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

C. Qiao, L. Li, R.T. Johns, and J. Xu, Pennsylvania State University

Summary
Injection of chemically tuned brines into carbonate reservoirs has been reported to enhance oil recovery by 5–30% original oil in place (OOIP) in coreflooding 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, is challenging because the complex interactions among ions in the brine and crude oil on the solid surface. In this work, we developed a multiphase and multicomponent reactive transport model that explicitly takes into account wettability alteration from these geochemical interactions in carbonate reservoirs.

Published experimental data suggest 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, whereas cations (Ca$^{2+}$, Mg$^{2+}$) decrease the oil-surface potential.

The developed model was first tuned with experimental data from the Stevns Klint chalk and then used to predict oil recovery for additional untuned experiments under a variety of conditions where IOR increased by as much as 50% OOIP, depending on salinity and oil acidity. The numerical results showed that an increase in sulfate concentration can lead to an IOR of more than 40% OOIP, whereas cations such as Ca$^{2+}$ have a relatively minor effect on recovery (approximately 5% OOIP). Physical parameters, including the total surface area of the rock and the diffusion coefficients, control the rate of recovery, but not the final oil recovery. The simulation results further demonstrate that the optimum brine formulations 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 of 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. To the best of our knowledge, this is the first model that explicitly and mechanistically couples multiphase flow and multicomponent surface complexation with wettability alteration and oil recovery for carbonate rocks specifically.

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

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-wet 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 with oil-wet reservoirs. In addition, fractured rocks, a water-wet matrix allows for water imbibition and countercurrent 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 (Anderson 1987; Morrow 1990; Peters 2012). The relative proportion of oil-wet and water-wet surfaces determines the overall capillary pressure, relative permeability, and residual oil saturation (ROS), which ultimately control oil recovery (Anderson 1987; Ustohal et al. 1998; Delshad et al. 2003; O’Carroll et al. 2005). Low-salinity seawater has been found to increase the proportion of the water-wet surface during spontaneous imbibition experiments in the Stevns chalk (Strand et al. 2006a, 2006b; Puntervold and Austad 2008; Strand et al. 2008; Puntervold et al. 2009). Favorable contact-angle hysteresis was observed during injection of low-salinity brine containing sulfate (Alotaibi et al. 2010; Yousef et al. 2010; Gupta and Mohanty 2011; Yousef et al. 2011; Yousef et al. 2012a, 2012b, 2012c). 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 SO$_4^{2-}$, Ca$^{2+}$, and Mg$^{2+}$ ions actively participate in surface reactions that alter wettability (Strand et al. 2003, 2006a; 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 (RezaeDoust et al. 2009). According to this mechanism, experimental studies reported the optimal ionic composition for IOR 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 (Hjelmeland and Larrrondo 1986; Strand et al. 2006b; Zhang et al. 2007; Puntervold and Austad 2008; Strand et al. 2008; Puntervold et al. 2009; Fathi et al. 2011).

Significant advances have been made in recent years to predict wettability alteration and oil recovery (Hegnesen et al. 2006; Jer-auld et al. 2008; Yu et al. 2009; Evje and Hiorth 2011; Andersen...
Fig. 1—Schematic of the governing equations for multiphase flow (oil and water) and multicomponent reactive transport. The two processes interact by means of solute transport and wettability alteration.

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 implicit-pressure/explicit-concentration-formulated code (PennSim Toolkit 2013) to solve the coupled multiphase-transport and chemical-reaction equations in this research (Fig. 1). The mass-conservation equations for oil and water phases are solved for the pressure and saturation sequentially. The watsaturation 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:

\[
\partial_t (\phi S_\text{w} \rho_\text{w}) + \nabla \cdot (\rho_\text{w} \mathbf{u}_\text{w}) = 0, \quad z = a, \ w, \quad \ldots \ldots \ldots \ldots \quad (1)
\]

where \(\phi\) is porosity (dimensionless) and \(S_\text{w}, \rho_\text{w}\) and \(\mathbf{u}_\text{w}\) are the saturation (dimensionless), fluid density (kg/m³), and volumetric flow rates (m³/s), respectively, 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:

\[
\mathbf{u}_\text{w} = \frac{k_{rw}}{\mu_\text{w}} \nabla (P_\text{w} - \rho_\text{w} g Z), \quad \ldots \ldots \ldots \ldots \quad (2)
\]

where \(k\) is absolute permeability (m²); \(Z\) is the depth (m); \(\mu\) and \(P\) are the viscosity (cp), gravitational constant (m²/s²), and the pressure of the fluid phase (Pa), respectively. The pressure difference between oil and water phases is the capillary pressure:

\[
P_{\text{cow}} = P_\text{o} - P_\text{w} \quad \ldots \ldots \ldots \ldots \quad (3)
\]

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

\[
S_o + S_w = 1 \quad \ldots \ldots \ldots \ldots \quad (4)
\]

The unknowns for the multiphase-flow system are the pressure and saturation of the different fluid phases.

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 and Lasaga 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 concentrations of the secondary species can be explicitly expressed by those of the primary species through the mass-action law (Lichtner et al. 1996). The mass-conservation equation for the primary species \( p \) is

\[
\frac{\partial}{\partial t} \left( M_p + \sum_{q=1}^{N_{sec}} \nu_{pq} M_q \right) + \nabla \cdot \left( F_p + \sum_{q=1}^{N_{sec}} \nu_{pq} F_q \right) = 0;
\]

where subscripts \( p \) and \( q \) represent the primary species \( p \) and secondary species \( q \) and \( \nu_{pq} \) represents the \((q,p)\) entry of the stoichiometry coefficient matrix. The number of primary species \( N_p \) equals \( N_{tot} - N_{sec} \), where \( N_{tot} \) is the total number of species and \( N_{sec} \) is the number of secondary 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 equations includes the aqueous-species concentration \( C_{i,a} \), the solid-surface-species concentration \( C_{i,s} \), and the oil-surface-species concentration \( C_{i,o} \), where the subscript \( i \) represents a species. Details of the reactive-transport-modeling formulation can be found in Yeh and Tripathi (1991), Steefel and Lasaga (1994), and Walter et al. (1994). The system of general equations is coupled with the mass-action law discussed later.

**Multiphase Reaction Network.** As illustrated in Fig. 2, the reaction network includes the interactions among \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{SO}_4^{2-} \), 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). 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. All aqueous reactions are fast and are assumed to be at equilibrium and are controlled by reaction thermodynamics (Lichtner et al. 1996; Langmuir 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 improved-oil-recovery (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 2005a). 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 through 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 and Morel 1990). The expression for the equilibrium constant of Reaction 2 is shown as an example:

\[
K_{eq} = \frac{\exp \left( \frac{F \psi_o}{RT} \right) \cdot [-\text{COOCa}^+] \cdot a_{H^+}}{[-\text{COOH}] \cdot a_{\text{Ca}^{2+}}},
\]

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

\[
\sigma_o = -\sqrt{8q_0 \ite^2 \text{mRT}} \sinh \left( \frac{-F \psi_o}{2RT} \right),
\]

where \( \sigma_o \) is the charge density at the oil/water interface \((\text{C/m}^2)\) calculated from \( \sigma_o = \sum z_i C_{i,o} \), where \( z_i \) is the charge carried by ion species \( i \); \( q_0 \) is the dielectric constant of water \((55.3, \text{ dimensionless})\); \( \ite\) is the permittivity of free space \( (8.854 \times 10^{-13} \text{ C/V} \cdot \text{m}) \); and \( I \) is the ionic strength of water \((\text{mol/kg water})\). The solid-surface potential can be calculated in a similar manner. The calculation follows the same method of Hoorth 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 \( >\text{CaOH} \) represents the reactive site on the calcite surface because \( >\text{CaOH}^- \) 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 et al. 2008; Fathi et al. 2010). Here we use the data...
interpolated from Evje and Hjorth (2011). Similar to the oil/water-interface reactions, the equilibrium constants of Reaction 5 can be written as

\[ K_5 = \exp \left( \frac{F \psi_s}{RT} \right) \frac{[> \text{CaSO}_4]}{[\text{CaOH}_2][\text{SO}_4^{2-}]} \]

where \( \psi_s \) is the solid/water-interface potential (mV), which can be calculated similarly to \( \psi_w \). Experimental results show that Ca\(^{2+}\), Mg\(^{2+}\), and SO\(_4^{2-}\) control surface potential, but Ca\(^{2+}\) or Mg\(^{2+}\) alone without SO\(_4^{2-}\) cannot alter wettability (Zhang et al. 2007). SO\(_4^{2-}\) alone, however, cannot alter wettability either (Strand et al. 2006a; Zhang et al. 2007). Reactions 1 through 5 show that SO\(_4^{2-}\) determines the potential at the solid surface, whereas 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 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), whereas 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 through 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, whereas a chalk surface is known to be positively charged, as shown in Reaction 4 (Hjorth et al. 2010). The electrostatic attraction between opposite charges leads to the oil sorption on the solid surface (Nasralla and Nasr-Elf-Din 2012). Those reactions represent the competitive adsorption of carboxylic acids and SO\(_4^{2-}\) on the chalk/water interface and the competitive compounding of Ca\(^{2+}\), Mg\(^{2+}\), and >CaO\(_{12}\) on the oil/water interface. Reactions 7 through 9 are aqueous-speciation reactions that are also important in determining pH. For all aqueous species (Ca\(^{2+}\), Mg\(^{2+}\), H\(^+\), and others), 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):

\[ \ln \gamma_i = - \frac{2A_i^2 \sqrt{I}}{1 + d_i^2 B \sqrt{I}} + b_i \]

where the parameters \( A, B, \) and \( b \) are temperature-dependent parameters taken from the EQ3 database (Wolery et al. 1990). The parameter \( d_i \) is the ion size, 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-Altention Model.
Most carbonate reservoirs are classified as having 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-contact angles (altered, water-wet) and advancing-contact angles (unaltered, oil-wet) varied in core experiments (Buckley et al. 1996; Drummond and Israelachvili 2004; Zhang and Austad 2005a; Aloaibi et al. 2010). According to Young’s equation, the contact angle has the following relation derived from the force balance:

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

where \( \gamma_{ow}, \gamma_{ws}, \) and \( \gamma_{ow} \) are the interfacial tension (IFT) (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 IFTs are determined by the surface concentration of ion species through Gibbs equation (Gibbs 1948). 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 surfaces of carbonates, which is justified in Appendix B, where the derivation is modeled after the Gibbs isotherm. The linear interpolation is shown in Eqs. 8 and 9:

\[ \cos \theta_{ow} = \cos \theta_{ow,0} + \frac{[> \text{CaSO}_4]}{[> \text{Ca}, \text{total}]} (\cos \theta_{ow,1} - \cos \theta_{ow,0}) \]

\[ \cos \theta_{ws} = \cos \theta_{ws,0} + \frac{[> \text{CaSO}_4](-\text{COO}^-)}{[> \text{Ca}, \text{total}]} (\cos \theta_{ws,1} - \cos \theta_{ws,0}) \]

where \([> \text{Ca}, \text{total}]\) represents the total concentration of the surface site on the carbonate surface. The contact angle \( \theta_{ow} \) on the water-wet surface (receding-contact angle) is interpolated by the concentration of the water-wet agent (saltate). The oil-wet contact angle \( \theta_{ws} \) (advancing-contact angle) is interpolated by the oil-wet agent (carboxylic group). The contact angles \( \theta_{ow,0}, \theta_{ow,1}, \theta_{ws,0}, \) and \( \theta_{ws,1} \) are input values representing the extreme cases (0 and 90° for water-wet, 90 and 150° for oil-wet).

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

\[ \text{WWF} = 1 - \frac{[> \text{CaSO}_4](-\text{COO}^-)}{[> \text{Ca}, \text{total}]} \]

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

\[ P_c(S_w, \text{WWF}) = \text{WWF} \cos \theta_{w} P_{c, w}^{\text{ww}}(S_w) \]
\[ + (1 - \text{WWF}) \cos \theta_{o} P_{c, o}^{\text{ww}}(S_w) \]  \hspace{1cm} (10)

where \( P_{c, w}^{\text{ww}}(S_w) \) and \( P_{c, o}^{\text{ww}}(S_w) \) are the capillary pressure functions for completely 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 et al. 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 are from Webb et al. (2005). The curves for intermediate wetting state were obtained by use of 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 (ROS) 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 et al. 2009). The relative permeability was assumed to depend on the endpoint relative permeability and relative saturation using the following equations:

\[ k_{ro} = k_{ro}^*(S^*)^{n_o} \]
\[ k_{rw} = k_{rw}^*(S^*)^{n_w} \]

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

\[ S^* = \frac{S_o - S_w}{1 - S_{nw} - S_w} \]

where \( S_{nw} \) is the initial water saturation and \( S_{nw} \) is the ROS. For the mixed and fractional wettability, the fluids were assumed to flow in parallel in both oil-wet and water-wet pore networks. Therefore, WWF was also used to linearly interpolate the relative permeability between completely water-wet and oil-wet cases, as follows:

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

where \( k_{ro, \text{ww}}^* \), \( k_{ro, \text{ow}}^* \), \( k_{rw, \text{ww}}^* \), and \( k_{rw, \text{ow}}^* \) are the oil and water endpoint relative permeability for the oil-wet or water-wet case. One set of relative permeability curves is shown in Fig. 3b, with the corresponding parameters (endpoint relative permeability and Corey exponent) in Table 2. In Fig. 3b, the oil-wet relative permeability function was adapted from Høgnesen et al. 2006. Increasing water wettability shifts the curves to the right, which favors 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 a noniterative implicit-pressure/explicit-concentration method (Coats 2000) 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 timestep size (Zysset et al. 1994). The calculation procedure for one timestep is shown in Fig. 4.

**Results and Discussion**

This section presents a validation of the model by use of the base-case scenario, sensitivity analyses of key 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.

**Table 2**—Corey’s relative permeability model parameters.

<table>
<thead>
<tr>
<th></th>
<th>( S_o )</th>
<th>( S_{nw} )</th>
<th>( n_o )</th>
<th>( n_w )</th>
<th>( k_{ro} )</th>
<th>( k_{rw} )</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 are from Høgnesen et al. (2006). The water-wet data were adjusted to represent a water-wet condition.

Fig. 3—Illustration of wettability-dependent capillary pressure and relative permeability. (a) Relative permeability for oil-wet (WWF = 0), water-wet (WWF = 1), and intermediate-wettability (WWF = 0.5) state. (b) Imbibition capillary pressure for oil-wet, water-wet, and two intermediate states with different WWF values: 0.52 and 0.82. Note that 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.

\[ P_c = \frac{\sigma_{w} - \sigma_{o}}{\cos \theta_{w} - \cos \theta_{o}} \]

\[ P_c = \frac{\sigma_{w} - \sigma_{o}}{\cos \theta_{w} - \cos \theta_{o}} \]

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Various core experiments have been performed to understand the mechanism and identify the optimal conditions for chemically tuned waterflooding (Austad et al. 2008; Fathi et al. 2010; Yousef et al. 2010, 2012a, 2012b). We used the data from Fathi et al. (2010) to validate our model and to obtain key parameters. We selected this data set because their experiments were consistently carried out at 110°C with different brine compositions while maintaining all other conditions, which allows easy comparison among different cases.

The experiments used homogeneous Stevns Klint chalk cores (3.8 cm in diameter and 7.0 cm in length) with porosity of approximately 45% and permeability between 1 and 2 md. 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 the initial water saturation. The oil used was diluted 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 4 weeks to restore to the reservoir condition, where mixed wettability has been established. The cores were then immersed in synthetic brine at 110°C, after which spontaneous imbibition began. The produced oil was collected over time, after which chromatographic wettability tests were performed to determine the water-wet fraction. Three different synthetic brines were used, including formation water (FW), seawater (SW), and seawater depleted in NaCl (SW0NaCl), as listed in Table 3. The comparison among cases allows identification of the important ions during the low-salinity-imbibition process.

During the spontaneous imbibition, the ions in the immersing brine were transported and diffused into the core. The chemical reactions altered the wettability and improved imbibition. Spontaneous imbibition causes countercurrent 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 through 5 with Dirichlet boundary conditions. The boundary pressure for both phases was set to be the backpressure; the boundary saturation for water was 1.0; and the brine concentration on the boundary was set to be the same as the imbibing fluid. The initial oil saturation determined from the experiments was used and the water-phase pressure was the same as the backpressure, whereas the oil-phase pressure was calculated from the capillary pressure relation in Eq. 3. The fluid initial water composition was the same as the formation water.

We performed 2D simulations by use of the radial symmetry of the core, where the core was discretized into 30 x 100 grid-blocks in the r, z coordinates, as shown in Fig. 5. Fig. 6 compares the oil-recovery data and the modeling output. The reaction-equilibrium $K_r$ value was tuned to match the base case. Here, we compare three methods of different levels of complexity in reproducing the oil recovery by use of brines of different composition. Method A was modeled after Høgnesen 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; and intermediate-wet functions were used for SW. These functions were chosen on the basis of our understanding of the wettability with respect to different water compositions. Method B includes the transport and adsorption reaction of SO$_2^-$ as the single reacting solute and calculates the wettability as a function of the adsorbed sulfate mass (Yu et al. 2009). The capillary pressure and relative permeability functions were obtained by interpolation by use of the equations $k_r = WWF \cdot k_r^{WWF}$ and $P_w = WWF \cdot P_w^{WWF}$, where WWF is calculated from the solid-surface fraction of sulfate ions (i.e., $C_{SO_2^-}/C_{total}$). The sulfate-adsorption reaction was modeled with the Langmuir isotherm without the effect of salinity. Method C is our mechanistic method with PennSim, 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. In the FW case, with fixed wettability, Method A reproduced the countercurrent flow and the subsequent oil production for the FW case. However, it overestimated the oil-production rates for SW and SW0NaCl when wettability alteration occurred. Method B cannot distinguish between the SW and SW0NaCl cases, as indicated by their overlapping oil-recovery curves. This is because of the over-simplified representation by use of a single component and single reaction. PennSim accurately matched the oil-recovery curves for the FW and SW0NaCl cases, and predicted approximately the recovery curve for SW (Fig. 6c). Our model reproduced the oil-

![Flow Chart](Image)
recovery decrease with increasing NaCl concentration for SW and SW0NaCl. Moreover, our model reproduced the measured wetting-area fraction 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. 2006a; Fathi et al. 2010).

Fig. 7 shows the profile evolution for the base-case scenario with SW0NaCl. The core was originally saturated with oil, whereas 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 because of increasing spontaneous imbibition. Oil saturation decreased from the initial 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50% on Day 20. The change occurred faster in the first 10 days, with the oil saturation reduced to 80–90% to a range of 30–50%

These reaction equilibrium constants are chosen to vary by one to two orders of magnitude in our sensitivity analysis. The multiple processes involve a large number of parameters. A sensitivity analysis was performed to understand the importance of different processes and parameters in the SW0NaCl case, and the most-effective fluid in improving oil recovery was compared with other types of 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 one to two orders of magnitude in our sensitivity analysis. Fig. 9a compares the oil-recovery curves generated by use of different equilibrium constants. A larger $K_r$ 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

<table>
<thead>
<tr>
<th>Species (mol/kg water)</th>
<th>FW</th>
<th>SW</th>
<th>SW0NaCl</th>
<th>SW0NaClSO4</th>
<th>SW0NaCl4SO4</th>
<th>SW0NaCl4Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$</td>
<td>0.009</td>
<td>0.002</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>0.126</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>Na$^+$</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>0.025</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>8.4</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>

Table 3— Synthetic-brine compositions used in experiments (Fathi et al. 2010) and simulations. 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; SW0NaClSO4 denotes seawater with no NaCl or SO$_4^{2-}$; SW0NaCl4SO4 denotes seawater with no NaCl and with the sulfate concentration adjusted to four times that of seawater; and SW0NaCl4Ca denotes seawater with no NaCl but with the calcium concentration adjusted to four times that in seawater.

**Sensitivity Analysis.** The multiple processes involve a large number of parameters. A sensitivity analysis was performed to understand the importance of different processes and parameters in the SW0NaCl case, and the most-effective fluid in improving oil recovery was compared with other types of brines in this research. As shown in Fig. 9a, 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 one to two orders of magnitude in our sensitivity analysis. Fig. 9a compares the oil-recovery curves generated by use of different equilibrium constants. A larger $K_r$ 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
oil recovery. However, in this case the salinity of water does not affect wettability alteration more oil-wet chalk surface and less oil recovery. Therefore, a smaller AN leads to a higher oil recovery (68% OOIP) than a larger AN (59% OOIP). This is consistent with experimental observations in the literature (Zhang and Austad 2005a; Strand et al. 2006a). 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 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. All diffusion coefficients lead to the same oil recovery on Day 80. The diffusion coefficient is important because diffusion controls the transport rate of the ions into the rock. Fig. 12b shows the corresponding sulfate-concentration profile on Day 10. Sulfate was 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 parameters control the ultimate amount of oil recovery. These include the chemical-equilibrium constants and crude-oil AN. Type II parameters, including the solid-
surface-site density and diffusion coefficient, control the rate of oil recovery. 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 predictions for five cases with different SO\textsubscript{4}\textsuperscript{2−} and Ca\textsuperscript{2+} concentrations for the same core and crude oil. Fig. 13 shows oil-recovery curves for all cases. Among these five cases, the SW\textsubscript{0NaCl4SO\textsubscript{4}} case has the greatest oil recovery of approximately 65% OOIP. The SW\textsubscript{0NaCl0SO\textsubscript{4}} case behaves the same as formation water, indicating no improved oil recovery without the presence of sulfate. Without sulfate, the carboxylic group is stable on the rock surfaces and the system remains oil-wet. With more

Fig. 7—Spatial and temporal evolution of the SO\textsubscript{4}\textsuperscript{2−}, Na\textsuperscript{+} 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.
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 are consistent with multiple experimental observations (Zhang et al. 2006; Fathie et al. 2011).

A decrease in oil recovery is observed with increased aqueous salinity, which is consistent with Fig. 7 and with experimental

![Fig. 8—Spatial and temporal evolution of the SO\(_2\) surface concentration, water-wet fraction, and oil saturation for the imbibition of SW. The corresponding oil-recovery curve is shown in Fig. 6c. The comparison of this figure with Fig. 7 explains the recovery differences.](image)

A decrease in oil recovery is observed with increased aqueous salinity, which is consistent with Fig. 7 and with experimental

<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</td>
<td>2.0 (Fathi et al. 2010)</td>
<td>4.8 (Holford et al. 1975)</td>
<td>0.2 (Borgwardt et al. 1986)</td>
</tr>
<tr>
<td>Chalk-surface total site density</td>
<td>3.0 nm(^2) (Brady et al. 2012)</td>
<td>5.0 nm(^2) (Davis and Kent 1990)</td>
<td>2.0 nm(^2) (Villalobos et al. 2001)</td>
</tr>
<tr>
<td>Oil-surface site density (nm(^2))</td>
<td>3.0 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 and Austad 2005a)</td>
<td>0.2 nm(^2) for AN = 0.17 mg-KOH/g (Zhang and Austad 2005a)</td>
</tr>
<tr>
<td>Diffusion coefficient (m(^2)/s)</td>
<td>1.43×10(^{-10}) (Hill 1984)</td>
<td>2.40×10(^{-10}) (Hill 1984)</td>
<td>5.10×10(^{-11}) (Hill 1984)</td>
</tr>
<tr>
<td>(\log K)(_{2})</td>
<td>−2.2 (Brady et al. 2012)</td>
<td>−1.2</td>
<td>−3.2</td>
</tr>
<tr>
<td>(\log K)(_{3})</td>
<td>−2.5 (Brady et al. 2012)</td>
<td>−1.5</td>
<td>−3.5</td>
</tr>
<tr>
<td>(\log K)(_{6})</td>
<td>3.4 (Brady et al. 2012)</td>
<td>4.4 (Megawati et al. 2013)</td>
<td>2.4 (Hioth et al. 2010)</td>
</tr>
<tr>
<td>(\log K)(_{5})</td>
<td>5.4</td>
<td>6.4</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 4—Parameters used in sensitivity analysis. The value for \(K\)\(_{6}\) was selected from the match of the base case because no such data were found in the literature. Other values selected are within the range from the literature.
Increasing Ca\(^{2+}\) concentration has a negligible effect, suggesting that Ca\(^{2+}\) concentration is not a limiting quantity for SW0NaCl and there are abundant divalent cations in seawater. Similar marginal effects of Ca\(^{2+}\) were also observed in experiments (Fathi et al. 2011).

**Limitations and Potential Improvements.** In the model validation in Fig. 6, the oil-recovery curves were matched for FW and SW0NaCl, whereas the oil recovery for SW was predicted. There are two main differences between the model prediction and experimental data. First, the predicted oil recovery for SW is larger than the experimental data in the first 5 days. There are multiple reasons that could have caused the discrepancy. The lack of the measured specific imbibition capillary pressure function for limiting wettability cases could be one reason for the discrepancy. Another possible factor is numerical diffusion introduced by the low-order finite-volume discretization. Numerical diffusion causes additional mixing between the imbibing and connate fluids and may overestimate the rates of wettability alteration. In addition, the ions were assumed to have the same diffusion coefficient. However, small ions such as Na\(^+\) can diffuse faster than large ions such as SO\(_4\)^{2-}. Surface adsorption/desorption reactions could also be dominated by kinetic effects, which violates the reaction-equilibrium assumption (Bruegger et al. 1988; Fuller et al. 1993). All these factors could lead to the mismatch of the oil-recovery rate in the first 5 days.

Second, the final oil-recovery factor for SW is underestimated. This can be because of the lack of accurate surface-chemistry data. Reaction 6 used in this model was not validated by experiments, but instead was tuned to provide a good match of the simulated data to the experiments. Whether the acidic-oil-component adsorption obeys the mass-action law is not clear. The diffusive-layer model used to predict the effect of surface potential on carboxylic-group adsorption could also be a constraint of the model. An independent measurement of the key reaction-equilibrium constant \(K_6\) could allow a conclusive validation of the model. Also, the relative permeability and capillary pressure data specific to the core experiments (at the initial wettability and final wettability) will lead to a complete validation of this model and better understanding of the system.

**Fig. 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 solid/water interface reactions (5 and 6) are very important. The specific values of these parameters can be found in Table 4.

**Fig. 10**—Oil recovery as a function of the total number of surface sites. A difference in the recovery rate is apparent at approximately Day 2. The ultimate recovery is the same, however. The adsorbing capacity, represented by TSS, affects the recovery rate.
Conclusion

We developed a model to understand and predict wettability alteration and improved oil recovery (IOR) 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 the complex interactions among different phases and species involved in chemically tuned water IOR. The model captured the interplay among aqueous species (Ca$^{2+}$, Mg$^{2+}$, SO$_4$$^2-$, CO$_3^{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 showed good consistency with experimental observations.

Our model improves the understanding of and provides a powerful tool for chemically tuned waterflooding. The findings 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, whereas Type II controls the rate of wettability alteration and rate of oil recovery. Type I includes the reaction-equilibrium constants and crude-oil acid number. Type II includes total surface sites of solid and the diffusion coefficient.
- The concentrations of ionic species, ionic strength, and oil acidity are important in the IOR process. The salinity should not be the single factor that is used to assess the effectiveness of the chemically tuned water.

Fig. 11—(a) Oil recovery as a function of the AN. (b) Water-wet fraction profile along the radial direction at Day 10. Crude-oil acidity affects the wettability alteration and oil recovery.

Fig. 12—(a) Predicted oil recovery with different values of diffusion coefficients. (b) The sulfate concentration in the aqueous phase (mol/kg water) profile on Day 10 for diffusion coefficient $1.43 \times 10^{-10}$ m$^2$/s. (c) The sulfate concentration in the aqueous phase (mol/kg water) profile on Day 10 for diffusion coefficient $5.1 \times 10^{-11}$ m$^2$/s. The oil-recovery rate (a) is very sensitive to the diffusion coefficient because the diffusion process dominates the solute transport (b) in these experiments.

Fig. 13—Oil-recovery prediction for five chemically tuned brines, where brine is the imbibing fluid at 110$^\circ$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.
Nomenclature

\[ a_i \] = the activity of species \( i \), dimensionless

\[ d_i^0 \] = the ion-size parameter for Debye-Hückel model

\( A_{ot} \) = area of the oil/solid interface, \( \text{m}^2 \)

\( A_{ow} \) = area of the oil/solid interface, \( \text{m}^2 \)

\( A_{ws} \) = area of the water/solid interface, \( \text{m}^2 \)

\( C_{i_s} \) = the concentration for the species \( i \), on the oil surface, \( \text{mol/m}^2 \)

\( C_{i_s} \) = the concentration for the species \( i \), on the solid surface, \( \text{mol/m}^2 \)

\( C_{i_w} \) = the concentration for the species \( i \), in the aqueous phase, \( \text{mol/m}^3 \)

\( D \) = diffusion coefficient, \( \text{m}^2/\text{s} \)

\( F \) = Faraday's constant, \( 9.648 \times 10^4 \text{C/mol} \)

\( F_p \) = molar rate of the primary species \( p \), mol/m·d

\( F_q \) = molar rate of the secondary species \( q \), mol/m·d

\( g \) = gravity factor, \( \text{m/s}^2 \)

\( I \) = the ionic strength of water, \( \text{mol/kg water} \)

\( k \) = permeability, \( \text{md} \)

\( k_r \) = relative permeability

\( K_{eq} \) = the equilibrium constant for the \( n \)th reaction, unitless

\( M_p \) = molar density of the primary species \( p \), \( \text{mol/m}^3 \)

\( M_q \) = molar density of the secondary species \( q \), \( \text{mol/m}^3 \)

\( N_p \) = the number of the primary species

\( N_{oc} \) = the number of secondary reactions

\( N_{tot} \) = the total number of species

\( P \) = pressure, \( \text{Pa} \)

\( P_r \) = the oil/water capillary pressure

\( R \) = the gas constant, \( \text{J/K} \cdot \text{mol} \)

\( R_i \) = reaction rate for the species \( i \), mol/m·s

\( S \) = saturation, dimensionless

\( T \) = the absolute temperature, \( \text{K} \)

\( u_i \) = fluid-volume flow rate, \( \text{m}^3/\text{d} \)

\( z_i \) = the charge carried by the species \( i \)

\( \alpha \) = phase subscript, \( w \), representing water phase and \( o \), representing oil phase

\( \gamma_i \) = the activity coefficient of species \( i \), \( \text{kg water/mol} \)

\( \gamma_{if} \) = the interfacial tension (IFT) of the oil/solid interface, \( \text{dynes/cm} \)

\( \gamma_{ow} \) = the IFT of the oil/water interface, \( \text{dynes/cm} \)

\( \gamma_{ws} \) = the IFT of the water/solid interface, \( \text{dynes/cm} \)

\( \varepsilon_0 \) = the dielectric constant of water, 55.3, dimensionless

\( \varepsilon_{ow} \) = the permittivity of free space, \( 8.854 \times 10^{-13} \text{C} \cdot \text{V}^{-1} \cdot \text{dm}^{-1} \)

\( \theta \) = the contact angle, degrees

\( \mu \) = viscosity, poise

\( \mu_i \) = chemical potential of species \( i \), \( \text{J/mol} \)

\( v_{pq} \) = the \( (q, p) \) entry in the stoichiometry matrix

\( \rho \) = density, \( \text{kg/m}^3 \)

\( \sigma_o \) = the charge density at the oil surface, \( \text{C/m}^2 \)

\( \phi \) = porosity, dimensionless

\( \psi_w \) = the oil/water-interface-charge-potential, \( \text{mV} \)

\( \psi_s \) = the solid/water-interface-charge-potential, \( \text{mV} \)

Acknowledgments

The authors gratefully thank the member companies of the Enhanced Oil Recovery JIP in the EMS Energy Institute at Pennsylvania State University at University Park, Pennsylvania, for their financial support.

References


Appendix A: Mass Conservation for Multiphase Reactive Transport System

This appendix derives the multiphase reactive-transport equation, Eq. 5. For the aqueous species, the mass-conservation equation for the primary species $i_a$ is

$$\frac{\partial}{\partial t} \left[ \phi S_v \rho_a C_{i_a} \right] + \nabla \cdot [ \mathbf{J}_a ] - D^v \nabla ( \rho_a C_{i_a} ) = R_{i_a}^{\text{eq}} + R_{i_a}^{\text{kinetic}} \quad i_a = 1, \ldots, n_{iw} \quad (A-1)$$

For the water/solid-interface species $i_{ws}$ and the oil/solid-interface species $i_{os}$, the mass-conservation equation is

$$\frac{\partial}{\partial t} \left[ (1 - \phi) \rho_{ws} C_{i_{ws}} \right] = R_{i_{ws}}^{\text{eq}} + R_{i_{ws}}^{\text{kinetic}} \quad i_{ws} = 1, \ldots, n_{ws} \quad (A-2)$$

$$\frac{\partial}{\partial t} \left[ (1 - \phi) \rho_{os} C_{i_{os}} \right] = R_{i_{os}}^{\text{eq}} + R_{i_{os}}^{\text{kinetic}} \quad i_{os} = 1, \ldots, n_{os} \quad (A-3)$$

For the oil/water-interface species $i_{ow}$, the mass-conservation equation is

$$\frac{\partial}{\partial t} \left[ (1 - \phi) \rho_{ow} C_{i_{ow}} \right] = R_{i_{ow}}^{\text{eq}} + R_{i_{ow}}^{\text{kinetic}} \quad i_{ow} = 1, \ldots, n_{ow} \quad (A-4)$$
where $C_i$ is the concentration of species $i$ in aqueous phase (mol/kg water); $C_{i,w}$ is the concentration of species $i$ on water/solid interface (mol/m$^2$); $C_{i,s}$ is the concentration of species $i$ on oil/solid interface (mol/m$^2$); and $D$ is the diffusion/dispersion coefficient (m$^2$/s); $A_{os}$ is the water/solid-interface area (m$^2$/g solid); $A_{ws}$ is the oil/water-interface area (m$^2$/g oil); and $A_{is}$ is the oil/solid-interface area (m$^2$/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 $R_{eq}$ and $R_{kinetic}$ (mol/s/kg water). These two terms can be the summation of multiple reaction-rate terms, depending on the number of reactions that involve 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, whereas the interface between brine and solid contains solid-surface sites that contain polar ions (Buckley 1994; Buckley and Liu 1998; Hirasaki and 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 on the basis of the specific surface area (SSA) of the rock. The total oil-surface area ($A_{ws} + A_{is}$) may vary depending on oil saturation. We define the solid-surface concentration ($C_{i,s}$) as

$$
C_{i,s} = \begin{cases} 
  \frac{A_{os}}{A_s} C_{i,w}, & \text{when } i = i_{ws}, \\
  \frac{A_{is}}{A_s} C_{i,w}, & \text{when } i = i_{is}. 
\end{cases}
$$

The oil/water-surface concentration can be defined similarly. Eqs. A-2 through A-4 can be rewritten as the mass conservation on the total solid surface and total oil surface:

$$
\frac{\partial}{\partial t} \left[(1 - \phi) p A_{s} C_{i} \right] = R_{eq}^{i} + R_{kinetic}^{i}, \hspace{1cm} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
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Changhe Qiao is a PhD degree candidate in the Department of Mathematics at the Pennsylvania State University. Qiao’s research interest includes compositional simulation, reactive-transport models, fast and robust linear solvers, and parallel computing. He holds a bachelor’s degree in computational mathematics from Peking University, China.

Li Li is an assistant professor in the Department of Energy and Mineral Engineering at Pennsylvania State University. She has worked for more than 10 years in understanding and predicting physical-, chemical-, and biological-process coupling in spatially heterogeneous subsurface. In addition to low-salinity flooding, Li has worked on a range of topics at the water/energy nexus, including geological carbon sequestration, microbe enhanced oil recovery, reservoir souring, and bioremediation.

Russell T. Johns is the Chair of the Petroleum and Natural Gas Engineering Program within the Department of Energy and Mineral Engineering at Pennsylvania State University. He also holds the Victor and Anna Mae Beighini Professorship of Petroleum and Natural Gas Engineering and the CMG Foundation Chair in fluid behavior and rock interactions. Before his current position, Johns served on the petroleum engineering faculty at the University of Texas at Austin from 1995 to 2010. He also has 9 years of industrial experience as a petrophysical engineer with Shell Oil and as a consulting engineer for Colenco Power Consulting, Baden, Switzerland. Johns has more than 200 publications in enhanced oil recovery, thermodynamics and phase behavior, unconventional gas engineering, multiphase flow in porous media, and well testing. He received the SPE Ferguson Medal in 1993 and served as coexecutive editor for SPE Reservoir Evaluation and Engineering from 2002 to 2004. In 2009, Johns was awarded the SPE Distinguished Member Award and in 2013 the SPE Faculty Pipeline Award. He is currently director of the Enhanced Oil Recovery Consortium and codirector of the Unconventional Natural Resources Consortium in the EMS Energy Institute at Pennsylvania State University. Johns holds a bachelor’s degree in electrical engineering from Northwestern University and master’s and PhD degrees in petroleum engineering from Stanford University.

Jinchao Xu is the Verne M. Willaman Professor of Mathematics, the Francis R. and Helen M. Pentz Professor of Science, and Director of the Center for Computational Mathematics and Applications at Pennsylvania State University. His research interests are in the design, analysis, and application of numerical methods, especially multilevel and adaptive finite-element methods, for systems of partial-differential equations and problems with direct applications to physics, biology, and engineering. Xu was a plenary speaker at the International Congress for Industrial and Applied Mathematics in 2007 and an invited speaker at the International Congress for Mathematicians in 2010. He is a fellow of the Society for Industrial and Applied Mathematics and the American Mathematical Society in the inaugural class.