Modeling Low-Salinity Waterflooding in Chalk and Limestone Reservoirs

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ABSTRACT: The injection of low-salinity brines can improve oil recovery in carbonate reservoirs by changing the rock wettability from being more oil-wet to being more water-wet. Existing models use an empirical dependence of wettability based on variables including equivalent salinity and ionic strength. We recently developed a process-based model that mechanistically includes the geochemical interactions between crude oil, brine, and the chalk surface that alter rock wettability. In this research, we extend the previous model by including mineral dissolution reactions, therefore enabling the modeling of low-salinity flooding in chalks and limestone cores with and without anhydrite, which is considered to be a key factor in controlling the extent of improved oil recovery (IOR). We examine the role of mineralogy by including surface complexation, aqueous reactions, and dissolution/precipitation of calcite and anhydrite in the extended model. These reactions, coupled with the equations of multiphase flow and transport, are solved simultaneously using an in-house simulator, PennSim. Relative permeability functions and residual oil saturation during flooding are adjusted dynamically according to the concentration of oil acids attached to the mineral surface. Core flooding experiments from the Stevns Klint (SK) chalk and a Middle Eastern carbonate with a small volume fraction of anhydrite are used to tune the reaction network and predict recovery. Simulation results agree with the observed effluent concentrations of SO$_4^{2-}$, Ca$^{2+}$, and Mg$^{2+}$ reported from chromatographic wettability tests and the measured recoveries under differing compositions in chalk and limestone cores. For the SK chalk without anhydrite, lower Na$^+$ and Cl$^-$ concentrations under constant SO$_4^{2-}$ conditions leads to IOR by as much as 6% OOIP. Lower salinity alone, however, does not lead to IOR in limestones without anhydrite. Instead, anhydrite dissolution provides a natural source of sulfate and increases oil recovery by 5% when injecting diluted formation water. Simulations of two-dimensional (2D) five-spot patterns using tuned reaction networks demonstrated that IORs from 5% to 20% OOIP can be obtained after two pore volumes are injected. These IORs are greatly dependent on the aqueous chemistry of the injected fluid and sweep. The results highlight the critical importance of understanding the mineralogy and including a mechanistic reaction model in the simulation of low-salinity water floods.

INTRODUCTION

Low-salinity water (LSW) has been reported in the literature to improve oil recovery significantly in sandstone and carbonate core experiments.$^{1-4}$ Here, we focus on the widely used term “low-salinity flooding,” although both experimental data from Austad et al.$^{1,5,6}$ and our model$^6$ suggest that improved oil recovery (IOR) is not solely caused by low salinity (total dissolved salt). Instead, it is the specific composition of the injection water—in particular, the concentrations of the wettability-altering species (SO$_4^{2-}$, Ca$^{2+}$, and Mg$^{2+}$)—that matters. The recoveries in core floods and imbibition tests vary greatly, depending on the aqueous chemistry used, the pore volumes injected (PVI), and the carbonate mineralogy.$^6,9$

Improved recoveries were ~5% to 40% OOIP for spontaneous imbibition tests in the Stevns Klint chalk and 5% to 20% OOIP in core flooding experiments in both the Stevns Klint chalk and a Middle Eastern limestone.$^6,2,10$ Diluted formation water without sulfate was found to improve oil recovery by 5% OOIP.$^2$ Diluted seawater was reported to improve oil recovery by 17% to 19% OOIP in a limestone core that contained anhydrite.$^3$ A single well tracer test at field scale also exhibited decreased residual oil saturation by seven saturation units from the injection of diluted seawater.$^{11}$

One of the primary mechanisms proposed for IOR by LSW flooding is wettability alteration from a more oil-wet state to a more water-wet state.$^{1,10}$ Chromatographic wettability tests with chemically tuned water confirmed wettability alteration by incremental sulfate adsorption onto the rock surface.$^6,12$ Wettability alteration was also confirmed in contact angle measurements on a flat plane carbonate surface, where smaller contact angles were reported with modified seawater.$^2$ Furthermore, capillary pressure reduction was observed in spontaneous imbibition tests when sulfate-containing seawater was injected, compared to sulfate-free water.$^{13}$ Shifts in relative permeability and decreases in residual oil saturation were demonstrated in core flooding experiments.$^{10}$

Wettability alteration could be caused by mineral dissolution, surface adsorption/desorption, and surface potential reduction.$^{2,4,15}$ Austad et al.$^1$ proposed that, for the Stevns Klint chalk outcrop, the concentrations of potential determining ions (PDIs) such as Mg$^{2+}$, Ca$^{2+}$ and SO$_4^{2-}$ greatly affected the oil recovery in spontaneous imbibition tests. They explained that, for mixed wet surfaces, both SO$_4^{2-}$ and carboxylic groups in the oil adsorb onto the rock surface, altering the surface charge from positive to negative. The negatively charged solid surface then attracts cations such as Mg$^{2+}$ and Ca$^{2+}$ to react with the adsorbed carboxylic group, which releases the carboxylic group.

Received: October 18, 2015
Revised: January 11, 2016

DOI: 10.1021/acs.energyfuels.5b02456
Energy Fuels XXXX, XXX, XXX−XXX
and causes the surface to become more water-wet. The notion that carboxylic groups leave the chalk surface was inferred from water vapor adsorption isotherms, where SO$_4^{2-}$ reduced the surface concentrations of adsorbed fatty acids.\textsuperscript{16} Spontaneous imbibition experiments with varied brine compositions support such chemical mechanisms.\textsuperscript{5,7,9,12} In addition to SO$_4^{2-}$, BO$_3^{2-}$ and PO$_4^{3-}$ were also found to improve oil recovery.\textsuperscript{17,18}

Experimental studies have revealed that the brine composition sufficient for enhanced oil recovery in Stevns Klint chalk was not necessarily effective for other carbonate minerals. Instead, diluted formation water and seawater were found to improve oil recovery the most for limestone and dolomites.\textsuperscript{7,18} Romanuka et al.\textsuperscript{18} performed spontaneous imbibition tests for Stevns Klint chalk, limestone, and dolomite cores and concluded that effective EOR fluids are significantly dependent on the rock mineralogy. Screening Amott imbibition experiments showed that additional SO$_4^{2-}$ did not lead to IOR for limestone and dolomite, as well as for the Stevns Klint chalk with diluted formation water. One possible reason for an increase in oil recovery for sulfate-free injection fluids in limestone is the increased sulfate concentration from dissolution of anhydrite in situ.\textsuperscript{5} In addition, SO$_4^{2-}$ and Mg$^{2+}$ were reported to improve oil recovery incrementally in core flooding experiments for limestone.\textsuperscript{19}

The above-mentioned experimental evidences have shown significant promise of LSW for IOR; however, at the same time, it has indicated the complexity of geochemical reactions involved in low-salinity flooding in different types of carbonate formations. Currently, there is no theory to quantify and explain many of these differences. Various modeling efforts have tried to capture the wettability alteration process. Wettability alteration has been modeled by interpolating capillary pressure, relative permeability, and residual oil saturation between two wetting states.\textsuperscript{20,21} Empirical relationships between wettability and water chemistry parameters were used including salinity, ionic strength, or total dissolved salts.\textsuperscript{20,22} Contact angles were also used to represent surface wettability.\textsuperscript{22} Although these relationships are valid under the given experimental conditions, they do not take into account complex surface reactions mechanistically and therefore cannot be used to predict wettability alteration under conditions that differ from where the empirical relationships are derived.\textsuperscript{23} Thus, a mechanistic model is needed to understand the dominant processes and to accurately predict wettability under varying mineralogical.

Qiao et al.\textsuperscript{8} developed a mechanistic model that coupled multiphase flow and transport using a detailed surface and aqueous multicomponent reaction network including adsorption/desorption that captures the competitive interactions among oil, brine, and the surface of the Stevns Klint chalk. Natural carbonate reservoirs, however, often contain minerals including anhydrite, dolomite, and quartz. These minerals could potentially affect surface reactions among rock, oil, and water, and therefore influence the oil recovery. For example, Austad et al.\textsuperscript{5} reported that anhydrite can play an important role in wettability alteration.

In this paper, we extend the multiphase reactive transport model by Qiao et al.\textsuperscript{8} to include limestone surface complexation and mineral dissolution/precipitation reactions. This extends the model in our in-house simulator PennSim\textsuperscript{24} to provide a unified model for low-salinity flooding in mineralogically different carbonate reservoirs. The model was calibrated using core experimental data from the Stevns Klint chalk and limestones with anhydrite. We first introduce the multiphase reactive transport equations, and then we describe the wettability alteration model and the mechanisms of altered wettability and oil recovery in different cores. Lastly, we use the new model to demonstrate the potential of LSW flooding at the field pattern scale.

\section*{METHODOLOGY}

We consider isothermal recovery processes with immiscible oil/water flow. Geochemical reactions occur in the aqueous phase and at the crude oil/brine-mineral interfaces. Desorption of the carboxylic group from the rock surface leads to more water-wet conditions, which further changes the relative permeability and residual oil saturation based on measured curves at two wettability end points. The major extension from our previous model\textsuperscript{8} includes the addition of calcite and anhydride dissolution/precipitation reactions, surface complexation with the surface site $>$CO$_3$ and additional aqueous complexation such as CaCl$^+$ and NaSO$_4$$^-$. [Note that the prefix “$>$” denotes the species at the solid surface.] In this section, we describe the governing equations that couple the flow, transport and reaction system, and the inputs to setup a simulation.

\textbf{Governing Equations.} The equation set describes the mass conservation of oil/water and chemical species, Darcy flow, and reaction kinetics and equilibrium. The physical meanings and units of the symbols are given in the Nomenclature section.

\textbf{Immiscible Oil/Water Flow Equations.} The mass conservation equations for immiscible oil and water phases are as follows:

$$\frac{\partial}{\partial t} (\phi \rho_o \rho_o) + \nabla \cdot (\rho_o \bar{u}_o) = 0 \quad \alpha = o, w$$

Darcy’s law governs the flow rate of each phase,

$$\bar{u}_o = k_{ow} \frac{P_o - \rho_o \rho Z}{\mu_o} \quad \alpha = o, w$$

The subscript “w” represents the water phase and subscript “o” represents the oil phase. Capillary pressure relates the pressure of oil and water phases:

$$P_{cow} = P_o - P_w$$

The saturation relation completes the set of equations:

$$S_o + S_w = 1$$

The primary unknowns for the multiphase flow system are $P_o$ and $S_w$.

\textbf{Reactive Transport Equations.} The mass conservation equation for the primary species $p$ is

$$\frac{\partial}{\partial t} (M_p + \sum_{q=1}^{N_p} \kappa_{pq} M_q) + \nabla \cdot (F_p + \sum_{q=1}^{N_p} \kappa_{pq} F_q) = 0 \quad p = 1, \ldots, N_p$$

where the first term is the accumulation of total moles and the second term is the total molar flux of a primary component $p$, the chemical building blocks of the reaction systems. The equations are based on the stoichiometric relationship among the species participating in reactions and reaction kinetics. The derivation of the reactive transport equations are given in Qiao et al.\textsuperscript{8} More details of reactive transport equations can also be found in Yeh and Tripathi,\textsuperscript{25} Lichtner,\textsuperscript{26} Steefel and Lasaga,\textsuperscript{27} and Walter et al.\textsuperscript{28} These equations solve for the concentrations of primary species in the aqueous phase and at the phase interfaces. Secondary species are solved using laws of mass action based on the concentrations of primary species. Reactive transport models have been widely used in subsurface biogeochemistry in the past decades,\textsuperscript{29-31} however, they are relatively new in applications of interest to the oil and gas industry.\textsuperscript{32-34}

\textbf{Multiphase Reaction Network.} Reactions are either kinetically controlled or at equilibrium, depending on the typical rates of the specific geochemical reactions. According to the geochemical convention, the reactions in the aqueous phase and surface
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Table 1. Multiphase Reaction Network\(^{44}\)

<table>
<thead>
<tr>
<th>number</th>
<th>reaction</th>
<th>(\log K_{eq}(25 , ^\circ C))</th>
<th>(\log K_{eq}(110 , ^\circ C))</th>
</tr>
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<tbody>
<tr>
<td>Oil/Water Interface Reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>(-COOH \leftrightarrow -COO^- + H^+)</td>
<td>-5.00</td>
<td>-5.00</td>
</tr>
<tr>
<td>O2</td>
<td>(-COOCA^+ \leftrightarrow -COO^- + Ca^{2+})</td>
<td>-1.20</td>
<td>-1.20</td>
</tr>
<tr>
<td>O3</td>
<td>(-COOMg^+ \leftrightarrow -COO^- + Mg^{2+})</td>
<td>-1.00</td>
<td>-1.30</td>
</tr>
<tr>
<td>Solid (Calcite)/Water Interface Reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>(&gt;CaOH + H^+ \leftrightarrow &gt;CaOH_2^+)</td>
<td>11.80</td>
<td>11.80</td>
</tr>
<tr>
<td>C2</td>
<td>(&gt;CaOH_2^+ + SO_4^{2-} \leftrightarrow &gt;CaSO_4 + H_2O)</td>
<td>-2.10</td>
<td>-3.25</td>
</tr>
<tr>
<td>C3</td>
<td>(&gt;CaOH_2^+ + CO_3^{2-} \rightarrow &gt;CaCO_3 + H_2O)</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>C4</td>
<td>(&gt;CO_2H \leftrightarrow &gt;CO_3^- + H^+)</td>
<td>-5.10</td>
<td>-5.10</td>
</tr>
<tr>
<td>C5</td>
<td>(&gt;CO_2 + Ca^{2+} \leftrightarrow &gt;CO_3^- + Ca^{2+})</td>
<td>-2.50</td>
<td>-3.40</td>
</tr>
<tr>
<td>C6</td>
<td>(&gt;CO_2Mg^+ \leftrightarrow &gt;CO_3^- + Mg^{2+})</td>
<td>-2.50</td>
<td>-3.40</td>
</tr>
<tr>
<td>Calcite–Water/Oil–Water Interface Reaction</td>
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<td></td>
</tr>
<tr>
<td>CO1</td>
<td>(&gt;CaOH_2^+(-COO^-) \rightarrow &gt;CaOH_2^+ + -COO^-)</td>
<td>-5.90</td>
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</tr>
<tr>
<td>Aqueous-Phase Reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>(H_2O \leftrightarrow H^+ + OH^-)</td>
<td>13.99</td>
<td>12.24</td>
</tr>
<tr>
<td>A2</td>
<td>(HCO_3^- \leftrightarrow H^+ + CO_3^{2-})</td>
<td>-10.33</td>
<td>-10.27</td>
</tr>
<tr>
<td>A3</td>
<td>(H_2CO_3 \leftrightarrow H^+ + HCO_3^-)</td>
<td>-6.35</td>
<td>-6.43</td>
</tr>
<tr>
<td>A4</td>
<td>(MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-})</td>
<td>-2.37</td>
<td>-2.46</td>
</tr>
<tr>
<td>A5</td>
<td>(NaSO_4 \leftrightarrow Na^+ + SO_4^{2-})</td>
<td>-0.70</td>
<td>-0.77</td>
</tr>
<tr>
<td>A6</td>
<td>(CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-})</td>
<td>-2.30</td>
<td>2.61</td>
</tr>
<tr>
<td>A7</td>
<td>(CaCl^+ \rightarrow Ca^{2+} + Cl^-)</td>
<td>-0.70</td>
<td>-0.54</td>
</tr>
<tr>
<td>A8</td>
<td>(MgCl^+ \rightarrow Mg^{2+} + Cl^-)</td>
<td>-0.15</td>
<td>-0.74</td>
</tr>
<tr>
<td>Mineral Dissolution/Precipitation Reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>(CaCO_3(s) + H^+ \rightarrow Ca^{2+} + HCO_3^-)</td>
<td>1.85</td>
<td>0.58</td>
</tr>
<tr>
<td>M2</td>
<td>(CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-})</td>
<td>-4.36</td>
<td>-5.34</td>
</tr>
</tbody>
</table>

\(^{44}\)\(K_{eq}\) values for oil/water interface reactions are taken from Brady and Krumhansl;\(^{15}\) \(K_{eq}\) for calcite surface reactions are taken from Pokrovsky and Schott;\(^{12}\) and Brady et al.;\(^{40}\) \(K_{eq}\) for aqueous and mineral reactions are taken from Wolery.\(^{37}\) \(K_{CO1}\) was fixed at -5.9 obtained from reproducing initial wettability of Fathi et al.\(^{8}\) The kinetic rate constant for reaction M1 is \(10^{-6.19} \text{ mol/(m}^2\text{s})\);\(^{34}\) the kinetic rate constant for reaction M2 is \(10^{-4.26} \text{ mol/(m}^2\text{s})\).\(^{35}\) The new additions in the reactions, compared to the previous model, \(^{4}\) include reactions C3–C6, A4–A8, M1, and M2.

Complexation on the rock and oil surfaces typically occur fast and are assumed to be at equilibrium.\(^{30}\) In contrast, mineral dissolution and precipitation are relatively slow and modeled with reaction kinetics.\(^{36}\) The reaction network, along with the thermodynamic and kinetic constants at 25 and 110 °C, are listed in Table 1. The primary species include aqueous ions HCO_3^-, CO_3^{2-}, SO_4^{2-}, SCN^-, Mg^{2+}, Ca^{2+}, Na^+, K^+, H^+, and surface species > CaOH_2^+, > CO_3^-, and - COO^-, where the prefixes “>” and “-” represent the species at the solid surface and oil surface, respectively. The extension from Qiao et al.\(^{1}\) includes calcite surface reactions (reactions C4–C6), aqueous reactions (reactions A4–A8) and mineral dissolution/precipitation reactions (reactions M1 and M2). The equilibrium constants for aqueous and mineral dissolution reactions are taken from the EQ3/6 thermodynamic database.\(^{37}\)

**Aqueous Complexation Reactions in Water.** The aqueous species include free ions HCO_3^-, CO_3^{2-}, SO_4^{2-}, SCN^-, Mg^{2+}, Ca^{2+}, Na^+, K^+, H^+, CO_3^{2-}, OH^-, and H_2CO_3, and complex ions MgSO_4, NaSO_4, CaSO_4, CaCl^+, and MgCl^+. An example, the equilibrium constant of reaction A4 is

\[
K_{eq,A4} = \frac{a_{Mg^{2+}}a_{SO_4^{2-}}}{a_{MgSO_4}}
\]

where the activities of the aqueous species (\(a_i\)) are calculated by

\[
a_i = \gamma_i \bar{C}_i
\]

Activity coefficients are determined using an extended Debye–Hückel model.\(^{54}\) High Na^+ and Cl^- concentrations reduce surface adsorption in two ways. First, higher concentrations lead to greater ionic strength and smaller activity coefficients of aqueous species (and, therefore, less surface adsorption). Second, Na^+ and Cl^- form aqueous complexes with SO_4^{2-}, Mg^{2+}, and Ca^{2+} through reactions A5, A7, and A8, which reduces the corresponding free-ion concentration available for surface adsorption. Therefore, reducing Na^+ and Cl^- concentrations can promote surface adsorption, which causes wettability alteration.

**Mineral Surface Reactions.** We considered the surface dissolution/precipitation of calcite and anhydrite (reactions M1 and M2 in Table 1). The mineral reaction rates are written based on the transition state theory (TST) rate laws.\(^{49}\) For example, calcite dissolution rate is expressed as follows:

\[
R_{CaCO_3} = A_{CaCO_3}k_{H^+} \exp \left(-\frac{E_a}{RT_a}\right) \gamma^\text{H+} \left(1 - \frac{a_{Ca^{2+}}a_{HCO_3^-}}{K_{eq,H^+}}\right)
\]

The last term in the parentheses above the equation indicates how far away the reaction is from equilibrium. If the reaction is at
equilibrium, the rate is zero. The Damköhler number (D) for this reaction is calculated as
\[ \text{D}_{\text{CaCO}_3} = \frac{K_{\text{CaCO}_3} \cdot C_{\text{Ca}^{2+}}} {v \cdot C_{\text{Ca}^{2+}} \cdot \text{total}} \]
where \( v \) is the flow velocity and \( C_{\text{Ca}^{2+}} \cdot \text{total} \) is the total \( Ca^{2+} \) concentration. The Damköhler number determines if the reaction is modeled using an equilibrium law or a kinetic rate law. Calcite dissolution provides a source for \( Ca^{2+} \) species and buffers pH. The calculated Damköhler number for anhydrite dissolution is more than 100 in the experimental cases studied later in this paper, indicating much faster dissolution rates than transport. Therefore, the anhydrite dissolution rate is modeled at equilibrium. Anhydrite dissolution is an important source or sink for sulfate and calcium.

In addition to the mineral dissolution reactions, we also consider the surface adsorption/desorption reactions on a calcite surface. Surface complexation models are typically used to describe the surface reactions.\(^{40-43} \) A calcite surface contains sites \( >\text{CaOH} \) and \( >\text{CO}_3\text{H}^+ \) which can adsorb aqueous ions and carboxylic groups and form surface species \( >\text{CaOH} \cdot \text{OH} \), \( >\text{CaO}_2\text{H}_\text{f} \), \( >\text{CO}_3\text{H} \cdot >\text{OH} \), \( >\text{CO}_3\text{H} \cdot \text{CO}_3\text{H}_\text{f} \), and \( >\text{CO}_3\text{H} \cdot >\text{CO}_3\text{H}_\text{f} \).\(^{44} \) In this research, two models are used to describe the complexation reactions: the electrical diffuse layer (EDL) and the nonelectrical diffuse layer (NEDL) model (the latter of which is also called the constant capacitance model).\(^{45,46} \) We used the relatively simple-to-implement NEDL model when the change of surface potential does not have a significant effect. The EDL model is used when there are significant surface potential changes, because of surface adsorption. Thus, the EDL model also affects the surface adsorption equilibrium. In the EDL model, the activity of an aqueous species is corrected through a Boltzmann factor, so the equilibrium constant for reaction C2 is expressed as follows:
\[ K_{\text{C2}} = \exp \left( \frac{-2\psi \cdot \text{mol}} {RT} \right) \left[ >\text{CaSO}_4 \right]_{\text{mol}} \frac{[>\text{CaOH} \cdot >\text{CO}_3\text{H}]} {[>\text{CaOH} \cdot >\text{CO}_3\text{H}]} \]
Here \([>\text{CaSO}_4] \) and \([>\text{CaOH} \cdot >\text{CO}_3\text{H}] \) are the surface concentrations (in units of mol/m\(^2\)). The surface potential (\( \psi \)) is calculated from the Gouy–Chapman theory,
\[ \sigma = \sqrt{8 \varepsilon \varepsilon_0 k_b T R} \sinh \left( \frac{F \psi} {2 R T} \right) \]

In the NEDL model, \( \psi \) is considered constant. The equilibrium constant for reaction C2 can be written then as
\[ K_{\text{C2}} = \frac{[>\text{CaSO}_4]_{\text{mol}}} {[>\text{CaOH} \cdot >\text{CO}_3\text{H}]} \]
here the constant surface potential term is lumped into \( K_{\text{C2}} \). A sensitivity analysis in Qiao et al.\(^{46} \) demonstrated the strong dependency of the oil recovery on the equilibrium constants. For aqueous reactions, the \( K_{\text{eq}} \) values are well-documented for a large range of temperature. For surface complexation, the \( K_{\text{eq}} \) values are empirical parameters related to intrinsic thermodynamic constants.\(^{45} \) The solid surface site densities for \( >\text{CaOH} \) and \( >\text{CO}_3\text{H}^+ \) are fixed at 4.1 \( \mu \text{mol/m}^2 \), based on a previous simulation study.\(^{40} \)

**Oil/Water Interface Reactions.** The active species on the oil/water interface include \( >\text{COOH} \), \( >\text{CO}_2 \), \( >\text{COO}^- \), and \( >\text{COOMg}^+ \). The \( >\text{NH}_4^+ \) oil surface sites are not included here because \( \text{COO}^- \) dominates the interaction between oil and water surfaces.\(^{40} \) Oil surface complexation reactions are described by either NEDL or EDL in a similar way as mineral surface reactions. Temperature effects for reactions on the oil surface are not considered to be as significant.\(^{40} \) The surface oil site total concentrations are fixed at 6 \( \mu \text{mol/m}^2 \).\(^{48} \)

**Interfacial Interactions and Wettability Alteration.** The calcite-water/oil interface reaction is represented by reaction C01. The species \( >\text{CaOH} \cdot (\text{COO}^-) \) is the adsorbed carboxylic group on the calcite surface. When the reaction goes from left to right, \( >\text{CaOH} \cdot (\text{COO}^-) \) desorbs and the system becomes more water-
spontaneous imbibition in a previous publication. Experimental studies also shows that the change in $S_w$ is negligible for high-salinity water and LSW. The initial water saturation was assumed to be constant. The water saturation remains high after alteration of the wettability. Even $S_w$ changes, the oil recovery will not be affected.

**Simulation Cases.** Table 2 lists the mineralogical compositions and parameters for the limestone and chalk cores. The Stevns Klint chalk in Fathi et al. and the Middle Eastern limestone in Strand et al. contain pure calcite, with 100% volume fraction in the solid phase. In contrast, the limestone cores from Austad et al. and Yousef et al. contain anhydrite. In these experiments, $k_w$ curves were not measured. A practical workflow for simulation of core flooding experiments where relative permeability curves are not measured is given as follows.

1. Tune $k_{wi}$ and $S_{wi}$ at the original wetting state to match oil recovery with injection of formation water where wettability alteration does not occur.
2. Tune $S_{wi}$ at the end-point water-wet state to match ultimate oil recovery.
3. Perform speciation calculations given the formation water composition to obtain $c_{sw}$. Namely, solve the nonlinear equation systems that describe the equilibrium condition of all reactions and conservation of the total concentration as the formation water. Perform speciation calculation given the LSW that leads to the most water wettability to obtain $c_{sw}$. Select either the NEDL or the EDL model so that $c_{sw} > c_{sw}^f$.
4. Perform simulations using the end-point parameters obtained in steps 1, 2, and 3.

**RESULTS AND DISCUSSION**

**Stevns Klint Chalk Outcrop (No Anhydrite).** The Stevns Klint chalk is comprised of 55% (volume) calcite with 45% pore space. The wettability can be altered by injection of ions that causes the oil acids to desorb from the surface, changing the rock to a more water-wet state. Austad et al. demonstrated this in imbibition tests where a core plug was immersed by aqueous solution containing $SO_4^{2-}$. Forced displacement experiments (core floods) also show that chemically tuned seawater injection leads to increased oil recovery in the same cores.

Table 2. Input Parameters for Simulation of Core Flooding Experiments

<table>
<thead>
<tr>
<th></th>
<th>Fathi et al.</th>
<th>Strand et al.</th>
<th>Austad et al.</th>
<th>Yousef et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCC®1</td>
<td>Core 2-21</td>
<td>Core SB</td>
<td>1st core flooding</td>
</tr>
<tr>
<td>core material</td>
<td>Stevns Klint chalk</td>
<td>Middle Eastern limestone</td>
<td>Limestone from the aqueous zone of an oil reservoir</td>
<td>Middle Eastern limestone</td>
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<td>mineral volume fraction</td>
<td>55% calcite</td>
<td>75% calcite</td>
<td>79% calcite, 3% anhydrite</td>
<td>71% calcite, 3% anhydrite</td>
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<td>porosity</td>
<td>0.45</td>
<td>0.25</td>
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<td>0.25</td>
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<tr>
<td>permeability</td>
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<td>2.7 mD</td>
<td>1.2 mD</td>
<td>39.6 mD</td>
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<td>calcite</td>
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<td>0.29 m²/g</td>
<td>0.29 m²/g</td>
<td>0.29 m²/g</td>
</tr>
<tr>
<td>anhydrite</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>dimensions</td>
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<td>38.0 mm</td>
<td>38.0 mm</td>
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<td>101.5 psi</td>
<td>145 psi</td>
<td>1000 psi</td>
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<td>100 °C</td>
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<tr>
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<td>NEDL</td>
<td>NEDL</td>
<td>EDL</td>
</tr>
<tr>
<td>$c_{sw}$</td>
<td>0.40 µmol/m²</td>
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<td>0.03 µmol/m²</td>
<td>0.17 µmol/m²</td>
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<tr>
<td>diffusion/ dispersion coefficient</td>
<td>0.0042 ft²/day</td>
<td>0.0020 ft²/day</td>
<td>0.0020 ft²/day</td>
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</tbody>
</table>

"Values were taken from the reference listed in the first row, unless otherwise specified. The 3% anhydrite was speculated, according to Austad et al. and Yousef et al. reported that the crushed powder is composed of 80% calcite, 13% dolomite, 6% anhydrite, and <1% quartz. The composition used in simulations was calculated for the porous media and by lumping dolomite with calcite without differentiating between the two. The specific surface area for limestone was taken from Shariatpanahi et al. The end-point concentrations were obtained from speciation calculations with water compositions at end-point oil-wet and water-wet states. The diffusion/ dispersion coefficient was determined from tracer effluent concentration curves."
Table 3. Synthetic Brine Compositions Used in Experiments and Simulations\textsuperscript{d}

<table>
<thead>
<tr>
<th>ion concentration (mol/kg water)</th>
<th>FW\textsuperscript{a}</th>
<th>SW\textsuperscript{b}</th>
<th>SW0NaCl\textsuperscript{c}</th>
<th>SW0NaCl4SO4\textsuperscript{d}</th>
<th>SW1/2M\textsuperscript{e}</th>
<th>NaCl-M\textsuperscript{f}</th>
<th>FW\textsuperscript{d}</th>
<th>seawater\textsuperscript{d}</th>
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<tbody>
<tr>
<td>HCO\textsuperscript{3}\textsuperscript{−}</td>
<td>0.009</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.000</td>
<td>0.003</td>
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<tr>
<td>Cl\textsuperscript{−}</td>
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<td>0.525</td>
<td>0.126</td>
<td>0.126</td>
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<td>SO\textsubscript{4}\textsuperscript{2}−</td>
<td>0</td>
<td>0.024</td>
<td>0.024</td>
<td>0.096</td>
<td>0.012</td>
<td>0.013</td>
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<tr>
<td>SCN\textsuperscript{−}</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.012</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>0.008</td>
<td>0.045</td>
<td>0.045</td>
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<td>0.045</td>
<td>0.013</td>
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<td>Ca\textsuperscript{2+}</td>
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<td>0.013</td>
<td>0.013</td>
<td>0.437</td>
<td>0.016</td>
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<td>0.504</td>
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<td>0.010</td>
<td>0.010</td>
<td>0.010</td>
<td>0.022</td>
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<tr>
<td>pH\textsuperscript{f}</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
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<tr>
<td>total ionic strength</td>
<td>1.116</td>
<td>0.658</td>
<td>0.258</td>
<td>0.474</td>
<td>0.682</td>
<td>0.608</td>
<td>4.159</td>
<td>1.149</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Legend: FW, formation water; SW, seawater; SW0NaCl, seawater depleted in NaCl; SW0NaCl4SO4, SW0NaCl with four levels of sulfate; SW1/2M, seawater that contains SCN\textsuperscript{−} and half the amount of SO\textsubscript{4}\textsuperscript{2−} in SW; and NaCl-M, NaCl solution with equal amounts of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and SCN\textsuperscript{−}.

\textsuperscript{b}Data taken from Fathi et al.\textsuperscript{6}

\textsuperscript{c}Data taken from Strand et al.\textsuperscript{56}

\textsuperscript{d}Data taken from Yousef et al.\textsuperscript{2}\textsuperscript{e}Data taken from Zlati et al.\textsuperscript{9}\textsuperscript{f}The pH in this study was determined by adding a calculated amount of a strong acid or base to the injection water, thus reproducing the experimental breakthrough curves\textsuperscript{6} with and without residual oil. The cores were filled with formation water initially.

Chromatographic Wettability Test. In chromatographic wettability tests, seawater with different compositions (SW\textsuperscript{d} in Table 3) is injected into a formation-water-saturated core and a core initially at residual oil saturation (here, S\textsubscript{or} = 0.25). The purpose of chromatographic wettability tests is to quantify the adsorption of sulfate. Figure 2A shows the breakthrough curves in a reference water-wet core without oil. The dispersion coefficients (0.0042 ft\textsuperscript{2}/day) were determined by reproducing the breakthrough curves (BTCs) of the non-reactive tracer SCN\textsuperscript{−}. The area between the BTCs for SCN\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} quantifies the amount of adsorbed SO\textsubscript{4}\textsuperscript{2−}, as discussed in Zhang et al.,\textsuperscript{9} which essentially measures the amount of surface sites available and the water-rock contact surface area.

We included all reactions in the simulations, except reaction CO1, because, at room temperature, the oil surface reactions were assumed to be inactive. Two simulations were performed to reproduce the experimental breakthrough curves\textsuperscript{6} with and without residual oil. The cores were filled with formation water initially. Figure 2B shows the predicted Ca\textsuperscript{2+} and Mg\textsuperscript{2+} concentrations. Because the injected seawater—water contains more Mg\textsuperscript{2+} and less Ca\textsuperscript{2+} than the formation water does, more Mg\textsuperscript{2+} adsorbed on the calcite surface, replacing adsorbed Ca\textsuperscript{2+} as the seawater contacted the rock surface, causing the Ca\textsuperscript{2+} concentration peak near 1.0 PVI. This is consistent with experimental observations.\textsuperscript{6,8} Both concentrations eventually returned to the injection concentrations.

Figure 2C shows the BTCs for cores at a residual oil saturation of 0.25. The surface area that is in direct contact with the aqueous phase is smaller than at the saturated conditions without oil, leading to a smaller difference between the SCN\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} curves. The SCN\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} breakthrough earlier than those in Figure 2A, because of the immobile residual oil and less available pore space for flow and less surface area for adsorption. The predicted Mg\textsuperscript{2+} and Ca\textsuperscript{2+} concentrations in Figure 2D are similar to those depicted in Figure 2B, except with an earlier and a smaller Ca\textsuperscript{2+} peak. The match of the BTCs with and without oil shows the validity of the model and parameters relevant to the physical processes when no oil reactions are included.

Forced Displacement. Forced displacement experiments were performed with successive injection of formation water (FW), seawater (SW), and seawater depleted in NaCl (SW0NaCl).\textsuperscript{6} The initial water saturation is 0.08.

Simulation studies are performed in two ways. Simulation A injected FW, SW, and SW0NaCl successively in Table 3; in simulation B, NaCl solution was injected with the same total molality of FW, SW, and SW0NaCl. As shown in Figure 3A, simulation A closely reproduced the experimental data. The oil recovery for simulation B, however, indicates that without SO\textsubscript{4}\textsuperscript{2−}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}, oil recovery was the same, even though the injection water has increasingly lower salinity. This indicates that, for the Stevns Klint chalk, it is the chemical composition of the injected water that matters, not salinity. This is very different from core flooding in limestones, where lower salinity has been shown to improve oil recovery.\textsuperscript{2,10,19,52}

Figure 3B shows the predicted BTCs of total SO\textsubscript{4}\textsuperscript{2−}, >CaSO\textsubscript{4}\textsuperscript{−}, and >CaOH\textsubscript{2}(−COO), as well as the pH for
simulation A. During the FW injection, >CaOH₂(−COO) maintained a high concentration while no sulfate sorption occurred (>CaSO₄ = 0). During the SW injection, the effluent concentrations and oil recovery did not change much until the seawater reached the outlet at ~3.0 PVI, when the total concentration of SO₄²⁻ increased with increasing >CaSO₄ and decreasing >CaOH₂(−COO). The high affinity of sulfate to the calcite surface, indicated by higher surface concentrations of >CaSO₄ than >CaOH₂(−COO), leads to increased oil recovery between 3.0 PVI and 4.0 PVI. From 4.0 PVI to 6.0 PVI, SW₀NaCl was injected with the same SO₄²⁻ concentration as in the SW case, but without NaCl. With the decrease in ionic strength, SO₄²⁻ activity increased so that the surface concentration of >CaSO₄ increased further while the aqueous total SO₄²⁻ decreased. With continued SO₄²⁻ injection, the total concentration eventually increased back to the inlet concentration at ~5.0 PVI. The increased sulfate adsorption reduces >CaOH₂(−COO), which causes the observed change in wettability toward a more water-wet state and the increased oil recovery. The predicted SO₄²⁻ and >CaOH₂(−COO) concentrations are consistent with the chemical mechanism proposed by Austad et al.¹ The pH of the effluent solution changes between 6.5 and 9.5 and is responsive to the changes in injection water composition. Effluent pH increased during the SW slug and decreased during the SW₀NaCl slug. After ~3 PVI, the pH change mirrored the change in >CaSO₄, indicating the dominant control of SO₄²⁻ sorption on the pH of the system.

**Limestone without Anhydrite from Strand et al.⁵⁶** The selected limestone core was composed of 75% calcite and 25% pore space by volume. Thus, most of the reactions are the same as those for the SK chalk. The limestone has a lower specific surface area (0.29 m²/g), compared to that of chalk (1.00 m²/g).

**Chromatographic Wettability Tests.** To explore the affinity of SO₄²⁻ toward the limestone surface, a chromatographic wettability test for a completely water-wet core is simulated. In the test, seawater that contains SCN⁻ and half of SO₄²⁻ of SW (SW₁/₂M) was injected (Table 3). A smaller diffusion/dispersion coefficient (0.002 ft²/day) than the SK chalk was obtained by reproducing the BTC of SCN⁻. As shown in Figure 4A, the predicted SO₄²⁻ concentration agrees well with the concentration data. The similarity between Figure 4A and Figure 2A indicates that the same equilibrium constants can be used to describe sulfate adsorption in limestone and in SK chalk.

**Surface Adsorption Test for Ca²⁺ and Mg²⁺.** A NaCl solution with equal amounts of Ca²⁺, Mg²⁺, and SCN⁻ (NaCl-M, see Table 3) was injected to test the calcite surface adsorption of Ca²⁺ and Mg²⁺ in a similar chromatographic wettability test.⁵⁶ As shown in Figure 4B, the breakthrough times of Ca²⁺ and Mg²⁺ are longer than SCN⁻, indicating that Ca²⁺ and Mg²⁺ are adsorbed on the surface. The adsorption reactions are independent from SO₄²⁻ adsorption and the carboxylic group, as the adsorption is observed without SO₄²⁻ and oils. Figure 4B shows the comparison of experimental and predicted BTCs for SCN⁻, Ca²⁺, and Mg²⁺ at 70 °C. The BTCs were matched with tuned K_Ca and K_Mg (−2.1 for both reactions), because of the increased temperature using the NEDL model, while other reaction parameters are the same as that in the simulation of Fathi et al.⁶.

The two simulations of the chromatographic wettability tests indicated no significant difference between chalk and limestone, regarding the surface reactivity behaviors of Ca²⁺, Mg²⁺, and SO₄²⁻. The difference in adsorption is a result of different porosity and specific surface area. That is, we can use the same reaction network listed in Table 1 to describe the surface complexations on the Stevns Klint chalk⁶ and the Middle Eastern limestone surfaces.⁵⁶

**Limestone with Anhydrite.** Anhydrite dissolution was reported in some low-salinity core floods and was regarded as the cause of the alteration in wettability when the injection fluids do not contain sulfate. Here, we examine our model results for two cases.

**Forced Displacement in Limestone Core with Anhydrite from Austad et al.⁵** Dilution formation water was found to improve oil recovery in limestone cores.²¹,⁵ Austad et al.⁵ observed tertiary IORs of 5% OOIP in limestone rocks with diluted formation water containing no sulfate. Sulfate was detected in the effluent when the core was flooded with deionized water, confirming the presence of anhydrite. The increased SO₄²⁻ concentration from dissolved anhydrite likely led to the wettability alteration and increased IOR. To test this hypothesis, we simulated the forced displacement experiments in Austad et al.³ where formation water (FW) and 100-times-diluted formation water (100x diluted FW) were injected successively.

Figure 5A shows that simulation A with anhydrite dissolution reproduced the incremental oil recovery with 100x diluted FW. In simulation B, where anhydrite dissolution was removed, Figure 5A indicates that the diluted FW does not lead to IOR. Figure 5B shows the predicted total effluent concentration of

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**Figure 3.** (A) Oil recovery from experiments and simulations for forced displacements with successive injection of FW, SW, and SW₀NaCl. The experimental data are taken from Fathi et al.⁶ (B) The dimensionless concentration of total SO₄²⁻, >CaSO₄⁻, and >CaOH₂(−COO) for simulation A. C₀ = 0.024 mol/kg water for SO₄²⁻ and 4.1 μmol/m² for surface species, >CaSO₄⁻, and >CaOH₂(−COO).

**Figure 4.** Breakthrough curves (BTCs) of chromatographic wettability tests in limestone cores: (A) SCN⁻ and SO₄²⁻ at 25 °C and (B) SCN⁻, Ca²⁺, and Mg²⁺ at 70 °C.
Ca\(^{2+}\) and SO\(_4\)\(^{2-}\) for simulation A. Upon the injection of 100× diluted FW, Ca\(^{2+}\) concentrations decreased while SO\(_4\)\(^{2-}\) concentrations increased. Since the injection water does not contain SO\(_4\)\(^{2-}\), the total SO\(_4\)\(^{2-}\) concentration indicates how much anhydrite is dissolved. As shown in Figure 5B, total SO\(_4\)\(^{2-}\) did not change much when the injection fluid composition was changed at ∼6.0 PVI. This is because the lower Ca\(^{2+}\) concentration in the injection water increased anhydrite dissolution while a smaller ionic strength decreases anhydrite dissolution. The net result is that anhydrite dissolution remained almost the same as that indicated by the almost-constant total SO\(_4\)\(^{2-}\) concentration. The concentration of free SO\(_4\)\(^{2-}\), however, increased by more than one order of magnitude, because Na\(^+\) and Ca\(^{2+}\) concentrations decreased with the 100× diluted FW, so that less aqueous complexation of NaSO\(_4\) and CaSO\(_4\)\(_{aq}\) were formed. Thus, additional free SO\(_4\)\(^{2-}\) was available to adsorb onto the solid surface to replace adsorbed oil acids, leading to an increased oil recovery of ∼5% OOIP.

**Forced Displacement in Composite Limestone with Anhydrite in Yousef et al.** Yousef et al.\(^2\) observed ∼20% OOIP incremental oil recovery with successive injection of seawater, 2× diluted seawater, and 10× diluted seawater into composite limestone cores. Anhydrite dissolution was verified in their experiments using nuclear magnetic resonance (NMR) measurements. The cores were originally oil-wet. The NEDL model failed to predict any alteration of wettability in our first attempt. An EDL model, however, reproduced the data, indicating the importance of including the surface potential changes in simulations with brines of different ionic strength.

Figure 6A shows that the model reproduced oil recovery data. Figure 6B shows the predicted breakthrough curves containing anhydrite. The same injection sequence as that reported by Yousef et al.\(^2\) was used. Unlike limestone B, chalk and limestone A show little IOR when seawater, 2× diluted seawater, and 10× diluted seawater were injected. (B) The ratio of the breakthrough concentration of adsorbed carboxylic acids >CaOH\(_2\)(−COO) with respect to its initial concentration at the condition of panel (C). Simulation input parameters are the same as those in Figure 3A for chalk, Figure 5A for limestone A, and Figure 6A for limestone B.

**Comparison of Chalk and Limestones.** Using the same input parameters for the previously discussed cases, we compare predicted oil recoveries for the different cores with the same injection water composition. The core floods for different mineralogies were modeled with the same parameters in NEDL as shown in Figures 3A and 5A; core floods for different mineralogies with the same parameters in EDL were modeled as shown in Figure 6A.

Figure 7A compares the oil recovery of chalk from limestone A (Austad et al.) and limestone B (Yousef et al.), both

![Image](https://example.com/image1.png)  
**Figure 5.** (A) Oil recovery for forced displacements in cores with anhydrite dissolution (simulation A) and without anhydrite dissolution (simulation B). (B) Breakthrough curves of Ca\(^{2+}\), total Ca\(^{2+}\), SO\(_4\)\(^{2-}\), and total SO\(_4\)\(^{2-}\) from simulation.

![Image](https://example.com/image2.png)  
**Figure 6.** (A) Oil recovery for forced displacement from core floods (Yousef et al.) and simulation. (B) Effluent concentration of chemical species. The units for Na\(^+\), total SO\(_4\)\(^{2-}\) and free SO\(_4\)\(^{2-}\) concentration are mol/kg water. The units for >CaOH\(_2\)(−COO) concentration are μmol/m\(^3\).

![Image](https://example.com/image3.png)  
**Figure 7.** (A) Oil recovery for chalk, limestone A, and limestone B when seawater, 2× diluted seawater, and 10× diluted seawater were injected. (B) The ratio of the breakthrough concentration of adsorbed carboxylic acids >CaOH\(_2\)(−COO), with respect to its initial concentration for each case in panel (A). (C) Oil recovery for chalk, limestone A, and limestone B; formation water (FW) and 100× diluted FW were injected. (D) The ratio of the breakthrough concentration of adsorbed carboxylic acids >CaOH\(_2\)(−COO), with respect to its initial concentration at the condition of panel (C). Simulation input parameters are the same as those in Figure 3A for chalk, Figure 5A for limestone A, and Figure 6A for limestone B.
the sulfate concentration decreased as seawater was diluted (even after anhydrite was dissolved). Limestone A and limestone B show significantly different behavior. The different IOR for limestone A and limestone B results from the use of NEDL for limestone A, while EDL is used for limestone B. Figure 7C compares the oil recovery of the three cores with FW and 100× diluted FW injected. Both limestone A and limestone B show increased oil recovery, although the extent of the increase is much smaller in limestone A. The differences in IOR might be caused by shifts in relative permeability curves, which should be measured for each core. In contrast, no IOR is observed for chalk. The >CaOH₂(−COO) concentrations in Figure 7D indicate that wettability alteration occurs for limestones but does not occur for chalk, because of the lack of anhydrite dissolution. The different responses of the chalk and limestones to the same injection water indicate the importance of anhydrite dissolution.

**Extension to the Field Scale Injection.** One concern in the core flood experiments is low permeability due to scale deposition and wettability alteration. To examine this, we simulated a quarter of a five-spot pattern using PennSim with the reaction network and parameters that reproduced core flood experiments (see Tables 1 and 2). Two homogeneous models and one heterogeneous model were simulated. The pattern size of 300 ft × 300 ft for all three models was discretized into uniform 20 × 20 grid blocks. No gravity is included. The first two homogeneous models used the input parameters of core flood experiments of Austad et al. and Yousef et al., respectively. The heterogeneous model used the same porosity, mineral composition, and end-point relative permeability of Yousef et al. and the permeability field was taken from an upsampling of the 41th layer of the permeability field in a SPE10 comparative solution project. The original permeability was for 60 × 220 grid blocks and was coarsened into 20 × 20 grid blocks. The grid coarsening was done by combining 3 × 11 fine grid blocks into one coarse grid block. The permeability was calculated by using an arithmetic mean. PennSim results for the 2-D five-spot pattern cases matched exactly with simulations using Eclipse for FW injection without wettability alteration.

Figure 8A compares the oil recovery curves for the 1-D homogeneous core floods and 2-D homogeneous five-spot patterns. Breakthrough in the 1-D simulations is delayed slightly compared to the 2-D model for both FW and 100× diluted FW injection water. Breakthrough is somewhat quicker in the 2-D homogeneous model, because of poorer sweep.

Figure 8. Oil recoveries for 1-D core floods and 2-D five-spot patterns in a homogeneous limestone reservoir, using (A) parameters of core flood experiments from Austad et al. and (B) parameters of core floods from Yousef et al.

Sweep is excellent in the 2-D models, however, so that ultimate oil recovery quickly approaches the 1-D values. This is expected since the mobility ratio is favorable in these floods (end-point mobility ratios are ~0.5). For both the 1-D and 2-D cases, the injection of 100× diluted FW produces ~5% OOIP more oil recovery than injection of FW at 2.0 PVI. This increase is significant and demonstrates that recovery can be enhanced with a realistic volume of water being injected.

Figure 8B shows the oil recovery of SW and 10× diluted SW injection for the same 1-D core and 2-D five-spot models. For both injection fluids, the 2-D five-spot patterns exhibit smaller oil recovery at 2.0 PVI than the 1-D core floods. For both 1-D and 2-D cases, injection of 10× diluted SW leads to ~20% OOIP more oil recovery at 2.0 PVI than the injection of SW alone.

Figure 9A shows the permeability field for a heterogeneous 2-D reservoir. The permeability field contains a high-permeability channel and therefore injection water breakthroughs occur much faster. Figure 9B shows a significantly decreased oil recovery and earlier breakthrough, compared to the homogeneous case, because of poor sweep efficiency, although the benefit of using LSW remains large (6% OOIP). The CPU time for the entire simulation on a MacBook Pro (Intel i5 2.3 GHz, 2011 version) was 307 s.

**Comparison with Previous Model.** The reaction network used in this paper is extended from a previous model. With more reactions, the current model is compared with the previous model for the case of flow in chalk and a series of injection brine compositions including formation water (FW), seawater (SW), SW depleted in NaCl (SW0NaCl), and SW0NaCl with four levels of sulfate (SW0NaCl4SO4). The brine composition is shown in Table 3. As is shown in Figure 10 for the current model with and without calcite dissolution, the simulations reproduce the decrease of >CaOH₂(−COO)− concentration on the rock surface. This indicates that the current model and the previous model predict the same trend of wettability alteration with the tested brine compositions. The effect of calcite dissolution is also tested, since calcite dissolution was regarded as being important during seawater injection processes. Figure 10 also indicates that although calcite dissolution is important when FW is injected, it does not affect the trend of wettability alteration.

**Model Limitations and Potential Improvements.** The model developed here offers a promising pathway to move forward with regard to understanding the chemical mechanisms for wettability alteration during low-salinity waterflooding. The
current model does have some limitations that may affect the predictive capability of this model.

Four mechanisms of interaction between crude oil, brine, and solid surfaces have been reported in the literature, including polar, surface precipitation, acid/base and divalent/multivalent ion binding. Here, we focus on the acid/base mechanism. We did not include ion binding because there is a lack of experimental and thermodynamic data for ion-bridging interaction. Moreover, it is challenging to study those mechanisms independently.

The use of EDL and NEDL models to reproduce the experiments for limestone A\(^2\) and limestone B\(^2\) is not desirable. This indicates that the key difference between different forms of CaCO\(_3\), limestone and chalk, should be identified. Collection of detailed aqueous geochemical data, including Ca\(^{2+}\), Mg\(^{2+}\), and \(\text{SO}_4^{2-}\) concentrations, and pH at the effluent, as well as measuring zeta potential at the oil and rock surface at high pressure and high temperature, will also allow further constraints on the geochemical reaction network.

**CONCLUSIONS**

In this research, we extended a previous mechanistic wettability alteration model to understand and predict the improved oil recovery (IOR) from low-salinity waterflooding conditions with diﬀering the aqueous composition and could accurately predict wettability alteration and recoveries, because of surface reactions. The main overall conclusions are as follows:

(i) The 1-D chromatographic wettability tests for the SK chalk and limestone cores were simulated. The predicted effluent concentration matched well with the experimental measurements.

(ii) Forced displacement experiments for the SK chalk and limestone cores were also simulated. The predicted oil recoveries also matched the experimental measurements well. The predicted effluent concentrations were consistent with experimental measurements.

(iii) Simulation of secondary recoveries for the 1-D core flooding models and 2-D five-spot models ranged from 5% to 20% OOIP at 2.0 PVI, using diluted formation water or diluted seawater. More importantly, the 2-D models demonstrated that LSW can yield excellent increases in recovery at realistic pore volumes injected (PVI).

Additional important conclusions include the following:

- The same set of reactions can be used for the wettability alteration model.
- The prediction of wettability alteration using the mechanistic model is accurate for the demonstrated experimental studies.
- Coreflooding experiments are lacking all data needed to predict recovery. Relative permeability curves should be measured at two wettability states.
- The nonelectrical double layer (NEDL) model cannot capture wettability alteration in the core floods of Yusef et al.\(^2\) The electrical double layer (EDL) model was required instead.
- In limestone cores with anhydrite,\(^2\) dilute water reduces ion strength and aqueous complexation of sulfate with cations. This enhances anhydrite dissolution and the availability of free \(\text{SO}_4^{2-}\), thereby improving the oil recovery. The simulation for the same limestone core but without anhydrite does not show IOR.
- The IOR at 2.0 PVI for 1-D core floods and 2D five-spot models is dependent on the rock mineralogy.

This is the first mechanistic model for carbonate rocks that considers the coupling of mineral dissolution and surface complexation reactions to predict low-salinity waterflooding recoveries and wettability changes for both chalk and limestone cores, with and without anhydrite. Other minerals could be added as needed in the reaction network for reservoir formations with different type of lithology.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors gratefully thank the member companies of the Gas Flooding JIP in the EMS Energy Institute at The Pennsylvania State University at University Park, PA for their financial support. Russell T. Johns holds the Victor and Anna Mae Beghini Faculty Fellowship in Petroleum and Natural Gas Engineering at The Pennsylvania State University.

**NOMENCLATURE**

- \(a_i\) = activity of species \(i\) (dimensionless)
- \(A, B\) = temperature-dependent parameters for the Debye–Hückel model (kg \(\text{water}^{1/2}/\text{mol}^{1/2}\))
- \(d\) = temperature-dependent parameter for the Debye–Hückel model (kg \(\text{water}/\text{mol}\))

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Figure 10. Comparison of the calculated surface fraction of >CaOH\(_2\)(=COO\(_{-}\)) for chalk from extended and previous models. Blue bars represent the values calculated by the previous model; red bars represent the values calculated by the current model; and green bars represent the values calculated by the current model, but without calcite dissolution.


\[ A_s = \text{bulk surface area of mineral species} \ m^2 \]
\[ D = \text{diffusion/dispersion coefficient tensor} \ (\text{ft}^2/\text{day} \text{ or m}^2/\text{s}) \]
\[ E_a = \text{activation energy} \ (\text{Btu}/\text{lb-mol} \text{ or J/mol}) \]
\[ F = \text{Faraday’s constant}; \ F = 9.648 \times 10^4 \text{ C/mol} \]
\[ F_r = \text{molar rate of the primary species} \ \text{mol/(m day)} \]
\[ F_s = \text{molar rate of the secondary species} \ \text{mol/(m day)} \]
\[ g = \text{standard gravitational constant} \ (\text{ft/day}^2 \text{ or m/s}^2) \]
\[ I = \text{ionic strength of water} \ (\text{mol/kg water}) \]
\[ K_{eq} = \text{equilibrium constant of reaction} \ r \]
\[ K = \text{permeability} \ (\text{md or m}^2) \]
\[ k_r = \text{relative permeability of phase} \ j \]
\[ M_p = \text{molar density of the primary species} \ \text{mol/m}^3 \]
\[ M_q = \text{molar density of the secondary species} \ \text{mol/m}^3 \]
\[ N_p = \text{number of primary species} \]
\[ N_{tot} = \text{total number of species} \]
\[ N_{sec} = \text{number of secondary reactions} \]
\[ P_i = \text{pressure of phase} \ j \ (\text{psi or Pa}) \]
\[ P_c = \text{capillary pressure between phase} \ j \text{ and a reference phase} \ (\text{psi or Pa}) \]
\[ Q_e = \text{total molar rate of primary species} \ \text{lb-mol/day} \text{ or mol/s} \]
\[ R = \text{universal gas constant} \; R = 8.31 \text{ J/(mol K) or 10.73 ft}^3 \text{ psi/(R lb-mol)} \]
\[ S_j = \text{saturation of phase} \ j \ (\text{dimensionless}) \]
\[ T = \text{temperature} \ (\text{R or K}) \]
\[ Z = \text{depth} \ (\text{ft or m}) \]
\[ z_i = \text{charge carried by species} \ i \]

\[ \varepsilon_0 = \text{dielectric constant of water} \; \varepsilon_0 = 55.3 \ (\text{dimensionless}) \]
\[ \varepsilon_r = \text{permittivity of free space} \; \varepsilon_r = 8.854 \times 10^{-12} \text{ C V}^{-1} \text{ dm}^{-1} \]
\[ \sigma = \text{charge density at the oil surface} \; \sigma = \text{C/m}^2 \]
\[ \psi_c = \text{specific interfacial potential} \ (\text{mV}) \]
\[ \psi_i = \text{solid/water interface potential} \ (\text{mV}) \]
\[ \psi = \text{molar density of phase} \ j \ (\text{mol/lb-mol} \text{ or mol/m}^3) \]
\[ \gamma = \text{activity coefficient of species} \ i \ (\text{kg water/mol}) \]
\[ \kappa = \text{the (i, j) entry in the stoichiometry matrix for the reactions in canonical form} \]
\[ \phi = \text{porosity} \ (\text{dimensionless}) \]
\[ \rho = \text{density} \ (\text{lb/ft}^3 \text{ or kg/m}^3) \]
\[ \mu_i = \text{viscosity of phase} \ j \ (\text{cP}) \]


(49) Hopkins, P.; Puntenvold, T.; Strand, S. Preserving Initial Core Wettability During Core Restoration of Carbonate Cores. Presented at the 29th International Symposium of the Society of Core Analysts, St. John’s Newfoundland and Labrador, Canada, 2015.


