A Mechanistic Model for Wettability Alteration by Chemically Tuned Water Flooding in Carbonate Reservoirs

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Abstract

Injection of chemically tuned brines into carbonate reservoirs has been reported to enhance oil recovery by 5% to 30% OOIP in core flooding experiments and field tests. One proposed mechanism for this improved oil recovery (IOR) is wettability alteration of rock from oil wet or mixed-wet to more water wet conditions. Modeling of wettability alteration experiments, however, are challenging due to the complex interactions among ions in the brine and crude oil on the solid surface. In this research, we developed a multiphase multicomponent reactive transport model that explicitly takes into account wettability alteration from these geochemical interactions.

Published experimental data suggests that desorption of acidic oil components from rock surfaces make carbonate rocks more water wet. One widely accepted mechanism is that sulfate (SO$_4^{2-}$) replaces the adsorbed carboxylic group from the rock surface while cations (Ca$^{2+}$, Mg$^{2+}$) decrease the oil surface potential. In the proposed mechanistic model, we used a reaction network that captures the competitive surface reactions among carboxylic groups, cations, and sulfate. These reactions control the wetting fractions and contact angles, which subsequently determine the capillary pressure, relative permeabilities, and residual oil saturations.

The developed model was first tuned with experimental data from the Stevns Klint chalk and then used to predict oil recovery changes with time for additional un-tuned experiments under a variety of conditions where IOR increased by as much as 30% OOIP, depending on salinity and oil acidity. The numerical results showed that an increase in sulfate concentration can lead to an IOR of over 40% OOIP, while cations such as Ca$^{2+}$ have a relatively minor effect on recovery (about 5% OOIP). Other physical parameters, including the total surface area of the rock and the diffusion coefficient, control the rate of recovery, but not the final oil recovery factor. The simulation results further demonstrate that the optimum brine formulation for chalk are those with relatively abundant SO$_4^{2-}$ (0.096 mol/kg water), moderate concentrations of cations, and low salinity (total ionic strength less than 0.2 mol/kg water). These findings are consistent with the experimental data reported in the literature. The new model provides a powerful tool to predict the IOR potential of chemically tuned waterflooding in carbonate reservoirs under different scenarios.

Introduction

Changing the ionic composition of injection water during waterflooding has been reported to lead to improved oil recovery in recent years (Yildiz and Morrow 1996; Lager et al. 2006; A. Yousef et al. 2012). Increases in oil recovery between 5% and 38% OOIP have been observed in sandstone core flooding experiments (Webb et al. 2004; McGuire and Chatham 2005; Lager et al. 2006). Incremental oil recovery by up to 40% OOIP has been demonstrated in carbonate cores (Zhang et al. 2007; Yousef and Al-Saleh 2010). Incremental oil recoveries from field tests, however, are generally smaller than those from core floods. Increases of 15% OOIP have been reported in sandstone reservoirs (Webb et al. 2004). Oil recovery of 50% OOIP using seawater injection in carbonate reservoirs such as in the Ekofisk field in the North Sea reservoir have been reported (Hallenbeck and Sylte 1991; Austad and Strand 2008; Yousef et al. 2012).

Wettability alteration of the rock from oil wet to water wet has been suggested as the primary mechanism for increased oil recovery during low salinity waterflooding in carbonates (Morrow 1990; Buckley and Liu 1998; Austad et al. 2012). Oil recovery is generally greater in water reservoirs because of the higher oil mobility owing to its lower affinity to rock surfaces. Water breakthrough is typically slower in water-wet rocks compared to oil-wet reservoirs. In addition, in fractured rocks, a water-wet matrix allows for water imbibition and counter current flow of oil. Most carbonate reservoirs are not completely oil wet; instead the rocks usually have mixed wettability depending on the nature of the mineral surface, oil
properties, and fluid-rock interactions (Morrow 1990; Anderson 1987; Peters 2012). The relative proportion of oil-wet and water-wet surfaces determines the overall capillary pressure, relative permeability, and residual oil saturation, which ultimately control oil recovery (Anderson 1987; Ustohal et al. 1998; Delshad et al. 2003; O’Carroll and Abriola 2005). Low salinity seawater has been found to increase the proportion of the water wet surface during spontaneous imbibition experiments using the Stevns chalk (Strand et al. 2006; Strand et al. 2008; Puntervold and Austad 2008; Puntervold et al. 2009). Favorable contact angle hysteresis was observed during injection of low salinity brine containing sulfate (Alotaibi et al. 2010; Yousef and Al-Saleh 2010; Gupta and Mohanty 2011; Yousef et al. 2011; Yousef et al. 2012). Incremental oil recovery differed significantly from 0% to 40% OOIP under various experimental conditions (Fathi et al. 2010).

Possible mechanisms for the observed wettability alteration include fine particle migration (Tang and Morrow 1999), ion exchange (Lager et al. 2006), mineral dissolution (Hiorth et al. 2010) and sorption and desorption of carboxylic groups (Zhang et al. 2007). For Stevns chalk, spontaneous imbibition and chromatographic wettability tests verified that SO4^2-, Ca^{2+} and Mg^{2+} ions actively participate in surface reactions that alter wettability (Strand et al. 2003; Strand et al. 2006; Zhang et al. 2007). Austad et al. (2008) suggest that sulfate adsorption on positively charged chalk surfaces and desorption of the carboxylic group from the surface reduces the affinity of the surface to oil (Strand et al. 2006; RezaeiDoust et al. 2009). According to this mechanism, experimental studies reported the optimal ionic composition for improved oil recovery in carbonates (Fathi et al. 2011). Other factors, including temperature, oil composition, and water phase composition, are also observed to play an important role in determining oil recovery (Hjelmland and Larrondo 1986; Strand et al. 2006; Zhang et al. 2007; Strand et al. 2008; Puntervold and Austad 2008; Puntervold et al. 2009; Fathi et al. 2011). Although wettability alteration is considered as a possible reason for incremental recovery, no mechanistic model exists that can be used to quantitatively link water and surface reactions, wettability, capillary pressure and relative permeability, and eventually oil recovery, and to predict oil recovery under different injection water composition conditions for carbonate rocks.

Significant advances have been made in recent years to predict wettability alteration and oil recovery (Hognesen et al. 2006; Jerauld et al. 2008; Yu et al. 2009; Evje and Hiorth 2011; Andersen et al. 2012). Jerauld et al. (2007) proposed a fully compositional model that included the transport of salts in the aqueous phase as an additional single-lumped component. They determined the relationship between the relative permeability and residual oil saturation, however, from linear interpolation of the wetting state using the salinity without tracking individual species. Yu et al. (2009) and Andersen et al. (2013) assumed a single wetting agent that modified the rock wettability through adsorption. The simplification of wettability alteration by including one or two chemical species is not sufficient to capture the complex interactions among multiple components in water, oil, and solid surfaces. Brady et al. (2012) used a surface complexation model with reaction networks relevant to carbonate rocks and sandstones (Brady and Krumpalns 2012; Brady et al. 2012; Brady et al. 2013). However, their reaction approach has not been coupled with multiphase flow to understand dynamic effects on wettability alteration. Other models with multiple chemical reactions either assumed that mineral dissolution modifies wettability (Evje et al. 2011; Andersen et al. 2012), or were designed only for sandstones where cation exchange was believed to be the mechanism of wettability alteration (Dang et al. 2013). In general, there is currently a lack of a detailed representation of the surface geochemical reactions and the corresponding wettability alterations in multiphase flow models.

In the geochemistry community, multi-component reactive transport models have been developed since the 1980s (Lichtner 1985; Steefel et al. 2005) and have been extensively used to understand and predict subsurface reactive transport processes in many applications (Davis et al. 2004; Li et al. 2010; Li et al. 2011). Applications of these complex surface reactions in improved oil recovery processes, although promising from a geochemistry point of view, have not yet been made to the best of our knowledge.

In this research, we develop a model that couples multiphase flow with detailed, mechanistic understanding of surface reactions to systematically investigate the complex interactions among multicomponent surface reactions, wettability, and oil recovery. We propose a reaction network for carbonates based on a double surface complexation model (Brady et al. 2012a, 2012b, 2013). The new model was tuned with data from a low salinity imbibition seawater experiment, where both porous media properties (porosity, permeability, capillary pressure and relative permeability) and geochemical reactions (aqueous and surface complexation reactions) play important roles. Simulations were carried out with this new model under an array of conditions to understand the controlling parameters during the chemically tuned waterflood. By chemically tuned waterflood, we refer to the injection of water that is adjusted in the ionic composition.

This paper is organized as follows. We first introduce the general multiphase flow and reactive transport equations, and then present the reaction network and the relationships between chemical concentrations, capillary pressure, and relative permeability. We then focus on the model validation with the base case experimental data and sensitivity analysis of the important parameters and processes in determining wettability and the oil recovery factor.

**Methodology**

In this section, we introduce the general multiphase flow and reactive transport equations, the reaction network, and the wettability alteration model. The finite-difference solution approach is presented at the end of this section.

Low salinity flooding involves both multiphase flow and geochemical reactions. The injected brine has ionic compositions different from the formation water. This difference perturbs the original thermodynamic equilibrium and leads to surface geochemical reactions, which alters the concentrations of surface species and potentially the wettability. The wettability controls capillary pressure and relative permeability, which in turn affect multiphase flow and recovery.
We have developed an IMPEC formulated code PennSim (PennSim Toolkit, 2013) to solve the coupled multiphase transport and chemical reaction equations in this research (see Fig. 1). The mass conservation equations for oil and water phases are solved for the pressure and saturation sequentially. The water saturation and water phase flux from the solutions of the multiphase flow equations are used in the reactive transport equations. Reactive transport equations are then solved sequentially for the spatial-temporal evolution of the concentrations of aqueous and surface species. The multiphase flow and reactive transport are linked through the interactions among surface reactions, wettability, relatively permeability, and capillary pressure.

**Multiphase Flow Equations.** The mass conservation equations of the immiscible oil and water fluid phases are as follows:

\[ \frac{\partial}{\partial t} (\phi s_o \rho_o) + \nabla \cdot (\rho_o \vec{u}_o) = 0, \quad \alpha = o, w \]  

where \( \phi \) is porosity (dimensionless); \( s, \rho, \) and \( \vec{u} \) are the saturation (dimensionless), fluid density (kg/m\(^3\)), and volumetric flow rates (m\(^3\)/s) for the oil and water phases. The subscript “w” is for the water phase, and the subscript “o” is for the oil phase. Darcy’s law governs the flow rate of different phases:

\[ \vec{u}_\alpha = \frac{kk_{ra}}{\mu_\alpha} \nabla (P_\alpha - \rho_\alpha g Z) \]  

where \( k \) is absolute permeability (m\(^2\)); \( Z \) is the depth (m); \( \mu, g, \) and \( P \) are the viscosity (cP), gravitational constant (m/s\(^2\)), and the pressure of the fluid phase (Pa), respectively. The pressure difference between oil and water phases is the capillary pressure:

\[ P_{cow} = P_o - P_w. \]

The capillary pressure \( P_{cow} \) and the relative permeabilities \( k_{rw} \) and \( k_{ro} \) depend on water saturation, pore structure, and wettability. The saturation relation completes the set of equations

\[ S_o + S_w = 1. \]  

The primary unknowns for the multiphase flow system are the oil pressure \( P_o \) and water saturation \( S_w \).

**Reactive Transport Equations.** Reactive transport equations describe the coupled process of solute transport and reactions. Compared with standard reactive transport models for water saturated porous media (Steefel et al. 1994), PennSim has varying water saturation and three interfaces (oil-water, oil-solid, and water-solid interfaces). The species are partitioned into primary and secondary species. The partition is determined in such a way that the concentration of the secondary species can be explicitly expressed by that of the primary species through the mass action law (Lichtner et al. 1996). The mass conservation equation for the primary species \( p \) is as follows:

\[ \frac{\partial}{\partial t} \left( \sum_{q=1}^{N_q} N_q v_{pq} M_q \right) + \nabla \cdot \left( \sum_{q=1}^{N_q} v_{pq} F_q \right) = 0 \quad p = 1, \ldots, N_p \]

where subscript \( p \) and \( q \) represent the primary species \( p \) and secondary species \( q \); \( v_{pq} \) represents the \((q, p)\) entry of the stoichiometry coefficient matrix. Here the number of secondary species \( N_q \) equals \( N_e \), where \( N_e \) is the number of independent reactions that are in equilibrium. The number of primary species \( N_p \) equals \( N_s - N_q \), where \( N_s \) is the total number of species. The definition of molar density \( M \), flux \( F \), and the derivation of Eq. (5) are in Appendix A. The set of unknowns for the reactive transport equation includes the aqueous species concentration \( C_{aq} \), the solid surface species concentration \( C_{ss} \), and the oil surface species concentration \( C_{so} \). Details of the reactive transport modeling formulation can be found in Yeh et al. (1991), Steefel and Lasaga (1994), and Walter et al. (1994). The system of general equations is coupled with the mass action law discussed below.

**Multiphase Reaction Network.** As illustrated in Fig. 2, the reaction network includes the interactions among Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4^{2-}\), and absorbed oil species. The reaction network includes aqueous reactions and surface complexation reactions at the oil-water, solid-oil and solid-water interfaces (Brady and Krumhansl 2012; Brady et al. 2012; Brady et al. 2013). The reactions on the solid-water interface include the adsorption of sulfate and the carboxylic group. The reactions on the oil-water interface include the dissociation of carboxylic acids and reactions between the carboxylic group and multivalent
cations. Aqueous reactions are also included. All of those reactions are considered to be fast reactions and are assumed to be at equilibrium and are controlled by reaction thermodynamics (Lichtner et al. 1996; Langmuir et al. 1997).

The concentrations of the polar components in crude oil largely affect the initial wettability and the wettability alteration by seawater (Strand et al. 2003; Fathi et al. 2011). For refined oil where polar components are removed, no low salinity water or seawater IOR effect has been observed (Hirasaki and Zhang 2004; Robertson 2007). The acid number (AN) quantifies the abundance of polar components in crude oil and has been shown to be crucial in low salinity flooding (Zhang and Austad 2005). Here we use AN to quantify the amount of carboxylic acids in the oleic phase.

The carboxylic acids represent the polar oil components. As shown in reactions (1)-(3) in Table 1, the carboxylic acids dissociate at the oil-water interface and react with ions in the water phase. The species at the oil-water interface occupies an oil surface site following Brady et al. (2012). A diffusive layer model is used to quantify the activity of the surface species and the electrostatic forces (Dzombak et al. 1990). The expression for the equilibrium constant of reaction (2) is shown as an example:

$$K_{2,eq} = \frac{\exp \left( \frac{E \psi_d}{RT} \right) [-COOCa^+] a_{H^+}}{[-COOH] a_{Ca^{2+}}}$$

where \([-COOH]\) and \([-COOCa^+\)] are the surface concentrations (mol/m²) of carboxylic acid and the surface complex of carboxylic calcium; \(a_{H^+}\) is the activity of \(H^+\) in aqueous phase (unitless); \(F\) is Faraday’s constant (9.648 × 10^4 C/mol); \(\psi_d\) is the oil-water interface charge potential (mV); \(R\) is the gas constant (8.314 J/K·mol); \(T\) is the absolute temperature (Kelvin). The surface potential is calculated using the Gouy-Chapman theory that relates the surface charge density to surface potential in the following form (Gouy 1910; Chapman 1913):

$$\sigma_o = -\sqrt{8\varepsilon_0 \varepsilon_m I R T \sinh \left( \frac{F \psi_d}{2RT} \right)}$$

where \(\sigma_o\) is the charge density at the oil-water interface (C/m²) calculated from \(\sigma_o = \sum_i z_i C_{i_o}\), where \(z_i\) is the charge carried by ion species \(i\); \(\varepsilon_0\) is the dielectric constant of water (55.3, unitless), \(\varepsilon_m\) is the permittivity of free space (8.854×10⁻¹² C V⁻¹ dm⁻¹); and \(I\) is the ionic strength of water (mol/kg water). The solid surface potential can be calculated in a similar manner. The calculation follows the same method of Hiorth et al. (2010). This surface complexation model integrates the effects of surface charge, solution ionic strength, temperature, and surface potential.

The reactions between brine and the calcite surface are represented by reactions (4) and (5) in Table 1. The species >CaOH represents the reactive site on the calcite surface because \(>\text{CaOH}_2^+\) was found to sorb strongly on the oil surface (Brady et al. 2012). Reaction (4) describes the hydration of the calcite surface site. The equilibrium constant is known to highly depend on temperature (Austad and Strand 2008; Fathi et al. 2010). Here we use the data interpolated from Evje and Hinthor (2011). Similar to the oil-water interface reactions, the equilibrium constants of reaction (5) can be written as:

$$K_s = \frac{\exp \left( \frac{E \psi_d}{RT} \right) [>\text{CaSO}_4^-]}{[>\text{CaOH}_2^+] a_{SO_4^{2-}}}$$

where \(\psi_d\) is the solid-water interface potential (mV), which can be calculated similarly to \(\psi_d\). Experimental results show that Ca⁡²⁺, Mg⁡²⁺ and SO₄²⁻ control surface potential however Ca⁡²⁺ or Mg⁡²⁺ alone without SO₄²⁻ cannot alter wettability (Zhang et al. 2007). SO₄²⁻ alone, however, cannot alter wettability either (Strand et al. 2006; Zhang et al. 2007). Reactions (1)-(5) show that SO₄²⁻ determines the potential at the solid surface while Mg⁡²⁺ and Ca⁡²⁺ complex with desorbed carboxylic acids from the solid-fluid interface, which allows sufficient change to occur. These reactions describe the different roles of different aqueous species. Reaction (6) in Table 1 represents the acid/base interactions between oil-water interface and solid surface. Ion binding is not included here because on calcite surfaces a positive surface charge dominates below a pH of 9.4 (Buckley and Liu 1998) while the experiment in Fathi et al. (2010) used a pH value of 8.4. The equilibrium constant for reaction (6) was obtained by history matching of the base case scenario.

Reactions (1)-(6) account for the electrostatic interactions between the oil-water interface and the solid surface. The crude oil-brine interface is known to carry a negative charge as represented in reaction (1), while a chalk surface is known to be positively charged as shown in reaction (4) (Hiorth et al. 2010). The electrostatic attraction between opposite charges leads to the oil sorption on the solid surface (Nasralla and Nasr-El-Din 2012). Those reactions simulate the competitive adsorption of carboxylic acids and SO₄²⁻ on the chalk-water interface and the competitive compounding of Ca⁡²⁺, Mg⁡²⁺ and >CaOH⁡₂⁺⁰ on the oil-water interface. Reactions (7)-(9) are aqueous speciation reactions in carbonate reservoirs. These reactions are also important in determining pH.

For all aqueous species (Ca⁡²⁺, Mg⁡²⁺, H⁺ etc.), the activity was calculated from
\[ a_i = \gamma_i C_i \]

where the activity coefficients were calculated according to the extended Debye-Hückel model (Helgeson et al. 1970),

\[ \ln \gamma_i = \frac{A_2 \sqrt{I}}{1 + a_i^0 B \sqrt{I}} + b_i. \]

The parameters \( A, B \) and \( b \) are temperature dependent parameters taken from the EQ3 database (Wolery and Jackson 1990). \( a_i^0 \) is the ion size parameter and \( I \) is the ionic strength of the brine. Note that with higher ionic strength, the activity coefficients are smaller, which leads to lower activity of specific species.

**Wettability Alteration Model.** Most carbonate reservoirs are classified to have mixed wettability (Buckley et al. 1996; Helland and Skjaeveland 2006). Here the rock surface is considered as containing both water wet and oil wet surfaces. Different surfaces can have different contact angles. Both receding (altered, water wet) contact angle and advancing (unaltered, oil wet) contact angle varied in core experiments (Buckley et al. 1996; Drummond and Israilachvili 2004; Zhang and Austad 2005; Alotaibi et al. 2010). According to the Young’s equation, the contact angle has the following relation derived from the force balance

\[ \cos \theta = \frac{\gamma_{os} - \gamma_{ws}}{\gamma_{ow}} \]  

(7)

where \( \gamma_{os}, \gamma_{os} \) and \( \gamma_{ow} \) are the interfacial tension (mN/m) between water and solid, between oil and solid, and between oil and water, respectively. The contact angle describes how much a mineral surface prefers one phase to another and is a result of the three phase (brine/oil/surface) interaction. The interfacial tensions are determined by the surface concentration of ion species through Gibbs equation (Gibbs 1928). The contact angle is then a function of surface concentrations on the interface. We model the contact angle as a linear function of surface concentration for the oil wet and water wet parts of carbonates, which is justified in Appendix B where the derivation is based on a Gibbs isotherm. The linear interpolation is shown in Eqs. (8) and (9) below.

\[
\cos \theta_w = \cos \theta_{w,0} + \frac{[> CaSO_4^2]}{[> Ca,\text{total}]} (\cos \theta_{w,1} - \cos \theta_{w,0}) \\
\cos \theta_o = \cos \theta_{o,0} + \frac{[> CaOH_2^+ (\text{COO}^-)]}{[> Ca,\text{total}]} (\cos \theta_{o,1} - \cos \theta_{o,0})
\]  

(8)

(9)

where \([> Ca,\text{total}]\) represents the total concentration of the surface site on the carbonate surface. The contact angle \( \theta_w \) on the water wet surface (receding contact angle) is interpolated by the concentration of the water wet agent (sulfate). The oil wet contact angle \( \theta_o \) (advancing contact angle) is interpolated by the oil wet agent (carboxylic group). The contact angles \( \theta_{w,0}, \theta_{w,1}, \theta_{o,0}, \text{ and } \theta_{o,1} \) are input values representing the extreme cases.

The surface concentration also determines the oil wet and water wet surface fractions. The water wet fraction \( (WWF) \) is calculated as a linear function of the surface site concentration as

\[ WWF = 1 - \frac{[> CaOH_2^+ (\text{COO}^-)]}{[> Ca,\text{total}]} \]

The change in relative permeability and capillary pressure functions have typically been determined by linear interpolation with respect to a wettability index (Delshad and Najafabadi 2009; Yu et al. 2009). Our model uses an experimentally verified wettability index as well as theoretical support from the Gibbs and Cassie’s equations (Gibbs 1928; Cassie 1948). The capillary pressure function follows the Leveret-Cassie equation (O’Carroll and Abriola 2005),

\[ P_c(S_w, WWF) = WWF \cos \theta_w P_c^{ww}(S_w) + (1 - WWF) \cos \theta_o P_c^{ow}(S_w) \]  

(10)

where \( P_c^{ww}(S_w) \) and \( P_c^{ow}(S_w) \) are the capillary pressure functions for complete water wet and oil wet surfaces. Eq. (10) has been experimentally verified to provide excellent predictions of the capillary pressure as a function of saturation (Ustohal et al. 1998; O’Carroll and Abriola 2005). Surface roughness has been included in the completely oil wet and completely water wet capillary pressures. One example of the capillary pressure for mixed wettability is shown in Fig. 3A, where the oil wet and water wet data is from Webb et al. (2005). The curves for intermediate wetting state were obtained by using Eq. (10). In Fig. 3B the x-intercept represents the maximum water saturation that can be achieved by spontaneous imbibition. Our model captures the fact that the residual oil saturation highly depends on wettability.

The Brooks-Corey formulation was used here to describe the relative permeability as a function of normalized fluid saturation and water wet fraction (Anderson 1987; Delshad and Najafabadi 2009). The relative permeability was assumed to
depend on the end-point relative permeability and relative saturation in the following equations:

\[
\begin{align*}
    k_{rw} &= k_{rw}^*(S^*)^{n_w} \\
    k_{ro} &= k_{ro}^*(1 - S^*)^{n_o}
\end{align*}
\]

where the normalized water saturation \( S^* \) was calculated as

\[
S^* = \frac{S_w - S_{wr}}{1 - S_w - S_{or}}.
\]

Here \( S_{wi} \) is the initial water saturation and \( S_{or} \) is the residual oil saturation. Linear interpolation between completely water wet and oil wet cases were used as follows:

\[
\begin{align*}
    k_{rw}^* &= WWF \ k_{rw,ww}^* + (1 - WWF)k_{rw,ow}^* \\
    k_{ro}^* &= WWF \ k_{ro,ww}^* + (1 - WWF)k_{ro,ow}^*
\end{align*}
\]

where \( k_{rw,ww}^*, k_{rw,ow}^*, k_{ro,ww}^* \) and \( k_{ro,ow}^* \) are the oil and water end point relative permeability for the oil wet or water wet case. One set of relative permeability curves are shown in Fig. 3B, with the corresponding parameters (end-point relative permeability and Corey-exponent) in Table 2. In Fig. 3B, the oil wet relative permeability function was adapted from Hognesen et al. (2006). With increasing water wettability, the curves shift right, which is more favorable for oil phase flow. The treatment is consistent with experimental findings (Owens and Archer 1971).

The simulation code PennSim was used to solve the multiphase flow equations. PennSim uses a finite volume discretization (Fung et al. 1992) and an non-iterative IMPEC (implicit pressure explicit composition) (Coats 2000) method to solve the governing equations. We sequentially obtained the immiscible multiphase flow solution and then a chemical reactive transport solution. The procedure uses an operator splitting technique with a strict restriction on time step size (Zysset et al. 1994). The calculation procedure for one time step is shown in Fig. 4. After the calculation for one time step is completed, the simulator begins the next time step calculation until the final desired time is reached.

**Results and Discussion**

This section presents a validation of the model using the base case scenario, discussion of sensitivity analyses of key input parameters, and the effects of various brine compositions on wettability and recovery. The ultimate recovery in this paper refers to the recovery factor at the end of 40 days when the oil production rate is very low. The discussion provides a mechanistic and quantitative understanding of processes involved in low salinity flooding and identifies the most important parameters.

**Base Case Simulations.** Various core experiments have been carried out to understand the mechanism and identify the optimal conditions for chemically tuned waterflooding (Austad and Strand 2008; Fathi et al. 2010; Yousef et al. 2010, 2011, 2012). We used the data from Fathi et al. (2010) to validate our model and to obtain key input parameters. We selected this data set because the oil recovery curves in their experiments were collected at 110°C with different brine compositions while maintaining all other conditions the same.

In the experiments, the homogeneous Stevns Klint chalk cores (3.8 cm in diameter and 7.0 cm in length) were used with porosity of about 45% and permeability between 1 and 2 mD \((10^{-12} \text{ m}^2)\). The cores were first cleaned with distilled water. After the drying process, the cores were saturated with formation brine and then flooded with oil to establish an initial water saturation. The oil used was distilled from acid-reservoir-stabilized oil with n-heptane to an equivalent acid number of 1.9 mg KOH/g. The cores were aged at 90°C for four weeks to restore to the reservoir condition, where mixed wettability has been established. The cores were then immersed in synthetic brine, after which spontaneous imbibition begins. The composition of the synthetic brine is given in Table 3, including formation water (FW), seawater (SW) and seawater depleted in NaCl (SW0NaCl). The experiments were all carried out at 110°C under various brine compositions as shown in Table 3. For each case, the produced oil was collected over time. After the spontaneous imbibition, chromatographic wettability tests were performed to determine the water wet fraction. The comparison among different cases identifies the important ions in the low salinity brine imbibition process.

As the core is immersed into brine, spontaneous imbibition began. The ions in the immersing brine were transported and diffused into the core. The chemical reactions altered the wettability and imbibition was improved. These conceptual processes were described using the discussed equations. Spontaneous imbibition causes counter-current flow, during which the volumetric flow rate of oil and water were equal, but in opposite directions. Spontaneous imbibition is simulated by solving Eqs. (1)-(5) with Dirichlet boundary conditions. The boundary pressure for both phases is set to be the back pressure; the boundary saturation for water is 1.0; the brine concentration on the boundary is set to be the same as the imbibing fluid. For initial conditions, the oil saturation is specified as determined from the experiments; the water phase pressure is the same as the back pressure while the oil phase pressure is calculated from the capillary pressure relation, Eq. (3). The fluid initial water
composition is the same as the water formation.

We performed 2-D simulations using the radial symmetry of the core where the core was discretized into 30×100 grid blocks in the r−z coordinates, as shown in Fig. 5. We modeled the experimental data from Fathi et al. (2010) to validate our model and to obtain important parameters. In addition, we compared the modeling results using three relative permeability and capillary functions of increasing complexity. The reaction equilibrium $K_r$ value was tuned to match the base case. Fig. 6 compares the oil recovery data and the modeling results. Here we used three methods to match the oil recovery using brines of different composition. Methods A, B and C model the wettability alteration with increasing level of detail. Method A was based on Hognesen et al. (2006), where fixed capillary pressure and relative permeability functions were used as is typically the case for multiphase flow simulations. Oil wet functions were used for FW; water wet functions were used for SW0NaCl; intermediate wet functions were used for SW. The choice of these functions is based on our understanding of the wettability with respect to different water compositions. Method B is based on Yu et al. (2010) and includes the transport and adsorption reaction of $\text{SO}_4^{2-}$ as the single reacting solute and calculates the wettability as a function of the adsorbed sulfate mass. The capillary pressure and relative permeability functions were obtained by interpolation using the equation $k_r = WWF \frac{k^w}{P_c} + (1 - WWF)k^m$ and $P_c = WWF P_c^w + (1 - WWF)P_c^m$, where $WWF$ is calculated from the solid surface fraction of sulfate ions, i.e. $\frac{C_{\text{SO}_4^{2-}}}{C_{\text{total,s}}}$. The sulfate adsorption reaction was modeled with the Langmuir isotherm and the effect of salinity was not considered. Method C is our mechanistic method as discussed in the methodology section. The reaction system explicitly included the effects of different ions on the reaction-driven wettability alteration.

The comparison of oil recovery curves shown in Fig. 6 shows the necessity of including the geochemistry details. For FW, when the wettability is fixed, Method A reproduced the counter-current flow and the subsequent oil production for the FW case. However, method A overestimated the oil production rates for SW and SW0NaCl when wettability alteration occurred. With method B, the oil recovery curve of SW overlaps with that of SW0NaCl, which indicates that method B cannot distinguish between the two cases because of the oversimplified representation using a single component and single reaction. PennSim accurately predicted the oil recovery curves for all three compositions (Fig. 6C). The fact that the oil recovery decreased with increasing NaCl concentration was reproduced from our simulation results for SW and SW0NaCl. Moreover, our model predicted the wetting area fraction measured in all experiments. The final water wet fractions simulated for FW (0.52), SW (0.67), and SW0NaCl (0.83) were within 5% of the experimentally measured values through chromatographic wettability tests (Strand et al. 2006; Fathi et al. 2010).

Fig. 7 shows the evolution of the 2D spatial profiles for the base case scenario with SW0NaCl. The core was originally saturated with oil, while the SW0NaCl solution was at the outside boundary of the core. Sulfate diffused into the core from the boundary. Over time, zones of high sulfate concentration expanded. Correspondingly, the water wet fraction of the core also expanded into the core and oil was produced from the boundary due to increasing spontaneous imbibition. Oil saturation decreased from the original 80-90% at the time zero to a range of 30-50% on day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to about 36% at the boundary and up to 70% at the center. At later times, the oil was produced slower primarily because of the decreasing positive capillary pressure. Na+ concentration was high early on because of the high initial water salinity. The brine inside the core became diluted during the imbibition process because seawater was depleted with NaCl. In this scenario, Na+ did not participate in sorption and acted as a tracer, the spatial evolution of which was only a result of the transport process. Compared to Na+, the $\text{SO}_4^{2-}$ propagation was slower because the transport was delayed by adsorption. The order of the propagation rate $(S_a + \text{WWF}C_{\text{SO}_4^{2-}} - C_{\text{Na}^+})$ reflects the driving force of the system: the solute diffusion perturbed the original surface chemical equilibrium, followed by altered wettability by the adsorption of sulfate, followed by water imbibition with a positive capillary pressure and oil production. The spatial profiles show high level of coherence, which demonstrates the tightly coupled multiphase and reactive transport within the core.

Fig. 8 shows the sulfate and water wet fraction profiles for SW. SW has seawater levels of NaCl while SW0NaCl has no NaCl. At any particular time, the water wet fraction at the altered locations was larger for SW0NaCl than SW, because there was more $\text{SO}_4^{2-}$ adsorbed on the surface in the SW0NaCl case than in the SW case. According to the extended Debye-Hückel model, the activity coefficients of aqueous species in SW0NaCl are larger because of a low total ionic strength. The activity coefficients vary with mixing of the formation water and the imbibing fluid. Before mixing, the activity coefficient of sulfate is 0.57 in SW0NaCl and 0.38 in SW. With the same concentration in SW0NaCl and SW, the activity of sulfate is 1.5 times greater in SW0NaCl than in SW. Therefore, more $\text{SO}_4^{2-}$ was adsorbed in the SW0NaCl case and the surface became more water wet. That is, high salinity leads to less wettability alteration and low salinity therefore achieves better improved oil recovery.

**Sensitivity Analysis.** The multiple processes involved here require a large number of parameters. Sensitivity analysis was carried out to understand the importance of various parameters in the SW0NaCl case, the most effective fluid in improving oil recovery compared to other brines in this research. As shown in Table 4, the tested parameters include specific surface area and surface site density of the chalk, diffusion coefficient, equilibrium constants, and the crude oil acid number.

Surface reaction equilibrium constants are important in determining the chemical equilibrium state and thus the surface wettability. The reported equilibrium constants of reactions (2), (3), (5), and (6) in the literature vary by orders of magnitude (Zhang and Sparks 1990; Hiorth et al. 2010; Brady and Krumhansl 2012). These reaction equilibrium constants are chosen to vary by 1 to 2 orders of magnitude for our sensitivity analysis because they represent the key interactions between ions ($\text{SO}_4^{2-}$,
**Ca^{2+}, Mg^{2+}** and interfaces (oil and solid).

**Fig. 9A** compares the oil recovery curves generated using different equilibrium constants. A larger $K_5$ means larger affinity of sulfate to the surface so that more sulfate can adsorb onto the solid surface. With the same surface site density, this will lead to a larger portion of sulfate-occupying surface sites, which therefore alters the rock surface to a more water wet state. As such, a larger capillary pressure is expected with a faster and greater oil recovery. **Fig. 9A** shows that with a $K_5$ value one order of magnitude larger, the ultimate oil recovery increased by 5% OOIP. In addition, the recovery rate was faster, because the increased water wettability increased the capillary pressure to larger positive values. When the $K_3$ value is one magnitude smaller than the base case, the wettability alteration is negligible, which leads to zero incremental oil recovery.

Larger equilibrium constants typically correspond to those under high temperature conditions. More sulfate is adsorbed on chalk with larger wettability-altering capacity under high temperature (Strand et al. 2008; RezaeiDoust et al. 2009). Our results here are consistent with the findings with the experimental results that low salinity seawater is more effective under high temperature conditions (Zhang et al. 2006).

The strength of the oil-rock bond was represented by $K_6$ because reaction (6) represents the interaction between the carboxylic group and chalk surface. A large $K_6$ value means oil has a larger tendency to attach onto the solid. **Fig. 9B** shows that smaller $K_6$ values lead to much greater oil recovery. The closeness between curves for the small and medium cases indicates that when the $K_6$ is small enough (less than $2.5 \times 10^5$), the recovery is not sensitive to the $K_6$ value.

**Figs. 9C and 9D** compare the oil recovery with different $K_2$ and $K_3$ values. The cations Ca$^{2+}$ and Mg$^{2+}$ compound with the carboxylic group on the oil surface and make the oil surface charge more neutral. The decrease of the negative charge enhances the oil release from the positively charged rock surface. The larger $K_2$ and $K_3$ values lead to a stronger tendency of Ca$^{2+}$ and Mg$^{2+}$ to attach onto the oil surface. **Figs. 9C and 9D** show negligible effects of $K_2$ and $K_3$. Ca$^{2+}$ and Mg$^{2+}$ have similar roles in the reaction system. Since there are sufficient divalent cations in the seawater, the cation compounding reaction is unlikely to be a limiting reaction. Therefore, reactions (2) and (3) play a relatively insignificant role compared to reactions (5) and (6).

**Fig. 10** shows the effect of the total number of surface sites (TSS) on oil recovery. The total number of surface sites was calculated as the product of chalk specific surface area (SSA, in units of m$^2$/g) and surface site density (SSD = number of sites/m$^2$). **Fig. 10** was obtained by varying the SSA with the same SSD. Varying SSD with the same SSA produces exactly the same plot. As observed from the figure, although the ultimate oil recovery is the same for all cases, a smaller TSS leads to faster oil recovery while a larger TSS leads to slower oil recovery. The difference is due to the difference in sulfate adsorption and transport. A larger TSS value means a larger number of surface sites to be occupied by sulfate for the same proportion of WWF. To reach the same wettability, more sulfate needs to be adsorbed and the wettability alteration takes a longer time. TSS, however, only controls the quantity of adsorbed mass and has no effect on the reaction equilibrium. The wettability alteration is the same with different TSS values and that leads to the same ultimate oil recovery.

The oil contains the carboxylic group (-COOH); larger acid numbers mean more -COOH to react with Ca$^{2+}$ and Mg$^{2+}$ and other aqueous species. The literature reports a range of surface density values between 3.1/nm$^2$ and 0.3/nm$^2$, which corresponds to acid numbers between 2.07 and 0.17 mg-KOH/g. **Fig. 11A** shows greater recovery with the smaller acid number. **Fig. 11B** shows the water wet fraction along the core radius for different acidic numbers in **Fig. 11B**. For the small AN, the core was altered to almost completely water wet (WWF=1) at the end of 20 days. For the large AN case, the water wet fraction is around 0.82. This difference leads to increases in the oil recovery curves. Such differences can be explained using reactions (1) and (6). Reaction 1 shows that larger -COOH concentration leads to larger H$^+$ and -COO$^-$ concentrations, which make the oil surface more negatively charged. With reaction (6), the increased -COO$^-$ concentration leads to more $>$CaOH$_2$(-COO). That is, more oil is adsorbed on the chalk surface, which results in a more oil wet chalk surface and less oil recovery. Therefore, a smaller acid number leads to a higher oil recovery (68% OOIP) than a larger acid number (59% OOIP). This is consistent with experimental observations in the literature (Zhang et al. 2005; Strand et al. 2006). If the oil does not contain acid at all, the rock is completely water wet and the spontaneous imbibition has the best recovery. However, in this case the salinity of water does not affect the oil recovery. To our best knowledge, the dependence on oil acidity was not included in any other low salinity models.

The impact of diffusion coefficient is shown in **Fig. 12A**. The diffusion coefficient is important because diffusion controls the transport rate of the ions into the rock at early time. **Fig. 12B** shows the corresponding sulfate concentration profile on the 10th day. Sulfate is transported faster with a larger diffusion coefficient, which led to more adsorbed sulfate earlier, and faster wettability alteration and oil recovery. However, the diffusion coefficient does not affect the ultimate wettability and oil recovery at 40 days.

From the sensitivity analysis, the parameters are classified into type I and type II according to their role in controlling the oil recovery curve. Type I controls how much oil can be recovered at 40 days. The parameters include the chemical equilibrium constants and crude oil acid number. Type II controls the rate of oil recovery. Type II parameters include the solid surface site density and diffusion coefficient. Most of these controlling variables (equilibrium constants, oil acidity and the diffusion coefficient) are temperature dependent, indicating the importance of temperature in the effectiveness of the chemically tuned waterfloods in carbonates.

**Effect of Brine Composition.** Here we use the parameters from the calibrated base case and compare five cases with different SO$_4^{2-}$ and Ca$^{2+}$ concentrations for the same core and crude oil. **Fig. 13** shows oil recovery curves for all cases. The labels for
the water composition are explained in the captions. Among these five cases, the SW0NaCl4SO4 case has the greatest oil recovery of about 65% OOIP.

The blue dashed curve (SW0NaCl0SO4) behaves the same as formation water, which means that if there is no sulfate in the water, there is no improved oil recovery. Without sulfate, the carboxylic group is stable on the rock surfaces and the system remains oil wet. With more sulfate in the seawater, the ultimate oil recovery increased (SW0NaCl4SO4) by 5% OOIP and the rate of the oil production was also faster. These results demonstrate the importance of sulfate in the wettability alteration process and is consistent with multiple experimental observations (Zhang et al. 2006; Fathi et al. 2011).

A decrease in oil recovery is also observed if we increase the aqueous salinity as SW0NaCl. The corresponding mechanism has been demonstrated in Fig. 7 and related paragraphs above. The role of salinity shown in the simulations is in agreement with existing experiments (Fathi et al. 2011). Increasing Ca\(^{2+}\) concentration has only a negligible effect as generally there is only a slight difference between SW0NaCl and SW0NaCl4Ca. This suggests that Ca\(^{2+}\) concentration is not a limiting quantity for SW0NaCl and there are abundant divalent cations in seawater. The marginal effects of Ca\(^{2+}\) were also observed in experiments (Fathi et al. 2011).

**Conclusion**

We developed a model to understand and predict wettability alteration and improved oil recovery for chemically tuned waterflooding in mixed wet carbonate reservoirs. The simulation results of spontaneous imbibition experiments demonstrated that our model can be used to describe accurately the benefits of chemically tuned water IOR. The model captured well the interplay of aqueous species like Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4^{2-}\), crude oil acidity and solid surface properties. The coupled mixed wettability and reactive transport model was capable of predicting the wettability alteration effects owing to chemical reactions. The oil recovery curves predicted for different brine compositions agreed well with experimental observations.

Our model improves the understanding of chemically tuned waterflooding and provides a powerful tool for future research. The findings also include:

- The surface complexation reactions control the wettability alteration process. The chemically tuned brine should be designed to promote oil component desorption from the rock. Moreover, because the oil recovery is sensitive to the equilibrium constants, the specific reservoir condition should be used in both experiments and simulation.
- There are two types of parameters. Type I controls the final wettability and ultimate oil recovery while type II controls the rate of wettability alteration and oil recovery. Type I includes the reaction equilibrium constants and crude oil acid number. Type II includes total surface sites of solid and diffusion coefficient.
- The concentration of ionic species, ionic strength and oil acidity all participate in the IOR process. The salinity should not be the single factor that assesses the effectiveness of the chemically tuned water.

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**Nomenclature**

- \(\alpha\) = phase subscript, w represent water phase and o represent oil phase
- \(\gamma_{ws}\) = the interfacial tension of the water-solid interface
- \(\gamma_{ow}\) = the interfacial tension of the oil-water interface
- \(\gamma_{os}\) = the interfacial tension of the oil-solid interface
- \(\gamma_i\) = the activity coefficient of species \(i\) (kg-water/mol)
- \(\varepsilon_0\) = the dielectric constant of water (55.3, unitless)
- \(\varepsilon_m\) = the permittivity of free space (8.854\times10^{-12} \text{ C V}^{-1} \text{d m}^{-1})
- \(\phi\) = porosity (dimensionless)
- \(\sigma_o\) = the charge density at the oil surface (C/m\(^2\))
- \(\theta\) = the contact angle
- \(\rho\) = density (kg/m\(^3\))
- \(\psi_o\) = the oil-water interface charge potential (mV)
- \(\psi_s\) = the solid-water interface potential (mV)
- \(\mu\) = viscosity (Poise)
- \(v_{pq}\) = the \((p,q)\) entry in the stoichiometry matrix
- \(A, B, b\) = temperature dependent parameters for the Debye-Huckel model
- \(a_{i}^{0}\) = the ion size parameter for Debye-Huckel model
- \(a_i\) = the activity of species \(i\) (unitless)
- \(C_{w_i}\) = the concentration for the species \(i\) in the aqueous phase (mol/m\(^3\))
- \(C_{w_o}\) = the concentration for the species \(i\) on the oil surface (mol/m\(^2\))
\( C_{i_s} \) = the concentration for the species \( i \) on the solid surface (mol/m²)
\( F \) = Farady’s constant (9.648 \times 10^4 \text{ C/mol})
\( F_p \) = molar rate of the primary species \( p \) (mol/m-day)
\( F_q \) = molar rate of the secondary species \( q \) (mol/m-day)
\( g \) = gravity factor (m/s²)
\( I \) = the ionic strength of water (mol/kg water)
\( k \) = permeability (mD)
\( k_r \) = relative permeability
\( K_{n,eq} \) = the equilibrium constant for the \( n \)th reaction (unitless)
\( M_p \) = molar density of the primary species \( p \) (mol/m³)
\( M_q \) = molar density of the secondary species \( q \) (mol/m³)
\( N_p \) = the number of the primary species
\( N_s \) = the total number of species
\( N_e \) = the number of equilibrium reactions
\( P \) = pressure (Pa)
\( P_c \) = the oil water capillary pressure
\( R \) = the gas constant (J/K·mol)
\( S \) = saturation (dimensionless)
\( T \) = the absolute temperature (Kelvin)
\( \nu \) = fluid volume flow rate (m³/day)
\( WWF \) = water wet fraction
\( z_i \) = the charge carried by the species \( i \)

References


Strand, S., Standnes, D. C. and Austad, T. 2006. New Wettability Test for Chalk Based on Chromatographic Separation of SCN<sup>&lt;</sup> 4<sup>&lt;</sup> and SO<sub>&lt;</sub> 4<sup>&lt;</sup> 2<sup>&lt;</sup>. Journal of Petroleum Science and Engineering 52(1): 187-197. http://dx.doi.org/10.1016/j.petrol.2006.03.021


Appendix A
This appendix derives the multiphase reactive transport equation, Eq. (5). For the aqueous species, the mass conservation equation for the primary species $i_w$ is as follows:

$$\frac{\partial}{\partial t} \left( \phi S_w \rho_w C_{i_w} \right) + \nabla \cdot \left( C_{i_w} \rho_w \vec{u}_w - D \nabla (S_w \rho_w C_{i_w}) \right) = R_{i_w}^{eq} + R_{i_w}^{kinetic}, i_w = 1, ..., n_w$$

(A-1)

For the water-solid interface species $i_{ws}$ and the oil-solid interface species $i_{os}$, the mass conservation equation is as follows:
\[
\frac{\partial}{\partial t} \left( (1 - \phi) \rho_s A_{ws} C_{i_{ws}} \right) = R^q_{ws} + R^{\text{kinetic}}_{ws}, \quad i_{ws} = 1, \ldots, n_{ws}
\]

(A-2)

\[
\frac{\partial}{\partial t} \left( (1 - \phi) \rho_s A_{os} C_{i_{os}} \right) = R^q_{os} + R^{\text{kinetic}}_{os}, \quad i_{os} = 1, \ldots, n_{os}
\]

(A-3)

For the oil–water interface species \(i_{ow}\), the mass conservation equation is as follows:

\[
\frac{\partial}{\partial t} \left( (1 - \phi) \rho_s A_{os} C_{i_{ow}} \right) = R^q_{ow} + R^{\text{kinetic}}_{ow}, \quad i_{ow} = 1, \ldots, n_{ow}
\]

(A-4)

where \(C_{i_{ws}}\) is the concentration of species \(i_w\) in aqueous phase (mol/kg water); \(C_{i_{os}}\) is the concentration of species \(i_{os}\) on oil-solid interface (mol/m²); \(C_{i_{ow}}\) is the concentration of species \(i_{ow}\) on oil-water interface (mol/m²); \(D\) is the diffusion/dispersion coefficient (m²/s); \(A_{ws}\) is the water-solid interface area (m²/g solid); \(A_{os}\) is the oil-solid interface area (m²/g solid); \(A_{ow}\) is the oil-brine interface area (m²/g solid). In Eq. (A-1), the first term is for mass accumulation, the second term is a transport term, which includes convection and diffusion, and the right hand side is the reaction term. The reaction rates are classified into equilibrium-controlled reaction rates and kinetically controlled reaction rates, denoted as \(R^q\) and \(R^{\text{kinetic}}\) (mol/s·kg water). These two terms can be the summation of multiple reaction rate terms, depending on the number of reactions that involves this species. Eqs. (A-2), (A-3) and (A-4) do not have the transport term because the interfaces are not mobile in our model.

The interface between brine and oil contains surface active sites as the polar components in crude oil hydrate, while the interface between brine and solid contains solid surface sites that contain polar ions (Buckley 1994; Buckley & Liu 1998; Hirasaki & Zhang 2004). The interface between the solid and oil phase is regarded as the part of the solid surface that is fully occupied with organic ion-containing sites. At the solid surface the competition between the oil and water species for the solid surface determines the proportion of the solid surface that is occupied by water and oil. This occupancy of solid surface sites determines the wettability.

The total solid surface area \((A_{os} + A_{ws})\) represents the total available surface area and is a constant calculated based on the specific surface area (SSA) of the rock. The total oil surface area \((A_{os} + A_{ow})\) may vary depending on oil saturation. We define the solid surface concentration \((C_{i,s})\):

\[
C_{i,s} = \begin{cases} 
\frac{A_{ws}}{A_s} C_{i_{ws}} & \text{when } i = i_{ws} \\
\frac{A_{os}}{A_s} C_{i_{os}} & \text{when } i = i_{os} 
\end{cases}
\]

The oil-water surface concentration can be defined similarly. Eqs. (A-2) – (A-4) can be rewritten as the mass conservation on the total solid surface and total oil surface, as

\[
\frac{\partial}{\partial t} \left( (1 - \phi) \rho_s A_{s} C_{i_s} \right) = R^q_{i_s} + R^{\text{kinetic}}_{i_s}
\]

(A-5)

\[
\frac{\partial}{\partial t} \left( (1 - \phi) \rho_s A_{o} C_{i_o} \right) = R^q_{i_o} + R^{\text{kinetic}}_{i_o}
\]

(A-6)

where \(C_{i_s}\) is the solid surface concentration that includes the oil-solid and water-solid species; \(C_{i_o}\) is the oil surface concentration that includes the oil-water species; \(A_s\) and \(A_o\) are the total surface areas of solid and oil. In this research, \(A_s\) is the total surface area and is calculated based on the specific surface area of the carbonate rocks, while \(A_o\) is a linear function of oil saturation.

We define the molar density of species \(i\) as

\[
M_{i} = \begin{cases} 
\phi S_w \rho_w C_{i_{ws}} & \text{for } i = i_{ws} \\
(1 - \phi) \rho_s A_s C_{i_s} & \text{for } i = i_s \\
(1 - \phi) \rho_s A_o C_{i_o} & \text{for } i = i_o
\end{cases}
\]

and the molar flow rate of species \(i\) as

\[
F_i = \begin{cases} 
C_{i_{aq}} \rho_w \bar{u}_w - D \nabla (S_w C_{i_{ws}}) & \text{for } i = i_{ws} \\
0 & \text{for } i = i_s \\
0 & \text{for } i = i_o
\end{cases}
\]
From these definitions we can write a general equation for the transport of chemical species
\[
\frac{\partial}{\partial t} M_i + \nabla \cdot F_i = \dot{R}_i\]
where all the reactions are assumed to be at equilibrium and the kinetic rates vanish. We followed the typical reactive transport formulation to partition the reactive species into primary and secondary species. The rate of production of a primary species \( p \) from the equilibrium reactions can be written as the total rates of production of secondary species
\[
\dot{R}_p^{eq} = - \sum_{q=1}^{N_{eq}} v_{qp} \dot{R}_q
\]
where \( v_{qp} \) represents the \((q,p)\) entry of the stoichiometry coefficient matrix. Here the primary species \( p \) or secondary species \( q \) can represent aqueous species, solid surface species or species on the oil-water interface. We can eliminate the reaction rates from Eqs. (A-1), (A-5), and (A-6) as
\[
\frac{\partial}{\partial t} \left( M_p + \sum_{q=1}^{N_{eq}} v_{qp} M_q \right) + \nabla \cdot \left( F_p + \sum_{q=1}^{N_{eq}} v_{qp} F_q \right) = 0, \quad p = 1, ..., n_p.
\]

**Appendix B**

One crucial step in our model is to relate surface geochemistry to surface contact angles. That relation was built by estimating interfacial tensions from a Gibbs isotherm. The contact angle was then estimated from Eq. (7). The change in interfacial tension can be quantified by the Gibbs adsorption equation (Gibbs 1926),
\[
d\gamma_{ws} = - \sum_i \Gamma_i d\mu_{i,ws}
\]
where \( d\gamma_{ws} \) is the differential change of the water and surface interfacial tension, \( \Gamma_i \) is the surface excess concentration of species \( i \) (mol/m²), and \( d\mu_{i,ws} \) is the differential change of the chemical potential of species \( i \) on the surface (kJ/mol). For surface-active species, the surface excess concentration \( \Gamma_i \) can be considered to be equal to the actual surface concentration without significant error (Rosen 2004), namely \( \Gamma_i = [i] \) where \([i]\) is the surface concentration of species \( i \) in mol/m². The chemical potential of surface species \( i \) can be calculated from
\[
\mu_{i,ws} = \mu_{i,ws}^0 + RT \ln a_{i,ws} = \mu_{i,ws}^0 + RT \ln([i])
\]
where \( \mu_{i,ws}^0 \) is the chemical potential of surface species \( i \) at a reference state. If we assume the activity coefficient \( \gamma_i \) has a weak dependence on the surface concentration \([i]\), then
\[
d\mu_{i,ws} = d(RT \ln (\gamma_i[i])) = RTd \left( \ln([i]) + \ln(i) \right) = \frac{RT}{[i]} d[i].
\]
Substitution of \( d\mu_{i,ws} \) into Eq. (B-1) gives
\[
d\gamma_{ws} = - \sum_i \frac{RT}{[i]} d[i] = -RT \sum_i d[i].
\]

**Equation (B-2)** indicates that the surface tension is linear with respect to the surface concentration. The above derivation is also valid for an oil-solid interface. In the low salinity flooding scenario, the change in \( \gamma_{ow} \) is not considered significant (Zhang et al. 2006). Therefore,
\[
d \cos \theta_w = d \left( \frac{\gamma_{os} - \gamma_{ws}}{\gamma_{ow}} \right) = \frac{d\gamma_{os} - d\gamma_{ws}}{\gamma_{ow}} = \frac{RT \sum_i d[i]}{\gamma_{ow}}.
\]

**Equation (B-3)** indicates that for an ideal system, \( \cos \theta \) is a linear function of surface concentration of sulfate. A linear interpolation can be used when we know extreme values of the contact angles. With \( \theta = \theta_o \) for fresh water and \( \theta = \theta_s \) for a sulfate surface concentration \( [Ca, total] \), at surface concentration of \( [CaSO_4] \) the effective contact angle is estimated by Eq. (8).
\[ \cos \theta_w = \cos \theta_0 + \frac{[CaSO_4^-]}{[Ca_{total}]} (\cos \theta_1 - \cos \theta_0). \]  

(8)

Table 1: The reaction network used, where “−” means the species on the oil-water interface, and “>” means the species on the solid surface. The remaining species are in the aqueous phase. All reactions are assumed to be at equilibrium.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reactions</th>
<th>( \log K_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil-water interface reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(-COOH \leftrightarrow -COO^- + H^+)</td>
<td>-3.98</td>
</tr>
<tr>
<td>2</td>
<td>(-COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+)</td>
<td>-2.20</td>
</tr>
<tr>
<td>3</td>
<td>(-COOH + Mg^{2+} \leftrightarrow -COOMg^+ + H^+)</td>
<td>-3.30</td>
</tr>
<tr>
<td>Solid-water interface reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&gt; CaOH^- + H^+ \leftrightarrow CaOH_2^-</td>
<td>9.81</td>
</tr>
<tr>
<td>5</td>
<td>&gt; CaOH_2^- + SO_4^{2-} \leftrightarrow CaSO_4^- + H_2O</td>
<td>3.30</td>
</tr>
<tr>
<td>6</td>
<td>&gt; CaOH_2^-(-COO^-) \leftrightarrow CaOH_2^- + -COO^-</td>
<td>-5.40</td>
</tr>
<tr>
<td>Aqueous phase reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(H_2O \leftrightarrow H^+ + OH^-)</td>
<td>-12.25</td>
</tr>
<tr>
<td>8</td>
<td>(HCO_3^- \leftrightarrow H^+ + CO_3^{2-})</td>
<td>-10.08</td>
</tr>
<tr>
<td>9</td>
<td>(H_2CO_3 \leftrightarrow H^+ + HCO_3^-)</td>
<td>-6.39</td>
</tr>
</tbody>
</table>

* The \( K_{eq} \) values are taken from literature. \( K_{eq} \) values for reaction (1)-(4) are from Brady et al. (2012); \( K_{eq} \) values for reaction (5) is from Hiorth et al. (2010) at 100 \(^\circ\)C; \( K_{eq} \) values (7)-(9) are from Wolery et al. (1990). The \( K_{eq} \) for reaction (6) is tuned to match the data.

Table 2: Corey’s relative permeability model parameters*

<table>
<thead>
<tr>
<th></th>
<th>( S_{wr} )</th>
<th>( S_{or} )</th>
<th>( k_{rw} )</th>
<th>( k_{ro} )</th>
<th>( n_w )</th>
<th>( n_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil wet</td>
<td>0.09</td>
<td>0.12</td>
<td>1</td>
<td>0.76</td>
<td>2.4</td>
<td>2</td>
</tr>
<tr>
<td>Water wet</td>
<td>0.09</td>
<td>0.12</td>
<td>0.3</td>
<td>0.60</td>
<td>2.4</td>
<td>2</td>
</tr>
</tbody>
</table>

* The oil wet data is from Hognesen et al. (2006). The water wet data was adjusted to represent a water-wet condition.

*Table 3: Synthetic brine compositions used in experiments (Fathi et al. 2010) and simulations.*

<table>
<thead>
<tr>
<th></th>
<th>FW</th>
<th>SW</th>
<th>SW0NaCl</th>
<th>SW0NaCl0SO4</th>
<th>SW0NaCl4SO4</th>
<th>SW0NaCl4Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO_3^-</td>
<td>0.009</td>
<td>0.020</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Cl^-</td>
<td>1.07</td>
<td>0.525</td>
<td>0.024</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>0</td>
<td>0.024</td>
<td>0.024</td>
<td>0</td>
<td>0.096</td>
<td>0.024</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.0008</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>0.029</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.052</td>
</tr>
<tr>
<td>Na^+</td>
<td>1.00</td>
<td>0.450</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>pH</td>
<td>8.4</td>
<td>8.1</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>Total Ionic Strength</td>
<td>2.198</td>
<td>1.305</td>
<td>0.506</td>
<td>0.410</td>
<td>0.794</td>
<td>0.662</td>
</tr>
</tbody>
</table>

* We use the same notation for different types of brine as those used in Fathi et al. (2010). FW denotes formation water; SW denotes seawater; SW0NaCl denotes seawater with no NaCl; SW0NaCl0SO4 denotes seawater with no NaCl nor SO_4^{2-}; SW0NaCl4SO4 denotes seawater with no NaCl and with the sulfate concentration adjusted to four times that of seawater; SW0NaCl4Ca denotes seawater with no NaCl but with the calcium concentration adjusted to four times that in seawater.
Table 4: Parameters used in sensitivity analysis. The value for $K_6$ was selected from the match of the base case as no such data was found in the literature. Other values selected are within the range from the literature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Medium</th>
<th>Large</th>
<th>Small</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area of chalk (m$^2$/g)</td>
<td>2 (Fathi et al. 2010)</td>
<td>4.8 (Holfordi et al. 1975)</td>
<td>0.2 (Borgwardt et al. 1986)</td>
</tr>
<tr>
<td>Chalk surface total site density (nm$^2$)</td>
<td>3 nm$^2$ (Brady et al. 2010)</td>
<td>5 nm$^2$ (Davis and Kent 1990)</td>
<td>2 nm$^2$ (Villalobos et al. 2001)</td>
</tr>
<tr>
<td>Oil surface site density (nm$^2$)</td>
<td>3 nm$^2$ for AN=1.9 mg KOH/g (Fathi et al. 2010)</td>
<td>3.3 nm$^2$ for AN=2.07 mg KOH/g (Zhang et al. 2005)</td>
<td>0.2 nm$^2$ for AN=0.17 mg KOH/g (Zhang et al. 2005)</td>
</tr>
<tr>
<td>Diffusion coefficient (m$^2$/s)</td>
<td>1.43 $\times 10^{-10}$ (Hill et al. 1984)</td>
<td>2.4 $\times 10^{-10}$ (Hill et al. 1984)</td>
<td>5.1 $\times 10^{-11}$ (Hill et al. 1984)</td>
</tr>
<tr>
<td>log($K_2$)</td>
<td>-2.2 (Brady et al. 2010)</td>
<td>-1.2</td>
<td>-3.2</td>
</tr>
<tr>
<td>log($K_3$)</td>
<td>-2.5 (Brady et al. 2010)</td>
<td>-1.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>log($K_5$)</td>
<td>3.4 (Brady et al. 2010)</td>
<td>4.4 (Hiorth et al. 2010)</td>
<td>2.4 (Hiorth et al. 2012)</td>
</tr>
<tr>
<td>log($K_6$)</td>
<td>5.4</td>
<td>6.4</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 1: Schematic diagram of the governing equations for multiphase flow (oil and water) and multi-component reactive transport. The two processes interact via solute transport and wettability alteration.

\[
\frac{\partial}{\partial t} (\phi S_w \rho_w) + \nabla \cdot (\rho_w \vec{u}_w) = 0
\]

\[
\frac{\partial}{\partial t} (\phi S_o \rho_o) + \nabla \cdot (\rho_o \vec{u}_o) = 0
\]

Solute transport $S_w, \vec{u}_w$

Wettability, relative permeability, and capillary pressure alteration $k_{rw}, k_{ro}, P_{cow}$

Reactive Transport

\[
\frac{\partial}{\partial t} \left( M_j + \sum_{i=1}^{N_{eq}} \nu_{ij} M_i \right) + \nabla \cdot \left( F_j + \sum_{i=1}^{N_{eq}} \nu_{ij} F_i \right) = 0
\]
Figure 2: Illustration of the multiphase reaction network in a pore of mixed wettability. (A) A mixed wet pore using a triangle model. (B) The ion species distribution on a water-wet surface. (C) The chemical ion species at the interfaces between crude oil, water, and solid.

Figure 3: Illustration of wettability dependent capillary pressure and relative permeability. (A) Relative permeability for oil wet (WWF=0), water wet (WWF =1) and an intermediate wettability (WWF=0.5). (B) Imbibition capillary pressure for oil wet, water wet and two intermediate states with different water wet fraction values, 0.52 and 0.82. Note in (B) the equilibrium water saturation under capillary pressure is the x-axis intercept. As the rock becomes more water wet, larger water saturation can be achieved by spontaneous imbibition.
Figure 4: Illustration of the flow chart for one time step in the IMPES solution.

Figure 5: Geometry of the model used in the experiments and simulations. The radial symmetry of the core allows for 2-D simulations instead of 3-D ones. The computational domain has 30 blocks in the radial $r$ direction and 100 grid blocks in the vertical $z$ direction. The gray blocks are boundary blocks with Dirichlet boundary conditions.
Figure 6: Comparison between experimental oil recovery and simulation results for formation water (FW), seawater (SW) and seawater depleted in NaCl (SW0NaCl) using three different simulation methods. The experimental data are the same for all cases and are represented using the symbols. Simulation A used fixed wettability functions adapted from Hogensen et al. (2006). Simulation B used a single adsorption reaction adapted from Yu et al. (2009). Simulation C used the model developed in this paper. Note that with simulation B, the curve for SW overlaps with the curves for SW0NaCl. Only (C) matches the trend in the experimental recovery curve for seawater.
Figure 7: Spatial and temporal evolution of the SO$_4^{2-}$, Na$^+$ concentrations, water wet fraction, and oil saturation for the imbibition of SW0NaCl. The horizontal axis is the radial distance from the center of the cylinder core and the vertical axis is the vertical distance from the base.
Figure 8: Spatial and temporal evolution of the $\text{SO}_4^{2-}$ surface concentration and water wet fraction for the imbibition of SW. The corresponding oil recovery curve is shown in Fig. 6(C). The comparison of this figure with Fig. 7 explains the recovery differences.
Figure 9: Oil recovery curves for different reaction equilibrium constant parameters for reactions (5) (A), (6) (B), (2) (C) and (3) (D). With the same brine compositions, the significant difference in the oil recovery illustrates that the chemical reactions are very important. The specific values of these parameters can be found in Table 4.

Figure 10: Oil recovery as a function of the total number of surface sites. A difference in the recovery rate is apparent around day 2. The ultimate recovery is the same however. The adsorbing capacity, represented by TSS, affects the recovery rate.
Figure 11: (A) Oil recovery as a function of the acid number (AN); (B) Water wet fraction profile along the radial direction at day 10. Crude oil acidity affects the wettability alteration and hence, oil recovery.

Figure 12: (A) Predicted oil recovery with different values of diffusion coefficients; (B) The sulfate aqueous concentration (mol/water kg) profile on day 10 for diffusion coefficient $1.43 \times 10^{-10}$ m$^2$/s; (C) The sulfate aqueous concentration (mol/water kg) profile on day 10 for diffusion coefficient $0.51 \times 10^{-11}$ m$^2$/s. The oil recovery rate (A) is very sensitive to the diffusion coefficient as the diffusion process dominates the solute transport (B) in these experiments.
Figure 13: Oil recovery prediction for five chemically tuned brines, where brine is the imbibing fluid at 110°C. A description of the abbreviations is shown in Table 3. Generally, the oil recovery at 40 days increases with the sulfate concentration and decreases with the total ionic strength. This is because there are adequate Ca$^{2+}$ and Mg$^{2+}$ in seawater so that adding those cations only has a marginal effect in such cases.