Effect of multi-component ions exchange on low salinity EOR: Coupled geochemical simulation study

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Abstract

The mechanism(s) of Low salinity water flooding (LSWF) has been extensively investigated for 15–20 years, as a cost-effective and environmentally friendly technique for improved oil recovery. However, there is still no consensus on the dominant mechanism(s) behind low salinity effect due to the complexity of interactions in the Crude oil/Brine/Rock (COBR) system. While wettability is most agreed mechanism of low salinity EOR effect. Nevertheless, the mechanism(s) behind the wettability change is debated between multi-component ion exchange (MIE) and double layer expansion (DLE) in sandstone reservoirs. This paper aims to investigate the effectiveness of MIE with a coupled geochemical-reservoir model using published experimental data reported by Nasralla and Nasr-El-Din [1].

We created core-scale numerical models with parameters identical to those used in the experiments. We simulated the low salinity effect using a commercial reservoir simulator, CMG-GEM, by coupling three chemical reactions: (1) aqueous reaction, (2) multi-component ion exchange, and (3) mineral dissolution and precipitation. We modelled the adsorption of divalent cations on the surface of the clay minerals during low salinity water injection. Simulation results were compared with the experimental results.

Simulation results show that the fractional adsorption of divalent cations (Ca$^{2+}$) increased almost 25% by injecting a 2000 ppm NaCl solution, compared to initial 10,000 ppm NaCl. Injecting a 2000 ppm of CaCl$_2$ solution, however, significantly increased the adsorbed Ca$^{2+}$ from 0.1 to 1, which implies the complete saturation of mineral surface with divalent cations. Moreover, injecting 50,000 ppm of CaCl$_2$ solution also demonstrated the same effect as the 2000 ppm CaCl$_2$ solution but with a faster rate.

Upon combining the simulation and experimental results, we concluded that the multi-component ion exchange is not the sole mechanism behind low salinity effect for two reasons. First, almost 10% additional oil recovery was observed from the experiments by injecting the 2000 ppm CaCl$_2$ solution, compared with 50,000 ppm CaCl$_2$ solutions. Even though in both cases the surface is expected to be fully saturated with Ca$^{2+}$ according to the geochemical modelling. Second, 6% incremental oil recovery was achieved from the experiments by injecting 2000 ppm NaCl solution compared with that of 50,000 ppm NaCl. Although 25% incremental adsorption of divalent cations (Ca$^{2+}$) were presented during the flooding of the 2000 ppm NaCl solution. Therefore, it is worth noting that the electrical double layer expansion due to the ion exchange needs to be taken into account to pinpoint the mechanism(s) of low-salinity water effect.

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1. Introduction

Oil and natural gas are expected to remain an important resource for future energy demand [2,3]. However, there is a pressing need to develop cost-effective techniques to enhance oil recovery in the period of low oil prices. Engineering the injected
water chemistry and using water wisely to enhance oil recovery is a novel and emerging research area, which is called low salinity water flooding [4–7], smart water flooding [8–12], designer water flooding [13–16], or ion tuning water flooding [17,18]. Many researchers found that low salinity water injection could achieve an incredible additional oil recovery in sandstone and carbonate reservoirs from both experiments and field tests [19,20].

Changing water flood salinity/chemistry can increase oil recovery from sandstone and carbonate reservoirs by 5–25%, though why this happens is unclear [13,17,19–29]. Several mechanisms have been proposed to describe how the low salinity effect (LSE) increases oil recovery, including: (1) fines mobilisation [30], (2) limited release of mixed-wet particles [30], (3) increased pH and reduced interfacial tension (IFT) similar to alkaline flooding [31], (4) multi-component ion exchange (MIE), (5) expansion of the double layer, (6) salt-in effect [12], and (7) osmotic pressure [32].

Although the mechanism(s) of low salinity water is still debated, two major advantages of low salinity water flooding over other enhanced oil recovery (EOR) techniques are: a) cost-effective (i.e., based on the relatively low cost of acquiring low salinity water), and b) relatively environmentally friendly. British Petroleum (BP) applied Low Salinity Water Flooding (LSWF) to the Endicott oil field in Alaska and achieved 26% additional oil recovery. In 2016, BP, ConocoPhillips, Chevron, and Shell will initiate the largest offshore low salinity water flooding project in Clair Ridge oil field (in the North Sea). Clair Ridge is expected to produce more than 40 million barrels of additional oil at a relatively low cost [33]. LSWF is also a promising technique for mature oil reservoirs where the production has significantly decreased, and further recovery is uneconomic.

However, the major disadvantage of LSWF is that the mechanism(s) by which it operates are uncertain. Several oil companies, such as BP [34], Shell [35], Saudi Aramco [36], and PetroChina [17,18,21,37] have conducted numerous lab experiments, i.e., Log-Inject-Log, Single Well Chemical Tracer Test (SWCTT), and field scale trials. Their results have shown that, while in some cases LSWF has achieved an additional 5–25% oil recovery, in other cases, only minor incremental oil recovery was observed [38].

Even though the mechanism(s) of low-salinity effect is still uncertain, the most agreed mechanism of LSWF is wettability alteration [39] where again two main theories are proposed to justify wettability alteration: (1) multicomponent ion exchange (MIE) [40–43], (2) expansion of electrical double layer (DLE) [1,18,44–47]. In this study we particularly focus on simulating the effect of multicomponent ion exchange on low salinity effect with a combination of geochemical modelling and experimental observations.

2. Model description

MIE theory is based on the water geochromatography where cation exchange is a normal phenomenon occurring on the surface of the minerals due to the different affinities of various cations towards the rock surface [48]. Meanwhile, crude oil/brine/rock (COBR) system is intrinsically in a thermodynamic equilibrium [20,49,50]. Injecting low salinity with different electrolyte concentration than formation brine will disturb the equilibrium system and variations in ionic concentration results in the substitution of divalent cations by the monovalent cations [40]. Also, the presence of divalent cations in the formation brine can bridge the rock and the crude oil as shown in Fig. 1 [40]. Theoretically, exchange with monovalent cations can release the crude oil from the rock surface, which alters the system to more water-wet thus increasing the recovery factor.

Fig. 1 represents four different adhesion mechanisms of polar ends (e.g. COOH–) of the crude oil on the clay surface (presented as grey boxes) which can be affected due to the cations exchange [51]. Lager, Webb [40] hypothesised that the Van der Waal, Cation exchange and ligand bonds are strong and can lead into the detachment of organometallic complexes (see Fig. 2).

![Fig. 1. Representation of the diverse adhesion mechanism occurring between clay surface and crude oil (Lager et al., 2008a).](image1)

![Fig. 2. Final relative permeability curves after history matching.](image2)
3. Core-scale numerical model

This paper aims to elucidate the dominant mechanism(s) of low-salinity effect with coupling the geochemical reactions. We created a one dimension core-scale model (Fig. 4) with the identical properties to Nasralla and Nasr-El-Din [1] experiments. We also conducted a set of core-scale numerical simulations by injecting either NaCl solution or CaCl₂ under secondary mode using various salinity. To create the core-scale numerical model, five steps were taken as following:

In step 1, we created a core-scale numerical model using block centred grids. In this study, the core plug was 5 inch in length and divided into 40 grids. In step 2, to simulate the capillary end effect, two additional blocks were placed at both sides of the core plug with 0.0001 porosity and high permeability of 1000 D [25]. In step 3, we use Corey correlation to history matching Ramez's experimental data, thus acquiring a set of representative relative permeability data.

In step 4, we defined the initial condition (e.g. saturation and pressure) based on Ramez’s experimental data. The core plug was saturated using a dead oil with an apparent viscosity of 3.7 cp at 212°F, and at the connate water saturation (Swc) at 32.6%. The composition of formation brine extracted from the experiment is shown in Table 1. In Step 5, the core was flooded using LS water at constant injection rate 0.5 ml/min, identical to the experiment. To validate the model, the simulation results was history matched against recovery factor and pressure drop (Fig. 3). While we did not explicitly investigate the non-uniqueness of history matching, we can use the derived relative permeability curve to investigate the effect of multi-component ion exchange on recovery factor.

The common practice to simulate the effect of LSWF is incorporating wettability alteration by treating relative permeability curves from mixed or oil wet to more water wet [52]. Two sets of relative permeability curves should be defined to represent HS and LS water effect. Also, an interpolant is used to interpolate between the two sets of relative permeability curves [48,53,54], although the correct interpolant is still an open research area. However, in this study, we aimed to examine the hypothesis that multi-component is a dominant mechanism behind low salinity effect. Therefore, we exclusively focused on geochemical reaction instead of oil recovery.

3.1. Geochemical model

Low salinity water injection can give rise to geochemical alteration due to the interaction of fluid–fluid and fluid–rock [55]. Understanding the geochemical variation is a key factor in pinpointing the mechanism(s) of the low salinity water effect thus constraining the uncertainties. The fully coupled geochemical and equation of state model were firstly introduced by Nghiem, Sammon [56]. In this study, we use CMG-GEM to simulate the effect of multi-component ion exchange on low salinity effect. The Ion-exchange takes place along with geochemical reactions where geochemical reactions can occur in two main groups: (1) aqueous reactions, (2) mineral dissolution/ Precipitation reactions [48].

Aqueous reactions are the spontaneous type of reactions and represented as the chemical equilibrium reaction, whereas mineral dissolution and precipitation reactions are rate dependent [57]. In this study, we consider the following mineral reactions in the numerical simulation, according to the water composition and mineralogy of the core plug (Table 2) published by Nasralla and Nasr-El-Din [1].

Aqueous reactions:

\[ \text{CO}_2(aq) + H_2O \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]  

\[ \text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O} \]

While the core plugs that were tested in Ref. [58] were Berea sandstone, these samples contain 2.8 wt% calcite. It is worth

![Fig. 3. History matched data (recovery factor vs. injected PV, left; pressure drop vs. injected PV, right).](image-url)

![Fig. 4. Simulated Core Plug. The colour code represents the water saturation distribution at initial condition.](image-url)
Table 1  
Formation brine composition (Nasralla and Nasr-El-Din, 2014).

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>54,400</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>10,600</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1610</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>107,000</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>176</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>370</td>
</tr>
<tr>
<td>TDS</td>
<td>174,156</td>
</tr>
</tbody>
</table>

Table 2  
Mineralogy of Berea core plug (Nasralla and Nasr-El-Din, 2014).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>BBS (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>85.0</td>
</tr>
<tr>
<td>Feldspar</td>
<td>6.4</td>
</tr>
<tr>
<td>Calcite</td>
<td>2.8</td>
</tr>
<tr>
<td>Illite</td>
<td>2.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3.8</td>
</tr>
</tbody>
</table>

noting that calcite is a volatile mineral and can easily dissolve in the formation brine. Hence, the following mineral reaction has also been modelled to incorporate mineral dissolution and precipitation effect.

Mineral reaction:

\[ \text{Calcite} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \] (3)

Ion exchange is the key reaction and again considering the water composition and presented minerals, the main cations prevailing in our system would be Na⁺, H⁺ and Ca²⁺.

Ions exchange reaction:

\[ \text{Na}^+ + \frac{1}{2} \text{(Ca - X₂)} \rightarrow \text{Na}^+ + \frac{1}{2} \text{Ca}^{2+} \] (4)

3.2. Reaction kinetics

In the geochemical modelling, the heart of the model is the equilibrium system [59]. In GEM, the chemical reaction is in equilibrium if the forward reaction rate and backward reaction rates are equal to Nghiem, Sammon [56], which can be replicated in the following equations;

\[ Q_a - K_{eq,a} = 0 \quad \alpha = 1, \ldots, R_{aq} \] (5)

\[ Q_a = \prod_{i=a}^{n_a} K_{i-1} \text{aq} \] (6)

The Qₐ is the activity of the products and Rₐq is the number of species in the intra-aqueous reaction; aₙ is the activity of each species; Kₑₐₑq is the chemical constant of the reaction; R is the universal gas constant; T is the fluid temperature, and vₐ is the stoichiometry coefficient of a component in the chemical reaction [56]. The activity coefficient can be taken approximately equal to the concentration of the species (In Molality) [48]. In GEM the equilibrium constants for the above reactions are calculated with a fourth order polynomial where T is in °C and followed by five predefined coefficients a₀ to a₄ (equation (7)) (the coefficients are shown in Table 3)

\[ \log(K_{eq}) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \] (7)

As mentioned earlier mineral dissolution/Precipitation reactions are rate dependant, hence other parameters such as the surface area and the activation energy are considered.

For the ions exchange, the selectivity coefficient is implemented over the equilibrium constant to overcome the challenge of calculating the activity coefficient of Na-X and Ca-X components. The selectivity coefficient concept (the degree to which an ion selective electrode responds to particular ion with respect to reference ion) follows the Gaines—Thomas convention (1953) [60], and it also can be defined as the ratio of two equilibrium constant of each cations adsorbing to the surface of the substrate (Clays). For the ions exchange reaction (4), it can be expressed as equation (8)

\[ K_{Na/ca} = \frac{\zeta(XNa - X) m(Ca^{2+})^{0.5}}{\zeta(XCa - X) m(Na^+)^{0.5}} \] (8)

where X denotes the clay mineral in the reservoir rock; \( \zeta(XNa - X) \) and \( \zeta(XCa - X) \) are the equivalent fractions of Na⁺ and Ca²⁺ on the exchanger respectively; \( m \) denotes the molality and \( \gamma \) is the activity coefficient. It should be noted that equilibrium constant is a thermodynamic variable whereas the selectivity coefficient is an operational variable. Also, in the simulation, selectivity coefficient is implemented over the equilibrium constant to overcome the challenge of calculating the activity coefficient of Na-X and Ca-X components. After constructing the coupled geochemical model, the fractional adsorption of divalent cations during the core flood with 2,000, 10,000 and 50,000 ppm solutions of NaCl and CaCl₂ was simulated, and were compared with the experimental data. The results are explained in subsequent section. The values for selectivity coefficient are based on experimental data and predefined in CMG-GEM.

4. Coupled numerical simulation results

4.1. Injecting NaCl solution

Na⁺ is a typical monovalent cation in the injected brine and formation brine. The interaction between injected Na⁺ and original crude oil/brine/rock can provide implications of the multi-component ion exchange. Therefore, we simulated NaCl solution injection with three different salinity, 2,000, 10,000 and 50,000 ppm, respectively. The rock properties in the numerical model are consistent with the experiments. We particularly studied the variation of the Na⁺ and Ca²⁺ concentrations in the solution and the Ca-X2 at the surface of the rock in a certain grid block (40 x 1).

First, we simulated 50,000 ppm NaCl solution injection. The concentration of Ca²⁺ in the one dimension model can be seen in
Fig. 4. Simulation results show that injecting a solution with different electrolyte concentration than the one in the connate water will cause salinity buffering in the core sample, and consequently ion-exchange occurs at the surface of the pores. As mentioned before while ion-exchange is an instantaneous reaction [57]. Consequently, three distinct salinity fronts will be generated (Fig. 5). The first front contains formation brine, and yet to be displaced by injection brine (red arrow). The second slug in the middle is followed by buffered brine (Green) at which the displacement is taking place, and concentration of Na$^+$ and Ca$^{2+}$ is changing from high salinity formation brine to the injection brine (green arrow). Then the trailing edge is followed by injected water where the composition is, to some extent, similar to the injected brine where in NaCl solutions (10,000 ppm), the concentration of Ca$^{2+}$ is almost zero (Blue arrow).

We also investigate the geochemical alteration in a certain grid block to elucidate the implication of low salinity effect and geochemical reactions. Grid block (40 1 1) was chosen to investigate the concentration of Na$^+$ and equivalent fraction Ca-X2, as shown in Figs. 6 and 7. Simulation results show that concentration of Na$^+$ in the solution decreased first, and then become constant. The variation of Ca$^{2+}$ concentration keep the same trend as Na$^+$ does, but the concentration of Ca$^{2+}$ drop to zero. The decrease of Na$^+$ is attributed to the lower salinity of the injected brine than the formation brine. Simulation results also show that the high concentration of Na$^+$ ions will favour Na$^+$ adsorption and remove Ca$^{2+}$ cations at the surface initially, although Ca$^{2+}$ has a higher affinity towards the clay surface (Fig. 7). This is consistent with the multi-component ion-exchange theory. Also, this phenomenon was observed in core-flooding experiments conducted by Lager, Webb [40].

We then simulate the geochemical reaction during 10,000 ppm NaCl injection, as shown in Fig. 8. Results show that the Ca$^{2+}$ concentration drop to zero similar to 50,000 ppm NaCl injection, but the concentration of Na$^+$ declines dramatically due to the lower salinity of injected brine. Fig. 9 also shows that Ca-X2 increases initially, and then drop to zero gradually. The increase of Ca-X2 is due to the fact that calcite in the core-plug start to dissolve which partially compensate the Ca$^{2+}$ reduction, hence the rate at which Na$^+$ concentration drops is faster than Ca$^{2+}$ concentration. Consequently, there will be a temporary increase in the Ca$^{2+}$ adsorption but eventually, the system will thermodynamically stabilize with a higher concentration of Na$^+$, and again a full desorption of Ca$^{2+}$ similar to 50,000 ppm injection (see Fig. 10).
Geochemical reaction with invading of 2000 ppm NaCl was also simulated. Simulation results show the trend of concentration variation is in line with 50,000 and 10,000 NaCl flooding. Na\(^+\) concentration decreases sharply, but the Ca-X\(^2\) increases initially, then it starts to drop. Fig. 11 shows the concentration of Ca-X\(^2\) falls slower compared to the injection of 50,000 and 10,000 ppm NaCl, which is due to the smaller differential concentration between Ca\(^2\)\(^+\) and Na\(^+\) ions in the system.

4.2. Injecting CaCl\(_2\) solution

Divalent cations are usually rich in the formation brines and injected brines. Also, divalent cations play a significant role in ion-exchange due to the strong affinity to adsorb at the surface of the rock [51]. Therefore, we have also simulated the CaCl\(_2\) flooding with various concentrations and investigated the geochemical reactions. Simulation results are given in Figs. 12 and 13. It is clear that the concentration of Ca\(^2\)\(^+\) increases because the concentration of Ca\(^2\)\(^+\) we injected (50,000 ppm) is much more than that (10,600 ppm) in the formation brine. However, it is worth noting that in all three cases (2000, 10,000 and 50,000 ppm CaCl\(_2\) solution) a spontaneous adsorption of Ca\(^2\)\(^+\) occurs to the point that the entire ions exchange sites are saturated by divalent cations.

5. Discussion

5.1. Predicting recovery based on MIE and coupled geochemical model

As mentioned earlier based on MIE theory, there should be an agreement between recovery factors and divalent cation adsorption/desorption. The higher is the adsorption, the lower the recovery should be. Fig. 14 represents the Ca\(^2\)\(^+\) adsorption/desorption during NaCl and CaCl\(_2\) solutions injection. We can make the following predictions based on simulation results and MIE theory.

1. 50,000 ppm NaCl solution should contribute the highest recovery because almost all the Ca-X\(^2\) are substituted by Na\(^+\), which leads to losing the ability to bridge between rock and crude oil.
2. Injecting 10,000 ppm NaCl has also resulted in the full desorption of divalent cations, hence, the recovery should be high and almost equal to 50,000 ppm NaCl solution.
3. Injecting 2000 ppm should result in lower recovery than previous cases since the adsorption of divalent cations increased by 20%.
4. Injecting all three concentrations of CaCl\(_2\) should result in equal recoveries and it should be lower than NaCl solutions.

5.2. Comparison with experimental observation

Fig. 15 shows the experimental observation of recovery factors achieved in core flooding experiment via different brine compositions (2,000, 10,000, and 50,000 ppm) [1]. Nasralla and Nasr-El-Din [1] observed lower recovery factors by injecting CaCl\(_2\) solutions compared to the NaCl at the same concentration, which can be considered as an agreement with MIE theory. However, injected different CaCl\(_2\) solutions produced different recoveries which are not consistent with the prediction as a result of multi-component ion exchange. Furthermore, geochemical simulation results from various NaCl concentration injection has no consistency with experimental data at all. Experimental results show that lower concentration of Ca\(^2\)\(^+\) has
a higher potential to improve oil recovery. This is also observed for various concentration of NaCl flooding [1].

It is worth noting that water chemistry has a significant impact on the zeta potential for both fluid–fluid, and fluid–rock [1]. Double layer expansion plays a dominant role in the difference of recovery factor as injected various CaCl₂ [1].

5.3. The impact of CEC on the recovery factor

CEC is an intrinsic parameters for clays, which can represent the ability of the surface of the clays to be adsorbed by the counter-ions. The magnitude of CEC ranges from 3 to 150, depending on the type of clays [61]. If MIE is the dominant mechanism, the CEC should presumably affect the flooding performance of LS. Hence, we simulated three extreme scenarios with CEC equivalent to 10, 50, and 150, respectively. Also, we monitored the adsorption/desorption of divalent cations to predict the recovery factor. Fig. 16 shows the adsorption of divalent cations by injecting CaCl₂ solution at concentration of 10,000 ppm injection. Simulation results indicate that the surface of rock is saturated with Ca-X₂ after injected 1 PV CaCl₂ solution for all three different CEC values. Also, CEC does not play a significant role to impact the surface Ca-X₂ saturation, although CEC will influence the time to reach the full surface saturation with divalent cations. Hence again, if MIE is the dominant mechanism it is not expected to observe higher recovery. However, it should be noted that the surface potential will affect the zeta potential and the repulsion forces (see Fig. 17).

5.4. Further discussion

In addition to cation bridging there are seven other mechanisms on which the organic materials can be bonded to the surface of the minerals [62,63], and three of those mechanisms; Cation Exchange, Ligand bonding, Anion bridging are highly affected by electrolyte concentration (Fig. 18). Furthermore Austad, Rezaeidoust [64] has also proposed other possible mechanisms where polar components in the crude oil can directly attach to the surface of the rock.

We simulation results suggest that MIE can affect the LSWF performance as one of the bonding mechanisms, but in this study, it has been shown that ion exchange cannot be the only mechanism of breaking those bonds. To break the bonds, there should be a repulsive force greater than the chemical bond strength, and the repulsive force can be explained by the concept of disjoining pressure [49]. The disjoining pressure is the direct function of electrical double layer (EDL), which can exhibit enough repulsion force for oil droplet to detach from the pore walls. However, there are still some challenges to confirm if DLE is the dominant mechanism. It was shown that the thickness of water film can be a few angstroms at high salinity [65], and while hypothetically low salinity should result in expansion of EDL, but in some cases atomic force microscopy experiment was inconsistent with this theory, and a higher disjoining pressure observed in high salinity [66,67] this was attributed to hydration and structural forces, which can eventually dominate in the low range (thin liquid film) [49]. However, wettability alteration is the most agreed mechanism during low salinity water flooding. In this study, geochemical simulation results show that the MIE cannot be credited as the only mechanism of low salinity water

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Fig. 14. Comparison between sorption of divalent cations CaCl₂ vs NaCl.

Fig. 15. Recovery factors observed in core flooding experiment (Nassalla and Nasr-El-Din, 2014).

Fig. 16. Effect of CEC on divalent cation sorption during 1% wt CaCl₂ solution injection.
flooding, but double layer expansion, induced by multi-component ion exchange, needs to be included to elucidate the mechanism(s) of low-salinity water flooding.

6. Condition for sequence of affinities

The relative affinity of metal cations to the clay surface depend on solutions, but the best approximation can be justified in terms of inner sphere, outer sphere and diffuse ion swarm [63]. Generally in the inner sphere, the electronic structure of the metal cation and surface function groups are dominant, and in the diffuse swarm layer only valency and surface charge are the governing factors. It should be noted that the solution pH can also extensively affect the extent of the diffuse swarm layer (Zeta potential), thus affecting adsorption process.

Our simulation results (Fig. 19) show that in all of the cases, the pH values were almost constant with different solutions. It is worth noting that the sequence of affinity will depend on charge density and the valency of the metal cations, thus following the below order;

\[ \text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{H}^+ \]

Generally, adsorption isotherm will depend on the cation concentration, valence and hydration radius.

7. Conclusions

Core-scale numerical model was created to investigate the impact of geochemical reaction on low salinity effect using CMG-GEM with a combination of published experimental results. The variation of Na\(^+\) and Ca\(^{2+}\) in the solution was studied, and Ca-X2 absorbed at the surface of rock as injecting 2,000, 10,000, and 50,000 ppm NaCl and CaCl\(_2\) solutions. The simulation results were compared with the experimental results. Moreover, we discuss further the mechanism(s) of wettability change induced by low salinity water flooding. Based on the results, the following conclusions can be drawn;

1. The presence of divalent cations in low salinity water plays a great role in the adsorption of Ca-X2 to the surface of rock due to the strong affinity to minerals compared with monovalent ions.
2. To observe the effect of LSWT there is expected to be a concentration difference between monovalent cations and divalent cations to enable monovalent cations substitute the divalent cations on the surface of the clay minerals.
3. Multi-component ion exchange (MIE) is not the only mechanism to interpret the low salinity effect. Divalent...
cations fully desorb at the surface of rock during 50,000 and 10,000 ppm NaCl solution injection, while in 2000 ppm solution, approximately 10% of available exchange sites are saturated with Ca\(^{2+}\). Based on MIE, it was expected to observe higher recovery with 50,000 and 10,000 ppm than 2000 ppm NaCl. It was not consistent with experimental data as 2000 ppm NaCl resulted in higher recovery.

(4) Double layer expansion needs to be considered to predict the performance of low salinity water flooding. Zeta potential test is recommended to conduct to preliminary assess the potential of low salinity water.

(5) The CEC of different clays may not have a significant impact on the ultimate surface saturation with divalent cations, but the surface potential may affect the repulsion forces and consequently the ultimate recovery factor.

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