Higher oil recovery after waterflood in carbonate reservoirs is attributed to increasing water wettability of the rock that in turn relies on complicated surface chemistry. However, calcite mineral reacts with aqueous solutions, and can alter substantially the composition of injected water by mineral dissolution. Carefully designed chemical and/or brine flood compositions in the laboratory may not remain intact while the injected solutions pass through the reactive reservoir rock. This is especially true for a low-salinity waterflood process, where some finely-tuned brine compositions can improve flood performances, whereas others cannot.

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At typical calcite reaction rates, local equilibrium is established immediately upon injection. Using an open-source algorithm (Charlton and Parkhurst 2011), we present a design tool to specify chemical/brine flooding packages that correct for composition alteration by carbonate rock.

Here, we present a comprehensive 1D reactive transport model and validate it against analytic solutions for rock dissolution, ion exchange, and longitudinal dispersion, each considered separately. A companion paper compares the proposed theory against experiments on core plugs of Indiana limestone that serve as high velocity probes for reaction-controlled and mass-transfer-controlled dissolution. Finally, in another companion paper, we give examples of how injected salinity compositions deviate from those designed in the laboratory for water-wettability improvement based on contact angles, zeta potentials, surface charge densities, and ion exchange. How to correct the design chemical packages for exposure to reactive rock is also discussed in there.
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Chemical Compositions in Salinity Waterflooding of Carbonate Reservoirs: Theory

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Abstract Higher oil recovery after waterflood in carbonate reservoirs is attributed to increasing water wetting of the rock that in turn relies on complicated surface chemistry. However, calcite mineral reacts with aqueous solutions, and can alter substantially the composition of injected water by mineral dissolution. Carefully designed chemical and/or brine flood compositions in the laboratory may not remain intact while the injected solutions pass through the reactive reservoir rock. This is especially true for a low-salinity waterflood process, where some finely-tuned brine compositions can improve flood performances, whereas others cannot.

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Keywords Modified Salinity Waterflood, Incremental Oil Recovery, Reactive Transport Modeling
1 Introduction

Carbonate reservoirs contain over 50% of current proven oil reserves Schlumberger (2020 (accessed May 31, 2020). Improved oil recovery is challenging in carbonates, primarily because of their complex heterogeneities. Importantly, carbonate rocks also exhibit significant aqueous solubility. This means that during waterflood, contact with the reservoir rock can significantly alter the injected brine chemistry. Any water-based flooding process that requires injection of chemicals, even simple brines, is plagued by alteration of the injection composition due to mineral dissolution and precipitation, and by adsorption and ion exchange with the porous-rock minerals. Oil-displacement processes that require specifically tailored laboratory chemical packages can be changed enough by rock interaction to be ineffective under field conditions.

A pertinent example is low-salinity waterflooding (LSW), in which injected brine is typically diluted compared with the *in-situ* brine. LSW is appealing because of its simplicity and low cost. Although extensively studied, the oil-recovery mechanism(s) of LSW remain fuzzy (Sohal et al. 2016; Purswani et al. 2017; Katende and Sagala 2019; Bartels et al. 2019; Hao et al. 2019). There is some consensus that injected brine compositions should be chosen to alter rock wettability towards more water wet by controlling, for example, surface charge at the rock/brine interface and/or by detaching asphaltene molecules from the rock surfaces (Norrman et al. 2018; Hu et al. 2018; Collini et al. 2020; Shaik et al. 2020). Mineral surface chemistry is a sensitive function of *in-situ* brine composition, in particular aqueous pH. In reactive porous media, chemical flooding packages devised in the laboratory do not transfer directly to field applications.

The goal of this work is to establish how carbonate rock changes brine chemistry during flow through a reactive porous medium. We provide a new tool to establish injection compositions that achieve the desired compositions in the pores of the rock. When flowing in a carbonate rock, aqueous compositions are altered by rock dissolution/precipitation kinetics and mass transfer of multiple minerals, ion exchange/adsorption on those minerals, initial reservoir CO₂ level, and solute dispersion, among others. As the solution brine composition adjusts during flow in a reactive rock, so do rock surface compositions in equilibrium with the pore solutions. Local crude oil/brine/rock wettability depends on both surface and bulk compositions, although the exact mechanism(s) for wettability alteration is not currently known.

Our computation methodology is that of transport in reactive porous media which has a rich history, e.g. (Steefel et al. 2005; Tournassat and Steefel 2019). In the specific case of aqueous flow in carbonate media, considerable effort has also been expended (Nasralla et al. 2015; Chandrasekhar et al. 2016; Korrani et al. 2016; Farajzadeh et al. 2017; Eftekhari et al. 2017; Maes and Geiger 2018; Bonto et al. 2019). With the exception of Maes and Geiger (2018) who use a Lattice-Boltzmann approach, all works approximate numerically the continuum convective mass-transport equations. Many researchers (Nasralla et al. 2015; Chandrasekhar et al. 2016; Korrani et al. 2016; Farajzadeh et al. 2017; Bonto et al. 2019) couple their in-house numerical transport codes with the well-documented and verified reactive-species equilibria calculated by a USGS code called PHREEQC (Parkhurst and Appelo 1999). Unfortunately, only Korrani et al. (2016) test their calculations against experiment. Few researchers evaluate surface species that are essential to understanding of surface
wettability. To our knowledge, no efforts include all effects of dissolution kinetics and mass transfer, ion exchange, and dispersion for multiple aqueous-reaction species in the bulk and at the surface. None utilize available open-source codes.

In our description of reactive flow in carbonate rock, we include hydrodynamic dispersion, kinetic and mass-transfer effects in the dissolution of calcite together with exchange reactions on clay, and calcite surface equilibria. Our 1D single-phase reactive-transport code is built on PHREEQC. To ascertain surface-charge density profiles, we include surface speciation equilibria.

Here, we focus on the general theoretical formulation and on the validation of the numerics by benchmarking against separate analytic solutions of reactive transport, ion-exchange dynamics, and tracer dispersion. In a companion paper, model comparison will be made to experimental ion-concentration histories from flow through Indiana limestone core plugs (Indiana Limestone Institute 1979). Application of our findings to examine in-situ compositions relevant for LSW will be addressed in a companion paper. Below we describe our theoretical approach followed by example calculations. Description and validation of the numerical approach outlined in the Supporting Information.

2 Theory

Prediction of aqueous compositions during frontal displacement through porous carbonate rock is a challenge because of the rock reactivity, and because of the involved speciation chemistry in the bulk aqueous and rock-surface phases. For example, Table 1 lists typical carbonate species and their equilibrium constants. In general, the convection-diffusion equation must be written for each element including aqueous speciation reactions, rock reaction kinetics, rock surface adsorption that includes ion exchange and surface ion complexation (Lake et al. 2003; Felder and Rousseau 2005; Al-Shalabi et al. 2014; Yutkin et al. 2018), and axial dispersion. Here we consider a 1D reactive transport model.

2.1 Reactive Transport

Tables 1 and 2 describe the species that participate in the aqueous phase-carbonate reactions, along with their equilibrium constants at ambient temperature for bulk and surface chemistry, respectively (Yutkin et al. 2018). Units for use in the equilibrium constants are listed to aid the reader. Table 2 is slightly changed from that of Yutkin et al. (2018) to include sodium surface species in reaction S6. The symbol > in Table 2 denotes species at the calcite surface in surface concentration units. Each of the bulk aqueous species, in addition to chloride ions, must be tracked during flow through a porous carbonate rock. This is a daunting task, especially when several reactive reservoir minerals, such as anhydrite and/or dolomite, are present in addition to calcite. We assume insignificant reactive loss of the minerals under typical conditions of low salinity waterflood. All aqueous species are in reaction equilibrium at ambient temperature.
To account for aqueous equilibrium reactions, we conserve element masses (Felder and Rousseau 2005; Al-Shalabi et al. 2014). During frontal displacement in a 1D reactive porous medium, conservation of element $i$ demands that (Yeh and Tripathi 1991; Steefel and Lasaga 1994; Walter et al. 1994; Qiao et al. 2015; Eftekhari et al. 2017)

$$
\frac{\varphi}{t} \frac{\partial C_{iE}}{\partial t} + (1 - \varphi) a_{V_n} \frac{\partial n_{iE}}{\partial t} + u \frac{\partial C_{iE}}{\partial x} = D_{iE} \frac{\partial^2 C_{iE}}{\partial x^2} + (1 - \varphi) a_{V_r} r_{iE}
$$

(1)

where $\varphi$ is the fluid-accessible porosity; $C_{iE}(t, x)$ is the $i^{th}$ element pore molar concentration; $a_{V_n}$ is mineral surface area per solids volume for species adsorption; $a_{V_r}$ is reactive mineral surface area per solids volume; $n_{iE}(t, x)$ is the adsorbed molar concentration of element $i$ on solid surfaces per unit solids volume; $t$ is time, $x$ is axial distance; $u$ is superficial velocity (i.e., $u/\varphi$ is the frontal advance rate); $D_{iE}$ is the dispersion coefficient of element $i$; and $r_{iE}$ is the net production rate of element $i$ from minerals per unit solids surface area (mol/m$^2$/s). All aqueous species are in reaction equilibrium as enumerated in Table 1, except for Reaction 6 for the carbonate mineral which is accounted for separately by dissolution reaction kinetics. Element concentrations are those of all aqueous species $j$ in Table 1.

$$
C_{iE} \equiv \sum_j s_{ij} C_j
$$

(2)

where $C_j$ is the concentration of species $j$ in the pores and $s_{ij}$ is the stoichiometric coefficient of element $i$ in species $j$. Likewise, the adsorbed element amounts are related to adsorbed species $j$ in Table 2 by

$$
(1 - \varphi) a_{V_n} n_{iE} \equiv \sum_k \varphi_k a_{V_k} \sum_j p_{ijk} n_{jk}
$$

(3)

where $\varphi_k$ is the volume fraction of mineral $k$; $a_{V_k}$ is the surface area per unit solid volume of mineral $k$; $n_{jk}(t, x)$ is the molar concentration of species $j$ adsorbed on mineral $k$ per unit solid area (mol/m$^2$); and $p_{ijk}$ is the stoichiometric coefficient of element $i$ in species $j$ adsorbed on mineral $k$. Table 2 lists typical surface species for carbonate rock (Yutkin et al. 2018).

The element dispersion term is given by the expression

$$
D_{iE} \frac{\partial^2 C_{iE}}{\partial x^2} \equiv \sum_j s_{ij} D_{Lj} \frac{\partial^2 C_j}{\partial x^2}
$$

(4)

where $D_{Lj}$ is the longitudinal dispersion coefficient of species $j$. Lastly, the element mineral dissolution rate in Equation 1 is expressed for minerals $k$ as

$$
(1 - \varphi) a_{V_r} r_{iE} \equiv \sum_k \varphi_k a_{V_k} r_{ik}
$$

(5)

where $r_{ik}$ is the net production rate of element $i$ from mineral $k$ per unit surface area of the solid (mol/m$^2$/s).
The boundary conditions for Equation 1 by Danckwerts (1953), and Pearson (1959) prescribe continuity of the flux of each species at the column inlet and outlet. When written in terms of elements $i$, these boundary conditions become

\[ u C_{iE0} = u C_{iE}(t,0) - D_{iE} \frac{\partial C_{iE}(t,0)}{\partial x} \]  
\[ \text{at } x = 0 \]  

and

\[ \frac{\partial C_{iE}(t,L)}{\partial x} = 0 \]  
\[ \text{at } x = L \]  

with

\[ D_{iE} \frac{\partial C_{iE}(t,0)}{\partial x} \equiv \sum_j s_{ij} D_{Lj} \frac{\partial C_{j}(t,0)}{\partial x} \]  

where $x = 0$ is the medium inlet and $x = L$ is the medium outlet.

Equations 1 – 8 are general. For our particular application to limestone rock, we consider only reactive calcite and combined ion exchange on calcite and clay minerals. We include clay as an adsorptive mineral because of the ion-exchange characteristics we find in our Indiana Limestone corefloods described in a companion paper. For the aqueous phase, Table 1 lists 12 species not including excess water. To this number we add any brine species that do not participate in the carbonate-reaction or ion-exchange equilibria. Because we consider brine as aqueous NaCl/CaCl$_2$ mixture, chloride ions added as a species. Table 2 lists another 8 surface reaction species denoted by the prefix $\succ$. Following all bulk and surface species is a challenge. However, when those species are in local equilibrium, only elements need be tracked (Al-Shalabi et al. 2014; Yutkin et al. 2018).

In our example calculations and experimental corefloods, there is no free gas phase, and Reaction 1 does not participate, although it is pertinent to reservoir simulations. As a result, the concentration of aqueous carbon dioxide in the water-filled pores of the medium is set by calcite equilibrium. In the remaining Reactions 3–10 in Table 1, there are 4 independent elements: sodium, calcium, hydrogen (sans excess water), and carbonate, i.e., carbon and oxygen appear in all species at a 3/1 ratio. There is no need to impose electroneutrality in Reactions 3–10 because each is charge-neutral (Al-Shalabi et al. 2014; Yutkin et al. 2018). Sodium ions do not originate from calcite dissolution. Consequently, Reactions 9 and 10 only occur when sodium ions are present in the aqueous brine. Because we consider NaCl/CaCl$_2$ brines, in addition to the 4 elements in Table 1, chloride ion becomes the 5$^{th}$ independent element. Overall electroneutrality is imposed on the brine. Once the profiles of the elements and corresponding aqueous species are established, surface-species concentration profiles follow from the known surface-reaction equilibria in Table 2. Implicit in the surface calculations is the assumption that reactive minerals remain in excess and are not depleted to alter rock porosity.

Not all element balances contain all terms in Equation 1. For example, chloride ions do not participate in ion exchange and in carbonate-species reactions. Consequently, for chloride ions, ion-exchange and reaction-rate terms are absent, and Equation 1 reads
\[ \phi \frac{\partial C_{\text{Cl}^-}}{\partial t} + \frac{u}{\phi} \frac{\partial C_{\text{Cl}^-}}{\partial x} = D_L \frac{\partial^2 C_{\text{Cl}^-}}{\partial x^2} \]  

(9)

The dispersion coefficient in Equation 9 does not have a species-specific subscript because all aqueous species in Table 1 are dilute, and have about the same aqueous molecular diffusion coefficients, \( D_m \approx 10^{-9} \text{ m}^2/\text{s} \). To understand the role of dispersion, we vary the longitudinal dispersion Péclet number, \( Pe_L = uL/D_L \). Equation 9 indicates that chloride ions behave as an ideal tracer. Without dispersion, chloride ions transport along the core as a salinity wave with no holdup (Pope et al. 1978).

Conversely, calcium retains all terms in Equation 1. Thus, we have that

\[ \phi \sum_{j=1}^{3} s_{ij} \frac{\partial C_j}{\partial t} + \frac{\varphi_2 aV_2}{\phi} \frac{\partial n_i}{\partial t} + u \sum_{j=1}^{3} s_{ij} \frac{\partial C_j}{\partial x} = \sum_{j=1}^{3} s_{ij} D_L \frac{\partial^2 C_j}{\partial x^2} + \varphi_1 aV_1 r_1 \]  

(10)

where \( i \) designates calcium. Table 1 indicates that calcium species \( j = 1 - 3 \) correspond to \( \text{Ca}^{2+}, \text{CaOH}^+, \text{CaHCO}_3^+ \) aqueous ions, respectively. We label mineral 1 as calcite. Mineral 2 represents adsorptive minerals including calcite and clay. On calcite and clays, sodium/calcium ion exchange obeys local equilibrium or

\[ \frac{\partial n_{\text{Ca}^{2+}}}{\partial t} = \frac{\partial n_{\text{Ca}^{2+}}}{\partial C_{\text{Ca}^{2+}}} \frac{\partial C_{\text{Ca}^{2+}}}{\partial t} \]  

(11)

where the ion-exchange isotherm \( n_{\text{Ca}}(C_{\text{Ca}^{2+}}) \) is specified by classical mass action demonstrated in Appendix B

\[ \frac{y_{\text{Ca}^{2+}}}{(1 - y_{\text{Ca}^{2+}})^2} = \left[ \frac{K_{\text{CaNa}C\text{EC}}}{C_{\text{Cl}^-}} \right] \frac{x_{\text{Ca}^{2+}}}{(1 - x_{\text{Ca}^{2+}})^2} \]  

(12)

In Equation 12, \( y_{\text{Ca}^{2+}} = 2n_{\text{Ca}^{2+}}/n_{\text{EC}} \), \( x_{\text{Ca}^{2+}} = 2C_{\text{Ca}^{2+}}/C_{\text{Cl}^-} \), \( K_{\text{CaNa}C\text{EC}} \), is the ion-exchange equilibrium constant, \( C_{\text{Cl}^-} = 2C_{\text{Ca}^{2+}} + C_{\text{Na}^+} \) and \( n_{\text{EC}} = 2n_{\text{Ca}^{2+}} + n_{\text{Na}^+} \) is the cation exchange capacity expressed in units of mole of total exchange sites per unit surface area. In adopting Equation 12, we assume that ion-exchange rates are fast and that local equilibrium in attained. However, typical clay minerals in reservoir rock occur in book stacks, and the assumption of the local equilibrium may be questioned (Mansa et al. 2017; Khoury 2019). For modeling purposes, it is convenient to use exchange capacity in equivalents per liter of pore volume, or \( C_{\text{EC}} = n_{\text{EC}} aV_2 \varphi_2/\varphi \) (Pope et al. 1978; Hill and Lake 1978a). From Equation 12, ion-exchange amounts depend directly on ion-exchange capacity and inversely on chloride-ion concentration.

The remaining term to specify in Equation 10 is the dissolution rate of calcite. We utilize the expression derived by Yutkin et al. (2018, Appendix A).

\[ r_1 = k_{\text{rxn}} \sqrt{K_{\text{SP}}} \left[ 1 - C_{\text{Ca}^{2+}} C_{\text{CO}_3^{2-}} / K_{\text{SP}} \right] \]  

(13)

where \( k_{\text{rxn}} \) is the intrinsic dissolution reaction-rate constant (m/s), and \( K_{\text{SP}} \) is the solubility product of calcium carbonate (i.e., \( K_6 \) in Table 1). Based on the extensive review of Morse and Arvidson (2002) and the references therein, we find that Equation 13 is experimentally verified. At low pH, \( k_{\text{rxn}} \) is a strongly increasing
function of hydrogen-ion concentration. At pH values above about 6, however, $k_{rxn}$ is constant at approximately $10^{-5}$ m/s under ambient conditions (Morse and Arvidson 2002).

Equation 13, however, does not account for the convective mass-transfer resistance encountered by the dissolving calcium and carbonate ions (Bird et al. 2007). For pH values less than about 10, Appendix A demonstrates that

$$r_1 = \frac{k_m \left( \frac{K_{SP}}{C_{CO_3^{2-}}} - C_{Ca^{2+}} \right)}{1 + k_m \sqrt{K_{SP}/(k_{rxn}C_{CO_3^{2-}})}}$$

where $k_m$ is the convective-diffusion mass transfer coefficient appropriate to flow through porous media (Bird et al. 2007). Expressions for the mass transfer coefficient in packed beds are available in Rexwinkel et al. (1997) and Bird et al. (2007, page 486). We adopt Equation 14 to quantify the dissolution kinetics of calcite.

### 2.2 Numerics

Numerical solution of Equations 10 – 14 along with Equation 1 written for carbonate, sodium, and hydrogen elements is challenging. All species in Table 1 must be accounted through Equation 2. We use the 1D explicit central finite-difference implementation of the publicly available PHREEQC code of the US Geological Survey (Charlton and Parkhurst 2011; Yutkin et al. 2018) along with the well-documented extensive aqueous chemistry speciation calculations embodied in PHREEQC. Implementation details are described in Appendix C of SI. Appendix C also benchmarks our numerics against the derived analytic solutions. Distances and times in the species profiles and histories below are dimensionless and reported as $x/L$ and $ut/\varphi L = PV$, respectively. Table 3 lists the pertinent parameters of the example calculations below unless otherwise noted.

In the calculations that follow, reaction and mass-transfer rates are varied through reaction and mass-transfer Damköhler numbers: $Da_{rxn} = 2 \varphi_1 a V_1 k_{rxn} L / u$ and $Da_m = 2 \varphi_1 a V_1 k_m L / u$, respectively. Ion-exchange strength is gauged through the cation exchange capacity ($CEC$), and dispersion is varied through the Péclet number: $Pe_L = u L / D_L$.

### 3 Validation of Results and Discussion

We outline the theoretical results in the order of ion exchange alone, mineral reaction alone, and combined ion exchange with mineral reaction. The roles of reaction rates, mass transport rates, cation exchange capacity, and dispersion are discussed as appropriate. We consider ion exchange alone first.

#### 3.1 Ion Exchange

Figures 1 and 2 illustrate the role of ion exchange for sodium/calcium exchange on clay minerals with no dispersion. Logarithmic concentration profiles at 0.5 PV injected are shown on the left and histories are shown on the right. Calcite mineral is inert (i.e., $Da_{rxn} = 0$). Cation exchange capacity is 0.345 eq/L pore fluid in
Figure 1 and $3.45 \times 10^{-3}$ eq/L in Figure 2, respectively. These values cover a range characteristic of Berea sandstone (Hill and Lake 1978b; Pope et al. 1978). The equilibrium exchange constant, $K_{CaNa}$ is 1500 m$^{-1}$, estimated from Hill and Lake (1978b); Pope et al. (1978). Equations 9 and 10 are solved for calcium (solid lines) and chloride ions (dotted lines). Sodium-ion concentrations (dashed lines) follow from electroneutrality. The initial values of calcium, sodium, and chloride concentrations are 0.1 M, 0.005 M, and 0.205 M, respectively. The corresponding injected concentrations are calcium = 0 M, sodium = 0.01 M, and chloride = 0.01 M. These compositions remain in all subsequent figures.

Examination of the calcium ion-exchange profiles in Figure 1a reveals a salinity shock dropping the calcium concentration from the initial porous-medium value of 0.1 M down to $4 \times 10^{-3}$ M. The calcium concentration behind the salinity shock is set according to equal rock adsorption of calcium at the initial and injected chloride concentrations outlined in Appendix C of SI. A zone of constant calcium concentration (at $4 \times 10^{-3}$ M) follows the salinity shock. This zone precedes a spreading-wave zone of calcium desorption from the rock surface (Hill and Lake 1978b). The fastest wave of this zone corresponds to the calcium concentration of $4 \times 10^{-3}$ M and penetrates out to about $x/L = 0.35$ where it intersects the salinity-induced zone. The slowest calcium concentration wave corresponds to zero injected calcium and penetrates out to about $x/L = 0.01$. There are four calcium-concentration zones in the column: the initial calcium concentration, the salinity-induced concentration zone behind the indifferent salinity wave, a spreading calcium desorption zone, and a final injected-concentration zone. Because hydronium ions are not involved in classical sodium/calcium mass-action ion exchange, there is no effect of pH on ion exchange. With no mineral reaction, injected hydronium ions simply flush those initially present. Chloride behaves as an inert tracer; sodium follows from charge balance. At a $CEC$ of 0.345 eq/L, washout of the ion-exchangeable calcium in Figure 1a takes many pore volumes. Even without rock or aqueous-phase reactions, ion exchange significantly alters injection chemistry. Detailed information on ion-exchange wave dynamics is available in Appendix C of SI.

Figure 2 illustrates the importance of the cation exchange capacity on concentration profiles (a) and histories (b) under the same conditions as those in Figure 1. However, the cation exchange capacity is lowered by a factor of 100 to $3.45 \times 10^{-3}$ eq/L. With the considerably lower ion-exchange capacity, much less calcium resides on the rock surface. As observed in Figure 2a, the abrupt calcium-concentration decline remains at the chloride tracer front but the salinity zone collapses. Spreading calcium desorption waves emanate directly following the tracer chloride wave. Washout of the exchangeable calcium in Figure 2b is much more extensive than that in Figure 1.

Figure 3 investigates the role of axial dispersion on classical sodium/calcium ion exchange, where the amount of dispersion is characterized by a longitudinal Péclet number of $Pe_L = 100$. The remaining conditions are identical to those in Figure 1. As anticipated, all shock fronts smooth with the calcium zone spreading more at the rear than at the front. The injected concentrations do not reach the column outlet for many pore volumes. Hydrodynamic dispersion, completely smears the constant salinity zone. The 1D advective algorithm
3.2 Mineral Reaction

Figures 4 – 6 report the effects of calcite dissolution on concentration profiles and histories with no ion exchange or dispersion. Injected and initial column conditions are the same as those in Figures 1 – 3. Figure 4 illustrates the role of the reaction Damköhler numbers between $10^{-3}$ and $10^2$ for a fixed mass-transfer Damköhler number of 100, large enough for mass transfer to have no effect. The reaction front proceeds through the medium at the frontal advance rate. For all $Da_{rxn}$, there is a reaction zone at the beginning of the reactive medium where calcite dissolves. Beyond that reaction zone, calcium concentration is constant: dissolution products are convected away as fast as they dissolve. At $Da_{rxn} \geq 10$, however, the injected solution beyond the narrow inlet zone reaches equilibrium with the carbonate rock. No further dissolution occurs. Because reaction Damköhler numbers are very large in reservoir applications, this result confirms our previous order-of-magnitude estimates that rock dissolution occurs at the injection wellbore (Yutkin et al. 2018). Consequently, once past the reaction zone, any rock-dissolution-based mechanisms in low salinity waterflood are impossible (Chen et al. 2017). From the corresponding concentration histories in Figure 4, rock reaction neither speeds nor slows species transport advance. Reaction kinetics does not cause tailing of the effluent concentrations as sometimes reported (Austad et al. 2015). Rather, effluent concentrations are constant after breakthrough and approach rock equilibrium for high reaction Damköhler numbers.

Figure 5 is identical to Figure 4, except that the mass-transfer Damköhler number varies between $10^{-3}$ and $10^2$ for a fixed $Da_{rxn} = 100$, characteristic of rock equilibrium beyond the narrow reaction zone. Concentration profiles and histories are similar to those in Figure 4 except for a weaker dependence on $Da_m$. Mass transfer slows dissolution kinetics observed in Equation 14. Beyond the reaction zone, the dissolution product concentrations are constant.

Figure 6 is identical to Figures 4 and 5, except now sodium, hydronium (i.e., pH), and chloride concentration profiles and histories are also shown in addition to calcium. $Da_{rxn} = 100$ and $Da_m = 10^4$ indicating local equilibrium beyond the reaction zone. Calcium concentrations repeat those in Figures 4 and 5. Sodium and chloride concentrations overlap at the particular values chosen for the calculations. pH profiles provide fascinating insight. At the initial column concentrations of calcium = 0.1 M; sodium = 0.005 M; and chloride = 0.205 M, the equilibrium pH in the column is 8.6 (Yutkin et al. 2018). Injected pH is 7 (not shown on the scale of the graph). However, after the reaction zone, calcite dissolution raises the pH from 7 to almost 10. Thus, rock reaction controls aqueous chemistry occurring during a displacement process. In our calculations, CO$_2$ is confined to the aqueous phase. In reservoirs however, CO$_2$ may be present as free gas and/or dissolved in oil phases. In which case, we find pH is controlled by CO$_2$ concentration in the reservoir. Therefore, composition design of advanced waterflooding processes should account for conditions expected in a reservoir, including CO$_2$ sources or sinks.
3.3 Ion Exchange and Mineral Reaction

Figures 7 – 10 reflect simultaneous mineral dissolution and ion exchange. Conditions are the same as those in the preceding figures. Figures 7 – 9 do not include dispersion, whereas Figure 10 does with $Pe_L = 100$. For these four figures, $Da_{rxn} = 100$ and $Da_m = 10^4$ again signifying local equilibrium beyond the reaction zone. All ion concentration profiles and histories in Figure 7, except those for pH, are virtually indistinguishable from those in Figure 1. At a CEC of 0.345 eq/L, ion exchange dominates reaction chemistry. Classical ion exchange is independent of pH. Thus, the pH profile and history in Figure 7 arise because of calcite dissolution. Injected pH (= 7) rises at the column inlet to approximately 9.9, as in Figure 6, but then falls to 9.25 near the salinity front. This is due to the ion-exchange salinity zone influencing aqueous chemistry in addition to calcite dissolution. With reaction chemistry alone in Figure 6, the pH remains at 9.9 up to the salinity shock. In the history of Figure 7b, breakthrough of the salinity-shock wave occurs at one pore volume followed by the salinity zone, by spreading ion-exchange waves, and, finally, by rock-reaction equilibrium concentrations.

Figure 8 is identical to Figure 7, except that more species are portrayed. Especially important is the profile and history of the $\beta$-plane surface charge density, $\sigma_\beta$. Since the calcite surface contains equal numbers of negative and positive sites (Yutkin et al. 2018), the $\beta$-plane charge governs the subsequent adsorption of charged aqueous species. For the conditions of Figure 8, $\sigma_\beta$ is positive at 0.95 $\mu$C/cm$^2$ initially in the core and falls to essentially neutral as the waterflood proceeds. The charge density in the $\beta$-plane depends on aqueous sodium and CO$_2$ concentrations. Sodium ions in Reaction S$_6$ disfavor Reaction S$_5$ and expose negative charge obtained through Reaction S$_3$. Therefore, although positively charged, adsorbed sodium ions promote negative charge density in $\beta$-plane. Additional aqueous CO$_2$ creates more aqueous bicarbonate ions that also make the $\beta$-plane more negative via reaction S$_3$ in Table 2. Figure 8 highlights the power of our reactive-transport model, because surface charge density is often thought to play an important role in reservoir wettability.

If the cation exchange capacity is lowered to $CEC = 3.45 \times 10^{-3}$ eq/L in Figure 9, the resulting concentration profiles and histories are not exactly the same as those in Figure 6 for reaction alone. Even at a low CEC, the fingerprints of ion exchange are visible. Figure 9 resembles more closely Figure 2 for ion exchange alone. The spreading waves of calcium desorption surprisingly overpower rock dissolution. However, in Figure 9b, the calcium concentration is set by calcite equilibrium (at $\sim 1.2 \times 10^{-4}$ M), contrary to zero calcium concentration in Figure 2b at large throughput (not shown in the figure). Finally, Figure 10 repeats Figure 7 but now with dispersion at a longitudinal Péclet number of $Pe_L = 100$. Remnants of Figure 9 are seen, but are smoothed, as expected.

4 Conclusions

This work studies numerically the 1D simultaneous reactive transport, mass-transfer, ion exchange, and dispersion during flow through a calcium-carbonate porous medium. Dissolved aqueous carbonate species are in equilibrium as is ion-exchange kinetics. Carbonate dissolution kinetics are quantified by a rigorous rate expres-
sion. The key to the modeling effort is the continuum mass conservation of elements. All aqueous carbonate and brine species are followed as is pH and CO$_2$. For the first time, equilibrium surface species are also followed including the surface charge density and zeta potentials during frontal displacement provided that pore-solution concentrations are not strongly influenced by surface equilibria. Because reaction kinetics are fast, as characterized by the reaction and mass transfer Damköhler numbers, injected pore solutions attain equilibrium with the carbonate rock except for a narrow zone near the medium entrance.

All results are obtained using the open source software PHREEQC, including aqueous speciation and numerical solution to the 1D transport equations. Because of the highly nonlinear coupled behavior of species during mineral dissolution and surface ion exchange, we have performed careful verification of the PHREEQC transport code against analytic solutions over a wide range of the input parameter values, and, where applicable, we have reported the reliability ranges. Currently, our model implementation is restricted to a single mineral but is readily extended to multiple minerals. We assert that 1D transport in the reactive porous media with the simultaneous and coupled bulk and surface speciation, ion exchange, and dispersion is well captured by the open source code PHREEQC. Our calculations provide a new tool to assess how injected aqueous brine solutions alter upon contact with reactive rock. Accordingly, effective in-situ brine packages can be designed to improve oil recovery from reactive-mineral reservoirs.
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**Table 1** Solution Equilibrium Reactions and Equilibrium Constants, $K$ (298 K) from PHREEQC database (Charlton and Parkhurst 2011)

| # | Reaction | $\log_{10}K$ | Units           |
|---|----------|--------------|----------------|
| 1 | CO$_2$(g) $\rightleftharpoons$ CO$_2$(aq) | -1.47 | mol L$^{-1}$ atm$^{-1}$ |
| 2 | CO$_2$(aq) + H$_2$O $\rightleftharpoons$ H$_2$CO$_3$ | -2.59 | - |
| 3 | H$_2$CO$_3$ $\rightleftharpoons$ H$^+$ + HCO$_3^-$ | -3.76 | mol L$^{-1}$ |
| 4 | HCO$_3^-$ $\rightleftharpoons$ H$^+$ + CO$_3^{2-}$ | -10.33 | mol L$^{-1}$ |
| 5 | H$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$ | -14 | mol$^2$ L$^{-2}$ |
| 6 | CaCO$_3$(s) $\rightleftharpoons$ Ca$^{2+}$ + CO$_3^{2-}$ | -8.48 | mol$^2$ L$^{-2}$ |
| 7 | CaOH$^+$ $\rightleftharpoons$ Ca$^{2+}$ + OH$^-$ | -1.22 | mol L$^{-1}$ |
| 8 | CaHCO$_3^+$ $\rightleftharpoons$ Ca$^{2+}$ + HCO$_3^-$ | -1.11 | mol L$^{-1}$ |
| 9 | NaHCO$_3$ $\rightleftharpoons$ Na$^+$ + HCO$_3^-$ | 0.25 | mol L$^{-1}$ |
| 10 | NaCO$_3$ $\rightleftharpoons$ Na$^+$ + CO$_3^{2-}$ | -1.27 | mol L$^{-1}$ |
| # | Reaction | $\log_{10} K_S$ | Units |
|---|----------|-----------------|-------|
| S1 | $\text{CaH}_2\text{O}^+ \Leftrightarrow \text{Ca}^+ - \text{OH}^- + \text{H}^+$ | -10 | mol/L |
| S2 | $\text{CaH}_2\text{O}^+ + \text{HCO}_3^- \Leftrightarrow \text{Ca}^+ - \text{HCO}_3^- + \text{H}_2\text{O}$ | 2 | L/mol |
| S3 | $\text{CaH}_2\text{O}^+ + \text{CO}_3^{2-} \Leftrightarrow \text{Ca}^+ - \text{CO}_3^{2-} + \text{H}_2\text{O}$ | 3 | L/mol |
| S4 | $\text{CO}_3^- + \text{H}^+ \Leftrightarrow \text{CO}_3^{2-} - \text{H}^+$ | 8 | L/mol |
| S5 | $\text{CO}_3^- + \text{Ca}^{2+} \Leftrightarrow \text{CO}_3^- - \text{Ca}^{2+}$ | 3 | L/mol |
| S6 | $\text{CO}_3^- + \text{Na}^+ \Leftrightarrow \text{CO}_3^- - \text{Na}$ | -1 | L/mol |

1 The hyphen appearing in the surface species distinguished between ions at the calcite surface (species to the left of the hyphen) and those at the $\beta$-plane (species to the right of the hyphen).
### Table 3 Summary of PHREEQC Input Parameters

| Parameter Name                  | Parameter Symbol | Value | Units   |
|--------------------------------|------------------|-------|---------|
| Core length                     | $L$              | 1     | m       |
| Core diameter                   | $D$              | 0.1   | m       |
| Specific surface area           | $a_v$, $a_{v2}$ | $10^5$| m$^{-1}$|
| Ion-exchange constant           | $K_{ex}$         | 1500  | m$^{-1}$|
| Reaction kinetic constant       | $k_{rxn}$        | $10^{-5}$ | m s$^{-1}$|
| Mass-transfer constant          | $k_m$            | $10^{-3}$ | m s$^{-1}$|
| Volumetric flow rate            | $Q$              | $1.4 \times 10^{-5}$ | m$^3$s$^{-1}$|
| Molecular diffusion coefficient | $D_m$            | $10^{-9}$ | m$^2$s$^{-1}$|
| Longitudinal dispersion coefficient | $D_L$         | $10^{-8}$ | m$^2$s$^{-1}$|
| Porosity                        | $\varphi$        | 0.1   | -       |
| Reynolds number                 | $Re$             | 1     | -       |
| Schmidt number                  | $Sc_m$           | 1000  | -       |
| Sherwood number                 | $Sh_m$           | 100   | -       |
Supporting Information for the Manuscript: Chemical Compositions in Low-Salinity Waterflooding of Carbonate Reservoirs: Theory

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1 About Supporting Information

This document and the manuscript were prepared using org-mode and exported to pdf (Dominik 2010). The resulting pdf file contains attachments with experimental data as well as the source code of the manuscript and supporting information including all PHREEQC input files, python code for automatic generation of PHREEQC input files for plotting. The org-file can be exported to a pdf format using elisp code snipper in the very last section. It requires latexmk command-line utility. Note that all python code blocks must be executed sequentially (including si code blocks) to generate all the figures.

Appendix A Derivation of Mass-Transfer Resistance

Although correct, Equation 13 does not account for the mass-transfer resistance of the dissolving species. To account for this resistance, we recognize that the concentrations appearing are those directly at the calcite surface inside the mass-transfer boundary layer

\[ r_1 = k_{rxn} \sqrt{K_{SP}} \left[ 1 - C_{Ca}^{S} C_{CO_3^{2-}}^{S} / K_{SP} \right] \]  

(A.1)

where the superscript \( S \) indicates concentrations directly adjacent to the mineral surface. The remaining symbols are defined in the main text. Both calcium and carbonate ions convectively diffuse across the mass-transfer boundary layer. However, once calcite ions dissolve into the aqueous phase at the rock surface, they participate in aqueous speciation equilibria described in Table 1. Based on the equilibrium constants in Table 1 we neglect calcium-reaction species \( CaOH^+ \) and \( CaHCO_3^- \), relative to calcium ion. Thus, the convective-diffusion flux of calcium is expressed as

\[ r_1 = k_m (C_{Ca^{2+}}^S - C_{Ca^{2+}}) \]  

(A.2)

where \( k_m \) is the convective-diffusion mass transfer coefficient appropriate to flow through porous media (Bird et al. 2007). However, carbonate ions readily react to form bicarbonate ions, according to Reaction 4 in Table 1 that depends on the solution pH.

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Accordingly, the flux of total carbonate across the boundary layer involves the sum of carbonate and bicarbonate-ion fluxes with local speciation equilibrium. Let $K = C_H / K_4$, where $K_4$ is the equilibrium constant for Reaction 4 in Table 1. Then total carbon mass-transfer flux is

$$r_1 = k_m (1 + K) (C^S_{\text{CO}_3^{2-}} - C_{\text{CO}_3^{2-}})$$

(A.3)

where the mass transfer coefficient is approximately the same for small aqueous ions. Equations A.1 – A.3 provide two independent expressions to eliminate the surface concentrations of calcium and carbonate ions in favor of their bulk concentrations. Let $\tilde{C}_i = C_i / \sqrt{K_{SP}}$. Algebra gives

$$\tilde{C}^S_{\text{Ca}^{2+}} = \frac{1}{2} [\tilde{C}_{\text{Ca}^{2+}} - (1 + K)(\beta + \tilde{C}^S_{\text{CO}_3^{2-}})]$$

and

$$\tilde{C}^S_{\text{CO}_3^{2-}} = \frac{1}{(1 + K)C^S_{\text{Ca}^{2+}} - C_{\text{Ca}^{2+}} + (1 + K)C_{\text{CO}_3^{2-}}}$$

(A.5)

where $\beta = k_m / k_{rxn}$. Substitution of the surface concentrations in Equation A.4 and A.5 into Equation A.1 gives the carbonate dissolution rate that includes mass transfer resistance. For pH values less than 10, the constant $K$ is larger than 10. Thus, asymptotic expansion of Equations A.4 and A.5 for large $K$ gives, respectively,

$$\tilde{C}^S_{\text{Ca}^{2+}} = (1 + \beta) \tilde{C}_{\text{Ca}^{2+}}$$

and

$$\tilde{C}^S_{\text{CO}_3^{2-}} = \tilde{C}_{\text{CO}_3^{2-}}$$

large $K$ (A.6)

When Equation A.6 is substituted into Equation A.1, Equation 14 is obtained. Note that Equation 14 is not the usual series sum of a mass transfer and a kinetic resistance. It reduces correctly to Equation 4 for large mass-transfer coefficients and to Equation A.2 or A.3 for large reaction rate constants.

Rexwinkel et al. (1997) well summarizes 120 experimental observations for mass-transfer coefficients in packed beds at different Péclet numbers. In our work for moderately high flow rates, $Pe_m = 6 \times 10^4$. From Rexwinkel et al. (1997) the Sherwood number, $Sh$, corresponding to this Péclet is about 100 for the employed flow conditions (see Table 3 of the main text) or

$$Sh = \frac{2k_m D_g}{D_m} \equiv 100$$

(A.7)

where $D_g$ is the average particle diameter in m, and $D_m$ is the molecular diffusion coefficient ($10^{-9} \text{ m s}^{-1}$). $D_g$ is obtained from $a_v$, as $D_g = 6 \pi a_v$. We set $a_v$ to $10^5 \text{ m}^{-1}$. Number substitution gives $k_m$ of the order of $10^{-3} \text{ m s}^{-1}$.

Figures 4 and 5 of the text show the effect of various $k_{rxn}$ and $k_m$ on calcite concentration profiles and histories using Equation A.6.

**Appendix B Mass-Action Binary Cation Exchange**

Aqueous ion exchange on a constant-charged anionic solid surface is a subcase of surface ion complexation on a charged solid surface (Yutkin et al. 2018; Sposito 1994; Soudek 1985). Following Soudek (1985), we write two ion-complexation equilibrium reactions, one for sodium ion at the surface and one for calcium ion at the surface. Sodium ion binds to the surface at the beta plane according to the mass-action half-reaction

$$>S^- + Na^+ \rightleftharpoons >S^-Na^+$$

(B.1)

where $>S^-$ denotes a negatively charged surface site and $K_{Na}$ is the sodium site-binding equilibrium constant.

For calcium ion, there are two choices of surface complexation half-reactions:

$$>S^- + Ca^{2+} \rightleftharpoons >S^-Ca^{2+}$$

(B.2)
or

\[ 2S^- + Ca^{2+} \xrightleftharpoons{K_{Ca}} S_2^- Ca^{2+} \]  \hspace{1cm} (B.3)

where \( K_{Ca} \) is the calcium site-binding equilibrium constant. In Equation B.2, calcium binds to one exchange site giving a bound complex with a positive net charge of one. Conversely, in Equation B.3, calcium shares two adjacent exchange sites giving a neutral bound complex. Site sharing can only take place when the sites are closely spaced along the surface. Experimental data suggest that exchange-site sharing is prevalent for clays (Grim 1968; Soudek 1985). Combination of Equations B.1 and B.3 to eliminate surface sites gives the classical 2-1 mass-action ion-exchange reaction

\[ >S^- Na^+ + Ca^{2+} \xrightleftharpoons{K_{CaNa}} >S_2^- Ca^{2+} + 2 Na^+ \]  \hspace{1cm} (B.4)

Mass-action equilibria for reactions B.1 and B.3, respectively, read (Soudek 1985)

\[ K_{Na} = \frac{(<S^- Na^+)> \exp(F\varphi_\beta/RT)}{(<S^-)[Na^+]}} \]  \hspace{1cm} (B.5)

and

\[ K_{Ca} = \frac{(<S_2^- Ca^{2+}> \exp(2F\varphi_\beta/RT))}{(<S^-)^2[Ca^{2+}]}} \]  \hspace{1cm} (B.6)

where the parentheses enclosing species indicate surface concentrations in mole per unit area, the brackets enclosing species indicate bulk solution concentrations in mole per unit volume, \( F \) is Faraday’s constant, \( \varphi_\beta \) is the electrostatic potential at the beta plane, \( R \) is the ideal gas constant, and \( T \) is absolute temperature. Likewise, for the combined mass-action law of Equation B.4, we have that

\[ K_{CaNa} = \frac{K_{Ca} K_{Na}^2}{K_{CaNa}} = \frac{(<S_2^- Ca^{2+}>)[Na^+]^2}{(<S^-)^2[Ca^{2+}]}} \]  \hspace{1cm} (B.7)

In this expression, the \( \beta \)-plane electrostatic correction cancels. When both sodium and calcium equilibrium constants are large, the surface completely neutralizes at the beta plane. There is no diffuse double layer. In this case, all exchange sites are occupied.

With the definitions given in the text, Equation 12 emerges from Equation B.7.

**Appendix C Validation of the PHREEQC Reactive-Transport Code**

To validate the PHREEQC reactive-transport platform, we compare the numerical results with the analytic solutions to reactive transport alone, to ion-exchange alone, and to dispersion alone.

**C.1 Analytic Solution of Reactive Flow**

This section outlines an analytic solution to the reactive transport in a porous media to validate the extended PHREEQC code. For no ion exchange, no dispersion, no mass-transfer resistance, and only calcium and carbonate species present in the aqueous phase, Equations 10 and 13 reduce to

\[ \varphi \frac{\partial C_{Ca^{2+}}}{\partial t} + u \frac{\partial C_{Ca^{2+}}}{\partial x} = \varphi_1 a V_{1} k_{rxn} \sqrt{K_{SP}} \left[ 1 - C_{Ca^{2+}}^2 / K_{SP} \right] \]  \hspace{1cm} (C.1)

Introduction of the relative time scale, \( \tilde{t} \equiv t - \varphi x / u \), greatly simplifies Equation C.1

\[ u \left( \frac{\partial C_{Ca^{2+}}}{\partial x} \right)_i = \varphi_1 a V_{1} k_{rxn} \sqrt{K_{SP}} \left[ 1 - C_{Ca^{2+}}^2 / K_{SP} \right] \]  \hspace{1cm} (C.2)

To simplify notation, let \( \tilde{C} = C_{Ca^{2+}} / \sqrt{K_{SP}} \) and \( \tilde{x} = x / L \), where \( L \) is the core length. Accordingly, Equations C.1 and C.2 reduce to
\[
\left( \frac{\partial \tilde{C}}{\partial \tilde{z}} \right)_t = 2Da_{\text{rxn}} \left( 1 - \tilde{C}^2 \right)
\]  

(C.3)

where \(Da_{\text{rxn}} = \phi V_1 k_{\text{rxn}} L/u\) is the reaction Damköhler number. For a uniform initial calcium concentration in the core, \(\tilde{C}(0, x) = \tilde{C}_\infty\), and a fixed injected concentration, \(\tilde{C}(t, 0) = \tilde{C}_0\), Equation C.3 integrates directly to the concentration profile behind a tracer front

\[
\frac{C_{Ca^{2+}}(t, x)}{\sqrt{K_{SP}}} = \chi \exp[2Da_{\text{rxn}}(x/L)] - (1)^n \chi \exp[2Da_{\text{rxn}}(x/L)] + (1)^n \quad \text{for } \hat{t} > 0; \quad n = \begin{cases} 0 & C_0 < \sqrt{K_{SP}} \\ 1 & C_0 > \sqrt{K_{SP}} \end{cases}
\]

(C.4)

where \(\chi = (1 + C_0/\sqrt{K_{SP}})/[1 - C_0/\sqrt{K_{SP}}]\). The power index \(n\) indicates whether the injected calcium concentration is below the solubility limit \((n = 0)\), giving net rock dissolution or is above the solubility limit \((n = 1)\), giving net rock precipitation. As defined, the calcium feed-concentration parameter \(\chi\) is positive for both values of \(n\).

Ahead of a water tracer, the solution is

\[
C_L = C_\infty \quad \hat{t} < 0
\]

(C.5)

Calcium concentration ahead of a water tracer is that of the initial fluid in the core, \(C_\infty\), which prima facie is in equilibrium with the rock. Equations C.4 and C.5 are validated below against the PHREEQC numerics.

C.2 Numerical Solution of Reactive Transport

The analytic solution in Equations C.4 and C.5 requires the Damköhler number, the solubility product, and initial (feed) concentration. PHREEQC does not use dimensionless parameters, thus the input parameters to PHREEQC are adjusted accordingly. PHREEQC does allow a custom kinetic expression. Thus, the code requires the following input parameters: the reaction rate constant \((k_{\text{rxn}}, \text{m s}^{-1})\), the specific surface area \((a_{V_1}, \text{m}^{-1})\), and the porosity, respectively, which are specified by “-parms”. The solubility product \((K_{SP})\) is fixed by PHREEQC.

A typical discretization consists of 100 cells. The code below shows PHREEQC RATES and KINETICS blocks that describe a simple kinetic expression for calcite dissolution-precipitation.

**Rates Calcite**

```
RATES Calcite
  -start
  10 KSP = 10^-8.48
  20 k_rxn = PARM(1)
  30 sr_cc = SR("Calcite")
  40 a_v = PARM(2)
  41 phi = PARM(3)
  50 rate = k_rxn*sqrt(KSP)*a_v*(1-phi)*(1-sr_cc)
  60 moles = rate*TIME
  70 SAVE moles
  -end
```

**Kinetics 1-100**

```
KINETICS 1-100
Calcite2
  -formula Calcite 1
  -m 10
  -m0 10
  -tol 1e-10
```
To validate the PHREEQC reaction-kinetics results, we designed the following numerical experiment. We chose a one meter long column with 0.1 m diameter, and 10% porosity. Also, we assumed $\alpha_{\Gamma_1} = 10^{5}$ m$^{-1}$. According to the famous Carman-Kozeny equation, this surface area corresponds to a 30 mD permeability, given all other parameters, which is a reasonable value (Carman 1997; Kozeny 1927). We assumed a literature value of $k_{\text{rxn}}$ of $10^{-5}$ m s$^{-1}$ from Morse and Arvidson (2002). To match the $D_{\text{a,rxn}}$ numbers from the analytical solution, an appropriate time step and step length are specified as directives in the TRANSPORT block. Upon discretization of the column into $N$ cells, the appropriate step size is $L/N$, where $L$ is column length in meters. The time step, therefore, is $1/N$ of the total time for the solute to pass through the column i.e., time step = $t_{\text{res}}/N$, where $t_{\text{res}}$ is the tracer residence time in the column. The code below features an example of the correct input to TRANSPORT block based on these parameters.

```
TRANSPORT
  -boundary_conditions flux flux
  -dispersivities 100*0
  -correct Disp true
  -diffusion_coefficient 0
  -cells 100
  -shifts 100
  -timestep 1.11 s
  -length 100*0.01 m
```

$D_{\text{a,rxn}}$ values are established by setting column dimensions and volumetric flow rate through the column. It is convenient to vary $D_{\text{a,rxn}}$ on a log scale. We chose the following Da numbers: 0.1, 1, and 10. To achieve $D_{\text{a,rxn}}$ of 1 with the above settings, volumetric flow rate should be set to 8.5 mL min$^{-1}$ or $1.413 \times 10^{-6}$ m$^3$s$^{-1}$. The higher or lower $D_{\text{a,rxn}}$ values are achieved by varying $k_{\text{rxn}}$.

C.3 Reactive Transport Results

Figure C.1 compares the analytical solution (lines) with numerical results (symbols). The left graph (a) shows the profiles of dimensionless Ca$^{+2}$ concentration inside the column at $ut/\varphi L = 0.5$ PV. Very good matches are observed for all $D_{\text{a,rxn}}$ values. Profile concentrations are usually impossible to verify by experiment, so it is useful to consider history data, which correspond to the effluent concentrations measured directly at the column outlet. These data are presented in the right graph (b). Very good matches are observed as well for the concentration profiles. PHREEQC captures reactive transport well.

C.4 Analytic Solution of Binary Cation Ion Exchange

This section provides an analytic solution to the 2-1 ion-exchange chromatography in a 1D porous medium, to serve as another validation of the PHREEQC code. The only aqueous species present are sodium, calcium, and chloride ions. The rock is insoluble. Ion exchange at the porous medium surface is in local equilibrium with the pore fluid, and obeys classic calcium/sodium mass action in Equation 12 favorable to the calcium ion. Ion exchange behaves differently than classical adsorption chromatography (Rhee et al. 1989), because all adsorption sites remain occupied with either sodium or calcium ions, and because chloride ion does not participate in the exchange process. Chloride ion provides electroneutrality in the pore fluid. These two constraints mean that chloride ion behaves as a tracer penetrating the porous medium at the injected frontal advance rate (i.e., at $x = ut/\varphi$) and at the injected concentration. To satisfy electroneutrality, sodium and calcium ions must follow chloride ion in the tracer salinity wave.
We consider first conservation of the calcium ion in the 1D column with no rock- and aqueous species chemical reactions, and with no axial dispersion. Upon dropping the subscript for calcium ion, Equations 10 and 11 read

\[ 1 + \frac{\varphi_2 a V}{\varphi} \frac{\partial n}{\partial C} \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = 0 \]  

(C.6)

where the ion-exchange isotherm obeys Equation 12. Equation C.6 is rewritten as

\[ \frac{\partial C}{\partial t} = \left( \frac{\partial x}{\partial t} \right)_C = \frac{u/\varphi}{1 + \frac{\varphi_2 a V}{\varphi} \frac{\partial n}{\partial C}} \]  

(C.7)

The derivative \( \frac{\partial x}{\partial t} \) is the wave velocity of a given calcium concentration. Because the exchange-isotherm slope is positive, calcium concentration waves transport through the porous medium slower than the chloride tracer does. Equation C.7 is an analytic solution to ion-exchange chromatography. All concentration waves emanating from the column inlet upon a step concentration injection at time zero follow from the integration of Equation C.7

\[ x = \frac{ut/\varphi}{1 + \frac{\varphi_2 a V}{\varphi} \frac{\Delta n}{\Delta C}} \]  

(C.8)

Because the isotherm slope, appearing in the denominator of Equation C.8, is positive, calcium concentration waves of higher concentration travel faster than those of lower concentration. When faster-moving waves overcome slower-moving ones, a shock wave evolves characterized by the expression (Pope et al. 1978; Rhee et al. 1989)

\[ x = \frac{ut/\varphi}{1 + \frac{\varphi_2 a V}{\varphi} \frac{\Delta n}{\Delta C}} \]  

(C.9)

where the symbol \( \Delta \) denotes a jump (concentration difference) across the shock. Equation C.8 and Equation C.9 provide the basis for constructing ion-exchange chromatography profiles and histories.

Consider first the behavior of the inert chloride ion. From Equation 1 with no dispersion, chloride ion transports as a shock wave at the frontal advance rate. Thus, to provide electroneutrality, sodium and calcium ions similarly transport at the frontal advance rate. Nevertheless, Equation C.9 remains valid, demanding that the calcium concentration directly behind the salinity shock obeys the constraint that

\[ \Delta n = n(C_S, C_{Cl0}) - n(C_{\infty}, C_{Cl\infty}) = 0 \text{ at } x = ut/\varphi L \]  

(C.10)

where \( n(C_{\infty}, C_{Cl\infty}) \) is the amount of calcium adsorbed at the initial calcium and chloride concentrations on the porous exchanger surface, and \( n(C_S, C_{Cl0}) \) is the amount of calcium adsorbed at the injected chloride concentration \( C_{Cl0} \) and at the calcium concentration directly behind of the salinity wave, \( C_s \) (Pope et al. 1978; Rhee et al. 1989). The constraint of zero calcium adsorption change in Equation C.10 establishes \( C_S \), the calcium concentration directly at the back of the salinity shock wave.

We now construct the calcium and sodium-ion profiles at the back of the fast-moving chloride salinity shock front. The analytic solution depends on whether the ion-exchanging rock loads with calcium ion (i.e., \( C_0 > C_{\infty} \) or adsorption), or whether calcium ion elutes from the exchanger surfaces (i.e., \( C_0 < C_{\infty} \) or desorption). We tackle each case separately.

In the loading direction, a shock wave develops behind the salinity wave front, corresponding to calcium concentrations between \( C_S \), that at the rear of the salinity shock, and \( C_0 \), the calcium concentration in the injected solution (Pope et al. 1978).
Equation C.11 describes a self-sharpening calcium shock wave that appears behind the salinity shock wave. This second shock moves with a velocity determined by the chord of the exchange isotherm at the injected chloride concentration, and between the injected calcium concentration and that in the salinity zone, $C_S$. The calcium ion-exchange shock wave lags the salinity tracer front because calcium must populate exchange sites.

Thus, the column concentration profile consists of three zones, each with constant calcium concentration: initial calcium concentration in the column $C_\infty$, followed by a salinity-wave zone with the concentration $C_S$, and finally a zone of injected concentration $C_0$.

Conversely, during calcium washout or elution, the higher concentration waves move ahead of the lower concentration waves, leading to the concentration waves separating ever more from each other. A concentration-spreading domain develops in the column, as illustrated in Figure C.3. Equation C.8 is obeyed for each concentration between $C_0$ and $C_S$:

$$x = \frac{ut}{\varphi} \left[ 1 + \frac{\varphi^2 a V_2}{\varphi^2} \frac{\partial n}{\partial C} \right] \quad C_0 \leq C \leq C_S$$

The fastest moving wave at $C_S$ intersects the salinity-wave zone also at $C_S$. The slowest moving wave at $C_0$ terminates the spreading zone.

The calcium concentration profile in the elution mode consists of four zones: initial calcium concentration in the column $C_\infty$, followed by a salinity-wave zone with constant concentration $C_S$, a spreading ion-exchange zone between $C_S$ and $C_0$, and finally a zone of constant injected concentration $C_0$. Equations 12, C.10, C.11, and C.12 complete the ion-exchange analytic solution.

C.5 Numerical Solution of Binary Cation Ion Exchange

PHREEQC supports ion-exchange calculations, which can be coupled with 1D transport. Ion-exchange is specified via EXCHANGE or SURFACE directives. PHREEQC uses half-reaction notation for defining EXCHANGE or SURFACE reactions. There is a small difference between these two directives, namely, in the dimensions of the input values as well as in the fact that SURFACE directive allows exchange sites to stay empty, whereas EXCHANGE sites are always fully occupied by species. If used correctly, both of these directives produce the same outcome. For example, in the case of the EXCHANGE directive, the binding constant of one of the ions is a reference, and its half-reaction constant is set to 1 ($\log_{10} K = 0$); another half-reaction constant is set relative to it. However, in the case of the SURFACE directive, both constants must be supplied, and their ratio controls exchange calculations. In this work, we used the EXCHANGE directive. A few simulations were tested with SURFACE directive and yielded the same results given the same input parameters. The initiation of SURFACE or EXCHANGE directive starts with the definition of SURFACE/SURFACE_MASTER_SPECIES and the main reactions in which they participate.

For this particular simulation, we set $K_{CaNa} = 1500 \text{ m}^{-1}$. PHREEQC uses the same expression for the equilibrium constant, but it uses activities instead of concentrations. The activity of an exchange species in PHREEQC is simply the number of moles (not equivalents) of the exchange species divided by total moles of the exchange sites. By adopting this convention, the value of $K_{CaNa} = 1500 \text{ m}^{-1}$ can be converted correctly into PHREEQC units, as shown below.

Assume that we have 0.0345 eq of exchanger in 1 L. Ca$^{2+}$ and Na$^+$ concentrations are $5 \cdot 10^{-3}$ and $50 \cdot 10^{-3}$ mol L$^{-1}$, respectively. Chloride concentration is charge-balanced. By solving for equilibrium values of exchange species, we obtain the corresponding surface concentrations $n_{S_2-Ca^{2+}} = 1.5 \cdot 10^{-2}$ eq/L and $n_{S_2-Na^+} = 4.5 \cdot 10^{-3}$ eq/L. Upon dividing these by the total exchange capacity and substituting in the PHREEQC equilibrium ion-exchange constant expression, we find a value of about 13, and $\log_{10} 13 \approx 1$, which is used in the code, see the example below.
EXCHANGE_MASTER_SPECIES

Z Z-

EXCHANGE_SPECIES

Z- = Z-; log_k 0  
Z- + Na+ = NaZ; log_k 0  
2Z- + Ca+2 = CaZ2; log_k 1

EXCHANGE 1-1000 
*equilibrate 1  
Z 0.0345

For the exchange-code block defined through SURFACE, high values for the half-reactions equilibrium constant must be specified to satisfy the condition of fully occupied exchanger.

SURFACE_MASTER_SPECIES  
Su Su-

SURFACE_SPECIES  
Su- = Su-; log_k 0  
Su- + Na+ = NaSu; log_k 10  
2Su- + Ca+2 = CaSu2; log_k 21

SURFACE 1-1000 
*equilibrate 1  
Su 0.0345

To compare PHREEQC results with the analytical solution, the following input conditions were specified. All calculations were high precision and with N = 1000 cells, unless explicitly stated otherwise. The column porosity, dimensions, and permeability do not affect exchange calculations, ut/ϕL = 0.5 PV, CEC = 0.0345 eq L⁻¹, and K_{CaNa} = 1500 m⁻¹ for all cases. For faster calculation, the ADVECTION directive was used instead of TRANSPORT, because exchange calculations without kinetics do not require time step discretization.

The term “loading” means C₀ > C∞, the term “unloading” means C₀ < C∞, and the S, 0, and ∞ subscripts match those in the manuscript. The initial and injected concentrations for each calculation are listed in Table C.1. Only concentration profiles, i.e. concentrations inside the column, were calculated for all exchange cases. Concentration histories are basically mirror images of the profiles.

C.6 Binary Ion-Exchange Results

Two ion-exchange only cases were pursued and labeled in Table C.1 as (1) equal-calcium concentration loading/unloading and (2) equal-chloride concentration loading/unloading. Each is presented below.

C.6.1 Case 1: Equal-Calcium Loading/Unloading

This case replicates the work by Pope et al. (1978). For the loading case, we show below an example SOLUTION input block for PHREEQC. Although our chosen concentration units are mol/L, PHREEQC employs molality units. Proper conversion between the two units is required.

SOLUTION 0 Injected solution  
  temp 25  
  pH 7 charge  
  units mol/L
Figures C.2 and C.3 compare concentration profiles, the analytic (symbols) and numeric (lines) calculations at $ut/\varphi L = 0.5 PV$ for equal-calcium loading and unloading, respectively. Figure C.2 reveals two shock waves separating three chromatographic zones in accordance with theory: an initial-concentration zone, a salinity zone following a salinity shock wave, and an injected-concentration zone. Numeric calculations from PHREEQC obey theory well with 1000 grid cells. Numerical dispersion is minimal. Refining the grid size by a factor of 2 or 3 provides minimal reduction in numerical dispersion.

Figure C.3 displays the unloading or washout direction for Case 1. Here four zones appear in the column confirming theory: an initial-concentration zone, a salinity zone following the salinity shock wave, a spreading desorption wave zone, and an injected-concentration zone. Again, numeric evaluation from PHREEQC is in good agreement with our analytic theory.

C.6.2 Case 2: Equal-Chloride Loading/Unloading

Figures C.4 and C.5 compare concentration profiles from the analytic (symbols) and numeric (lines) calculations at $ut/\varphi L = 0.5 PV$ for equal-chloride loading and unloading, respectively. This case is unusual because nothing happens to the chloride concentration profile. There are now one shock and two zones in the column. Because the initial and injected chloride concentrations are identical, Equation C.10 eliminates the salinity zone. There is now a shock wave lagging behind the tracer-salinity wave, specified by Equation C.9 between the initial and injected calcium concentrations. Agreement with the numeric PHREEQC platform is excellent.

Figure C.5 gives the Case 2 unloading (desorption) profile corresponding to Figure C.4. Again, the salinity zone disappears. Thus, in contrast to Figure C.3, there are three zones in the column: an initial calcium concentration zone, a spreading wave calcium desorption zone, and an injected calcium concentration zone. 1D PHREEQC algorithms correctly capture this behavior.

We assert that the 1D aqueous species transport in reactive porous media with ion exchange is captured well by PHREEQC.

C.7 Analytic Solution of Dispersion

To validate the PHREEQC platform for the 1D solute dispersion alone, we make use of the known solution to Equation 9 subject to the Dankwerts boundary conditions in Equations 6 and 7 (Lapidus and Amundson 1952; Danckwerts 1953; Ogata and Banks 1961; Hashimoto et al. 1964; Gupta and Greenkorn 1974; Lake 1989, eq.5.5-16, and references therein)

$$\tilde{C}(\tilde{t}, \tilde{x}) = \frac{1}{2} \text{erfc} \left[ \frac{(-\tilde{t}) \sqrt{PeL}}{\sqrt{\tilde{t}} \sqrt{2}} \right] + \frac{1}{2} \exp(\text{PeL}) \text{erfc} \left[ \frac{(\tilde{x} + \tilde{t}) \sqrt{PeL}}{\sqrt{\tilde{t}} \sqrt{2}} \right]$$

where $\tilde{C} = (C - C_0)/(C_\infty - C_0)$ with the subscript s0 and $\infty$ denoting initial and injected solute concentrations; $\tilde{t} = ut/\varphi L$, $\tilde{x} = x/L$, and $PeL = uL/D_L$ is the longitudinal Péclet number.
C.8 Numerical Solution of Dispersion

Tracer flow implementation is PHREEQC is the same as in the example above. TRANSPORT directive must be used to account for dispersion. Initial and injected solution tracer composition, which contain different concentrations of a tracer, must be provided. Additionally, the inlet and outlet boundary conditions must be specified as well as the dispersivity \((\alpha = L/PeL)\), diffusion coefficient, length of the column, time step and number of pore volumes flushed (see the example below). We use the same column parameters as in the calculations above. The ion molecular diffusion coefficient is equal to \(10^{-9} \text{ m}^2 \text{s}^{-1}\).

```
TRANSPORT
  -boundary_conditions flux flux
  -dispersivities 0.01
  -length 100*0.01
  -correct_disp true
  -diffusion_coefficient 1e-09
  -cells 100
  -shifts 200 # 2 PV
  -time_step 11.1 s
```

The choice of boundary conditions needs to be specified. Apart from the closed-end boundary condition, PHREEQC offers two more BC options, called “constant” and “flux” for the inlet and outlet. Each option is shown below

\[
C(x, t) = C_{inj}, \quad \text{where} \quad x = 0 \text{ or } 1 \tag{C.14}
\]

and

\[
C(x, t) = C_{inj} + \frac{D}{L} \frac{\partial C(x, t)}{\partial x}, \quad \text{where} \quad x = 0 \text{ or } 1 \tag{C.15}
\]

Additionally, PHREEQC has instruction “-correct Disp true”, which accounts for dispersion in the first and last cells (otherwise set to “false”; the inlet and outlet cells do not have dispersion).

The “flux” boundary condition in PHREEQC, written for the inlet is identical to Equation 6. However, there seem to be no correct choice for BC at the outlet that would correspond to Equation 7. According to van Genuchten and Parker (1984), we write

\[
uC_{iE} = uC_{iE}(t, L^-) - D_{iE} \frac{\partial C_{iE}(t, L^-)}{\partial x} \quad \text{at} \quad x = L^- \tag{C.16}
\]

where \(L^-\) means that the concentration is evaluated inside the column, just right before exit. A common assumption is that \(C_{iE}(t, L^-) = C_{iE}(L^-)\). With the fine-enough grid, such an assumption should be fulfilled. Then, we can rewrite Equation C.17 as

\[
\frac{\partial C_{iE}(t, L)}{\partial x} = 0 \quad \text{at} \quad x = L \tag{C.17}
\]

Therefore, the PHREEQC boundary condition “flux” can be used to model finite experimental columns, requiring a fine-enough mesh, such that \(C(N - 1) \approx C(N)\), where \(C(N)\) is concentration in the \(N^{th}\) cell. For this reason, we chose to set “-correct Disp” to “true”.

C.9 Dispersion Results

Figure C.6 compares the analytic (lines) and numeric solutions (symbols) from Equation C.13 and from PHREEQC, respectively. For the Péclet numbers larger than about 10, agreement of PHREEQC with the analytic solution is acceptable. However, for the Péclet numbers less than about 10, deviation is substantial.
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C.1 Dimensionless Ca$^{2+}$ dissolution concentration (a) profiles at $ut/\varphi L = 0.5$ injected pore volumes and (b) effluent history with no ion exchange, no mass transfer resistance, and no aqueous speciation equilibrium reactions. Reaction Damköhler numbers are 0.1, 1, and 10. Injected calcium and carbonate-ion concentrations are zero. The lines are from analytic theory in Equation C.4 for $n = 1$. The open symbols give the corresponding numerical calculations.

C.2 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5$ PV. Case 1, equal-calcium loading. The initial column concentrations are calcium = 5 mM; sodium = 50 mM, chloride = 60 mM. The injected concentrations are calcium = 5 mM; sodium = 30 mM, chloride = 40 mM.

C.3 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5$ PV. Case 1, equal-calcium unloading. The initial column concentrations are calcium = 5 mM; sodium = 30 mM, chloride = 40 mM. The injected concentrations are calcium = 5 mM; sodium = 50 mM, chloride = 60 mM.

C.4 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5$ PV. Case 2, equal-chloride loading. The initial column concentrations are calcium = 5 mM; sodium = 40 mM, chloride = 50 mM. The injected concentrations are calcium = 10 mM; sodium = 30 mM, chloride = 50 mM.

C.5 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5$ PV. Case 2, equal-chloride unloading. The initial column concentrations are calcium = 10 mM; sodium = 30 mM, chloride = 50 mM. The injected concentrations are calcium = 5 mM; sodium = 40 mM, chloride = 50 mM.

C.6 Comparison of the analytic (lines) and numeric (symbols) solutions for tracer concentration history over a range of Péclet numbers (log-spaced from 1 to 100). The boundary conditions for PHREEQC model are “flux” with continuous dispersion coefficient.
Fig. C.1 Dimensionless Ca$^{2+}$ dissolution concentration (a) profiles at $ut/\varphi L = 0.5$ injected pore volumes and (b) effluent history with no ion exchange, no mass transfer resistance, and no aqueous speciation equilibrium reactions. Reaction Damköhler numbers are 0.1, 1, and 10. Injected calcium and carbonate-ion concentrations are zero. The lines are from analytic theory in Equation C.4 for $n = 1$. The open symbols give the corresponding numerical calculations.
Fig. C.2 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\phi L = 0.5\ PV$. Case 1, equal-calcium loading. The initial column concentrations are calcium = 5 mA, sodium = 50 mA, chloride = 60 mA. The injected concentrations are calcium = 5 mA; sodium = 30 mA, chloride = 40 mA.
Fig. C.3 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $\alpha L/\varphi^2 L = 0.5$ PV. Case 1, equal-calcium unloading. The initial column concentrations are calcium = 5 mM; sodium = 30 mM, chloride = 40 mM. The injected concentrations are calcium = 5 mM; sodium = 50 mM, chloride = 60 mM.
Fig. C.4 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $u t / \varphi L = 0.5 \ PV$. Case 2, equal-chloride loading. The initial column concentrations are calcium = 5 mM; sodium = 40 mM, chloride = 50 mM. The injected concentrations are calcium = 10 mM; sodium = 30 mM, chloride = 50 mM.
Fig. C.5 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5\text{ PV}$, Case 2, equal-chloride unloading. The initial column concentrations are calcium = 10 mM; sodium = 30 mM, chloride = 50 mM. The injected concentrations are calcium = 5 mM; sodium = 40 mM, chloride = 50 mM.
Fig. C.6 Comparison of the analytic (lines) and numeric (symbols) solutions for tracer concentration history over a range of Péclet numbers (log-spaced from 1 to 100). The boundary conditions for PHREEQC model are “flux” with continuous dispersion coefficient.
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   C.1  Summary of concentrations used in each calculation       20
| Calculation                | Ion   | $C_0$, M | $C_\infty$, M |
|---------------------------|-------|----------|---------------|
| Equal-Calcium Loading     | Na$^+$| 0.030    | 0.050         |
|                           | Ca$^{2+}$ | 0.005    | 0.005         |
|                           | Cl$^-$ | 0.040    | 0.060         |
| Equal-Calcium Unloading   | Na$^+$| 0.050    | 0.030         |
|                           | Ca$^{2+}$ | 0.005    | 0.005         |
|                           | Cl$^-$ | 0.060    | 0.040         |
| Equal-Chloride Loading    | Na$^+$| 0.030    | 0.040         |
|                           | Ca$^{2+}$ | 0.010    | 0.005         |
|                           | Cl$^-$ | 0.050    | 0.050         |
| Equal-Chloride Unloading  | Na$^+$| 0.040    | 0.030         |
|                           | Ca$^{2+}$ | 0.005    | 0.010         |
|                           | Cl$^-$ | 0.050    | 0.050         |
