pH values compared to plain water, which can change the surface chemistry between brine and carbonate rocks significantly and this effect was studied here by performing single phase core experiments under reservoir conditions. On the other hand, transfer of CO2 into the gas phase would bring about extraction of oil compounds and hence presence of C3-C10 components can be significantly important in the interactions. It is conceivable to have rock dissolutions when CO2-enriched brines invade a carbonate reservoir rock (Ross, et al., 1982). Also, it is known that intermediate hydrocarbon components (such as C3-C6) can play a crucial role in phase behaviour of CO2-Oil systems (Holm & Josendal, 1974) and these components can be found in solution gases. Therefore, to represent a more realistic oil system, the live oil used in this study was made by recombining the crude oil with a four component gas. Therefore, investigation of CWI performance in carbonate reservoirs using a rich recombined oil sample can be of great interests.

To the best of our knowledge, this is the first time that the pertinent interactions in oil/carbonated-water/rock system at elevated pressure and temperatures of an oil reservoir would be reported, which can add more information to practical aspects of this enhanced oil recovery (EOR) method. The dissolution effects of carbonated water on carbonate rocks was studied comprehensively. Also, the level of CO_2 content of carbonated water was halved and a tertiary CWI was performed to observe the significance of the level of carbonation on the pore-scale and core-scale events. Observations from this integrated research confirm that the performance of CWI should be investigated at true reservoir conditions using multi-components live oil and reservoir core. Any simplification, e.g. one component make-up gas or reduced pressure/temperature of the reservoir conditions would be misleading and would change the pore-scale events and oil recovery. Adding another angle to our analyses, a series of compositional measurements was carried out to examine if the dynamic interactions (i.e. CO2 transfer and third-phase formation) in secondary and tertiary carbonated water injections can bring about compositional changes to the oil produced from coreflood experiments. Inasmuch as our experiments can demonstrate, it appears that there is a substantial level of pore-scale and core-scale advantages for carbonated water (in-situ gaseous-phase formation) against plain CO2 and even CO2-WAG, which are highly prone to CO2 segregation.

**Supplementary materials can be found in document added as “Supporting Information” to explain statements and findings highlighted in this paper.

2. Methodology

Interactions between oleic phase and carbonated water (CW) depend primarily on the light to intermediate components of the oil and hence, the pore-scale visualization experiments were designed to investigate the importance of intermediate components. Carbonated water injection was employed in two scenarios to evaluate the extent of third-phase formation in tertiary and secondary injection modes. Also, it has been aimed to comparatively study the impact of carbonation level. Four visualization and five coreflood experiments were performed (more information in section 1 of Supporting Information).

One of the laboratory issues that may affect our understandings is the impact of time and injection rate on the experimental results and observations. In the processes controlled by mass transfer (i.e. CO2 transfer from aqueous phase to oil), the time of interactions would play an important role on the outcome of the experiments. Therefore, coreflood experiments at high and low rates were performed to observe the impact of injection rate. It should be pointed out that the low rate experiments were followed with a bumped flow (high rates) at the end of coreflooding for reducing possible end-effects. The nominal rate of fluid flow through the reservoir would be around 1 ft/day (Ahemd, 2010), which would correspond to the low rate experiment. The consistency between high and low rate experiments would indicate the integrity of experimental approach and the results of coreflood experiments in terms of dimension and time.

3. Rock and fluid properties

A composite carbonate core formed with five core plugs was used in this study. Between the core plugs of the composite, we put filter papers infused with carbonate powders. The average permeability (measured with formation brine) and porosity of the composite core can be found in Table 1. We used a same core for all tests, which could make the results comparable. After each test, the core was cleaned at 110 ^{o}C (this is 10 C higher than the test temperature) and 1000 psi using sequential injection of toluene and methanol. Subsequently, similar initialization procedure was followed to establish *Swi* and age the core. For initialization of the core before each test, the core was vacuumed and then, saturated with formation brine. After that, the permeability of the core was measured. For establishing water saturation, a viscous mineral oil was injected to displace the formation brine. The viscous mineral oil was sequentially displaced with lighter mineral oils (which are miscible). Subsequently, dead crude oil was injected to displace light mineral oil for 2 pore volume. To age the core, the dead crude oil was being injected for three weeks with injection rate of 1.5 PV/week.

It is plausible that carbonated water and the minerals existing in carbonate rocks would react due to low pH of the CO2-enriched brine. Therefore, it would be expected that the core may undergo changes to some extents in terms of porosity and permeability. However, it should be noted that surface of pores covered with oil may interact with carbonated water in much lesser extent compared to naked rocks. The second row of Table 1 indicates that permeability decreased by 5% and porosity increased 1.5% after five coreflood experiments. However, as we will see, the results of water injection in two different experiments (CF-2 and CF-5, please see Supporting Information for numbering of the experiments) demonstrate an acceptable repeatability, which indicates the negligible impact of the changes of the rock on displacement performances.

Table 1: Properties of individual core plugs and the composite core made for the coreflood experiments.

Sample #	Porosity, %	Permeability, mD	Length, cm	Pore Volume, cm3	Swi (%PV)
Initial	25.83	96.21	25.84	75.127	17.64
After 5 corefloods	26.22	91.81	25.84	76.261	16.94

Live oil was made using dead crude oil pre-equilibrated with a four-component gas (C1 – C4). The composition of the make-up gas can be found in Table 2. In the case of secondary seawater injection, seawater was pre-equilibrated with associated gas to prevent stripping of the oil light components as water contacts with resident oil. This design of the experiments can replicate equilibration of invading water with oil in near wellbore and consequently, the injected water would become saturated with the gas in the reservoir. Also, methane content of oil plays an important role on interactions taking place between live oil and CW and extended injection of water may adversely strip methane of the live oil. Therefore, the experiment would represent the processes taking place in the main body of oil reservoir, i.e. away from injection well. Properties of live fluids can be found in Table 3. Ionic composition of formation and seawater can be found in section 2 of Supporting Information.

Table 2: Composition of the make-up gas, which was recombined with the crude oil to make the live oil.

	Experimental Comp.(% mole)
Methane (C1)	53.4264
Ethane (C2)	25.7866
Propane (C3)	13.245
Butane (C4)	7.542
Total	100

Table 3: Properties of the fluids

Properties	Sea Water	Carbonated SW	Half-saturated carbonated seawater	Live Oil
Gas content (ccGas/ccinj.)	3.28	22.33	11.7	82.4
Viscosity (cP)	0.350	0.374	0.355	0.83
Swelling factor	1.01	1.03	1.01	1.30

4. Results and discussions

4.1. Rock and aqueous phase interactions

One crucial aspect of CWI in carbonate rocks is the possible interactions between rock and CW. For that, a series of single phase injection of CW into carbonate core plugs was carried out under reservoir conditions. The knowledge and data generated from these tests, using tailored brine compositions, can be used to model geochemical processes during CWI. X-ray diffraction (XRD) was performed on both sides of one core plug in order to estimate composition of the rock as shown in Table 4. It should be noted that the Aluminium detected by XRD was originated from the sample holder (which is made of Aluminium) and not from the core sample.

Table 4: Mineralogy of a core plug as measured by XRD

Mineral	Content (%)
Calcite	**93.3 ± 4.9**
Gypsum	**3.3 ± 2.5**
Quartz	**2.25 ± 1.65**
Aluminium	**1.15 ± 0.75**

Having saturated the core with formation water, carbonated seawater injection was performed and continued for an extended period of time (12 PV injection) with different injection rates. Properties of the core used for single phase test can be found in section 3 of Supporting

Information. The injection started with an injection rate of 10 cc/hr for 5 PV. Then, the injection rate was increased to 20 cc/hr which was continued for 4 PV. Finally, the injection rate was increased to 30 cc/hr and injection continued until approximately 3.5 PV. Figure 1 summarizes the permeability ratio (normalised to initial permeability) obtained during CWI for the three injection rates. For practical purposes, Darcy law would adequately express the changes in flow properties of the rock. The results of the calculated k show that there had been some reductions in the core permeability during carbonated sea water injection at the lower injection rate of 10 cc/hr. However, the core permeability seems to have bounced back up to the initial value during the higher injection rates of 20 cc/hr and 30 cc/hr, which can be attributed to remobilisation of particles at higher rates.

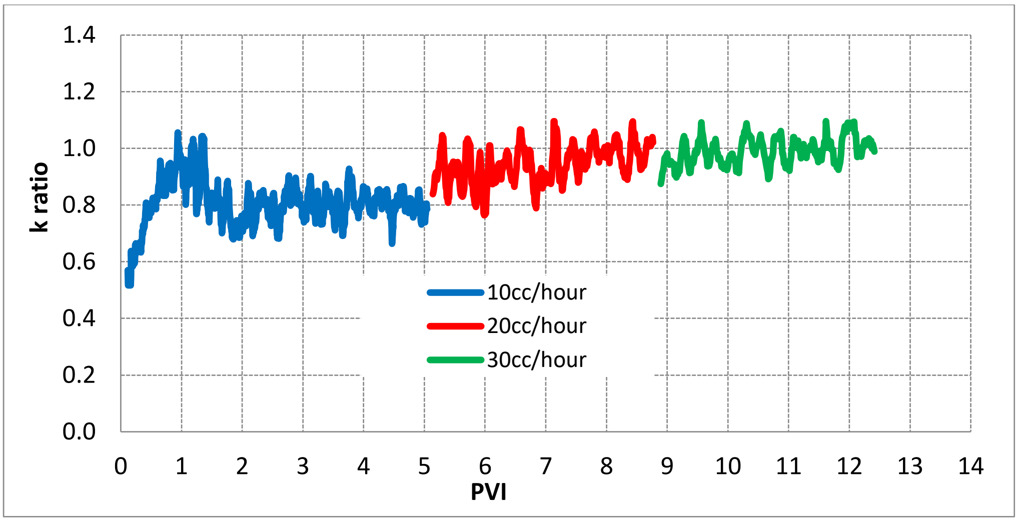

Figure 1: Variation of permeability (ratio of measured permeability to initial permeability) during carbonated water injection. Permeability was calculated directly from differential pressure data using Darcy Law. The variations in first pore volume injected of the test is due to displacement of formation brine with seawater and it represents a transient period of brines replacement. Hence, the first pore can not express true change in permeability.

When CO_2 dissolves in water, carbonic acid is formed, which dissolves carbonate minerals according to the following equations (Matter, et al., 2007):

$H_2O + CO_2 \leftrightarrow H_2CO_3$ (1)

$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$ (2)

$CaMg(CO_3)_2 + H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$ (3)

In our case, the solvent is seawater that contains sulphate anions which “may” lead to calcium sulphate precipitation (de Souza & Fjelde, 2013). This reaction is governed by:

$Ca^{2+} + SO_4^{2-} + xH_2O \leftrightarrow CaSO_4 \times xH_2O$ (4)

where x is equal to 0 (anhydrite), $^1/_2$ (hemihydrate), or 2 for gypsum. Three injection rates were examined during CSW (carbonated sea water) injection i.e., 10, 20 and 30 cc/hr. Analyses of produced brine have indicated that notably higher calcium ion concentrations were identified, which confirms rock dissolution. Also, higher concentrations of Mg^{+2} and SO_4^{-2} could be found in the effluent due to dissolution of gypsum and dolomite minerals of the rock. A complete analysis of effluents can be found in section 3 of Supporting Information. At high injection rates, the contact time between brine/CO_2/rock are shorter. As a result, less rock is dissolved in the injected CSW. Also, at higher rates, slight scales formed in the pores can be pushed out. To identify the impact of geochemical interactions (dissolution) on CO2 consumption, CO2 content at the outlet of the core was measured during the single phase test. The CO2 content of the produced brine was drop 0.5 unit (i.e. 22.3 cc/cc dropped to 21.8 cc/cc). This change in CO2 content can be assumed negligible for EOR purposes.

To identify the impact of dissolution on rock texture, high resolution CT (computed tomography) images of the core plugs before and after CWI was obtained. As illustrated in Figure 2, compared to CT image of the original rock (middle image), the dark patches formed on the top (very inlet of the core) shows the rock dissolution, which made the core hallow. However, the dissolution was focussed at the inlet face and as carbonated water advanced into the core, the extent of dissolution was considerably diminished, which left the end of core plug unaffected. In summary, interactions between carbonated water and carbonate rock would lead to dissolution but this dissolution would be limited to inlet face, i.e. injection well. Moreover, it should be reiterated that rock surface covered with oil may interact with carbonated water in much lesser extent compared to naked rocks.

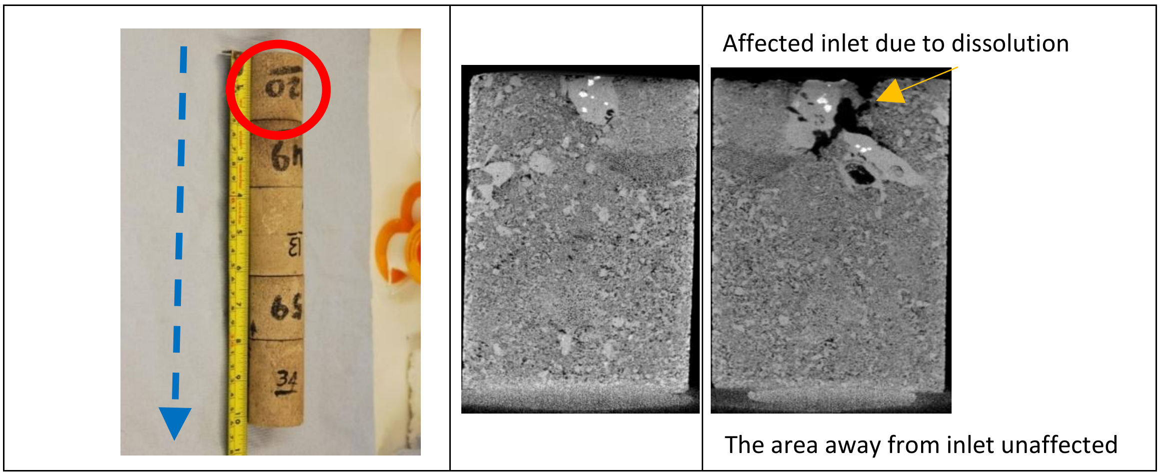

Figure 2: CT images of the core plug at the inlet before (middle image) and after (right image) the CWI. Left image indicate the flow direction (blue arrow) and the position (red circle) of the core plug in the composite. In the right image, compared to middle image, the dark patches formed on the top (very inlet of the core, pointed by a yellow arrow) shows the rock dissolution, which made the core hallow. End of core plug was unaffected by CWI.

4.2. Pore-scale visualizations

The micromodel experiment was performed on the recombined live oil at reservoir pressure and temperature, i.e. 100^{o}C and 3100 psig. Details of micromodel properties can be found in (Sohrabi, et al., 2015). Secondary and tertiary carbonated seawater injections were considered. The micromodel was aged for a day. The observation acquired from glass micromodel tests would be used interpret mass transfer aspects of coreflood experiments where real reservoir rocks were used. In the first experiment, dead crude oil was used and oil swelling was identified as the main mechanism of oil recovery. Using dead crude oil, no gas phase was formed during carbonated water injection. For more information, please see section 4 in Supporting Information.

In the tertiary mode, after injection of CWI for 1.5 hour, a third (gaseous) phase started to form within the oil phase due to CO_2 transfer from the carbonated water into the resident live oil. Figure 3 depicts a magnified section of micromodel to highlight the occurrence of two mechanisms by third-phase formation; (i) swelling of and reconnection of the oil trapped after waterflood and (ii) migration of the third-phase concurrently within the mobilized oil. Therefore, apart from the higher swelling introduced by the third-phase, a three phase flow region would occur during CWI, which can in turn bring about additional benefits of three phase flow characteristics. The gas phase would appear in the form of tiny bubbles (pointed by red arrows in Figure 3) within the oil phase, which can be linked to high interfacial tension between the new gaseous phase and oil phase, which can reflect the third-phase is mainly composed of methane in early stages as also confirmed by other works (Seyyedi, et al., 2017). More information about third phase behaviour in can be found in section 5 of Supporting Information.

However, in the secondary injection scenario, a direct contact between the carbonated water and the in-situ oil exists at the front of secondary CWI, which would facilitate the CO_2 transfer whereas, in tertiary scenario of CWI, the injected carbonated water would be mixed with the preceding plain water, which may weaken the strength of CO_2 dissolution. The formation of third-phase was delayed for 1 pore volume injected in tertiary CWI. However, it was observed that the formation of third-phase took place ahead of the CW front, which indicates a much stronger CO_2 transfer in secondary CWI processes.

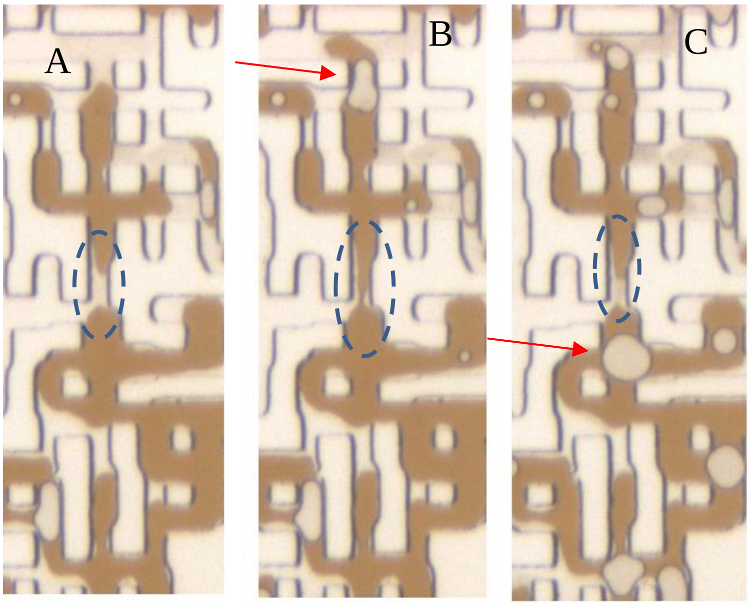

Figure 3: Three snapshots of a magnified section of the micromodel to indicate the swelling and reconnection of the oil phase (highlighted with blue dashed circle). The third-phase (red arrows) would become mobile as its saturation grows and it flows with the reconnected oil concurrently.

Towards end of CWI injection, a unique phenomenon was observed (which is reported for the first time) that, the third-phase volume would have a decreasing trend. Figure 4 illustrates the sequence of images taken in the late stages of secondary CWI. As can be seen, this reduction in third-phase volume cannot be explained by gas production since we analyzed stationary oil and gas blobs. Evidently, the third-phase has interacted with the surrounding oil and the interface between oil and gas vanished, which resulted in a brighter liquid phase formed towards the end of CWI period. In other words, the third phase is mainly composed of CO2 (towards the end of interactions), which is in agreement with the quantitative findings of (Seyyedi, et al., 2017) and gaseous CO2 would extract intermediate components of oil. This process can bring about favorable conditions for miscibility between gaseous and oleic phases. This direct observation would demonstrate that presence of intermediate components in preparation of live oil would more realistically replicate the processes taking place during CWI. Ignoring these crucial components in recombination stage would lead to misrepresentation of the pore-scale events. At the end of CWI, this remained liquid phase can be a suitable target for any miscible displacement due to its characteristics (miscibility between gaseous and oleic phases) as judged by the color.

Also, other factors such as CO_2 content of carbonated water was investigated as a pertinent parameter controlling the performance of carbonated water injection. A scenario can exist where the invading carbonated water in the reservoir would lose its CO2 content as it advances into the reservoir. The CO_2 transfer from carbonated water into the oil is mainly controlled by partitioning coefficient defined with Equation 5;

$$k_{CO2} = \frac{(X_{CO2})_{Oil}}{(X_{CO2})_{Water}} \qquad (5)$$

Where X is solubility of CO_2 into aqueous and oleic phase. Partitioning coefficient would be constant at fixed thermodynamic conditions, i.e. pressure and temperature. This parameter would dictate how much CO_2 departs from the carbonated water. To examine the impact of carbonation level, a visualization experiment was designed to inject half-saturated carbonated water. At the end of CWI, another batch of seawater (saturated with the associated gas) was injected to shrink the oil for calculating the improved oil recovery achieved by CWI. The tertiary CWI (half-saturated) led to reduction in oil saturation (S_o) from 0.6 to 0.53 (0.07 unit). The reduction in carbonation level resulted in a drop in additional oil recovery by tertiary CWI, i.e. 0.14 and 0.07 reduction in S_o in fully-saturated and half-saturated, respectively. The time at which third-phase formation started was delayed for 4.5 hours in half-saturated, which is 3 hours later than fully-saturated experiment. More importantly, injection of half-saturated CW led to a reduction in the amount of the third-phase formed within the oil phase. Quantitative estimation of the gas saturation in the micromodel indicates that 0.053 of the porous pattern was occupied by the third-phase. In summary, Figure 5 shows the oil saturation at the end of the injection scenarios and the maximum third-phase saturation determined during different scenarios of CWI. The best performance of CWI was obtained in secondary injection. The different response to various injection scenarios can be explained by amount of third-phase formed during CWI.

From these direct visualizations, it was identified that third-phase would stay where it was nucleated (i.e. within resident oil), which implies a high critical gas saturation (Seyyedi & Sohrabi, 2017) before it started to move. The mechanism of high critical gas saturation is analogous to depletion process where gas remains immobile fore relatively high critical gas saturations [(Kortekaas & Poelgeest, 1991) and (Firoozabadi, et al., 1992)]. Moreover, at later stages of CWI, the third-phase would possess a significant concentrations of CO2 (Seyyedi, et al., 2017). Therefore, from our visualizations linked to findings reported by others, it can be rationalized that CWI would lead to considerable CO2 trapping due to third-phase formation, which is more than conventional estimations linked to CO2 solubility in oil alone. Trapping CO2 in the third-phase can act as an enhanced mechanism for CO2 storage during CWI in oil reservoirs. In coreflood experiments performed in this work, another evidence is discussed to highlight the enhanced CO2 storage capacity during CWI.

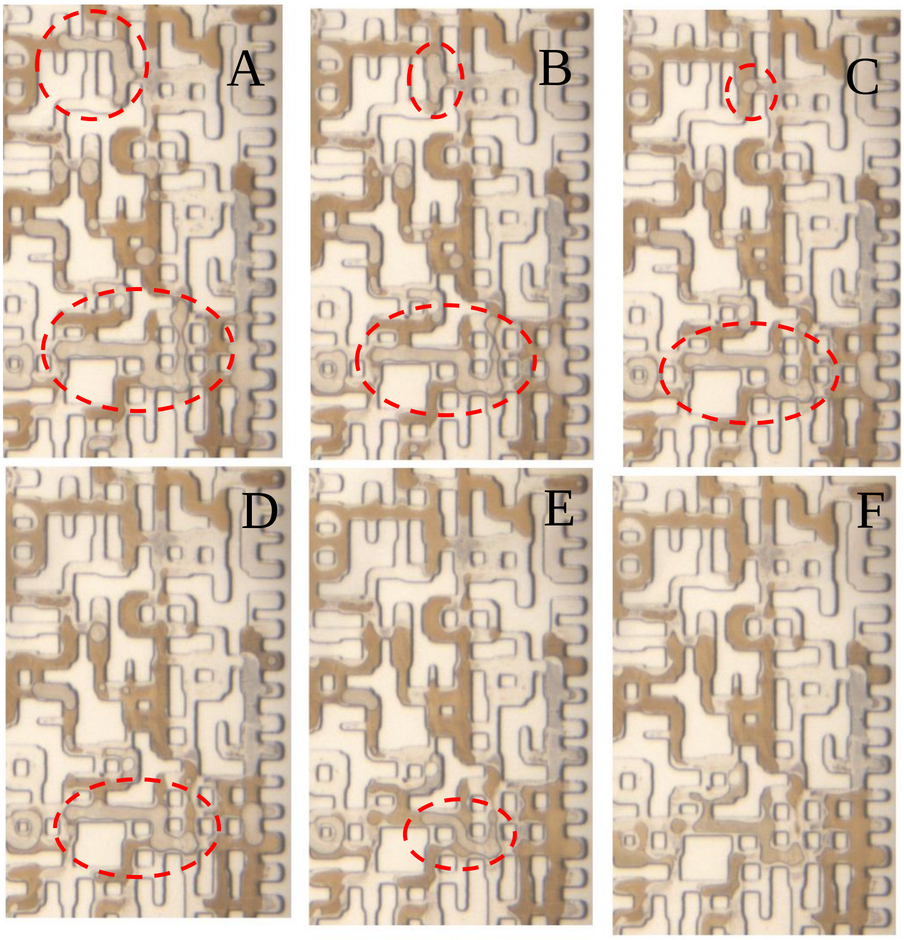

Figure 4: Snapshots of magnified section of the micromodel demonstrating the disappearance of the third-phase in the very late stage of CWI. The red circles highlight two large third-phase bubbles while CWI was being injected.

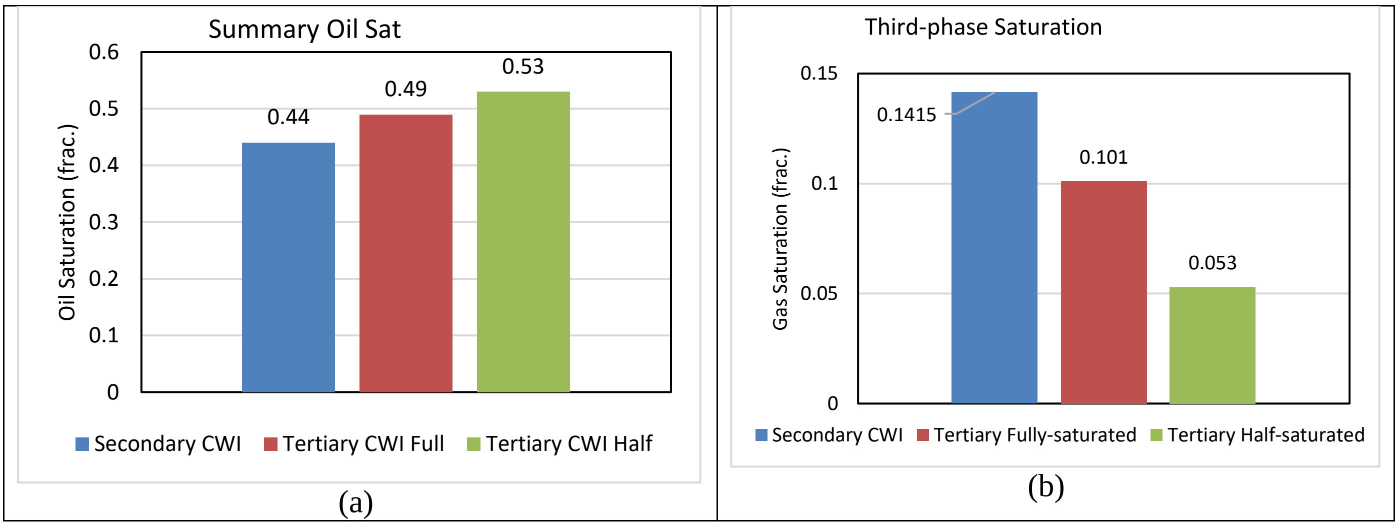

Figure 5: Oil saturation in the micromodel estimated at the end of three visualization experiments. Third-phase saturation in the micromodel estimated during three visualization experiments. Oil saturation after waterflood was approximately 0.6 (similar in all experiments).

4.2.1. *Discussions (in-situ WAG type EOR)*

One of the main implication of third-phase formation is the creation of three phase flow region in which two phase flow characteristics would no longer dictate the saturation distributions. In water injection in laboratory experiments, the remaining oil is mainly controlled by the residual oil saturation usually determined through SCAL (special core analysis laboratory) measurements. However, in the case of three phase flow which can be related to Stone 1 formulations (Stone, 1970), the residual oil saturation can be expressed by Equation 6 (Fayers, 1989);

$$S_{om} = S_{row} - a\, S_{gt} \qquad (6)$$

Where S_{om} is the minimal oil saturation in three phase region related to S_{row} (residual oil saturation in two phase water injection) and S_{gt} (trapped gas saturation). The *a* coefficient would be a constant between 0.5 and 1. Figure 6 demonstrates a sequence of snapshots taken from a magnified section of micromodel, which describes visually the consistency of Equation 6 with concept of third phase formation. As can be seen, after waterflooding, an isolated oil blob (S_{orw}) has started to liberate a gaseous phase (Figure 6-A), which resulted in swelling of the (oil+gas) blob (Figure 6-B). The swollen part in the oil+gas blob is highlighted with blue circles in Figure 6-B. Subsequently, the swollen (oil+gas) blob has become reconnected with an adjacent blobs and it shrank back to the original saturation albeit with a high immobile gas saturation housed inside the (oil+gas) blob. In other words, *the sum of oil and gas saturation would remain constant whilst the gas (third-phase) saturation grows, which would consequently reduce the oil saturation accordingly*. Although this semi-empirical relationship (Equation 6) was suggested for cyclic WAG process, we have a good number of visualization evidence confirming the analogy between the third-phase formation and in-situ WAG type injection, where the gas is formed in an intelligent manner with a high trapped saturation and hence high efficiency for reduction of remaining oil in place after waterflood. It should be pointed out that the third phase formation would create a local three phase flow with higher trapped gas saturation whereas, the cyclic injection of gas and water in WAG injection would require a fairly good sweep efficiency of both injection fluids, i.e. water and gas, to bring about reduction of oil saturation. Thus, carbonated water injection (under live oil conditions) can create an *"in-situ WAG"* type of EOR, which is much pronounced than cyclic WAG with poor sweep efficiencies. Furthermore, the third-phase formed in CWI has high tendency to remain inside the oil, which significantly increase the critical gas saturation.

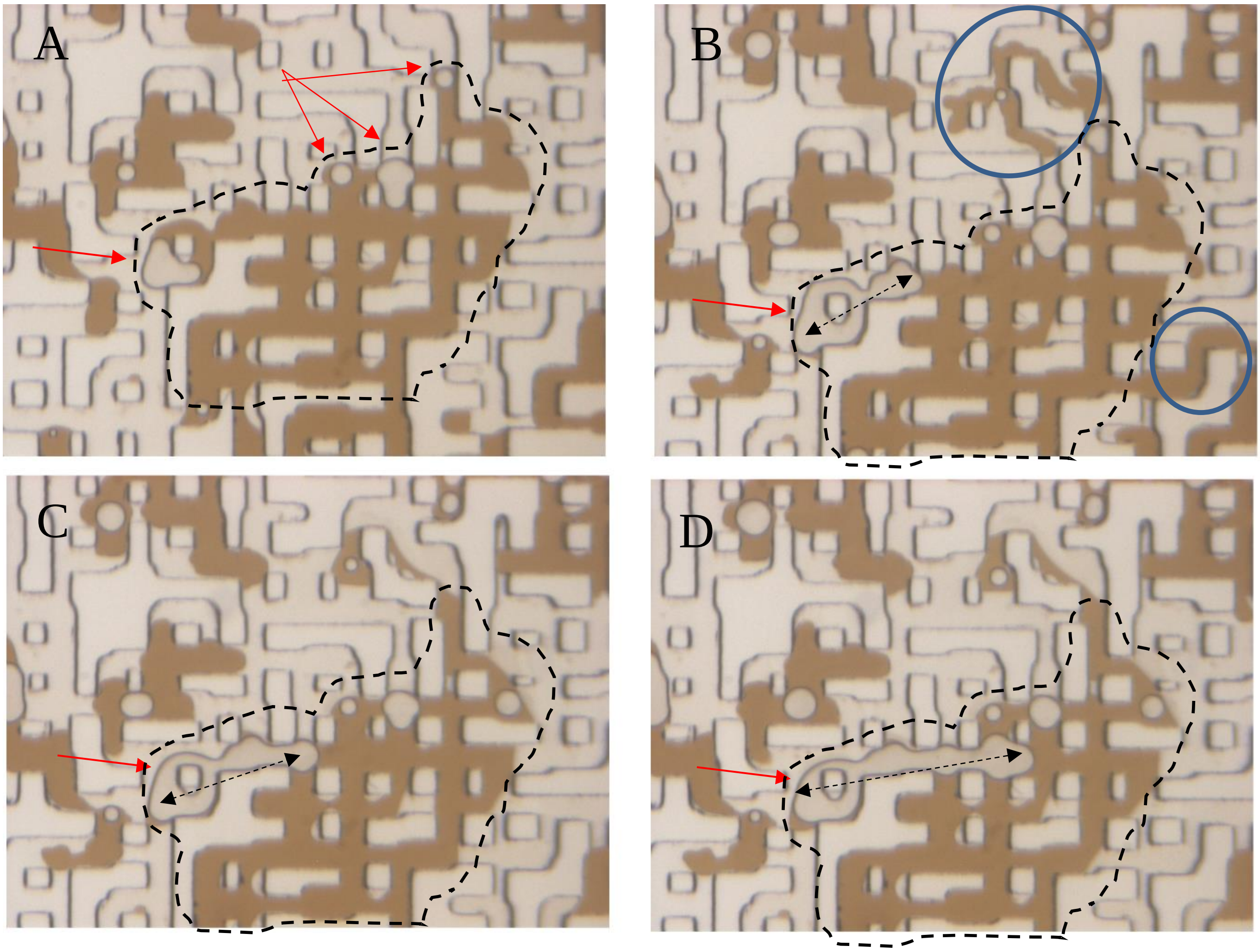

Figure 6: A sequence of snapshots taken from a magnified section of micromodel during tertiary CWI to explain the relationship between remaining oil saturation and third-phase formation. The black dashed drawing illustrate a remaining oil and gas ganglion. (A) Early stage of CWI, (B) oil started to swell (blue circles) and reconnect (black arrow), (C) the oil saturation became similar to original remaining oil, and (D) further growth of the third-phase inside the source oil. The red arrows point to the gaseous third-phase.

4.3. Coreflood experiments

Compared to visualisations in glass micromodels, a more representative porous media was used in coreflood experiments to obtain more realistic displacement patterns and wettability conditions. A further advantage of coreflood experiments is that, samples of the fluids produced during the experiments can be analysed for compositional effects and frontal advancements of different fluids. Details of experimental setup and procedure can be found in section 6 of Supporting Information.

4.3.1. Tertiary Injection of Carbonated Seawater

Two waterflood experiments at different injection rates (5cc/hour and 60cc/hour) were performed. After the termination of each water flood, bump flow injection was performed in order to surpass possible end-effects. In all coreflood experiments, after bump flood periods, the injection rate was switched back to the original rate of corresponding experiments. For instance, at end of bump periods with original rate of 5 cc/hour, the injection rate was set at 5 cc/hour for one pore volume to make sure that the remaining oil was immobile. Details of low rate coreflood (i.e. 5 cc/hour) can be found in section 6.2 of Supporting Information.

In the case of the high rate (60cc/hour that corresponds to the flow velocity of 18ft/day) experiment, a tertiary CWI was carried out to evaluate the performance of carbonated water to recover the residual oil after waterflooding. In the secondary water injection period, the seawater was pre-equilibrated with the associated gas in order to avoid any mass transfer and stripping the light components of the oil (the extent of methane dissolution from oil to water is approximately 0.2% $\frac{mole\ methane}{mole\ water}$ (Seyyedi, et al., 2017)). Figure 7 demonstrates the full sequences of plain seawater with tertiary CWI. When the injection fluid was switched to carbonated seawater, an additional oil recovery of 15.3% was achieved, which can be considered as a significant improved oil recovery in tertiary mode. The dP started to rise but the oil production was seen after 1 pore volume of tertiary CWI. The rise in dP is attributed to gradual formation of the third-phase at the inlet, which bring about a three phase flow and hence, higher dP. As the oil production continued, dP started to drop. This drop of dP can be attributed to factors; (i) significant oil production corresponds to substantial drop in oil saturation and lower oil saturation would favor easier water flow as the displacing fluid and also, (ii) as identified directly in micromodel experiments, the third-phase would become miscible with the oil phase towards the later stages of CWI (demonstrated in Figure 4), which can lead to disappearance of the gas phase. Therefore, these two factors have acted to bring about a declining dP trend.

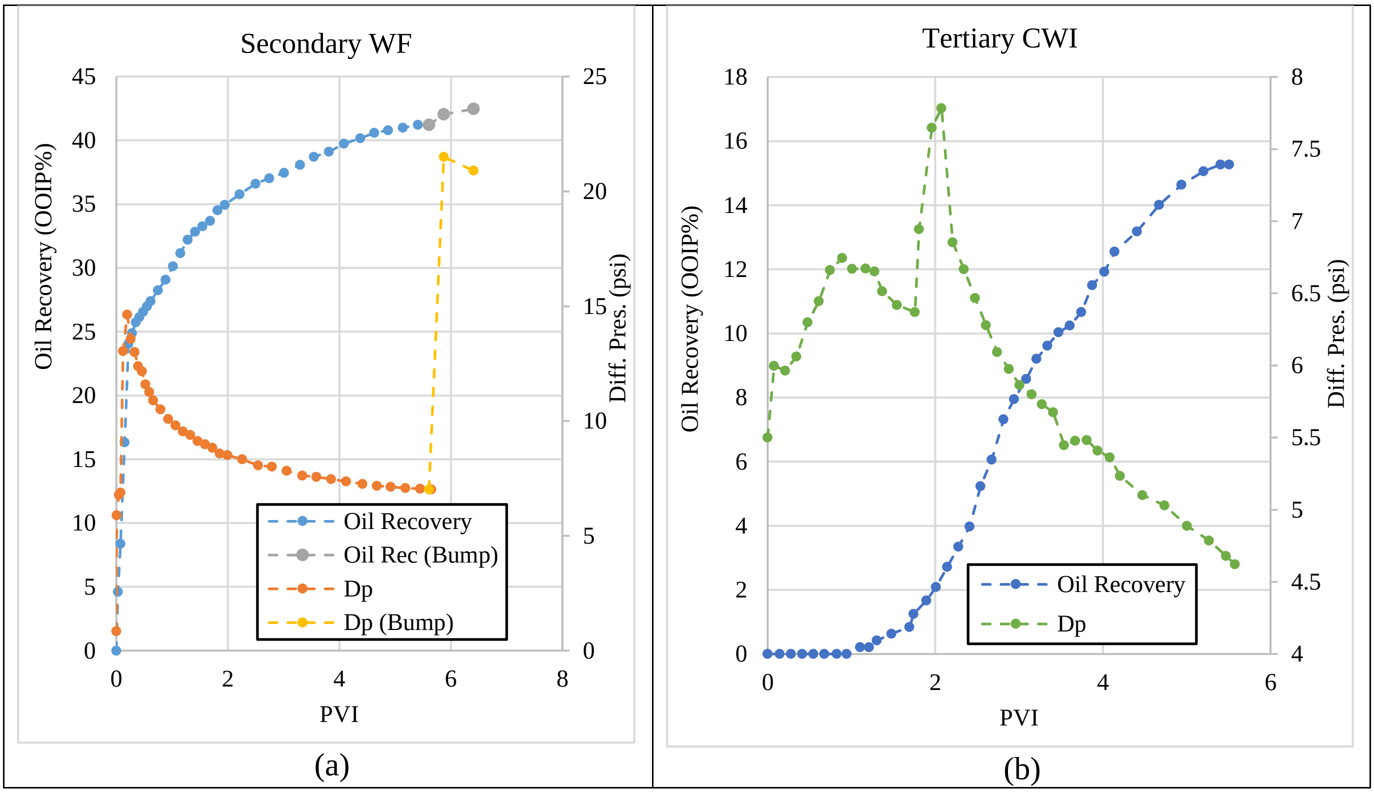

Figure 7: Fig7a is profiles of oil production and differential pressure during secondary water injection followed by bump flood. Fig 7b on right hand side shows profiles of oil production and differential pressure during tertiary CWI.

4.3.2. Secondary Carbonated Seawater Injection

In micromodel experiments, it was identified that the formation of the third-phase and additional oil recovery was much more pronounced in secondary mode. Two coreflood experiments with two different injection rates (at 5cc/hour and 60cc/hour) were performed in secondary mode. Figure 8 demonstrates the oil recovery and differential pressure profiles of secondary CWI and secondary waterflood performed in the same core under high and low injection rates. In the case of low rate CWI, the secondary CWI resulted in 66.4% oil recovery whereas, the plain seawater injection led to 39.9%. Therefore, augmentation of the seawater with CO_2 improved the oil recovery by 26.5%. The breakthrough time of carbonated water was recorded at the approximately same time compared to the seawater injection in both cases (i.e. low sand high rates). As identified in micromodel experiments, the significance of the third-phase formation is not considerable at the front of carbonated water before the water breakthrough, which makes the breakthrough time identical between the two tests. The differential pressure during CWI is higher than that of the seawater injection, which can be attributed to the formation of the gaseous third-phase. Occurrence of three-phase flow would normally cause higher dP across the core.

In the oil recovery profiles, in addition to similar breakthrough, there is one feature to be highlighted: the amount of oil produced during the bump flood is similar in both coreflood experiments. The oil produced in the bump flood is mainly due to surpassing the capillary end-effect, which is an indication of existing capillary forces in the core. Thus, similar behavior in the bump flood can be indirectly interpreted as similar capillary forces in two experiments. In other words, it appears that the wettability regime during water injection and carbonated water injection is not significantly different and hence, the carbonated seawater would not effectively alter the wettability state. It should be pointed out that the interpretation of wettability states of wateflood and CWI has been indirectly inferred from coreflood information. There may occur changes from dissolution and low pH of CW however, it appears that the possible changes would not affect the displacement characteristics such as breakthrough time and bump flood performance. This may disagree with other works that reported changes in contact angles but apart from uncertainty in contact angle measurements in systems where droplet volumes can be significantly affected by CO2 dissolution, our displacement experiments could not demonstrate an effective wettability alterations by carbonated water injection.

The fourth coreflood experiment was conducted at the high rate (right plot in Figure 8). 63.8% of original oil in place was recovered during secondary CWI whereas, 42% of oil recovery was obtained in secondary plain seawater injection. Therefore, 21.8% additional oil recovery was achieved due to carbonated seawater injection. Like the experiments performed at the low rate, the breakthrough of the displacing phase (water) occurred at almost the same time in both experiments. In terms of dP behavior, the differential pressure of secondary CWI is generally higher than that of plain seawater injection, which can be also attributed to formation of a gaseous third-phase. However, it should be pointed out that the dP at late stage of secondary CWI dropped below the water flood experiment, which is similar to dP behaviour observed in tertiary CWI. Nonetheless, the performance of secondary CWI was remarkably similar at low and high rates.

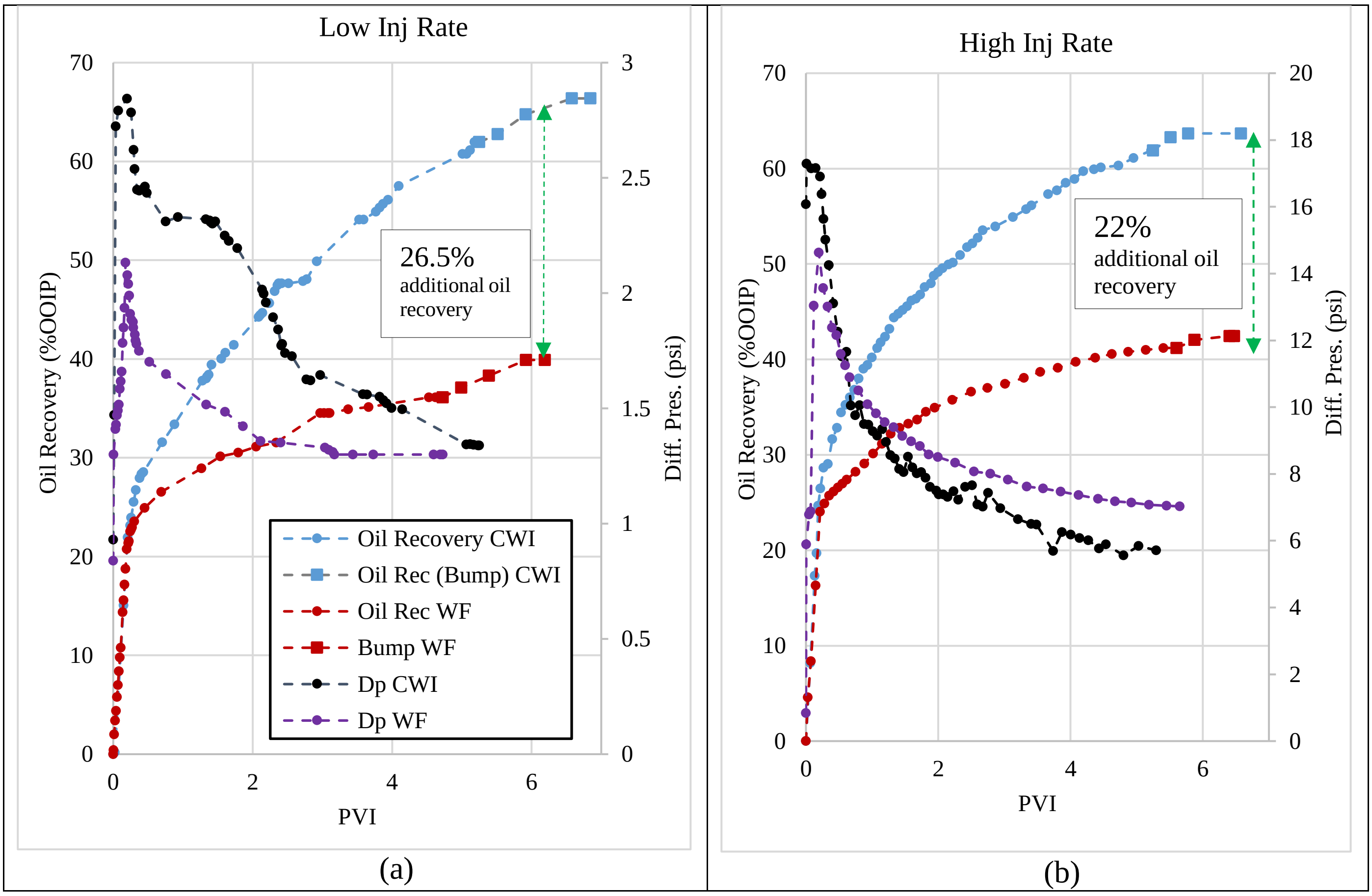

Figure 8: Curves on the left plot (Fig8a) shows Profiles of oil production and differential pressure during secondary water injection followed by bump flood (CF-1) and secondary CWI followed by bump flood (CF-2). Injection rate was 5 cc/hr in both experiments. Compared to water injection, 26% additional oil recovery was obtained when secondary CWI was employed. Fig8b on right hand side plot illustrates Profiles of oil production and differential pressure during secondary water injection followed by bump flood (CF-3) and secondary CWI followed by bump flood (CF-4). Compared to water injection, 23% additional oil recovery was obtained when secondary CWI was employed. Injection rate was 60 cc/hr in both experiments.

4.3.3. Half-saturated carbonated water (Tertiary CWI)

The objective of this part of the study was to investigate the impact of carbonation level on the performance of CWI. Tertiary carbonated seawater was injected after the secondary seawater injection. The outcome of pore-scale visualization test has highlighted "qualitatively" and mechanistically the importance of carbonation level in performance of CWI in terms of time of response and ultimate recovery. In core-scale, the rate of injection was set at 60 cc/hr and the experiment were carried out at 3100 psi and 100°C.

Figure 9 illustrates the results of coreflood experiments performed at tertiary mode using fully-saturated and half-saturated carbonated seawater. Comparatively speaking, the difference in oil recovery of plain seawater injection between two tests is 1.6% which demonstrates an acceptable degree of repeatability between the secondary waterflood sequences of the tests. Likewise, profiles of differential pressure across the core have indicated a repeatable behaviour. Having reached to remaining oil saturation to waterflood, the carbonated seawater was injected with carbonation level of 50%. An additional oil recovery of 9.8% was achieved, which indicates a good potential for carbonated water injection even though water was only half-saturated.

As can be seen in Figure 9, the oil recovery of the fully-saturated case is 5.5% higher than that of the half-saturated CWI. This change in oil recovery would indicate that the additional oil recovery by CWI would depend on CO2 content of the injection fluid. But, interestingly, the additional oil recovery in half-saturated case is $^2/_3$ of the fully-saturated case. In other words, the CO2 content was halved but the oil recovery did not drop proportionately. Therefore, it appears that the benefits of carbonated water injection cannot be estimated linearly from its CO2 content.

The results of these two coreflood experiments can be employed to identify an important process during carbonated water injection in large scales. As carbonated water invades porous media, it loses its CO2 content to oil but the effectiveness of displacement (oil recovery) would not diminished proportionately and it appears that the small quantities of CO2 transfer to the resident oil can trigger the gas phase formation. Moreover, the third-phase can form like a rarefaction wave, which would advance in a progressive manner inside the invaded zone. In other words, areas closer to injection point would experience high gas saturations and, although the CO2 content of carbonated water would drop, the process of gas phase formation would not stop throughout the invaded zone. Therefore, there would be a monotonically decreasing trend of gas saturation between injecting and producing points, which would grow continuously. This overall view on the performance of carbonated water is in agreement with continuous oil production after water breakthrough observed in coreflood experiments even in half-saturated carbonated water. More information on CO2 content of half-saturated CW and profiles of CO2 production can be found in section 6.3 of Supporting Information.

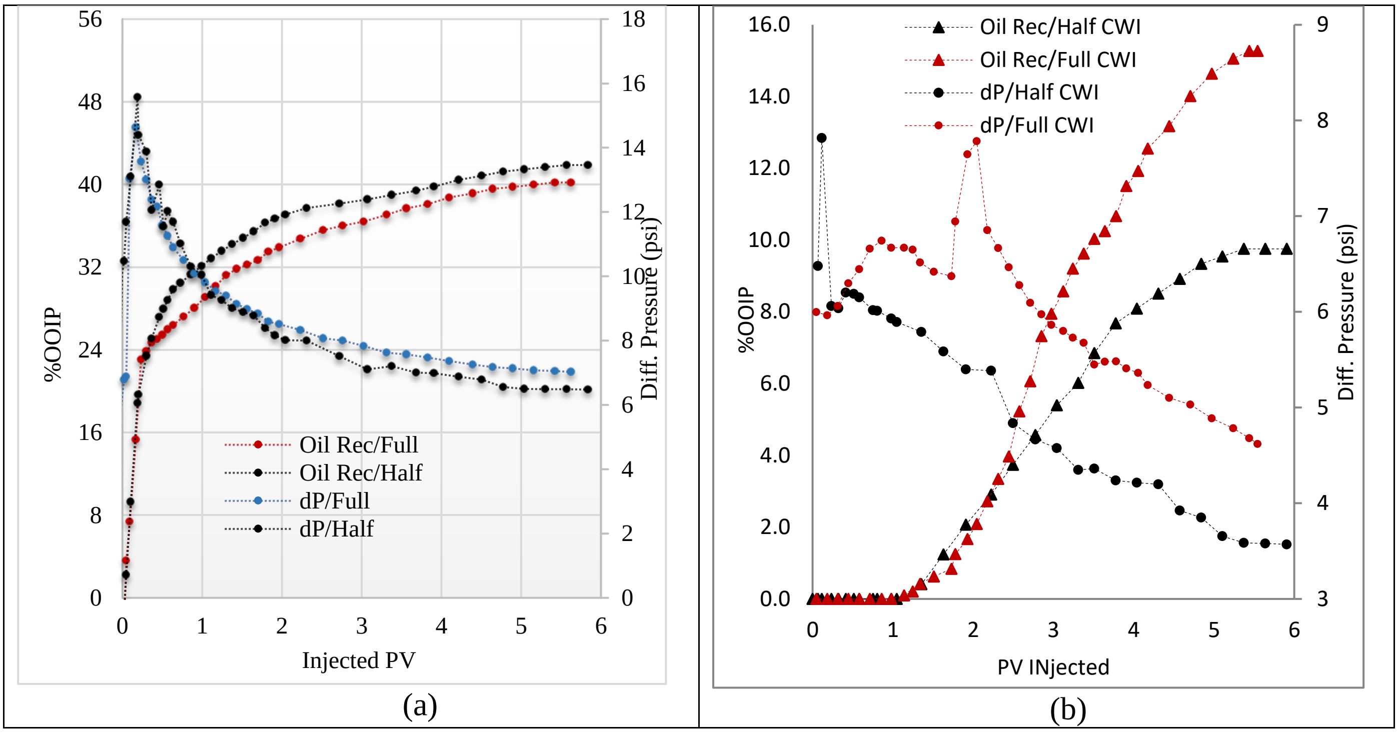

Figure 9: Fig9a shows Oil recovery and differential pressure profiles obtained during secondary seawater injection sequences of fully and half saturated carbonated injection experiments. Fig9b illustrates oil recovery and differential pressure profiles obtained during tertiary carbonated seawater injection sequences of fully and half saturated cases.

4.3.4. Discussions

4.3.4.1.Impact of flow rate in fluid displacement

Figure 10 illustrate the comparison of oil recovery profiles during water injection and carbonated water injection experiments at different injection rate. As can be seen, the low injection rate plus the corresponding bump floods would produce a similar oil recovery if compared to high rate cases. Evidently, the breakthrough happened in the same pore volume injected, which indicates the resident oil was displaced similarly in two cases. The similarity between the low rate plus bump flood with the high rate indicates that the difference between low and high rate is mainly due to the end-effects rather than different displacement patterns. The improved oil recovery by secondary CWI was markedly similar in low and high rate experiments indicating that the performance of CWI would not be influenced by the injection rate. However, we believe that the low injection rate would be more representative of the processes occurring in the main body of the reservoir where the nominal flow velocity would be in the range of 1 ft/day.

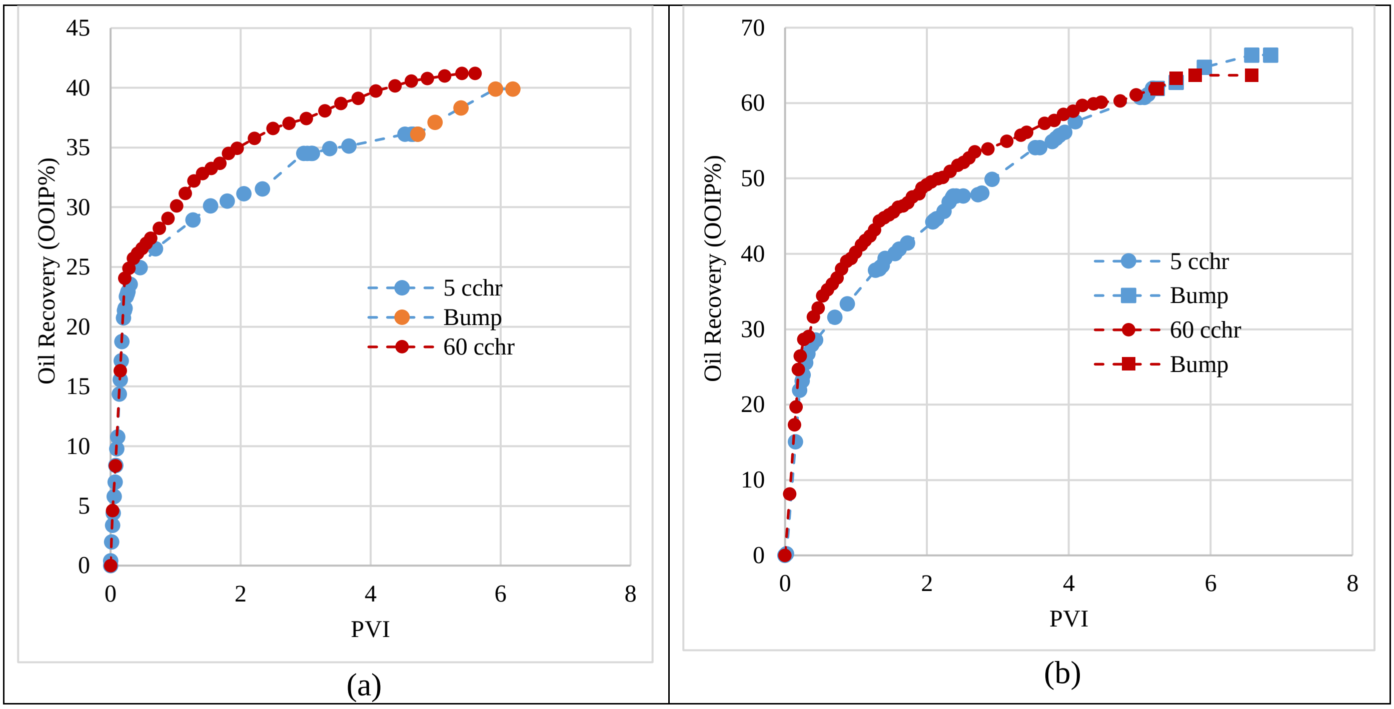

Figure 10: Fig10a shows oil production profiles in seawater injection experiments at two different rates, i.e. 5 and 60 cc/hr. The ultimate oil recovery in both cases are almost exactly the same (41% in high rate versus 40% in low rate + bump flood). The breakthrough occurred almost the same. Fig10b illustrates oil production profiles in secondary CWI experiments at two different rates, i.e. 5 and 60 cc/hr. The ultimate oil recovery in both cases are almost exactly the same (64% in high rate versus 66% in low rate + bump flood). The breakthrough occurred almost the same.

4.3.4.2.Advancement of CO_2 and Water in CWI

Our coreflood rig is equipped with a real-time CO_2 analyzer, which enables us to determine the CO_2 concentration in a gas stream, i.e. produced gas. Figure 11 shows the profile of water and CO_2 during the secondary CWI performed at high rate of 60 cc/hr. As can be seen in Figure 11b, CO_2 was seen slightly earlier than water in the effluent. The only source of CO_2 was the carbonated water and appearance of CO_2 slightly earlier than water would reveal that CO_2 may move faster through the resident oil due to diffusive flow of CO_2. Given that one of the significant advantages of employing CWI is the better sweep efficiency and better transfer of CO_2 (Blackford, 1987), this finding would imply that CO_2 can also diffuse through the oil phase and this process cannot be ignored. Also, once the aqueous phase did breakthrough, the CO2 concentration slightly increased reflecting that, the water was not completely depleted from its CO2 content. This may imply that in the scale (i.e. 25.84 cm) the front of carbonated water would still give CO2 to the resident oil. Compared to previous findings (Seyyedi, et al., 2017) where water became completely depleted from its CO2 in a 20 metre medium, this finding would indicate that the CO2 transfer depends on the length of the porous media.

As depicted Figure 11a, there is a significant difference between CO2 produced in the outlet and CO2 injected in the inlet of the core, particularly in later stages of CWI. Interestingly, although oil production reached to a plateau, CO2 content of the effluent did not reach to the injected CO2 content. This clearly indicates an important mechanism favorably causing CO2 retention (trapping) in the porous medium. This mechanism is related to the substantial capacity of the third-phase to take in CO2, as previously demonstrated in (Seyyedi, et al., 2017). As discussed above in direct visualizations third-phase would exhibit a high critical gas saturation before it started to move, which would change the CO2 storage capacity more than conventional estimations linked to CO2 solubility in oil alone. Therefore, retention of CO2 in the third-phase can act as an enhanced mechanism for CO2 storage during CWI in oil reservoirs.

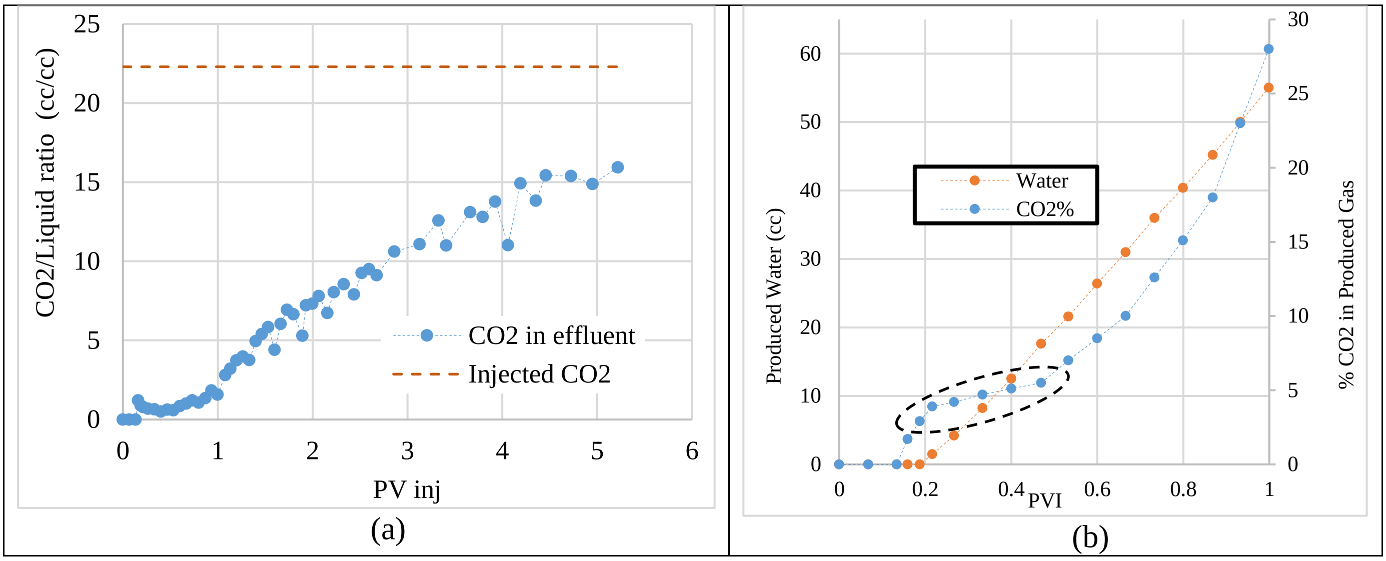

Figure 11: Fig 11a shows profiles of CO_2 production (expressed in ratio of CO2 to total liquid produced) in secondary CWI performed at high rate (60 cc/hr). The significant difference between injected CO2 and produced CO2 in the later stages would indicate retention of CO2 in porous media due to CO2 transfer into the third-phase. Fig 11b illustrates profiles of water and CO_2 production in secondary CWI performed at high rate (60 cc/hr). The CO_2 did breakthrough slightly earlier than water due to CO_2 diffusion through the oil. After water breakthrough, insignificant increase in CO_2 concentration occurred as highlighted by a black dashed circle. The volumetric measurements reported in this figure are all in room or standard conditions.

4.4. Compositional Analysis of produced oil

In this part, compositions of oil samples produced during secondary and tertiary carbonated water injection were measured by a series of gas chromatography (GC) analysis. Figure 12 illustrates the oil recovery profiles obtained during the secondary and tertiary carbonated water injection experiments, which highlighted how the produced oil samples were collated to represent early, mid, and late stages of oil production by carbonated water. The oil samples produced from coreflood experiments were then compared with original oil (named "STOCK

OIL SAMPLE"). To analyse the compositional changes, the area below each peak of GC measurement was calculated and the results were plotted versus molecular weight of the detected compound. Therefore, each figure would show area (which represents concentration) versus molecular weight of the oil compounds. Figure 13 shows the results of compositional analyses performed on the oil samples produced during secondary and tertiary carbonated water injection. Broadly speaking, all the samples produced during tertiary CWI were marginally heavier than the original oil in place. This implies that the formation of third-phase would result in slight extraction of intermediate components into the gaseous phase. Also, the oil sample produced in the early stages of this coreflood experiment is heavier that the mid stages. However, at the later stages, the oil samples became heavier again.

Also, the extent of compositional variations is more pronounced in secondary scenarios (as can be identified in Figure 13b). This difference can be attributed to the amount of oil interacting with the injected CWI. Therefore, the interactions between CW and live oils would be primarily dependent on the amount of oil present in the porous medium. It should be noted that in the low molecular weight components (i.e. MW of below 100), the produced oil samples have exhibited a very low concentration compared to "STOCK OIL SAMPLE", which indicates the extraction of light to intermediate components into the new gaseous phase. In other words, the mechanisms inferred from visualizations (i.e. formation of low mobility new-phase, which would lead to extraction) can be verified from the results of compositional analyses.

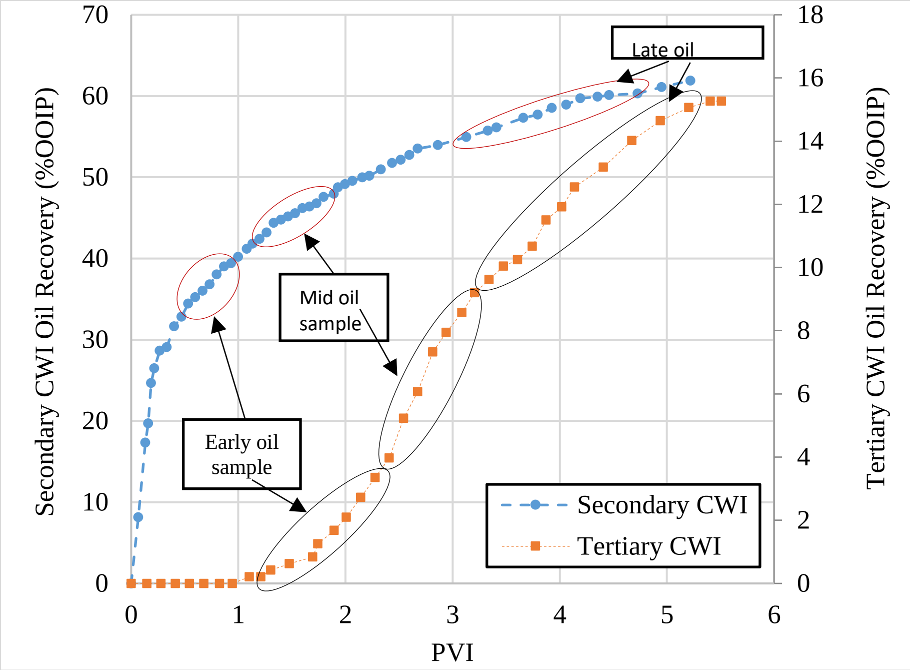

Figure 12: Oil recovery profiles of secondary and tertiary carbonated water injection tests to explain the selection of the oil samples. Three different oil samples were analyzed; early, mid, and late.

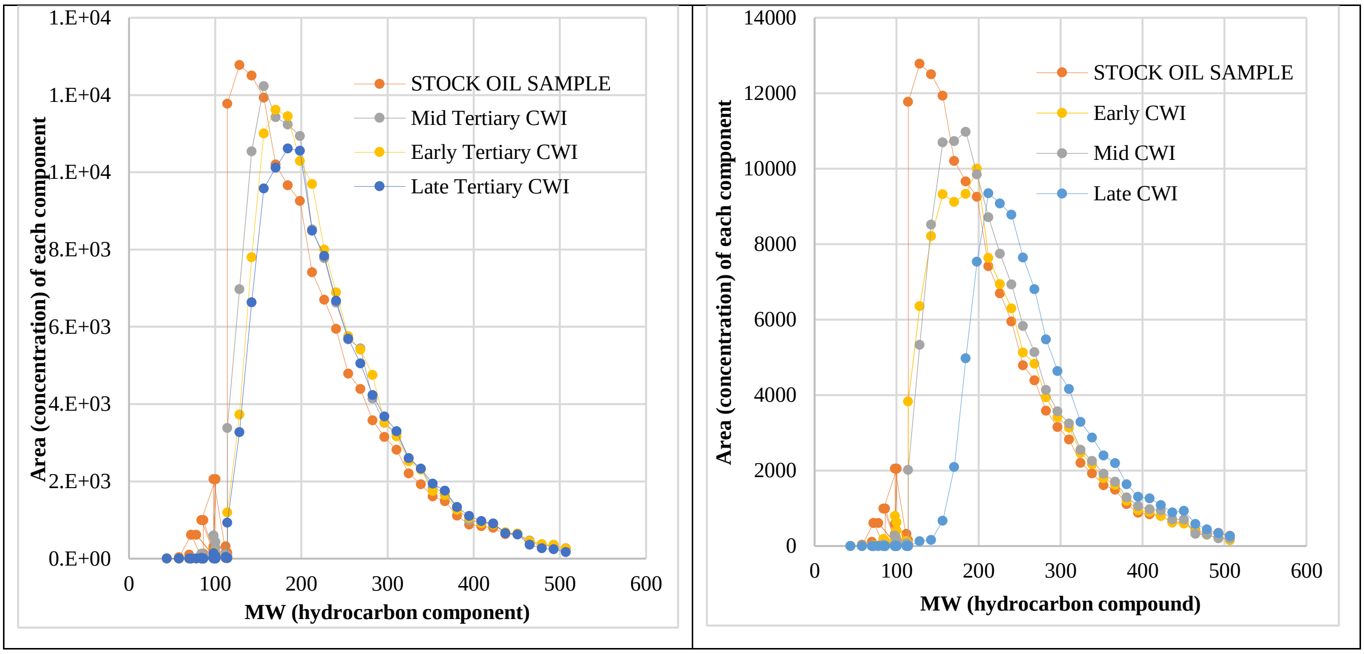

Figure 13: Compositional analysis of oil samples collected during tertiary (left) and secondary (right) carbonated water injection. The concentration of each hydrocarbon was plotted in the form of area beneath each GC peak versus molecular weight of the corresponding compounds.

Figure 14 shows the molecular weight of the oil samples at different stages of the tertiary and secondary coreflood experiments. The non-monotonic behaviour in the compositional analysis can be manifested in the magnitude of molecular weights. Like the compositional analysis, the molecular weight of the oil samples exhibited a higher value compared to the original oil. Therefore, there is a clear similarity between the composition behaviour in tertiary and secondary carbonated water injection modes. However, as can be seen Figure 14, the significance of the compositional variations was more noticeable in the secondary CWI, which is in agreement with direct visualisation experiments.

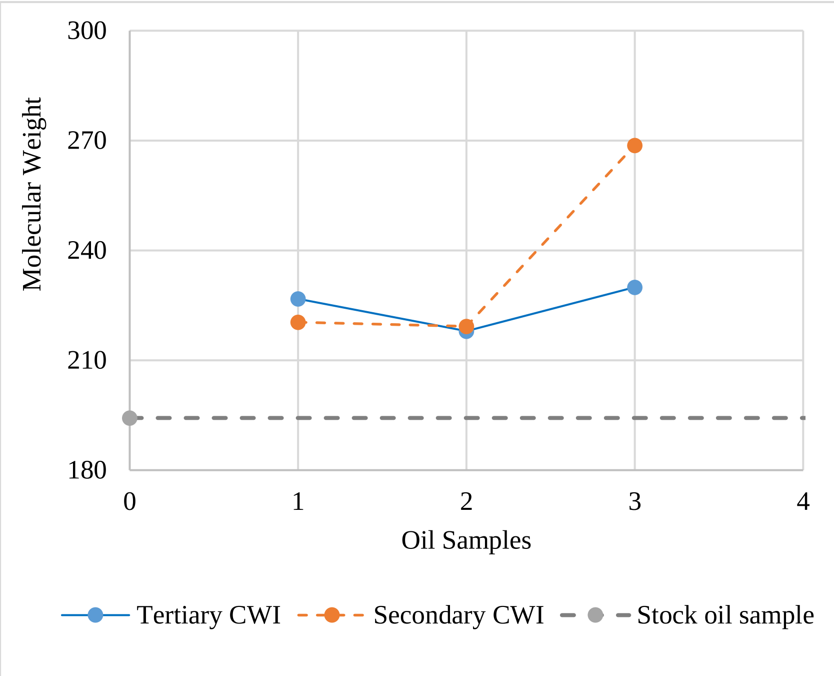

Figure 14: Molecular weights of the oil samples collected during tertiary and secondary carbonated water injection as compared with molecular weight of the stock oil sample.

5. Conclusions

For carbonate oil reservoirs, the unique advantage of this study is the comprehensive results presented to identify various aspects of CWI at high pressure (3100 psi) and temperature (100C) using recombined live oil with a four-component associated gas. From brine-rock interaction tests, CT images of the inlet core has directly revealed that rock dissolution has been localised and limited to the inlet core plug. From pore-scale visualizations, formation of gaseous third-phase was identified as the predominant mechanism controlling the improved oil recovery by CWI. In secondary CWI, the third-phase formation triggered in the very early stage of carbonated water displacing the resident oil. It was identified that an in-situ three-phase region would be generated where carbonated water meets the resident live oil. Therefore, an *"in-situ WAG"* three-phase flow would be built up with the enhanced pore-scale advantages.

Five coreflood experiments were carried out at different carbonated seawater injection scenarios. In secondary and tertiary CWI, significant amount of additional oil were observed.

The difference between tertiary and secondary modes can be attributed to less oil available in tertiary mode to take CO2 from the flowing CW. Similar performance at different injection rates demonstrated that the coreflood experiments were designed adequately to be uninfluenced by the laboratory artefacts. As identified in the coreflood experiments, the injection rate would not alter our judgment about the effectiveness of carbonated water. It was identified that retention of CO2 in the third-phase can act as an enhanced mechanism for CO2 storage during CWI in oil reservoirs. Also, from waterflood and CWI breakthrough time and recovery curves, it can be concluded that CWI cannot bring about effective wettability alterations in carbonate rock systems.

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