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Bulk and Surface Aqueous Speciation of Calcite: Implications for Low-Salinity Waterflooding of Carbonate Reservoirs

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Summary

Low-salinity waterflooding (LSW) is ineffective when reservoir rock is strongly water-wet or when crude oil is not asphaltenic. Success of LSW relies heavily on the ability of injected brine to alter surface chemistry of reservoir crude-oil/brine/rock (COBR) interfaces. Implementation of LSW in carbonate reservoirs is especially challenging because of high reservoir-brine salinity and, more importantly, because of high reactivity of the rock minerals. Both features complicate understanding of the COBR surface chemistries pertinent to successful LSW. Here, we tackle the complex physicochemical processes in chemically active carbonates flooded with diluted brine that is saturated with atmospheric carbon dioxide (CO$_2$) and possibly supplemented with additional ionic species, such as sulfates or phosphates.

When waterflooding carbonate reservoirs, rock equilibrates with the injected brine over short distances. Injected-brine ion speciation is shifted substantially in the presence of reactive carbonate rock. Our new calculations demonstrate that rock-equilibrated aqueous pH is slightly alkaline quite independent of injected-brine pH. We establish, for the first time, that CO$_2$ content of a carbonate reservoir, originating from CO$_2$-rich crude oil and gas, plays a dominant role in setting aqueous pH and rock-surface speciation.

A simple ion-complexing model predicts the calcite-surface charge as a function of composition of reservoir brine. The surface charge of calcite may be positive or negative, depending on speciation of reservoir brine in contact with the calcite. There is no single point of zero charge; all dissolved aqueous species are charge determining. Rock-equilibrated aqueous composition controls the calcite-surface ion-exchange behavior, not the injected-brine composition. At high ionic strength, the electrical double layer collapses and is no longer diffuse. All surface charges are located directly in the inner and outer Helmholtz planes.

Our evaluation of calcite bulk and surface equilibria draws several important inferences about the proposed LSW oil-recovery mechanisms. Diffuse double-layer expansion (DLE) is impossible for brine ionic strength greater than 0.1 molar. Because of rapid rock/brine equilibration, the dissolution mechanism for releasing adhered oil is eliminated. Also, fines mobilization and concomitant oil release cannot occur because there are few loose fines and clays in a majority of carbonates. LSW cannot be a low-interfacial-tension alkaline flood because carbonate dissolution exhausts all injected base near the wellbore and lowers pH to that set by the rock and by formation CO$_2$. In spite of diffuse double-layer collapse in carbonate reservoirs, surface ion-exchange oil release remains feasible, but unproved.

Introduction

LSW refers to improved oil recovery achieved by waterflooding a reservoir with brine of lower salinity than that of the field brine. The process is alluring because of simplicity, favorable economics, and large potential. In some applications, seawater is injected, a fluid not commonly viewed as “low” salinity. Precise definition of LSW is lacking. In principle, spiking injection water with specific anions and/or cations has the potential to improve recovery (Strand et al. 2006; Zhang et al. 2007b; Sorbie and Collins 2010; Alshakhs and Kovscek 2015; Austad et al. 2015; Puntervold et al. 2015) without need for lower salinity.

Starting in the middle 1990s, the pioneering work of Morrow and colleagues popularized LSW of sandstones. Fines release was highlighted as one of several proposed recovery mechanisms (Jadhunandan and Morrow 1995; Yildiz and Morrow 1996; Tang and Morrow 1997, 1999, 2002; Zhang and Morrow 2006; Zhang et al. 2007b). Later studies of LSW in sandstones (Webb et al. 2004; Lager et al. 2007, 2008a, b) confirmed the oil-recovery findings of Yildiz and Morrow (1996), but did not experimentally observe fines release. These authors (Webb et al. 2004; Lager et al. 2007, 2008a, b) introduced multicomponent ion exchange (MIE) from which oil releases by aqueous ions exchanging at the rock surface.

LSW of carbonate reservoirs, the focus of this work, was initially dismissed because carbonate rock typically contains no clays. Austad and coworkers, however, showed a positive response of carbonate rocks to LSW (Zhang and Austad 2006; Strand et al. 2006; Zhang et al. 2007a; Rezaeidoust et al. 2009; Fathi et al. 2010; Puntervold et al. 2015). These authors also promulgated a version of MIE as an LSW oil-recovery mechanism. In a landmark contribution, Youssef et al. (2011) detailed the viability of LSW with seawater in a Middle East carbonate. Later works experimentally confirm the earlier findings of successful oil recovery by LSW in carbonate rock (Zahid et al. 2012; Chandrasekhar and Mohanty 2013; Alshakhs and Kovscek 2015).

Several helpful reviews on LSW are available (Lager et al. 2008a; Buckley and Morrow 2010; Morrow and Buckley 2013; Sheng 2014; Myint and Firoozabadi 2015). Fascinatingly, Sheng (2014) introduced 15 disparate physical mechanisms for LSW oil displacement. Multiple and coupled mechanisms likely conspire. Definitive confirmatory experiments are lacking. Nevertheless, there is consensus on three observations:

- LSW recovers only crude oil. Improved recovery with clean oils is not found.
- Some wettability alteration toward more-water-wet rock is requisite, but not complete water-wetting (Brady et al. 2015).
- Rock/water interactions are important.

The surface charge of the mineral interfaces appears to play a critical role. This last observation engendered a large number of ancillary studies on silica, clay, and calcite/water interfaces and their ion-exchange behavior, especially recently (Lager et al. 2008a; Sorbie and Collins 2010; Nasralla and Nasr-El-Din 2012; Alotaibi et al. 2011; Alotaibi and Youssef 2015; Alshakhs and Kovscek 2015; Brady...
et al. 2015; Myint and Firoozabadi 2015; Puntevold et al. 2015; Qiao et al. 2016). Fundamental studies (Ricci et al. 2013; Alshakhs and Kovscek 2015; Brady et al. 2015; Lashkarbolooki et al. 2016; Mugele et al. 2016) of the calcite/water interface, including molecular simulation (Kerisit and Parker 2004; Sakuma et al. 2014; Qiao et al. 2016), also garnered attention. These results generally support the surface-charge-recovery concepts of DLE and MIE.

Carbonate reservoirs are unique in several ways. Foremost, carbonate rock is “reactive” in that it alters the injected-brine composition by dissolution/precipitation. In particular, we demonstrate that injected brine almost immediately equilibrates with carbonate rock. Thus, the assessment of aqueous speciation chemistry is paramount to LSW (Al-Shalabi et al. 2014; Qiao et al. 2014, 2016). Also pertinent to LSW in carbonates are high-salinity brine and lack of clay content, both of which affect the DLE recovery mechanism.

Because LSW strongly depends on rock-brine chemistry, this paper also ascertains the equilibrium compositions of the calcite-mineral/water interface, appropriate to reservoir brine compositions. We discover that aqueous CO$_2$ in the reservoir is critical to rock/brine equilibration. Reservoir sources of aqueous CO$_2$ are injected seawater saturated with atmospheric CO$_2$ at 350 ppm (10$^{-3.44}$ bar), CO$_2$-saturated crude oil, and, at times, CO$_2$-rich gas phase. Because aqueous CO$_2$ is such an important driver of carbonate equilibria, its effect is investigated over a broad range of concentrations. Aqueous CO$_2$ concentration in the reservoir is varied from essentially zero (10$^{-8}$ mol/L) to very high (1 mol/L). Importance of the specific crude oil cannot be ignored, but here we focus on rock/brine interactions in promoting LSW oil recovery.

In the following sections, we establish that equilibrium reaction with calcite rock controls brine composition in the reservoir. An important corollary is that for all laboratory experiments involving water in carbonate rocks, the aqueous brine must be pre-equilibrated. Following this discussion, we demonstrate the importance of aqueous speciation in controlling surface-charge behavior under reservoir conditions. We conclude by summarizing how surface and bulk aqueous speciation negate many of the proposed mechanisms by which LSW is anticipated to perform.

**Methodology**

**Calcite/Solution Kinetics.** Carbonate rocks consist mainly of crystalline calcite, and include smaller amounts of dolomite, anhydrite, and dolostone (Folk 1959, 1962; Lucia 2007). Because these minerals exhibit significant water solubility, they are considered “reactive,” meaning that rock dissolves/precipitates under the influence of water chemistry (Stumm and Morgan 1996; Sposito 2008).

Given sufficient exposure time, carbonate rock equilibrates with the surrounding aqueous phase. Fig. 1 shows the injection of an aqueous electrolyte solution into a porous carbonate rock. Inlet species molar concentration is $C_{i0}$, where the tilde under $C$ denotes a vector of species. During traverse through the rock, the aqueous ionic species react with mineral surfaces (Fig. 1). Upon exiting the porous mineral/water interface, appropriate to reservoir compositions. We discover that aqueous CO$_2$ in the reservoir is critical to rock/brine equilibration. Reservoir sources of aqueous CO$_2$ are injected seawater saturated with atmospheric CO$_2$ at 350 ppm (10$^{-3.44}$ bar), CO$_2$-saturated crude oil, and, at times, CO$_2$-rich gas phase. Because aqueous CO$_2$ is such an important driver of carbonate equilibria, its effect is investigated over a broad range of concentrations. Aqueous CO$_2$ concentration in the reservoir is varied from essentially zero (10$^{-8}$ mol/L) to very high (1 mol/L). Importance of the specific crude oil cannot be ignored, but here we focus on rock/brine interactions in promoting LSW oil recovery.

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The fast kinetics of carbonate dissolution is important. First, carbonate rocks equilibrate with the flooding solution over extremely short distances. Similarly, laboratory core plugs a few centimeters in length come into equilibrium with the waterflooding solution. Second, injected-brine composition is not what occurs in the pores of the medium. In LSW, reactive rock changes the injected-brine composition substantially, a fact that is not normally considered. Third, changes in aqueous composition are critical to LSW because of the sensitivity of the process to water chemistry. To understand the role of ion-complexing surface chemistry in LSW, a detailed understanding of the rock/aqueous-solution equilibria is mandatory. Fourth, the proposed “rock-dissolution” mechanism of LSW-improved oil recovery (Buckley and Morrow 2010; Hiorth et al. 2010; Zahid et al. 2012; Al-Shalabi et al. 2014; Lashkarbolooki et al. 2016) is not applicable (unless the injected brine completely dissolves the rock). Injected brine equilibrates with carbonate rock almost immediately after exiting the injection well. Thereafter, the rock no longer dissolves (or precipitates) and can no longer eich to release oil. The fact that carbonates equilibrate rapidly with brine necessitates a detailed understanding of aqueous-speciation chemistry (Al-Shalabi et al. 2014; Alotaibi and Yousef 2015; Qiao et al. 2014, 2016).

**Calcite/Solution Bulk Equilibria.** The chemistry of calcite/water equilibrium involves numerous aqueous species. Fortunately, considerable information is available (Stumm and Morgan 1996). Appendix B lists the currently accepted species reactions and corresponding equilibrium constants at ambient temperature (Charlton and Parkhurst 2011; Al-Shalabi et al. 2014; Parkhurst and Apello 2014; Qiao et al. 2016). When rock equilibration is achieved, species chemical-reaction equilibria are obeyed (Felder et al. 2015):

\[
K_j(T) = \prod \left( \gamma_i \cdot C_{iL} \right)^{n_i},
\]

where \(K_j(T)\) is the \(j\)th reaction equilibrium constant at temperature \(T\), and \(\gamma_i\) is the dilute-solution activity coefficient of species \(i\) (\(\gamma_i\) approaches unity as concentrations approach zero). Element mass balance completes the equilibrium calculation (Charlton and Parkhurst 2011; Al-Shalabi et al. 2014; Parkhurst and Apello 2014; Felder et al. 2015):

\[
C_{iL} = C_{i0} + \sum_j n_i \xi_j,
\]

where the subscript \(j\) denotes the \(j\)th independent chemical reaction, \(\xi_j\) is the extent of the \(j\)th reaction (Felder et al. 2015) (in mol/L), and \(n_i\) is the stoichiometric coefficient of species \(i\) in reaction \(j\). Eq. 4 means that species concentrations exiting the porous medium are those entering plus those produced (or consumed) by chemical reaction with minerals. Impostion of solution electroneutrality is unnecessary because all speciation reactions conserve charge (Stumm and Morgan 1996; Al-Shalabi et al. 2014). Substitution of Eq. 4 into Eq. 3 yields coupled nonlinear algebraic expressions to calculate the extent-of-reaction vector \(\xi\). Eq. 4 then establishes the equilibrium-species concentrations \(C_{iL}\). On the basis of the available species identifications (Al-Shalabi et al. 2014), our calculation of calcite/sodium chloride (NaCl) brine chemistry specifies 10 independent equilibrium reactions, as listed in Table 1. Given reaction stoichiometry, equilibrium constants, and activity coefficients, Eqs. 3 and 4 are solved simultaneously by two different numerical methods. First, Newton iteration is used in MATLAB (2015). Second, PHREEQC software (Charlton and Parkhurst 2011; Parkhurst and Apello 2014) is adopted. Excellent agreement is found between the two procedures. Appendix B details the numerical solutions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>(\log_{10}K)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{CO}_3^{2-} \rightleftharpoons \text{CO}_2^{2+})</td>
<td>-1.47</td>
<td>mol/L atm</td>
</tr>
<tr>
<td>2</td>
<td>(\text{CO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3)</td>
<td>-2.59</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>(\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-)</td>
<td>-3.76</td>
<td>mol/L</td>
</tr>
<tr>
<td>4</td>
<td>(\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-})</td>
<td>-10.33</td>
<td>mol/L</td>
</tr>
<tr>
<td>5</td>
<td>(\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-)</td>
<td>-14</td>
<td>(mol/L)^2</td>
</tr>
<tr>
<td>6</td>
<td>(\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-})</td>
<td>-8.48</td>
<td>(mol/L)^2</td>
</tr>
<tr>
<td>7</td>
<td>(\text{CaOH}^- \rightleftharpoons \text{Ca}^{2+} + \text{OH}^-)</td>
<td>-1.22</td>
<td>mol/L</td>
</tr>
<tr>
<td>8</td>
<td>(\text{CaHCO}_3^- \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-)</td>
<td>-1.11</td>
<td>mol/L</td>
</tr>
<tr>
<td>9</td>
<td>(\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-)</td>
<td>0.25</td>
<td>mol/L</td>
</tr>
<tr>
<td>10</td>
<td>(\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^+ + \text{CO}_3^{2-})</td>
<td>-1.27</td>
<td>mol/L</td>
</tr>
</tbody>
</table>

Table 1—Solution-equilibrium reactions and equilibrium constants, \(K\) (298 K). The \(\log_{10}K\) values are from Charlton and Parkhurst (2011) and Parkhurst and Apello (2014).

**Calcite/Solution Surface Equilibria.** Because of the proposed importance of the aqueous-calcite surface charge to the LSW process, elucidation of surface equilibria is paramount. Atomic structure of the calcite/water interface has been extensively studied, specifically the [104]-face, because it is predominant (Fenter et al. 2000; Pokrovsky et al. 2000; Geissbühhler et al. 2004; Kerisit and Parker 2004; Heberling et al. 2011; Ricci et al. 2013; Sakuma et al. 2014). We adopt the corresponding [104]-interface structure shown in Fig. 2, which reveals that all surface carbonate ions are raised and tilted so they are slightly out of plane. Each surface calcium ion is surrounded by six carbonate anions in an octahedral arrangement. In turn, each carbonate-anion-exchange site is surrounded by six calcium cations; which reveals that all surface carbonate ions are raised and tilted so they are slightly out of plane. Each surface calcium ion is surrounded by six carbonate anions in an octahedral arrangement. In turn, each carbonate-anion-exchange site is surrounded by six calcium cations;
charges adopted by Heberling et al. (2011) for the calcite/water interface. We do not account for edge and corner sites but invoke surface-charge numbers of ±1. From the crystal-lattice structure, the maximum number of ion-exchange sites on a [104]-calcite surface is 5 nm⁻² each for calcium and carbonate sites. This value was experimentally confirmed by Möller and Sastri (1974). We picture the calcite/water interface as electroneutral but with equal and opposite cationic- and anionic-exchange charge densities of ±80 μC/cm².

Fig. 2—A view of calcite [104]-crystal plane. Red balls are oxygen, blue balls are calcium, and black balls are carbon. Green lines indicate real crystal edges and have length of 0.95 nm. Beneath the plane is bulk calcite and above the plane is the interface, which is indicated by truncated bonds within the square bounded by green lines. There are five ion-exchange sites of calcium and carbonate per nm². These are counted the following way: two calcium from the center of the square (face calcium) plus \( \frac{1}{4} \) calcium from the edges of the square (edge calcium), and plus \( \frac{1}{4} \) from the corners (corner calcium) gives 4.5 calcium sites per 0.9025 nm². Extrapolating this number gives 5 sites/nm².

Fig. 3a is a schematic of ions distributed near the calcite surface. As discussed previously, the lattice surface, or 0-plane, is on average electrically neutral, demanding a net surface-charge density of \( \sigma_0 = 0 \). Nevertheless, the calcite/water interface acquires charge in the presence of aqueous electrolytes because of the specific adsorption of charge-bearing aqueous species. For simple aqueous electrolytes, specific adsorption occurs primarily by ion complexation or ion binding with oppositely charged surface sites. Calcite immersed in water is both a cation- and anion-exchange mineral. Because all aqueous ionic species potentially exchange, there is no one potential- or charge-determining ion (Somasundaran and Agar 1967; Thompson and Pownall 1989; Pierre et al. 1990; Zhang and Austad 2006; Zhang et al. 2007a). Because the proclivity for exchange is not the same for all aqueous ions, a nonzero surface-charge density, \( \sigma_b \), arises at the \( \beta \)-plane or inner Helmholtz plane (Grahame 1947; Newman and Thomas-Alyea 2004; Berg 2010). The remaining charge at the surface is distributed in the diffuse electrical double layer, commencing at the \( d \)-layer or the outer Helmholtz plane, highlighted in Fig. 3a. Because the calcite/water interface at the 0-plane is neutral, the charge density in the diffuse electrical double layer, \( \sigma_b \), balances that in the \( \beta \)-plane (i.e., \( \sigma_b + \sigma_0 = 0 \)).

In this work, ion complexing or ion binding of a solution counter ion with the oppositely charged surface site involves a significant enough specific chemical interaction to dehydrate partially the complexing ion. Conversely, all ions in the diffuse region remain fully hydrated. This feature is illustrated in Fig. 3a: Ions in the \( \beta \)-plane are closer to the calcite-exchanging ions and are partially dehydrated, whereas ions in the diffuse layer are fully hydrated. Of course, ions have different hydrated sizes so that the \( \beta \)- and \( d \)-planes are not strictly uniform layers. Our analysis does not include this detail (Levine et al. 1967).

Following others (Davis et al. 1978; Dzombak and Morel 1990; Hiemstra and Riemsdijk 1996), we recognize surface-ion complexing as an equilibrium chemical reaction analogous to Eq. 3, but expressed with surface concentration for each surface complex. Because all aqueous ions potentially exchange at calcite-surface sites, a large number of surface complexes is possible. Fortunately, considerable information is available on the calcite/water interface (Somasundaran and Agar 1967; Möller and Werr 1972; Siffert and Fimbel 1984; Thompson and Pownall 1989; Van Cappellen et al. 1993; Pokrovsky et al. 2000; Nystrom 2001; Wolters et al. 2008; Hiorth et al. 2010; Alotaibi et al. 2011; Heberling et al. 2011; Heberling et al. 2011; Alshakhs and Kovscek 2015). We adopt the five preliminary surface reactions listed in Table 2, where the symbol > denotes surface species.

Table 1 reveals that many ionic species are present in the calcite-equilibrated brine and may ion exchange at the calcite/water interface. In particular, sodium and chloride ions are dominant species at high brine concentrations and may participate in ion-exchange equilibria. It is commonly accepted, however, that sodium and chloride ions are inactive at the calcite/water interface (Somasundaran and Agar 1967; Möller and Werr 1972; Siffert and Fimbel 1984; Thompson and Pownall 1989; Van Cappellen et al. 1993; Pokrovsky et al. 2000; Nystrom 2001; Wolters et al. 2008; Hiorth et al. 2010; Alotaibi et al. 2011; Heberling et al. 2011; Austad et al. 2015; Puntervold et al. 2015). Unfortunately, no direct evidence is available to confirm or refute this view.

The five surface reactions listed in Table 2 listed are based on previous modeling of measured \( \zeta \)-potentials (Van Cappellen et al. 1993; Pokrovsky et al. 2000; Nystrom 2001; Wolters et al. 2008; Hiorth et al. 2010; Alotaibi et al. 2011; Heberling et al. 2011; Heberling et al. 2011). Each has been identified by separate spectroscopic studies (Pokrovsky et al. 2000; Heberling et al. 2011). Also, except for sodium and chloride ions, these are the dominant aqueous species in calcite-equilibrated waterflooding, as shown below. Inclusion of additional surface-complexing reactions awaits experimental justification.

We write mass-action equilibrium expressions for the surface reactions in a surface-complexation model (SCM). For example, for the first surface reaction, \( S_1 \) in Table 2, reaction equilibrium gives

\[
K_{S_1}(T) = \frac{\left(\text{CaOH}^{-}\right)^{\gamma_{H^+}} C_{H^+} \exp\left(-\frac{F \phi_b}{RT}\right)}{\left(\text{CaH}_2\text{O}^{-}\right)^{\gamma_{H^+}}}, \quad \text{reaction equilibrium}
\]

where \( K_{S_1} \) is the surface-ion-complexing equilibrium constant, the symbol > stands for surface species in the 0- or \( \beta \)-planes, and parentheses denote surface concentrations in mol per area. \( \gamma_{H^+} \) is the activity coefficient of hydronium ion in solution, and
\( \varphi_\beta \) is the electrostatic potential at the \( \beta \)-plane (also at the 0-plane in Fig. 3b). The exponential factor is a Boltzmann-activity correction to account for the electrostatics of the charged \( >\text{CaH}_2\text{O}^+ \) sites. Similarly, mass-action equations are written for reactions \( S_2 \) through \( S_5 \) (Table 2 and Appendix C). Determination of the surface-complexing equilibrium constants, \( K_S \), is discussed in the Results section.

![Fig. 3—Schematic of the calcite/water interface. The calcite surface charge at the 0-plane is zero. Charge at the surface arises from unequal ion complexing at the \( \beta \)-plane. The diffuse double layer beginning at the distance \( x_d \) neutralizes the \( \beta \)-plane charge. Electrostatic profile of the calcite/water interface is shown when the \( \beta \)-plane is positively charged. Note that the profile is constant between the 0- and \( \beta \)-planes because the calcite surface is electrically neutral. The potential at the \( d \)-plane identifies the \( \zeta \)-potential.](image)

Table 2—Surface-complexation reactions and corresponding equilibrium constants, \( K_S \) (298 K). The \( \log_{10}K_S \) values are refined from Hiorth et al. (2010) and Heberling et al. (2011).

<table>
<thead>
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</tr>
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<tbody>
<tr>
<td>( S_1 )</td>
<td>( \text{CaH}_2\text{O}^+ \rightleftharpoons \text{CaOH}^- + \text{H}^+ )</td>
<td>-10</td>
<td>mol/L</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>( \text{CaH}_2\text{O}^- + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^- + \text{H}_2\text{O} )</td>
<td>2</td>
<td>L/mol</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>( \text{CaH}_2\text{O}^- + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3^- + \text{H}_2\text{O} )</td>
<td>3</td>
<td>L/mol</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>( \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CO}_3^\text{H}^- )</td>
<td>8</td>
<td>L/mol</td>
</tr>
<tr>
<td>( S_5 )</td>
<td>( \text{CO}_3^\text{H}^- + \text{Ca}^2+ \rightleftharpoons \text{CO}_3\text{Ca}^+ )</td>
<td>3</td>
<td>L/mol</td>
</tr>
</tbody>
</table>

Overall surface-charge neutrality is imposed, with the \( \beta \)-plane charge set by the number density of specifically adsorbed ion complexes. The \( d \)-plane charge density (i.e., that in the diffuse layer) is set by Poisson-Boltzmann (Verwey and Overbeek 1948; Berg 2010), as outlined in Appendix C:

\[
\sigma_d = -\frac{\varphi_d}{\varphi_d} \sqrt{2 \varepsilon \kappa \sum_i C_i \left[ \exp\left( \frac{-z_i F \varphi_d}{RT} \right) - 1 \right]} .
\]
where \( \varphi_d \) is the electrostatic potential at the \( d \)-plane. For example, if \( \varphi_d \) is negative, net positive charges must be distributed in the diffuse layer because of a negative electrostatic potential, and vice versa. In our analysis, the \( d \)-plane is defined as the plane of no-slip so that \( \varphi_d \) corresponds to the \( \zeta \)-potential. Finally, Gauss’ law relates the potentials \( \varphi_d \) and \( \varphi_d \) through a constant integral capacitance between the inner and outer Helmholtz planes (Newman and Thomas-Alyea 2004; Berg 2010).

A qualitative electrostatic-potential profile for the calcite/water surface is displayed in Fig. 3b for a positively charged \( \beta \)-plane. The potential remains constant at \( \varphi_0 = \varphi_d \) between the calcite surface and the inner Helmholtz plane because the 0-plane surface is neutral. \( \varphi(x) \) then falls linearly between the inner and outer Helmholtz planes because that region is assumed devoid of charge. Finally, charge balance is achieved in the diffuse double layer of thickness, \( \lambda \), the Debye length given by (Verwey and Overbeek 1948; Newman and Thomas-Alyea 2004; Berg 2010)

\[
\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_r k T}{2F^2 I}}
\]

where \( \varepsilon \) is the dielectric permittivity of water, \( \varepsilon_0 \) is the dielectric permittivity of free space, and \( \varepsilon_r \) is the relative permittivity or dielectric constant of water. \( F \) is Faraday’s constant, \( R \) is the ideal-gas constant, \( I = 0.5 \sum z^2 C_i \) is the aqueous-solution ionic strength, \( z_i \) is the valence of dissolved species \( i \), and \( C_i \) is the bulk aqueous molar concentration of that species.

If the \( \beta \)-plane charge is negative, the potential profile in Fig. 3b reverses sign and increases from negative \( \varphi_d \) at the 0-plane to zero as \( x \to \infty \). Because many aqueous ions contribute to the \( \beta \)-plane charge, the \( \zeta \)-potential (= \( \varphi_d \)) of calcite can be either positive or negative depending on solution composition. There is no unique point of zero charge. Many different solution compositions lead to a net-neutral \( \beta \)-plane. Numerical solution of the surface-complexing model is again by Newton iteration, outlined in Appendix C.

According to Eq. 7, when ionic strength increases, \( \lambda \) shrinks. At high-enough ionic strength, the diffuse double layer collapses completely. Only when \( \lambda \) is larger than approximately 1 nm (2–4 water layers) does a diffuse double layer exist. Fig. 4 displays the Debye length at ambient temperature as a function of aqueous ionic strength. DLE can only occur if the reservoir-equilibrated brine falls into the upper-left shaded corner of Fig. 4, irrespective of reservoir-rock mineralogy. At least 10-times-diluted seawater is necessary to permit DLE. We assert that DLE is not applicable in most carbonate LSW applications.

**Results and Discussion**

**Calcite/Solution Bulk Equilibria.** Fig. 5 portrays what happens to injected-brine concentrations during flow through and equilibration with carbonate reservoir rock. Equilibrium-aqueous-species concentrations in calcite rock are graphed as a log-log function of injected-brine ionic strength. Influent brine is saturated with atmospheric CO2(g) at 350 ppm (10−3.44 bar). This means that injected-brine pH is 5.65. Similarly, reservoir brine is equilibrated with CO2(g) at the same partial pressure of 10−3.44 bar and remains so during flooding. All species in Table 1 are graphed except dissolved CO2, CO2(aq), and carbonic acid, H2CO3, the concentrations of which are fixed and minor [by equilibration with CO2(oil) and CO2(g), where applicable]. Except for very-low ionic-strength injected brines, reservoir ionic strength is identical to that injected. pH in the reservoir, however, changes substantially to an alkaline value of approximately 8.3. At the highest ionic strengths, the pH diminishes to approximately 7.9 because of activity-coefficient corrections. All calcite-rock-generated aqueous species are less than 10−3 mol/L, relatively independent of ionic strength, until greater than \( I \approx 1 \) mol/L (near seawater), where there are substantial changes. These again arise from activity-coefficient interactions. Aside, possibly, from the brine-based species (Na+, NaHCO3, NaCO3, and Cl−), the calcite-parent ions of calcium, bicarbonate, and carbonate control surface speciation and, hence, the calcite-surface charge (in the \( \beta \)-plane). Fig. 5 reveals that the flooding brine is not what exists in the reservoir: ionic strength...
is not altered significantly, but pH is. Concentrations of the dominant ions known to bind at the calcite/water surface are strongly influenced by rock equilibration. The charge of the calcite/water interface is controlled by rock equilibration and not by injected brine.

To emphasize the importance of rock equilibration, Fig. 6 investigates the role of reservoir CO$_2$ either as free gas or dissolved in oil. Fig. 6 graphs aqueous-species concentrations as a function of $p$CO$_2$ in the reservoir on log-log scales. Injected NaCl brine is saturated with CO$_2$(g) at $10^{-3.44}$ bar, resulting in $10^{-5}$ mol/L of CO$_2$(aq). The aqueous phase in the calcite rock contains the same amount of dissolved CO$_2$ (i.e., $p$CO$_2$ = 5).

![Image of Fig. 5](image_url)  
**Fig. 5**—Reservoir-calcite/water-equilibrium-species concentrations as a function of injected ionic strength (from NaCl) on log-log scales. Injected NaCl brine is saturated with CO$_2$(g) at $10^{-3.44}$ bar, resulting in $10^{-5}$ mol/L of CO$_2$(aq). The aqueous phase in the calcite rock contains the same amount of dissolved CO$_2$ (i.e., $p$CO$_2$ = 5).

![Image of Fig. 6](image_url)  
**Fig. 6**—Reservoir-calcite/water-equilibrium-species concentrations as a function of aqueous $p$CO$_2$ in the reservoir on log-log scales (CO$_2$ concentration increases from right to left). Injected brine at 1.5 mol/L NaCl is saturated with CO$_2$(g) $10^{-3.44}$ bar, resulting in $10^{-5}$ mol/L of CO$_2$(aq), pH = 5.65. Henry's constant = 0.034 mol/kg bar at 273 K.
**Fig. 7** explores the possibility of changing the injection-brine pH to alter alkalinity in the reservoir. Concentrations of the major ion-exchanging species are reported for various inlet alkalinitites adjusted by dilute sodium hydroxide in 1.5 mol/L NaCl injected brine. Inlet brine contains no dissolved carbon. Up to injected pH = 11, the reservoir pH is unchanged from 8.5. This value appears because of buffering by dissolved carbonate species. Likewise, the ion-exchanging-species concentrations remain constant until a pH value of approximately 11. Above this inlet pH, reservoir pH rises, but only to approximately 10, even with an injected value four orders of magnitude larger. Carbonate buffering is strong and does not permit much alteration of reservoir pH. Again, equilibration of the injected brine with the rock changes the calcium, bicarbonate, and carbonate ion concentrations and, hence, rock-surface chemistry.

Carbonate aqueous chemistry is critical to LSW. Injected-brine speciation alters dramatically by reaction equilibration with the rock. Because of buffering and especially because of the presence of reservoir CO2, pH values in the reservoir do not deviate much from approximately 8, no matter what pH is injected. The proposed saponification mechanism for LSW (i.e., activation of surface-active soaps) (Buckley and Morrow 2010; Sheng 2014; Myint and Firoozabadi 2015) is not expected to contribute at this low alkalinity. Because surface chemistry of the mineral interface is controlled by aqueous speciation, careful attention must be paid to actual ionic concentrations that evolve in the reservoir. In particular, all ancillary laboratory studies must be performed with rock-equilibrated aqueous solutions at reservoir conditions, including temperature and especially CO2 levels, something that is rarely contemplated. Figs. 5 through 7 provide a glimpse into a large range of possible LSW injection schemes. Many other salinities, particular ions, rock minerals, and temperatures, may be pursued depending on the specific reservoir and LSW process under consideration.

**Calcite/Solution Surface Equilibria.** Aqueous speciation controls the surface-charge behavior of aqueous-immersed calcite. Because all aqueous ions present have the potential for ion exchange, the surface-chemistry landscape is immense, with no single charge-determining species. We first consider laboratory studies at low ionic strengths where ζ-potential measurements are possible. This exercise calibrates the SCM and provides physical insight into the calcite-surface structure. We then extend the SCM to brines that might be used in LSW of carbonate reservoirs.

**Low Ionic Strength.** Most laboratory information on aqueous-calcite-surface behavior is from ζ-potential measurements at relatively low ionic strength, typically less than 0.1 mol/L (Somasundaran and Agar 1967; Thompson and Pownall 1989; Van Cappellen et al. 1993; Wolthers et al. 2008; Alotaibi et al. 2011; Heberling et al. 2011; Alshakhhs and Kovscek 2015; Alotaibi and Yousef 2015). At high ionic strength, ζ-potentials are small and measurements imprecise. We consider the experimental measurements of Heberling et al. (2011). These authors carefully pre-equilibrate the aqueous solution with calcite mineral and verify the resulting aqueous-solution behavior against separate equilibrium calculations (by use of the PHREEQC code). Because the ζ-potentials are strong functions of ionic strength, Heberling et al. (2011) performed their experiments at approximately constant ionic strength. They also equilibrated the aqueous brine with fixed CO2(g) partial pressures, a point emphasized previously. Few ζ-potential studies on calcite pay close attention to the important details that control aqueous speciation and, accordingly, the surface chemistry of the calcite/water interface.

**Fig. 8** shows the experimental ζ-potentials of Heberling et al. (2011) as a function of pH for ionic strengths nominally at 0.1 mol/L (open symbols). Three data sets are seen corresponding to equilibration with differing partial pressures of CO2 gas. A larger partial pressure demands larger amounts of CO2 dissolved in the aqueous phase, making the solution more acidic and limiting the range of pH values at fixed ionic strength. Note that calcite is charged both positively and negatively at each CO2 partial pressure. Further, each partial pressure exhibits a separate point of zero charge, equivalently an isoelectric point, where the ζ-potential crosses zero. pH alone does not determine calcite-surface charge, as it does for oxide minerals (Stumm and Morgan 1996).
The zero point of charge in Fig. 9 is pH = 8.75, as in Fig. 8. Surprisingly, charge densities of all surface complexes at the inner Helmholtz plane are less than 10 to 20% of the maximum possible. This means that approximately 30% of each ion-exchange capacity is surface-complexed (the remaining 70% is uncomplexed). The two main surface complexes are \( \text{Helmholtz plane} \) are less than 10 to 20% of the maximum possible. This means that approximately 30% of each ion-exchange capacity is surface-complexed (the remaining 70% is uncomplexed). The two main surface complexes are

The SCM is enlisted in Fig. 9 to illustrate why the calcite \( \beta \)-plane charge changes sign from positive to negative and why it does so at different pH values upon different saturations of aqueous-dissolved CO\(_2\). The left abscissa gives the \( \beta \)-plane surface concentrations, \( \Gamma _\beta \), of five ion complexes in Table 2 as a function of pH at a fixed \( \text{PCO}_2 \) of \( 10^{-3.44} \) bar corresponding to the pH value range of 8 to 9 in Fig. 8. The fifth species, > CaOH in Table 2, is not displayed because its surface density is one order of magnitude smaller and is constant over this pH range. Surface-complex densities reported on the left abscissa are relative to the maximum anion (or cation) exchange capacity (\( \Gamma _\text{max} = 5 \text{ nm}^{-2} \) corresponding to \( 80 \mu \text{C/cm}^2 \)). The net-charge density in the \( \beta \)-plane is shown as a solid line and reported on the right abscissa in units of \( \mu \text{C/cm}^2 \). Ordinals in parentheses labeling each surface complex correspond to the valence of that complex in the \( \beta \)-plane. For example, the divalent CO\(_2\) ion in the surface species > CaCO\(_3\) exhibits a valence of \((-2\) \) in the \( \beta \)-plane.

The main distinction between charge characterization of the calcite/water interface in laboratory experiments and that at reservoir conditions is the much higher ionic strength. Fig. 10 reports SCM predictions (right abscissa) of \( z' \)-potentials (upper solid line) and \( \beta \)-plane charge densities \( \sigma _\beta \) (lower solid line), as a function of injected-brine pH at 1.5 mol/L ionic strength (seawater) in a reservoir exposed to atmospheric CO\(_2\)(g). Bulk aqueous-species concentrations appear on the left abscissa. For injected pH values less than approximately 11.5, there is a positive \( \beta \)-plane charge. High ionic strengths do not neutralize the \( \beta \)-plane and, hence, the surface. At an ionic strength of 1.5 mol/L, the Debye length in Fig. 4 is approximately 0.3 nm; therefore, the diffuse double layer...
completely collapses directly onto the \( \delta \)-plane. Nevertheless, below injected pH values of 11, SCM demonstrates a small positive \( \zeta \)-potential of approximately 1 mV, barely measurable by available laboratory techniques. Small but finite values of \( \zeta \)-potential remain at high ionic strength because sodium ions scavenge carbonate and bicarbonate ions (Reactions 9 and 10 in Table 1), thereby raising the charge density in the \( \beta \)-plane. This observation accentuates that equilibrium-solution speciation controls surface charge.

At pH values greater than 11, the \( \beta \)-plane charge turns increasingly negative because all surface-complex reactions shift by mass action toward ever-more-negative charge. The collapsed diffuse-double-layer electrostatic potential \( \sigma_\beta \) follows suit. Aqueous speciation in the reservoir brine controls the surface charge. We assert that carbonate rock/water surfaces remain charged and participate in ion-exchange reactions even at high ionic strengths relevant to LSW (Møller and Werr 1972). However, DLE is no longer operative.

The observation that ion exchange on calcite is active at high ionic strength is crucial to the LSW of carbonate reservoirs. One proposed mechanism of improving waterflood performance is to displace asphaltic carboxylates tightly bound to the rock surface by ion complexing and bridging by tailored solution ions (Lager et al. 2006, 2007, 2008a, b; Strand et al. 2006; Zhang and Austad 2006; Zhang et al. 2007b; Sorbie and Collins 2010; Zahid et al. 2012; Austad et al. 2015; Puntervold et al. 2015; Qiao et al. 2016). MIE is strongly coupled to rock/brine-surface chemistry. Ion-exchange oil release appears feasible in carbonate rocks even at high salinity and deserves more experimental attention.
Conclusions
Successful design of LSW in carbonate reservoirs presents severe challenges because rock/water reactions and highly concentrated brines cloud the understanding of COBR surface chemistries. Calcite rapidly equilibrates with aqueous solution within very short distances, even at high flow rates in fractures. The result is that injected-brine pH is altered substantially because of buffering by dissolving rock. Depending on the CO2 content of the reservoir, it is difficult to achieve alkalinities much different from pH 8.3 upon equilibration with calcite. Rock/water-surface chemistry is controlled by aqueous speciation present in the reservoir and not that injected. These findings are not changed when more-realistic brines are injected other than sodium chloride (illustrated in Figs. 5 through 7). We caution that all pertinent laboratory experiments should be performed with aqueous solutions that are pre-equilibrated with the rock and have CO2(aq) levels carefully adjusted to those anticipated in the field.

Surface-charge behavior is important to the success (or failure) of LSW. It is controlled by reservoir aqueous composition. Our preliminary effort to understand the electrical behavior of the calcite/water interface successfully predicts measured \( \zeta \)-potentials and confirms the critical role of aqueous speciation. This exercise permits estimation of surface charge under more-realistic LSW conditions. We find that because the calcite-surface lattice is neutral, surface charge of the calcite/water interface is at the inner Helmholtz plane. Because of ion-exchange reactions, surface charge may be positive or negative depending delicately on aqueous speciation in the reservoir. At brine ionic strengths beyond approximately 0.1 molar (\( \approx \)5,000 ppm of total dissolved salt, based on NaCl), the diffuse double layer collapses completely onto the outer Helmholtz plane. There is no "diffuseness" to the diffuse double layer. This does not mean that the calcite surface is overall neutral; ion exchange remains active and is quite important to LSW. Future work will focus on the important role of crude oil and MIE in LSW.

Our findings draw inferences concerning several proposed LSW oil-recovery mechanisms. Because of the high brine concentrations in carbonate reservoirs, diffuse DLE is precluded. Likewise, fines release is not possible for the same reason. In addition, carbonate rocks contain minimal or no clays. Because aqueous equilibration with carbonate rock is essentially instantaneous, the proposed dissolution LSW mechanism is not possible. Within a short kinetically controlled equilibration distance, rock no longer dissolves. Calculations of aqueous speciation under reservoir conditions suggest a pH that is too low for significant activation of oil-soluble acids into effective surfactants. Thus, the saponification mechanism for LSW is doubtful even if highly alkaline brine is injected. However, ion exchange remains active on calcite surfaces at high ionic strengths, suggesting that ligand-ion-exchange oil release is feasible in carbonate rocks.

We stress the importance of rock/brine equilibration under reservoir conditions when considering LSW. A simple but effective formulation is presented for scoping calculations of LSW performance.

Nomenclature

\[
\begin{align*}
a_i & = \text{first Truesdell-Jones equation ion-specific parameter, length} \\
\alpha_i & = \text{activity of species } i, \text{ where upper index } \epsilon \text{ denotes equilibrium state when specified, mol/L} \\
A & = \text{first Davies equation parameter, } \sqrt{\text{mol/L}} \\
b_i & = \text{second Truesdell-Jones equation ion-specific parameter, L/mol} \\
B & = \text{second Davies equation parameter, } \sqrt{\text{mol/L/nm}} \\
\bar{C} & = \text{constant integral capacitance between the inner and outer Helmholtz planes} \\
C_i & = \text{ith species concentration, where bottom tilde denotes vector of concentrations, mol/L} \\
C_i \bar{C} & = \text{ith species concentration at position } L, \text{ mol/L} \\
D & = \text{aqueous-salt diffusion coefficient, length}^2/\text{time} \\
D_\text{Da} & = \text{Damkohler number: } D_\text{Da} \equiv t_{\text{res}}/t_{\text{dis}}, \text{ unitless} \\
D_\text{g} & = \text{grain size, length} \\
f & = \text{vector of equations in the last column of Table B-1} \\
F & = \text{Faraday’s constant, charge/mol} \\
I & = \text{ionic strength, mol/L} \\
k_{\text{m}} & = \text{convective mass-transfer coefficient, length/time} \\
k_{\text{ion}} & = \text{intrinsic dissolution rate constant, length/time} \\
K_{\text{eq}} & = \text{equilibrium constant of } j\text{th reaction, units depend on reaction} \\
K_{\text{eq}} & = \text{equilibrium constant of } i\text{th surface reaction, units depend on reaction} \\
K_{\text{SP}} & = \text{solubility product of calcium carbonate, mol}^2/\text{L}^2 \\
L & = \text{characteristic length, length} \\
P_e & = \text{Peclet number, } u_0/D, \text{ unitless} \\
r_A & = \text{calcium carbonate dissolution rate in water, mol/length/time} \\
R & = \text{ideal gas constant, volume } \times \text{pressure}/(\text{temperature } \times \text{mol}) \\
S_i & = \text{ith surface reaction, unitless} \\
S_{\text{dis}} & = \text{characteristic rock-dissolution time, time} \\
S_{\text{m}} & = \text{characteristic mass-transport time, time} \\
S_{\text{res}} & = \text{residence time in the porous medium, time} \\
S_{\text{ro}} & = \text{characteristic reaction time for calcium carbonate rock, time} \\
T & = \text{absolute temperature, K} \\
u & = \text{frontal advance rate, length/time} \\
v & = \text{characteristic velocity, length/time} \\
z_i & = \text{valence of } i\text{th species, unitless} \\
y_{H+} & = \text{activity coefficient of hydronium ion in solution, unitless} \\
y_i & = \text{dilute-solution activity coefficient of species } i, \text{ unitless} \\
\Gamma & = \text{ion-exchange capacity, where index denotes the state, unitless} \\
\delta & = \text{gap/fracture thickness, length} \\
v & = \text{dielectric permittivity of water, Farads/m} \\
u_0 & = \text{dielectric permittivity of free space, Farads/m} \\
u & = \text{relative permittivity of water, unitless} \\
C \bar{e}_{\text{avg}} & = \text{average dielectric constant in diffuse layer} 
\end{align*}
\]
\[\zeta = \text{zeta potential, energy/charge}\]
\[\kappa = \text{scaling constant, length = time \times concentration}\]
\[\lambda = \text{Debye length} = \sqrt{\frac{RT}{2\pi F}} \text{ length}\]
\[\mu_i^e = \text{Chemical potential of species } i; \text{ symbol } ^e \text{ denotes the standard-state Gibbs free energy of aqueous species } i, \text{ while } e \text{ indicates chemical potential at equilibrium, energy}\]
\[\nu_{ij} = \text{stoichiometric coefficient of species } i \text{ in } j \text{ reaction, unitless}\]
\[\xi_i = \text{extent of the } j \text{ reaction, where bottom tilde denotes vector of extents, mol/L}\]
\[\sigma_{i,j} = \text{net surface charge density, where } 0, \beta, \text{ and } d \text{ denote different planes, charge/area}\]
\[\phi_{i,j} = \text{electrostatic potential at } 0-, \beta-, \text{ and } d-\text{planes, energy/charge}\]

**Other Notations**

- \(\text{CaHCO}_3\) notation used to denote surface species, where \(>\) denotes mineral surface
- \(\text{CO}_2(\text{aq})\) denotes aqueous \(\text{CO}_2(\text{g})\)
- \(\text{CO}_2(\text{g})\) denotes \(\text{CO}_2\) in gas phase
- \(\text{CO}_2(\text{oil})\) denotes \(\text{CO}_2(\text{g})\) dissolved in oil phase
- \(P_{\text{CO}_2}\) denotes partial pressure of \(\text{CO}_2(\text{g})\)
- \(p_{\text{CO}_2} = -\log_{10}[\text{CO}_2(\text{aq})]\)
- \(p_{\text{H}_2}\) denotes aqueous \(\text{CO}_2(\text{g})\)

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Appendix A—Calcium Carbonate Dissolution Kinetics

Mineral dissolution occurs in sequential steps, including ion transfer between the crystal-lattice surface and the immediately adjacent aqueous solution, and transport of released solvated ions into bulk aqueous solution. The characteristic time for mineral dissolution/precipitation, $t_{\text{dis}}$, is the sum of the characteristic reaction and mass-transport times: $t_{\text{dis}} = t_{\text{rxn}} + t_{\text{trxn}}$. Equivalently, the resistance to dissolution is the sum of the resistance for mineral-surface ion dislodgement and resistance for flushing dislodged solvated ions into solution. We estimate each characteristic time in order.

To establish $t_{\text{rxn}}$, we formulate a simple linear expression for pure calcium carbonate rate of dissolution into aqueous solution, $r_A$ (mol/m²/s). Fig. A-1 illustrates the dissolution process. Our goal is to quantify the intrinsic rate constant $k_{\text{rxn}}$ (cm/s) from experimental data on $r_A$. We begin with the rock equilibrated with brine.

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Fig. A-1—Dissolution of solid calcium carbonate into aqueous solvated ions directly at the solid/liquid interface.

Rock/Brine Equilibrium. When the dissolution/precipitation reaction is in equilibrium, as denoted by superscript \( e \), reaction equilibrium demands that

\[
\mu_{CaCO_3(e)} = \tilde{\mu}_{Ca^{2+}} + \tilde{\mu}_{CO_3^{2-}} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \Quad
in carbonate matrix domains as \(\approx 1\) \(\mu\)m. Therefore, the characteristic reaction time for calcium carbonate rock \([i.e., t_{\text{diss}} = (a_l k_{\text{diss}})^{-1}]\) lies between 15 milliseconds and 1.5 seconds. Molecular kinetic steps occurring at the calcite-aqueous surface are rapid.

Evaluation of \(t_{\text{diss}}\) also requires \(t_m\), the time scale to transport solvated ions away from the mineral surface. This exercise demands consideration of different transport modes depending on the pertinent length scales of the porous medium (Kim and Santamarina 2016). For fractures, the Péclet number, \(Pe\), is defined as \(u d / D\) (Bird et al. 2007), where \(D\) is the aqueous-salt-diffusion coefficient, typically \(10^{-5}\) cm\(^2\)/s, and \(u\) is the frontal advance rate approximated here as 10 to 100 ft/D. For either velocity, \(Pe \gg 1\); mass transport in fractures is convection dominated.

Convection in fractures is quantified here by Darcy flow through a slit of gap thickness, \(\delta\). The Graetz theory for plug flow in a slit under fully developed mass transfer (Bird et al. 2007) gives a convective-mass-transfer coefficient of \(k_m = 5D/\delta\) or \(5 \times 10^{-4}\) cm/s, which is within the range of the carbonate-surface kinetic-rate constant. The characteristic fracture-mass-transfer time follows from \(t_m = (a_l k_m)^{-1}\) or 30 milliseconds when we adopt a roughness size of 1 \(\mu\)m. Accordingly, the characteristic dissolution-time constant, \(t_{\text{diss}} = (a_l k_m) + t_m\), ranges from 45 milliseconds to 1.5 seconds, independent of the frontal advance rate.

Conversely, for mass transport away from dissolving grains in matrix zones, the characteristic length appearing in the Péclet number is the grain diameter, chosen here as \(\approx 20\) \(\mu\)m. Even for imbibition velocities of 1 ft/D, \(Pe < 1\). On the pore scale, solvated ion transport is dominated by diffusion. Here, the mass-transfer coefficient \(k_m = 2D / \delta\) (Bird et al. 2007, page 686) or 0.01 cm/s. Again, assuming a characteristic grain-roughness size of 1 \(\mu\)m, the characteristic diffusion-time constant in the low-permeability matrix, \(t_m = (a_l k_m)^{-1}\), is 2 milliseconds. We conclude that dissolution time in rock matrix blocks is again \(t_{\text{diss}} = 45\) milliseconds to 1.5 seconds, independent of the frontal advance rate. For both high- and low-permeability zones of carbonate rocks, the kinetics of rock dissolution is fast, at the longest a few seconds. We use this finding in the main text to establish that local equilibrium sets the carbonate-reservoir-brine composition.

**Appendix B—Calcite/Aqueous-Electrolyte Bulk Equilibria**

In this work, we use PHREEQC software with its default database (phreeqc.dat) for calculation of bulk equilibrium speciation. However, the PHREEQC procedure was validated as described here. At equilibrium,

\[
K_j = \prod a_i^{n_i} = \exp \left( \sum \frac{\nu_j \mu_i}{RT} \right) \tag{B-1}
\]

where \(K_j\) is the \(j\)th independent reaction equilibrium constants, \(a_i = \gamma_i / C_i\) is the activity of species \(i\), \(\mu_i\) is the standard-state Gibbs free energy of aqueous species \(i\) in the dilute solution or Henry’s standard state, and \(\nu_j\) is the stoichiometric coefficient of species \(i\) in reaction \(j\). \(R\) is the ideal-gas constant, and \(T\) is absolute temperature. The exponential argument in Eq. B-1 is a function of temperature only; \(\mu_i\) for each species is tabulated at standard conditions. Therefore, the exponential argument can be evaluated as a function of temperature by use of the Gibbs-Helmholtz relation and the standard enthalpy of reaction (Felder et al. 2015).

At high (> 1 mM) ionic strength, activity coefficients cannot be assumed as unity. Ionic strength of a solution is defined by

\[
I = \frac{1}{2} \sum z_i^2 C_i \tag{B-2}
\]

where \(z_i\) is the valence of species \(i\) and \(C_i\) is the molar concentration of charged species \(i\). The Davies (1962) equation is used to calculate the activity coefficient for each charged species; it is given as

\[
\log_{10} \gamma_i = -A \left( \sqrt[3]{\frac{I}{1 + \sqrt[3]{I}}} - 0.3 I \right) \tag{B-3}
\]

where \(A\) is a constant that depends only on temperature \([0.5085 (\text{mol/L})^{0.5} \text{ for } 25\degree\text{C}]\). For uncharged species, the Setschenow (1899) equation evaluates the activity coefficients:

\[
\log_{10} \gamma_i = b_i I \tag{B-4}
\]

where \(b_i\) is assumed to be 0.1 M^{-1} for all the uncharged species, unless otherwise specified. Along with mass conservation listed in Table B-1 and the solubility product of calcium carbonate (Reaction 6 in Table 1), Eqs. B-1 through B-4 establish the aqueous-speciation-equilibrium concentrations.

The set of eight nonlinear algebraic equations shown in the last column of Table B-1 was programed in MATLAB (2015) and solved for the extent-of-reaction vector \(\xi\) by use of the Newton-Raphson method with an \(L_2\)-norm convergence threshold of \(10^{-16}\):  

\[
\xi_{i+1} = \xi_i - \frac{\left[ \frac{df(\xi)}{d\xi} \right]^{-1} f(\xi)}{\frac{df(\xi)}{d\xi} \xi} \tag{B-5}
\]

where subscript \(i\) denotes the \(i\)th iteration.

Constant CO2 pressure was imposed on the system, fixing both CO2(aq) and H2CO3 concentrations. Ionic-strength variation resulting from dissolution of calcite or CO2 was iterated in the Davies equation (Eq. B-3) until less than a 5% difference was reached. This value was then used to convert concentrations to activities. The vector of initial guesses for the Newton-Raphson algorithm was 10^{-4} for all concentrations.

To compare the MATLAB results with PHREEQC software, the default database was changed to run simulations with the Davies activity correction. The MATLAB code and PHREEQC gave identical results. After validation, the PHREEQC software was used to calculate bulk speciation for all species shown in Table B-1 at both low and high ionic strengths. PHREEQC uses extended Debye-Hückel equations (applicable from 0 to 0.1 mol/L ionic strength) or WATEQ extended Debye-Hückel equations, which allow for activity correction at higher ionic strengths (Truesdell and Jones 1974):

\[
\log_{10} \gamma_i = -\frac{A_i^2 \sqrt{I}}{1 + B_i a^2 \sqrt{I}} + b_i I \tag{B-6}
\]
where $z_i$ is the valence of aqueous species $i$, and $A$ and $B$ are constants dependent only on temperature $[0.5085 (\text{mol/L})^{0.5} + 3.3 (\text{mol nm}^2/\text{L})^{0.5}]$, respectively, at $25^\circ\text{C}$, $I$ is ionic strength, and $\gamma_i$ is activity coefficient. If $b_i = 0$, Eq. B-6 is the extended Debye-Hückel equation; otherwise, it is the WATERQ extended Debye-Hückel. In the extended Debye-Hückel equation, $a_i^0$ is the ion-size parameter, whereas in the WATERQ extended Debye-Hückel equation, $a_i^B$ and $b_i$ are ion-specific parameters fitted from the mean salt-activity-coefficient data. In the PHREEQC database (see the PHREEQC standard database, phreqc.dat), these parameters are specified for each ion. If they are not present, PHREEQC resorts to the extended Debye-Hückel or to the Davies (1962) equation. For uncharged species, $A$ is zero, and Eq. B-6 reduces to the Setschenow (1899) equation (Eq. B-4); the $b_i$ parameter is specified for each species.

### Definitions

<table>
<thead>
<tr>
<th>Definitions</th>
<th>Mass-Balance Equations*,**</th>
<th>Equilibrium Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1 = [\text{CO}_2^{(aq)}]$</td>
<td>$C_1 = P_{\text{CO}_2} K_1$</td>
<td>$\log_{10} \gamma_i = -A_i^i \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$;</td>
</tr>
<tr>
<td>$C_2 = [\text{H}_2\text{CO}_3]$</td>
<td>$C_2 = C_1 K_2$</td>
<td>For charged species</td>
</tr>
<tr>
<td>$C_3 = [\text{HCO}_2^-]$</td>
<td>$C_3 = C_1 + \xi_1 - \xi_2 + \xi_4 + \xi_5$</td>
<td>$\log_{10} \gamma_i = b_i I$;</td>
</tr>
<tr>
<td>$C_4 = [\text{CO}_3^{2-}]$</td>
<td>$C_4 = C_1 + \xi_1 - \xi_2 + \xi_4 + \xi_5$</td>
<td>For uncharged species</td>
</tr>
<tr>
<td>$C_5 = [\text{H}^+]$</td>
<td>$C_5 = C_3 + \xi_1 + \xi_2 + \xi_3$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_6 = [\text{OH}^-]$</td>
<td>$C_6 = C_3 + \xi_1 + \xi_2 + \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_7 = [\text{Ca}^{2+}]$</td>
<td>$C_7 = C_4 + \xi_1 + \xi_2 + \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_8 = [\text{Na}^+]$</td>
<td>$C_8 = C_4 + \xi_1 + \xi_6$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_9 = [\text{Cl}^-]$</td>
<td>$C_9 = C_4 + \xi_1$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_{10} = [\text{CaOH}^+]$</td>
<td>$C_{10} = C_9 - \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_{11} = [\text{CaHCO}_3^-]$</td>
<td>$C_{11} = C_9 - \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_{12} = [\text{NaHCO}_3]$</td>
<td>$C_{12} = C_9 - \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
<tr>
<td>$C_{13} = [\text{NaCO}_3]$</td>
<td>$C_{13} = C_9 - \xi_5$</td>
<td>$K_{i}C_{j}^{z_i} (C_{j}^{z_j}) = 0$;</td>
</tr>
</tbody>
</table>

*The numbering on extents in the Mass-Balance Equations column refers to the reaction numbers in Table 1 but shifted by two, so that Reaction 3 in Table 1 corresponds to $\xi_i$. **In the Mass-Balance Equations column, the superscript 0 denotes inlet or initial concentrations.

### Appendix C—Surface-Calcite/Aqueous-Electrolyte Equilibria

Let $\sigma_0$, $\sigma_b$, and $\sigma_d$ denote the surface-charge densities in Fig. 4 at the calcite surface, at the $\beta$-plane, and in the diffuse layer extending outward from the $d$-plane, respectively. Overall electroneutrality demands that $\sigma_0 + \sigma_b + \sigma_d = 0$. However, the crystal structure of calcite at the (104)-face specifies that the density of calcium-lattice ions at the surface be the same as that of surface-carbonate-lattice ions; therefore, $\sigma_0$ is zero. Thus, the governing relation for the SCM is

$$\sigma_b + \sigma_d = 0.$$  \hspace{1cm} (C-1)

We must specify these two surface-charge densities. To quantify $\sigma_b$, equilibrium-site-binding chemical reactions are introduced. As discussed in the text, we chose the five preliminary surface reactions listed in Table 2, where $>$ denotes surface ions. As illustrated in the text, mass-action equations are applied to each of the five site-binding reactions. These are rewritten as follows:

$$K_{S1}(>\text{CaH}_2\text{O}^+)-(<\text{CaOH})_{\beta}^H\text{ exp}\left[\frac{-F \varphi_b}{RT}\right] = 0,$$  \hspace{1cm} (C-2)

$$K_{S2}(>\text{CaH}_2\text{O}^+)\gamma_{\text{HCO}_3}^\beta <\text{CaHCO}_3^\beta \text{ exp}\left[\frac{-2F \varphi_b}{RT}\right] = 0,$$  \hspace{1cm} (C-3)

$$K_{S3}(>\text{CaH}_2\text{O}^+)\gamma_{\text{CO}_3}^\beta <\text{CaCO}_3^\beta \text{ exp}\left[\frac{2F \varphi_b}{RT}\right] = 0,$$  \hspace{1cm} (C-4)

$$K_{S4}(>\text{CO}_3^-)\gamma_{\text{H}^+}^H <\text{CO}_3\text{H}^+ \text{ exp}\left[\frac{F \varphi_b}{RT}\right] = 0,$$  \hspace{1cm} (C-5)

$$K_{S5}(>\text{CO}_3^-)\gamma_{\text{Ca}^{2+}}^d <\text{CaCO}_3^\beta \text{ exp}\left[\frac{2F \varphi_b}{RT}\right] = 0,$$  \hspace{1cm} (C-6)

where curved parentheses (i) denote surface concentrations in number (sites) per unit area, and $\varphi_b$ is the electrostatic potential at the $\beta$-plane. To understand the origin of the $\beta$-plane electrostatic potential appearing in Eqs. C-2 through C-6, we write the excess chemical potential for each surface species at the $0$- and $\beta$-planes as $RT \ln (<S_i>)_0 + z_i F \varphi_b$ and $RT \ln (<S_i>)_\beta + z_i F \varphi_b$, respectively, where ($<S_i>$)0
and \( (> S_i) \) denote species \( i \) surface concentrations in the 0- and \( \beta \)-planes. Substitution of these relations into reaction-equilibria criteria provides Eqs. 2 through 6 because \( \phi_\beta = \phi_0 \) because of the calcite-surface-lattice electroneutrality. The surface-complexing equilibrium constants, \( K_b \), are listed in Table 2. Reaction equilibria at ion-exchange sites are augmented by conservation of total sites or

\[
\Gamma_{\text{max}} = (> \text{CaH}_2\text{O}^+) + (> \text{CaHCO}_3^-) + (> \text{CaCO}_3^-) + (> \text{CaOH}), \quad \ldots \quad (C-7)
\]

\[
\Gamma_{\text{max}} = (> \text{CO}_3^-) + (> \text{CO}_3\text{Ca}^+) + (> \text{CO}_3\text{H}), \quad \ldots \quad (C-8)
\]

where \( \Gamma_{\text{max}} = 5 \text{ nm}^{-2} \) is the equal anion- and cation-exchange capacities of the calcite-lattice surface. Not all ions can reach this maximal value. \( \Gamma_{\text{max}} \) for large ions, for example \( \text{Zn}^{2+} \), should be corrected to consider steric limitations (Davis and Kent 1990). Finally, charge density at the \( \beta \)-plane is defined by the surface concentrations of specifically adsorbed charged ions, as illustrated in Fig. 3:

\[
\sigma_i = (> \text{CaH}_2\text{O}^+) + 2(> \text{CaHCO}_3^-) - (> \text{CaOH}) - (> \text{CaHCO}_3^-) + 2(> \text{CaH}_2\text{O}^+) = \Gamma_{\text{max}} \quad (C-9)
\]

Next, the expression for the surface-charge density in the diffuse layer, \( \sigma_d \), is obtained from the Poisson-Boltzmann equation written for constant dielectric permittivity (Verwey and Overbeek 1948; Newman and Thomas-Alyea 2004; Berg 2010):

\[
\varepsilon \frac{d^2 \phi}{dx^2} = - \sum_i \sigma_i F \exp \left[ - \frac{z_i F \phi(x)}{RT} \right]. \quad \ldots \quad (C-10)
\]

where the linear coordinate \( x \) extends from the 0-plane. Eq. C.10 is rearranged to

\[
\frac{d}{dx} \left( \frac{d \phi}{dx} \right)^2 = - \frac{2F}{\varepsilon} \sum_i \sigma_i \exp \left[ - \frac{z_i F \phi}{RT} \right] \left( \frac{d \phi}{dx} \right) \quad (C-11)
\]

and integrated subject to boundary conditions of the asymptotic approach to zero potential far from the surface. The result is

\[
\left( \frac{d \phi}{dx} \right)^2 = \frac{2RT \sum_i \sigma_i}{\varepsilon} \left\{ \exp \left[ - \frac{z_i F \phi}{RT} \right] - 1 \right\} \quad (C-12)
\]

Evaluation of Eq. C.12 by Gauss’ law at the \( d \)-plane [i.e., \( \sigma_d = -\varepsilon (d \phi/dx)_d \)] provides Eq. 6 in the main text. We replace the bulk relative permittivity of water by an average value of 50 over the distance from the \( d \)-plane to infinity. The final step is a relation between potentials \( \phi_\beta \) and \( \phi_d \), which follows from Poisson and Gauss:

\[
\phi_\beta - \phi_d = - \frac{\sigma_d}{C_2} \quad (C-13)
\]

where \( C_2 \) is the constant integral capacitance between the inner and outer Helmholtz planes. \( C_2 \) is determined by the ratio of the local dielectric permittivity to the width of the region. We adopt a relative dielectric constant of 15 in this region, which has a width of 0.22 nm. As listed in Table 3, an integral capacitance of 13 \( \mu \text{F/cm}^2 \) emerges, a physically acceptable value.

Given the bulk aqueous-species concentrations from Appendix B, Eqs. 6, C.1 through C.9, and C.13 are solved by Newton iteration in MATLAB for the variables \( \sigma_d, \phi_\beta, \phi_d \) and the seven surface-species concentrations in Table 2.

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