

Effects of Slug Size, Soaking, and Injection Schemes on the Performance of Controlled Ions Water Flooding in Carbonates

Nikoo Moradpour, Marzhan Karimova, Peyman Pourafshary,* and Davood Zivar



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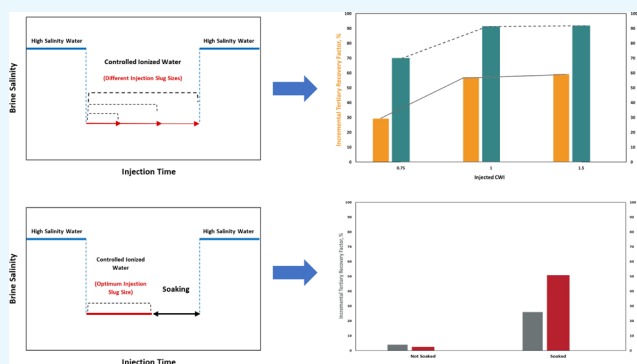
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ABSTRACT: The results of many previous studies on low salinity/controlled ions water (CIW) flooding suggest that future laboratory and modeling investigations are required to comprehensively understand and interpret the achieved observations. In this work, the aim is co-optimization of the length of the injected slug and soaking time in the CIW flooding process. Furthermore, the possibility of the occurrence of several governing mechanisms is studied. Therefore, the experimental results were utilized to develop a compositional model, using CMG GEM software, in order to obtain the relative permeability curves by history matching. It was concluded that CIW slug injection, concentrated in the potential-determining ion, can increase oil recovery under a multi ion exchange (MIE) mechanism. The wettability of the carbonate rocks was changed from a mixed or oil wet state toward more water wetness. However, there is a CIW slug length, beyond which extending the length does not significantly improve the rock wettability, and consequently, the oil production, which is known as the optimum slug size. This implies that the optimization of the injection process, by minimizing the slug size, can decrease the need for the CIW supply, therefore lowering the process expenditure. Moreover, if the exposure time of the rock and CIW is increased (soaking), a higher level of ion substitution is probable, leading to more oil detachment and production. Rock dissolution/precipitation (leading to a pH change) was found to have a negligible contribution.



1. INTRODUCTION

Based on the oil demand trend and oil prices, co-optimization is required to maximize crude oil production while the production cost is minimized.^{1,2} Water flooding is widely used as a conventional secondary oil recovery technique to improve the oil sweep efficiency. Alongside, it is known as a practical method to maintain reservoir pressure. As it is cost-effective and convenient to supply and implement, the idea of changing the concentration and/or composition of the injection water, to extract residual oil and achieve higher oil recovery in a tertiary stage, first attracted attention more than 50 years ago.³

The effect of injecting diluted sea water, synthetic low-salinity brines, ion-treated brines [known as controlled ions water (CIW)], and the controlling parameters on the microscopic water sweep efficiency has been investigated by many experimental and modeling works in both sandstone and carbonate rocks.⁴ A considerable number of the hydrocarbon-bearing reservoirs in the world, nearly 60%, are in carbonate rocks.⁵ On the other hand, the available research literature and pilot tests for low-salinity water (LSW) flooding in carbonates are limited, compared to sandstones, because of the increased complexity encountered when dealing with geochemical interactions in heterogeneous carbonate rocks. Up to 40%, incremental oil recovery can be obtained by injecting the

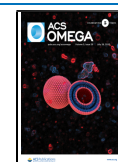
treated brines.⁶ However, the dominant driving mechanisms causing the incremental oil recovery by LSW is still a subject of controversy. Different mechanisms such as rock dissolution/precipitation,^{7–12} double-layer expansion,^{11,13–18} and wettability alteration are proposed to explain the mechanisms of incremental oil recovery by LSW in carbonates. The main reasons for this ambiguity and inconsistency are the numerous controlling parameters (such as initial wettability, rock mineralogy, resident fluids, etc.) and the complexity of the crude oil, brine, and rock (CBR) interactions.

Most of the conclusions in the literature have found wettability alteration as a consequence of multi ion exchange (MIE) as the responsible mechanism for incremental oil recovery by LSW injection in carbonate rocks. This mechanism is actuated by potential determining ions (PDIs), which are typically Ca^{2+} , Mg^{2+} , and SO_4^{2-} for carbonate rocks.^{19–22} The

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significant positive effect of the presence of sulfate ions has been reported in experimental studies.^{8,15,23,24} Various studies have confirmed the substantial effect of sulfate ions on the occurrence of wettability alteration in carbonates, as they found that sulfate-free brines did not change the core sample wettability toward water wetness, but sea water did.^{10,25–28} In their experimental investigations, AlQuraishi et al. stated that the higher sulfate content of sea water, rather than formation water, resulted in a lower contact angle, more negative surface charge (by zeta potential), and lower IFT values, all of which indicate a more water wet condition.²⁹

The net charge of the surface of carbonate rocks is usually positive at a neutral pH of 6.5–7.5, attracting negatively charged ends of crude oil (i.e., carboxylic acids) that causes the rock wettability to change to an oil or mixed wet state. When CIW-containing PDIs are injected, SO_4^{2-} ions approach the positive rock surface and reduce the net charge so that Ca^{2+} and Mg^{2+} cations can reach the surface and access the attached negative ends of the oil, therefore facilitating the oil detachment process by breaking the attraction bonds between oil molecules and the rock surface, as illustrated in Figure 1. At

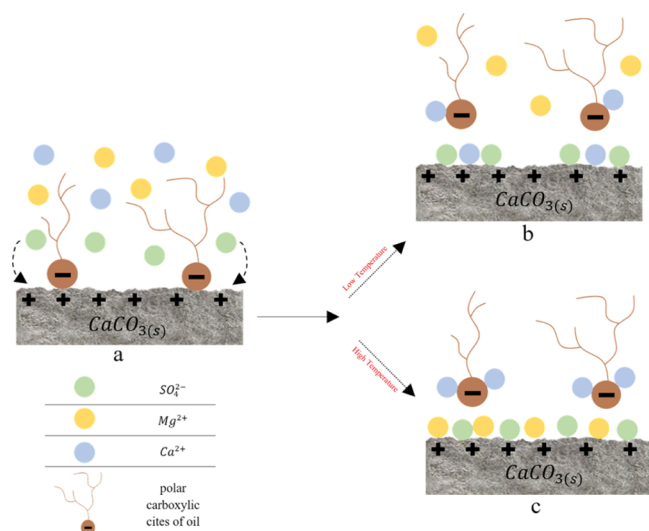


Figure 1. Negatively charged components of oil (a) detached from the positive carbonate rock surface by ion exchange applied by PDIs at low (b) and high (c) temperatures.

this stage, the repulsive force between the positive rock surface and the cations, attached to the oil, leads to the desorption of oil from the carbonate rock.²¹ The activity of Mg^{2+} cations increases at elevated temperatures, and they replace the Ca^{2+} cations connected to the rock surface, resulting in even more oil detachment. This latter reaction is more likely to happen if rock dissolution occurs, thereby providing higher concentrations of SO_4^{2-} and Mg^{2+} ions. Hence, the rock wettability changes to more water wet because of the presence of adequate concentrations of PDIs in the injected water.^{12,22,30–33}

Many researchers have shown that increased oil production under different low salinity/CIW injection schemes into limestone and dolomite core samples, and measurements of surface-related properties (contact angle, IFT, and zeta potential), indicated the advantageous role of decreasing the brine salinity or increasing the sulfate ion concentration in incremental recovery because of wettability alteration.^{12,32,34–36} For example, Yousef et al. indicated that 10

times diluted water decreased the contact angle values which clarified the fact that LSW modifies the rock surface charge which leads to incremental oil recovery by core flooding.³⁷ According to Mohammadkhani et al., the highest oil recovery (97.8%) was obtained by the lowest connate water saturation and the lowest salinities for both connate and injected water. In addition to MIE, precipitation of anhydrite (CaSO_4), that alters the wettability toward more water wetness, can be another reason for enhanced oil recovery.³⁸

Of late, a few studies have been conducted on the numerical simulations in carbonates to analyze the effect of the injected water composition, especially PDIs on CBR interactions. Wu and Bai³⁹ proposed a conceptual mathematical model to investigate how capillary pressure and relative permeability were affected by LSW. In this model, the relative permeability, capillary pressure, and residual oil saturation are salinity-dependent. It is also assumed that the relative permeability to the water phase remains unchanged, whereas the relative permeability to the oil phase increases with a decrease in salinity. The proposed model was verified with single-phase (one dimensional) flow, two-phase flow, and flow through a fractured rock (double porosity). The simulated results were in good agreement with analytical and experimental observations. One more mathematical model for spontaneous imbibition experiments in chalk core plugs was proposed by Hiorth and Evje.⁴⁰ The shifting of wettability to a highly water wet condition was observed. Interpolation of the relative permeability and capillary pressure was implemented as a function of the dissolution of the calcite (CaCO_3) mineral. During the calcite dissolution, the wettability changes toward a highly water wet condition.

Dang et al.⁴¹ developed a model by taking ion-exchange mechanisms and geochemical reactions into account. They interpolated relative permeability curves based on the concentration of Ca^{2+} and verified their model by the experimental results published by Fjelde et al. and Rivet. A multiphase, multicomponent mechanistic model by Sharma and Mohanty⁴² was developed in UTCHEM/IPHREEQC. They applied the ion exchange process leading to wettability alteration and rock dissolution, as presented by Zhang et al. and Hiorth et al., respectively.^{43,44} By their model, surface potential results indicated a surface charge alteration during LSW injection that is consistent with experimental results. The oil recovery results, matched with production data achieved by two experimental works, confirmed the validity and accuracy of the model. The acid concentration (acidic compounds of oil) attached to the rock surface was obtained from the geochemical analysis by the software and found to be decreased by injecting LSW. This parameter was used for the interpolation of the relative permeabilities.

To find the responsible production mechanism(s) for a 4–8% incremental oil recovery, Nasralla et al. conducted a geochemical modeling using PHREEQC and concluded that, based on the calcium concentration alteration trend, rock dissolution cannot be the main driving mechanism and the wettability alteration, according to zeta potential and contact angle results (referring to another work by them⁴⁵), caused oil desorption and enhanced production.⁴⁶ In a later study, their experimental and simulation results showed that LSW injection is able to accelerate oil production which is an important parameter economically. They used the shell in-house simulator (MoReS) to attain the relative permeability curves in order to input into field-scale modeling. The up-scaled

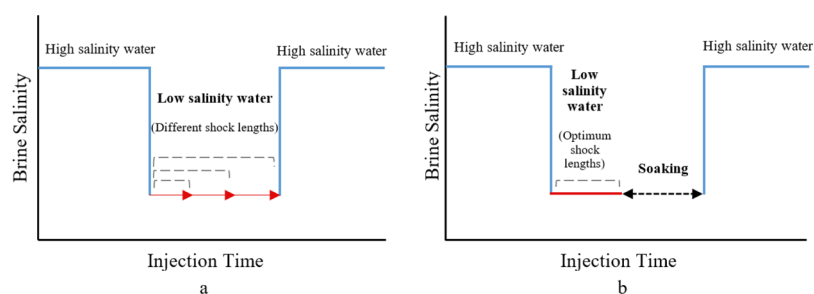


Figure 2. Illustration of the idea of (a) different slug lengths injection and (b) soaking after slug injection and before the next water flooding.

model indicated a 6–7% OOIP incremental oil recovery because of higher oil relative permeability provided by low salinity brine.⁴⁷

Al-Shalabi et al. used the experimental results (Mohanty and Chandrasekhar, and Yousef et al.) to validate and optimize their comprehensive modeling work. They concluded that low salinity brine does not affect the relative permeabilities of oil and brine similarly. Using the UTCHEM simulator, oil residual saturation, endpoint relative permeability, and exponents were calculated as a function of the contact angle estimated through injected water salinity. Afterward, they developed a fundamental LSW injection model modifying the capillary desaturation curve using trapping numbers. According to their outcomes, residual oil is a function of trapping number which is a function of the contact angle which is again, a function of electrical double layer thickness. Ultimately, they proposed that surface charge alteration and rock dissolution can change rock wettability toward a more water wet state.^{16,48–53}

To date, many parameters related to the process of low salinity/CIW injection such as injected brine salinity, composition, temperature, pH, and injection mode, have been investigated and optimized for different desired implementation conditions. To optimize the process economically, it is interested to allocate lower time and expenditures to the modification of the water salinity and constituent ions. Therefore, designing an optimized scenario to achieve the highest feasible oil recovery, with the lowest expenditure, will make low salinity/CIW flooding a more practicable EOR method. Accordingly, a new idea is to minimize the injection slug size of CIW to affect the CBR interaction in a shorter time and increase oil production in a more efficient way. This short period of CIW flooding is called shock injection in our study, which is mainly focused on engineering the injected water composition regarding PDIs in order to find the underlying mechanisms responsible for oil recovery. The lowest contact angle was observed in the disk soaked in the brine of 10 times diluted, high salinity water (HSW), and Mg^{2+} and SO_4^{2-} ions. This agrees with the mechanism of multicomponent ion exchange dictated by PDIs in carbonate rocks. They conducted a core flood test of the HSW–CIW–HSW scenario, with a slug size of 0.5 PV for the second injection step, as a CIW slug flooding. OOIP (51.9 and 4.35%) were recovered after injecting secondary HSW and the slug injection, respectively.⁵⁴ In a subsequent study by our research team, different slug sizes of 0.75, 1, 1.5, and 2 PV, for CIW slug injection, were applied on carbonate core samples to investigate the optimum injection scheme.⁵⁵ It was concluded that CIW flooding can increase oil recovery even at low slug size injections. Furthermore, they indicated that the longer the slug size, the

higher oil recovery is obtained as the rock surface has been exposed to ion exchange reactions for longer time. This method can be improved by “soaking” the core samples after slug injection, which means allowing the core to be soaked with the injected CIW, before the next HSW flooding, in order to provide PDIs with more time to affect the CBR interactions and change the rock wettability. The positive effect of soaking was observed in the higher oil recovery of 12.8% by the CIW rather than the 1.3% recovery of the nonsoaked core sample.

According to these observations in the literature, it is implied that to achieve the highest possible benefit from low salinity/CIW injections, there is no need to inject more and more treated waters which makes the process costly and maybe impractical. Indeed, smaller injection slug sizes (slug injection), as depicted in Figure 2a, and soaking, as illustrated in Figure 2b, are able to change the rock wettability toward more water wetness to such a favorable extent that its prolonged effect can even increase the oil recovery in the following second HSW injection.

Although the contributing mechanisms in the LSW process are vastly investigated by the researchers, the idea of the injected slug size optimization as well as soaking of the porous media by CIW is not well matured. On the other hand, to the best of our knowledge, a detailed modeling analysis of different slug sizes and soaking time on CBR interaction and relative permeability in carbonates has not been studied in the literature. Therefore, we investigated this hypothesis by developing a geochemical model in the core scale. The objective is to study the effect of CIW slug injection and soaking on CBR parameters such as wettability and relative permeability and to optimize the mentioned process. To do so, the developed model is tuned based on the presented experimental results in our previous study.⁵⁵ Then, the changes in relative permeability curves because of the injection of different slug sizes of CIW are studied. The contribution of the soaking time in the CIW flooding process is discussed by using relative permeability curves. The dissolution and or precipitation of the minerals are also presented to check the effect of CIW on the rock mineralogy.

2. METHODOLOGY AND MATERIALS

Five CIW slug injection experiments with different injected pore volume lengths have been chosen to use in this study.⁵⁵ The carbonate rock from the same formation, in addition to identical test conditions (temperature, pressure, etc.), was utilized in all the experiments. The injection rate was 0.1 cm^3/min and was kept constant for all the scenarios with the confining pressure set to be 1000 psi.

For the first three core flooding experiments, the implemented scenario was the injection of 2 PV of HSW

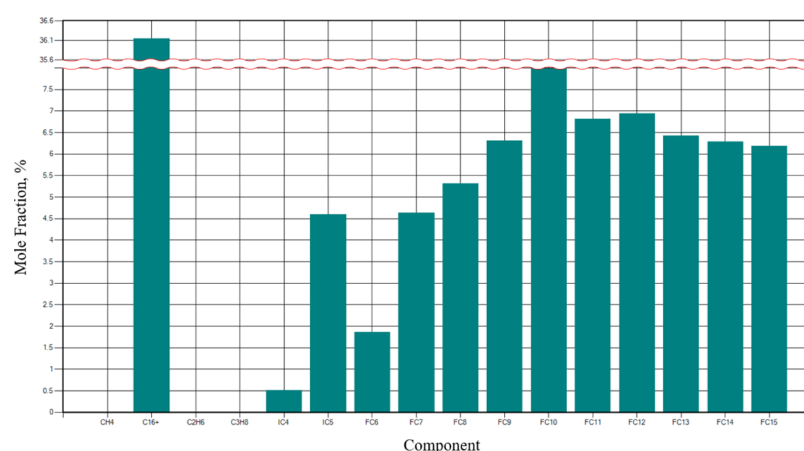


Figure 3. Composition of the crude oil after lumping.

from a carbonate reservoir into all the limestone core samples, followed by different CIW slug lengths ranging from 0.75 to 1.5 PV. Afterward, HSW was injected for 2–3 PV to make sure that no mobile residual oil remained in the cores. Two other core flood tests were carried out to evaluate the idea of soaking, where both core samples were flushed with 7 PV HSW in the first step and then 1 PV of CWI in the second step. As a third step, 10 PV HSW was injected in one of the core samples unceasingly and into the other core sample after 48 h of soaking. The brine's composition, oil and rock samples, and core flooding procedure were similar to our previous experiments mentioned in Fani et al.

Our model was developed, and the history matched, by the abovementioned experiments to analyze the effect of slug and soaking on CBR interactions. The following input data were used in the model.

2.1. Core Sample. The carbonate core samples used in this study show similar physical properties, where the porosity and permeability of the core samples are in the range of 12.91–15.9% and 3.1–4.2 mD, respectively. X-ray diffraction analysis of the core samples showed 98 and 2 wt % of calcite and quartz minerals, respectively, in the carbonate rock. The water-saturated cores were first flooded with oil to attain irreducible water saturation, and subsequently, they were aged in the same oil to mimic the initial oil wet condition of the reservoir rock. The contact angle measurements for the aged cores by Fani et al.⁵⁵ indicated that the initial wettability of the rock is strongly oil wet (contact angle = 152°).

2.2. Crude Oil Sample. A light Omani crude oil was used in this study.⁵⁵ The specific gravity and density of the oil are 0.837 and 0.815 g/cm³, respectively, according to PVT calculations by CMG WINPROP and also experimental measurements. Additionally, the oil viscosity is 8.94 cp at room temperature and 3.47 cp at 87 °C.

The Peng–Robinson equation of state was used in this study in order to generate the PVT behavior of the numerical simulation. We used a lumping technique to build a pseudo-component C₁₆^{*}, for the components C₁₆ to C₂₆, to reduce the compositional cost. The component content of the lumped composition is depicted in Figure 3. Also, the oil viscosity of the PVT model was tuned using experimental oil viscosity values.

2.3. Brine Sample. Two different types of brines were used in the experiments which are (1) HSW as a representative of the formation brine and (2) CIW as a representative of

injection water. The composition of the CIW is the same as HSW, but it is rich in terms of SO₄²⁻. The details of the composition and concentration of the brines are illustrated in Table 1.

Table 1. Composition and Concentration (in ppm) of the Brines

water	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Fe ²⁺	Cl ⁻	SO ₄ ²⁻
HSW	37640	7847	1310	356	134	66511	69
CIW	3880	788	403	50	22	6575	916

3. MODEL DESCRIPTION

A two-dimensional model has been developed in order to simulate experiments. The model consists of 30, 1, and 6 grid blocks in the *i*, *j*, and *k* directions, respectively. The length of grid blocks in the *i* direction is equal to the length of the core samples, and the area of the grid blocks in the *j*–*k* plane is equal to the areal cross section of the core samples. As the fluid flow is assumed to be only in one direction of *i* and the inlet cross section area of the cylindrical core sample and cubic model are identical, the cubic model is preferred to use because of model simplification.

We used an adaptive implicit mode which can optimize both the computational cost and the simulation stability (numerical dispersion). When adaptive implicit mode (threshold switching) is selected, the calculation method in each grid block and each time step is switched to implicit if the changes in water saturations or hydrocarbon component global mole fractions exceed the specified value. The tolerance of convergence of Newton's method has been tightened in order to reduce the residue. We also specified the maximum changes in the global mole fraction and aqueous reactions during Newtonian iterations. If the change of global mole fraction and aqueous reactions of any component exceeds 0.1, the time step size is reduced and the time step is repeated. Note that, refining the time step further, or reducing the maximum change of global mole fraction (total mole fraction of present fluids in each grid block) and aqueous reactions, had an insignificant change on the results. Hence, our simulations are essentially fully converged with this numerical control. A typical view of the simulation model is shown in Figure 4.

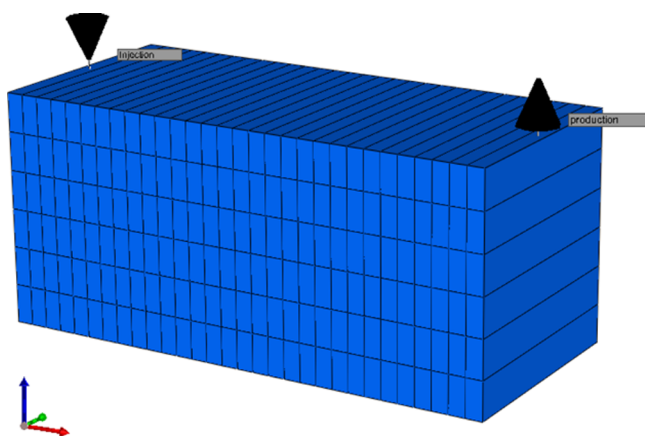
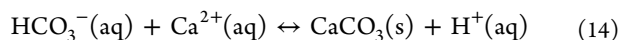
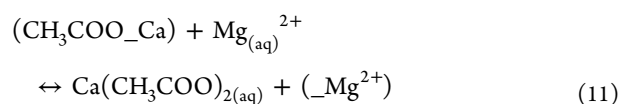
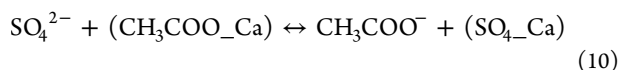
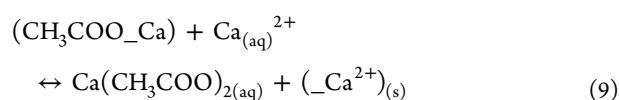


Figure 4. Homogeneous model representative of core samples.

The geochemical reactions in the numerical simulation can be divided in two different types: (1) aqueous reactions and (2) mineral precipitation/dissolution reactions as



Because the phase distribution and relative permeability are directly dependent on the rock wettability, it is of interest and importance to estimate the relative permeability before and after CIW injection in order to verify the responsible driving mechanism. Hence, oil and water relative permeability values are interpolated in each block cell, based on the concentration of SO_4^{2-} ions as the main PDI. The concentration of SO_4^{2-} was chosen as an interpolation parameter because it is assumed to be responsible for wettability alteration. In addition, LSW contains higher concentration of SO_4^{2-} than HSW. Relative permeability values were generated based on Corey's correlation for limestone rock as eqs 15 and 16.

$$\begin{aligned} K_{\text{rw}} = &a \times \frac{(S_w - S_{w,\text{crit}})}{(1 - S_{w,\text{crit}})} - b \times (S_w - S_{w,\text{crit}}) \\ &\times \left[\frac{(S_w - S_{\text{orw}})}{(1 - S_{w,\text{crit}} - S_{\text{orw}})} \right]^2 \\ &+ c \times \left[\frac{(S_w - S_{w,\text{crit}})}{(1 - S_{w,\text{crit}} - S_{\text{orw}})} \right]^4 \end{aligned} \quad (15)$$

$$K_{\text{row}} = d \times \frac{(S_o - S_{\text{orw}})}{(1 - S_{\text{orw}})} \times \left[\frac{(S_o - S_{\text{orw}})}{(1 - S_{w,\text{con}} - S_{\text{orw}})} \right]^2 \quad (16)$$

where K_{rw} and K_{row} are water and oil relative permeabilities, S_w and S_o are water and oil saturation at each point, $S_{w,\text{crit}}$ is critical water saturation, S_{orw} is residual oil saturation after water-flooding, and $S_{w,\text{con}}$ in connate water saturation. The coefficients a , b , c , and d vary for different CBR conditions.

As mentioned before, the concentration of SO_4^{2-} in CIW is significantly higher than in HSW. Hence, following injection schemes of HSW-CIW-HSW, the concentration of SO_4^{2-} is

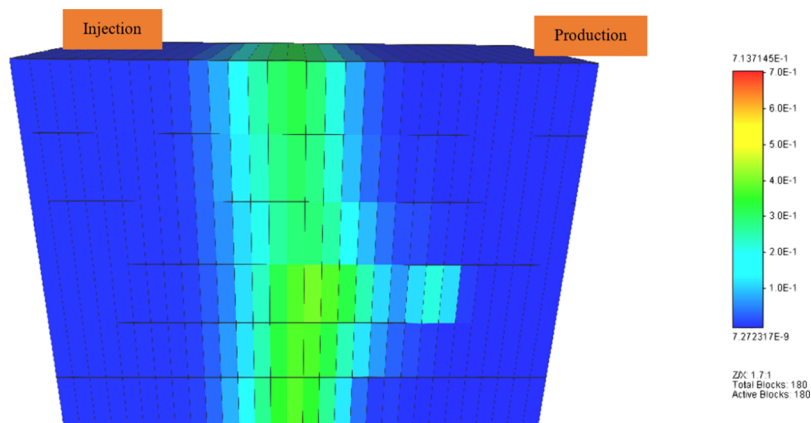


Figure 5. Example of oil relative permeability distribution after CIW injection.

subject to variability in each grid cell which alters the relative permeability through MIE. The relative permeability interpolation has been conducted based on the concentration of SO_4^{2-} (λ) which provides us with a weighting factor (ω) to interpolate between the relative permeabilities, before and after the CIW injection, in each grid cell. Figure 5 indicates an example of the altered oil relative permeability by CIW slug injection.

Oil and water relative permeability values and the weighting factor are calculated as below

$$K_{rw} = \omega K_{rw}^{\text{LSW}} + (1 - \omega) K_{rw}^{\text{HSW}} \quad (17)$$

$$K_{ro} = \omega K_{ro}^{\text{LSW}} + (1 - \omega) K_{ro}^{\text{HSW}} \quad (18)$$

$$\omega = \frac{\lambda - \lambda^{\text{HSW}}}{\lambda^{\text{LSW}} - \lambda^{\text{HSW}}} \quad (19)$$

where K_{rw} is the calculated water relative permeability, K_{ro} is the calculated oil relative permeability, K_{rw}^{LSW} is the water relative permeability (LSW injection), K_{rw}^{HSW} is the water relative permeability (HSW injection), K_{ro}^{LSW} is the oil relative permeability (LSW injection), K_{ro}^{HSW} is the oil relative permeability (HSW injection), ω is the weighting factor, λ is the overall concentration of the SO_4^{2-} , λ^{HSW} is the concentration of the SO_4^{2-} in HSW, and λ^{LSW} is the overall concentration of SO_4^{2-} in LSW.

3.1. History Matching. To obtain the best possible simulation by CMG GEM, the available effective parameters such as the coefficients in Corey's relative permeability correlations (eqs 15 and 16), interpolation indices, and oil and water relative permeability values, in each water saturation, were tuned to achieve the most accurate possible match with experimental data, as shown in Figure 6. It is worth noting that the pressure drop curves and recovery curves were simulated and matched the experimental data, simultaneously, by the error of less than 10%. As shown in subfigures (a–e) of Figure 6, the tuned models are able to predict the experimental results with a high degree of confidence.

3.2. Simulation Accuracy. The comparison between the recovery factors generated by the developed models and the experimental data of the CIW slug and soaking tests by linear regression is calculated and illustrated in subfigures (a–e) of Figure 7. The results of all the cases show an R -squared parameter of more than 95% which is acceptable and reliable. Higher errors in some points may be because of late production affecting the experimental results; however, the estimated ultimate recoveries at each production stage, by the model, are rigorous and in perfect agreement with the experimental curves.

The average values of relative errors for all curves are indicated in Table 2, which are less than 5% and acceptable. The relative error for each data point was calculated by eq 20.

$$\text{Relative error} = \frac{\text{experimental data} - \text{simulation data}}{\text{experimental data}} \times 100 \quad (20)$$

4. RESULTS AND DISCUSSION

The successful effect of PDIs on changing the carbonate rock wettability toward more water wetness, which desorbs oil droplets from the rock surface, was observed by our models. PDIs substitute oil droplets attached to the rock surface

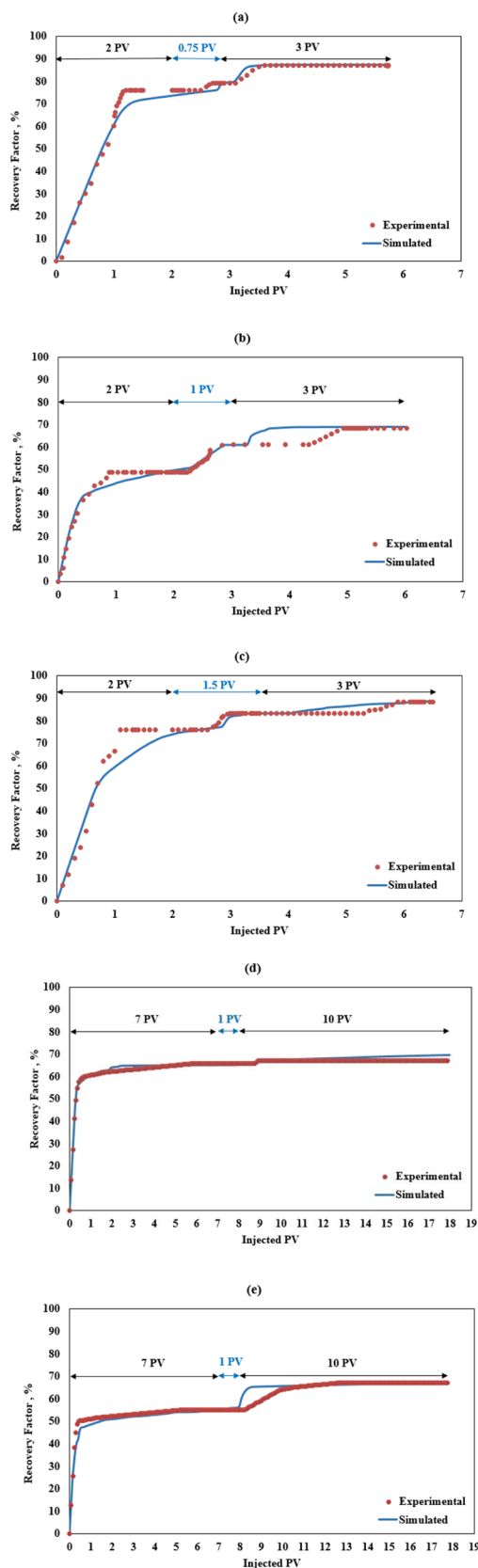


Figure 6. Results of simulated cases compared with experimental data for 0.75 PV (a), 1 PV (b), and 1.5 PV (c) CIW slug injection and 1 PV CIW injection without (d) and with (e) soaking time.

through ion-exchange reactions (eqs 8–11) and so make more mobile residual oil available to be swept, and produced, by

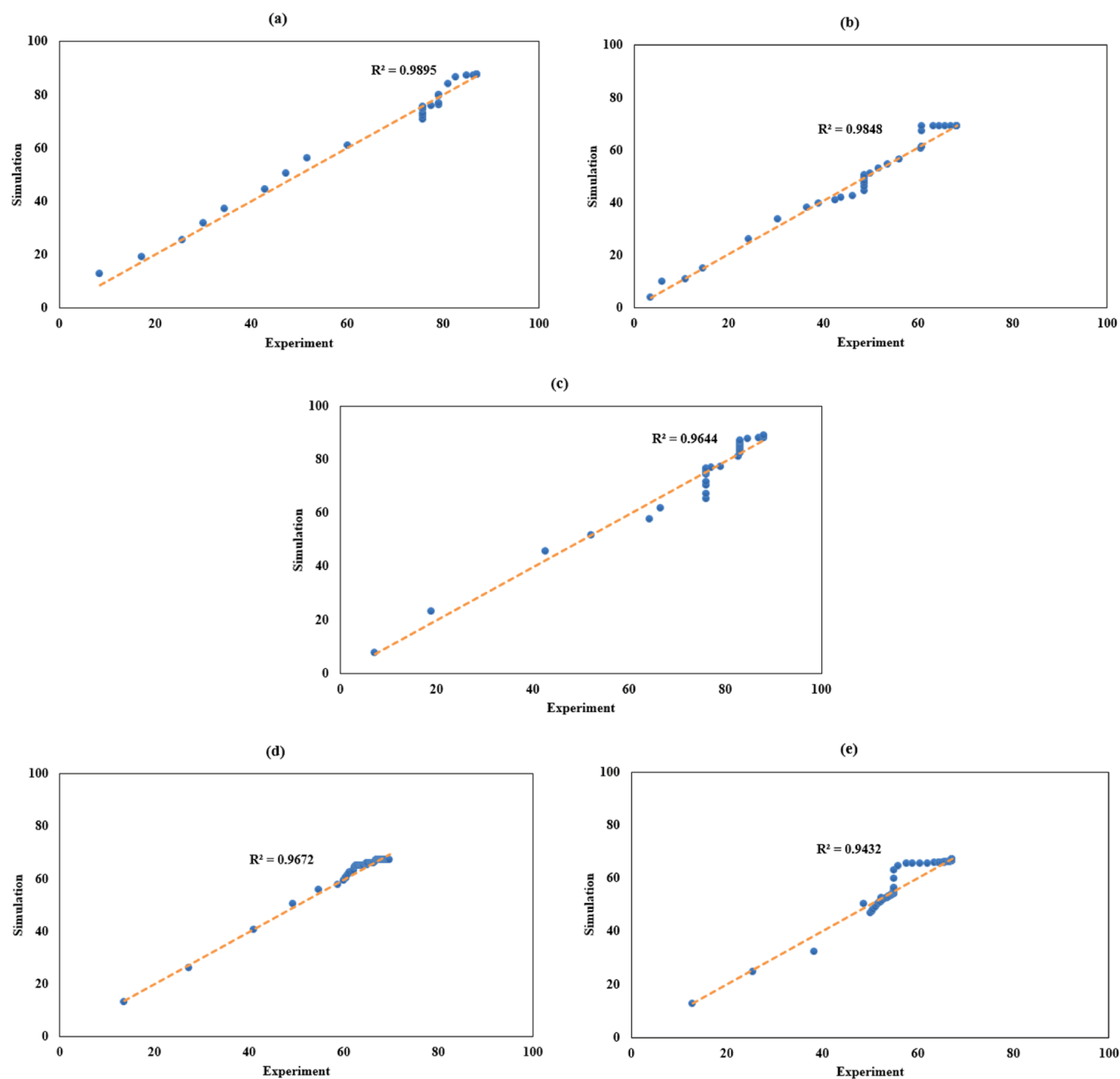


Figure 7. Recovery factor errors of simulation results for 0.75 PV (a), 1 PV (b), and 1.5 PV (c) CIW slug injection and 1 PV CIW injection without (d) and with (e) soaking time.

Table 2. Average of Relative Errors of Simulation Results Compared to Experimental Measurements

case#	1	2	3	4	5
error (%)	2.86	3.27	3.51	1.66	2.7

either the same CIW slug or the next HSW slug. Comparing the relative permeability curves before and after CIW flooding can be considered as evidence of wettability alteration.

4.1. Effect of Slug Size. The improved production suggests the positive synergistic effect of conventional and CIW injection under different injection schemes. The core relative permeability curves before and after CIW injection for cases 1–3 are depicted in subfigures (a–c) of Figure 8. It is assumed that relative permeabilities do not change by the second HSW flooding and only the detached oil drops by the

previous LSW injection is swept in this step resulting in incremental oil recovery. It can be concluded that, in all the cases, CIW injection caused wettability alteration which can be proposed as the responsible mechanism for oil detachment from the rock surface, redistribution of oil and water, and enhanced recovery. In all cases, oil relative permeability has increased while water relative permeability has decreased. This result conveys that CIW injection has helped oil production improvement by providing an easier flow path for oil toward the production well.

In order to compare the effect of slug length, the recoveries in the tertiary production stage are considered in Figure 9. The elongation effect of wettability alteration caused two incremental oil productions in each scenario. By increasing the slug length from 0.75 PV to 1 PV, oil recovery increases to

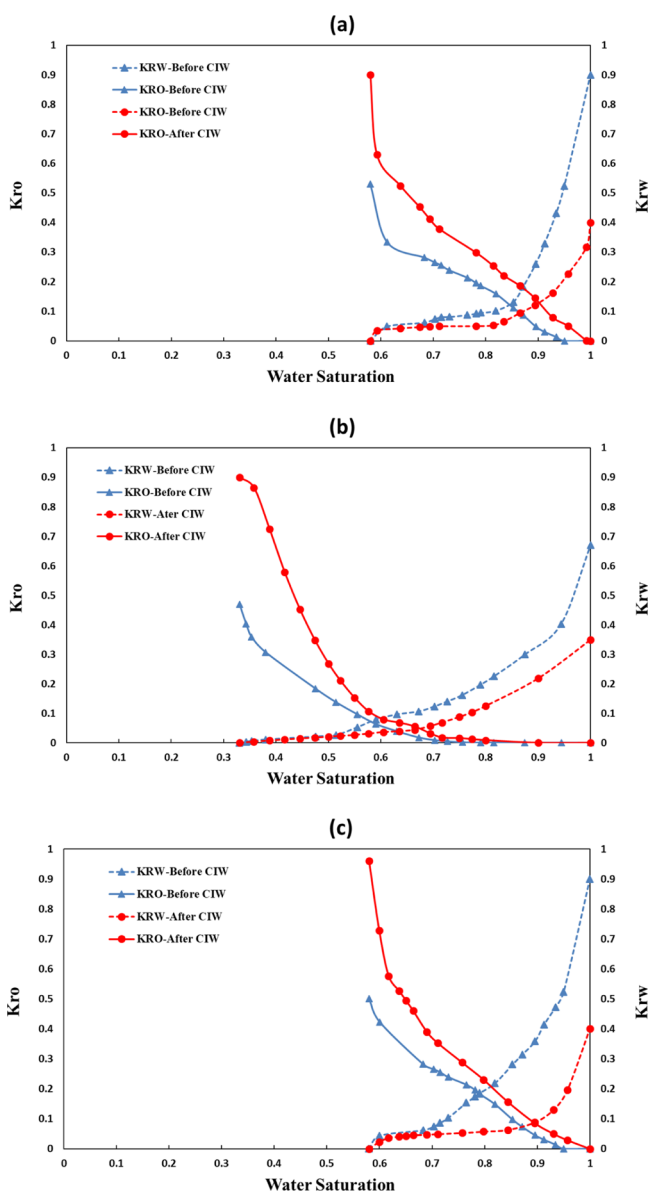


Figure 8. Relative permeability curves before and after 0.75 PV (a), 1 PV (b), and 1.5 PV (c) CIW slug injection.

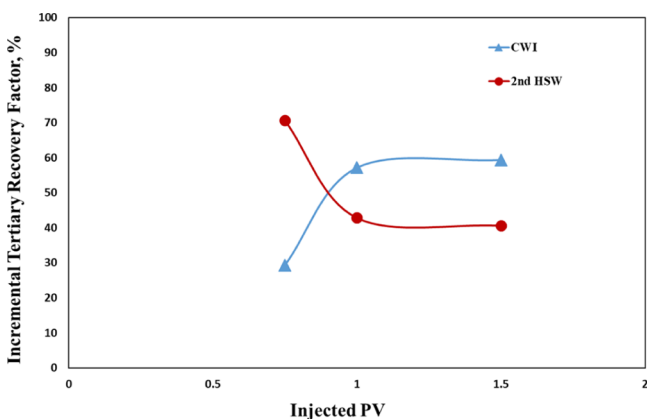


Figure 9. Incremental oil recovery by CIW slug injection and the preceding second HSW flooding.

27.9%. However, extending the slug length injection to 1.5 PV enhances the oil recovery by only 2.22%. On the other hand, the detached and redistributed mobile oil can still be swept by switching to HSW injection. The two curves in Figure 9 imply that (1) longer CIW slug injection yields higher oil recovery because of a higher multicomponent ion exchange on the rock surface which allows for more oil desorption. (2) Extending CIW slug length provides a longer time for the water slug to sweep the detached oil toward the production well. In this way, less mobile oil is left for the proceeding HSW flooding to recover. The decreasing trend of the production by HSW (red line) conveys this conclusion. (3) In order to design a CIW flooding process, it is necessary to optimize the design by considering the cost of the project. Hence, the longest slug length is not necessarily the most appropriate option. According to the experimental and simulation results, 1 PV is the optimum length concerning incremental oil recovery for CIW injection into the limestone cores.

As depicted in Figure 10, CIW changed K_{ro} in case #1 by 69.81%. In case #2, this was significantly increased to 91.49%.

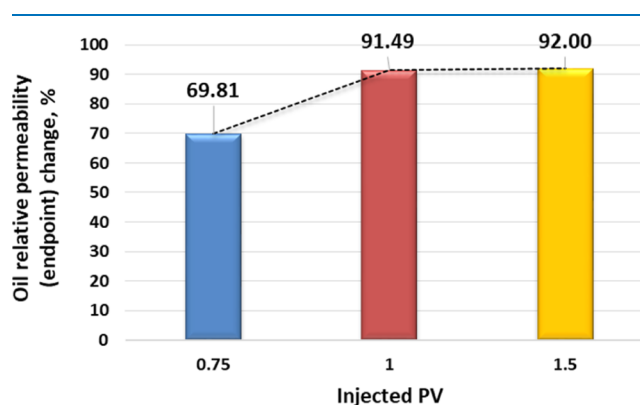


Figure 10. Comparison of the variations in oil relative permeability endpoints before and after different CIW slug injection schemes.

However, increasing the CIW slug injection to 1.5 PV, in case #3, the oil relative permeability alteration reached 92%. This very slight increase in wettability alteration, by switching from 1 PV to 1.5 PV, indicates that the wettability shows no further change after a specific slug length, which can be considered as an optimum economic option. Ion exchange between CIW and the rock surface cannot occur indefinitely, and stops after a particular level of ion exchange, even if more PDIs are injected.

One other available way to investigate wettability status and alteration is the intersection of the oil and water relative permeability curves. According to Wheaton,⁵⁶ when relative permeability curves are depicted based on water saturation, the interception of the curves occurring is an indicator for the wettability state. If the intersection occurs at water saturations lower than 50%, the rock system is oil wet. However, for intersections moving toward higher water saturations than 50%, the rock becomes more water wet. Any EOR process regarding wettability modification aims to redirect the rock wettability toward a more water wet status rather than the initial condition. Figure 11 displays the magnitude of variation in the water saturation at the intersection point in the relative permeability curves before and after CIW flooding. This value increased from 4.1 to 8.9% by switching from 0.75 PV to 1 PV of slug length. However, after extending to 1.5 PV, the saturation of the intersection changed to 10.1% which is only

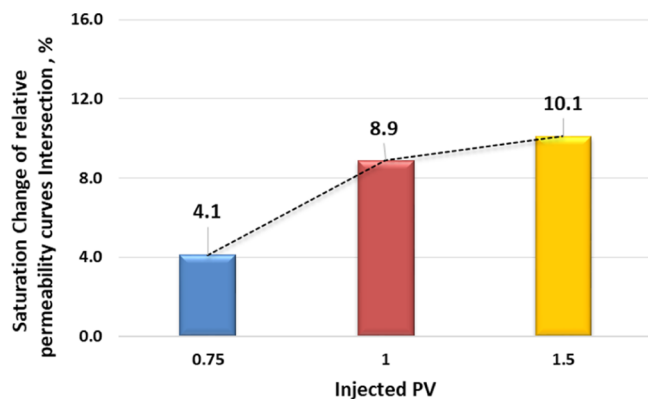


Figure 11. Comparison of the variations in the intersection points of relative permeability curves before and after CIW slug injection.

1.1% higher than the 1 PV injection. This confirms that the magnitude of the wettability alteration by 1 PV of CIW slug is high enough to produce the required oil detachment and can be considered as the optimum slug length. It is notable that compared to core-scale experiments, maybe 1 PV is not applicable in field scale because of large field or sector pore volume and smaller slug sizes of LSW/CIW would be more feasible to apply.

4.2. Effect of Soaking. To investigate the hypothesis of after-slug soaking and the possibility of achieving higher oil recovery, two more core flood tests were modeled using the same procedure as the slug length tests. The optimum CIW slug length of 1 PV was applied to the soaking tests.

The properties, mainly lower absolute permeability values, of the cores used in these tests are relatively different from the previous cores in cases 1–3. Therefore, longer HSW flooding periods were applied in cases #4 and #5. Despite the slug tests, case #4 and case #5 yielded only one incremental recovery step which is probably because of the lower absolute permeability values that restricts the oil sweeping by the same short CIW flow that detaches the oil droplets from the rock surface. Therefore, the detached oil remains in the core to be recovered by the following HSW injection.

Figure 12 demonstrates the oil and water relative permeability curves relating to cases 4 and 5 before and after CIW injection. The very small variation in the oil relative permeability endpoint, and the intersection of the curves in case #4 (Figure 12a), illustrates the fact that the CIW could not change the rock wettability highly enough to significantly improve the oil recovery. Comparing Figure 12b of case #5, with case #4, one can easily conclude that in this case, the magnitude of wettability alteration is much higher than case #4. Oil and water relative permeability endpoints were significantly elevated, and decreased, respectively. Moreover, the variation of the intersections implies a remarkable change in the wettability state of the rock toward more water wetness. The negligible change in relative permeabilities, besides the slight oil production in case #4, shows that wettability alteration is the governing mechanism and any other helping mechanisms do not have any significant contribution.

When the rock was immediately flooded by HSW after CIW injection, the rate of ion exchange was not high enough to generate a significant EOR effect. Consequently, according to Figure 13, a very small reduction (0.6%) in the residual oil was attained after the tertiary injection in case #4. On the contrary, in case #5, oil production increased significantly, leading to a

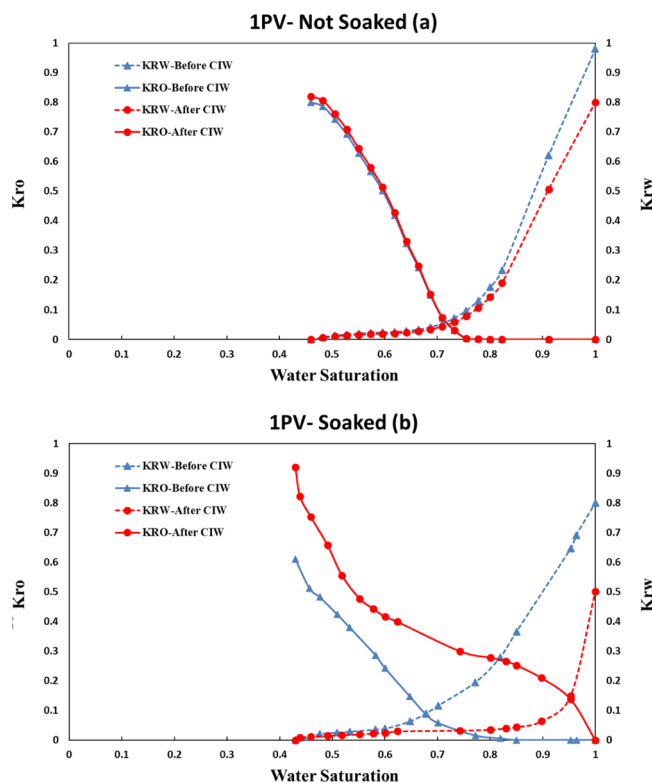


Figure 12. Relative permeability curves before and after 1 PV CIW slug injection without (a) and with (b) soaking time.

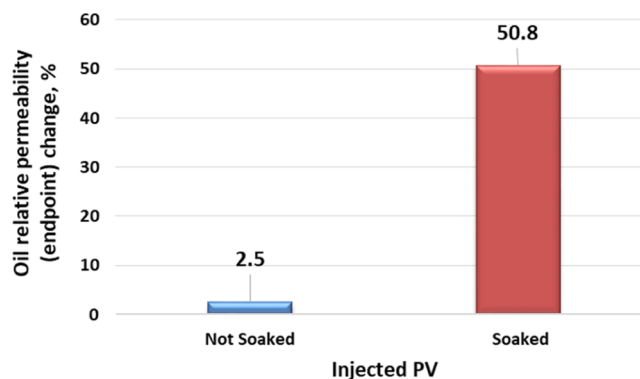


Figure 13. Comparison of the variations in oil relative permeability endpoints before and after CIW injection without and with soaking time.

12.8% OOIP incremental oil recovery and a 5.8% reduction of residual oil saturation. Soaking allows the rock surface and the present PDIs to undergo a higher level of ion exchange, the rate of which requires more exposure time to desorb oil droplets sufficiently to make the injection scenario economically feasible. In conclusion, we can claim that the idea of soaking time is confirmed to be advantageous with regard to oil recovery improvement.

The variations in oil relative permeability endpoint and the intersection of the oil and water relative permeability curves are shown in Figures 13 and 14.

In Figure 13, it can be seen that in case #5, soaking the rock after the CIW injection can change the rock surface wettability to a much higher extent such that the oil relative permeability endpoint increases to 50.82%, rather than before CIW injection. However, case #4 shows only a 2.5% improvement

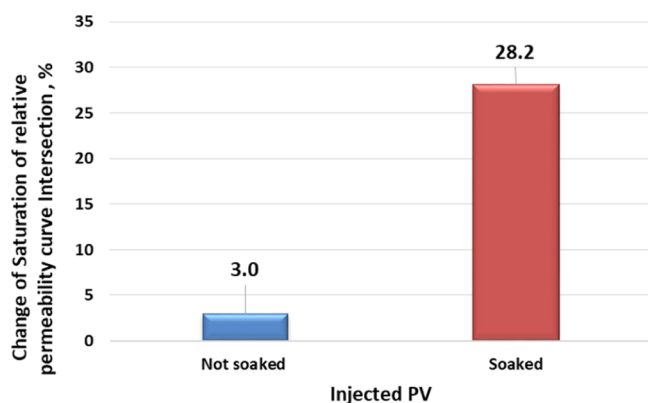


Figure 14. Comparison of the variations in the intersection points of relative permeability curves before and after CIW injection without and with soaking time.

after CIW injection which is considerably lower than case #5. The same point can be concluded from Figure 14. Comparing the saturation change of the intersection, it can be concluded that the rock surface has undergone a significantly higher level of ion exchange, and consequently, wettability alteration. These conclusions are the indications of the time-dependency of the process of wettability alteration which was similarly observed by Mahani et al.⁵⁷ However, it should be noted that the magnitude of the soaking effect for application requires more investigations because of greater injection rates and formation bulk volume conditions.

4.3. Rock Dissolution/Precipitation. The injected water contains lower Ca^{2+} ions which causes a concentration difference between the ions present in the aqueous and solid phases. This can be a driving force for calcite rock dissolution to compensate for the deficiency of Ca^{2+} ions in the aqueous phase, leading to a pH increase because of the hydroxide ion (OH^-) release (reactions 12 and 13). On the other hand, the reprecipitation of the calcite mineral releases H^+ , which is again a reason for the pH reduction (eq 14).

The dissolved solid calcium ions can help the oil production because the adsorbed oil droplets detach from the solid surface with the released Ca^{2+} ions and enter the aqueous phase ready to be swept and produced. This means a pH increase shows

the presence of rock dissolution which can help the wettability alteration besides other mechanisms, such as ion exchange.⁵⁴

If rock dissolution happens during CIW injection, the pore volume variation in the simulated slug injection experiments is depicted in Figure 15a. Very low pore volume changes (up to 0.014%) indicate that the contribution of rock dissolution to the obtained oil recovery is negligible. Additionally, based on Figure 15b, the changes in the calcite mineral mole fraction was also negligible, implying a very slight magnitude of rock dissolution. Esene et al. stated the similar conclusion that the contribution of rock dissolution to oil recovery is not significant, and the main driving mechanism is wettability alteration to a more water wet condition.⁵⁸

In Figure 16, the pH values of the aqueous phase at three stages of initial, during CIW injection, and final points, are

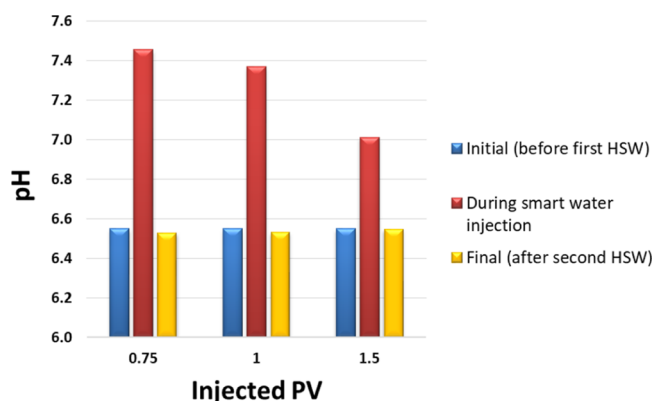


Figure 16. Initial, during CIW injection, and final pH values in different injection schemes [depicted for grid cell of (15, 1, 4)].

depicted. The presented pH values are related to similar grid cell of (15, 1, 4) for all the injection schemes, as a representative cell. Considering reactions 13 and 14, besides the mentioned figures, it can be concluded that by increasing the slug length, the precipitation reaction which decreases the pH value (because of H^+ generation) is activated to a higher extent. In case #1, rock dissolution is more dominant than precipitation (negative changes in calcite mineral), which

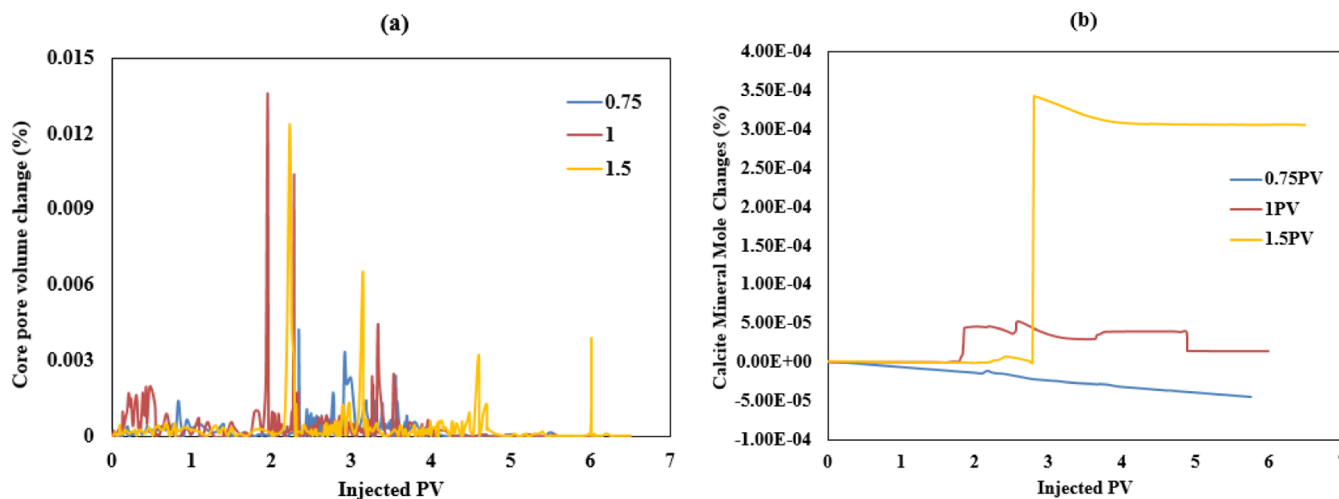


Figure 15. Changes in the core pore volume (a) and calcite mineral mole fraction (b) during HSW–CIW slug–HSW flooding in different injection schemes.

results in a higher pH according to reaction 13, while in case #3, mineral precipitation (positive changes in calcite mineral) is considerably higher because of the H^+ production, as stated in reaction 14. Similar to the deductions from Figure 15, pH analysis suggests that rock dissolution/precipitation cannot be the main producing mechanism because the highest pH increase is less than 1, which is not high enough to yield the achieved recoveries. This conclusion is confirmed by the small pH increase (ranging from 6.55 to 7.5) and normal pressure drop results reported in Fani et al.⁵⁵

5. CONCLUSIONS

The injection of the low salinity/CIW is getting attention because of its advantages. Tertiary low salinity/CIW flooding increases the ultimate oil recovery after conventional water flooding in the secondary production stage. Through a modeling study on the effect of slug length and soaking, on the magnitude of wettability alteration of carbonate rocks, based on laboratory works by the same research team, the following conclusions were obtained:

- The designed CIW enhanced the oil recovery in the tertiary injection mode in the carbonate rock. The greater the slug length of the CIW is, the higher the recovery is. However, the increasing trend reaches a plateau from a specific slug length onward.
- CIW injection changed the wettability of the carbonate rock samples from mixed wet, or preferentially water wet, toward a more water wet condition even with a small slug length, leading to enhanced oil recovery. This verifies the wettability alteration as the mechanism responsible for the oil recovery which is actuated at every slug length.
- There is an optimum length for CIW injection between secondary and tertiary HSW flooding, beyond which, no significant wettability alteration and consequently oil production is achieved. Therefore, using this optimum CIW slug injection reduces impractical long CIW injections, which are costly. The optimum slug length can be determined by evaluating the variations in the relative wettability curves, residual oil saturations, and incremental recovery factors.
- The positive EOR effect of the applied change in wettability is continued in the next HSW flooding. In other words, proceeding with the HSW flooding can increase oil recovery by sweeping the residual oil detached by the previous stage.
- As MIE is a time-dependent reaction, allowing the core sample to be soaked by the CIW for 48 h yielded a significant oil recovery which indicates a higher level of ion substitution by PDIs during soaking time. This idea can be implemented, after the optimum slug length injection, to increase oil recovery if the job duration is not a matter of concern.
- MIE is the main governing mechanism of CIW injection rather than rock dissolution/precipitation. Insignificant change in pore volume, calcite mineral content, pH, and pressure drop results verifies this conclusion. However, extending the slug length, higher, but still slight calcite mineral precipitation was observed.
- To design a low salinity/CIW injection process, it is important to take economic issues into consideration. Hence, optimization of the length of low salinity/CIW

slug and the provided soaking time can help lower the costs of water preparation (desalination, ion treatment, etc.).

■ AUTHOR INFORMATION

Corresponding Author

Peyman Pourafshary – School of Mining and Geosciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan;
orcid.org/0000-0003-4600-6670;
Email: Peyman.Pourafshary@nu.edu.kz

Authors

Nikoo Moradpour – School of Mining and Geosciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan
Marzhan Karimova – School of Mining and Geosciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan
Davood Zivar – Centre of Research in Enhanced Oil Recovery, Universiti Teknologi PETRONAS, Perak 32610, Malaysia

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsoomega.0c01766>

Notes

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