

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, and the Python code for automatic generation of PHREEQC input files for plotting. The org-file can be exported to a pdf format using elisp code snippet 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

$$r_1 = k_{rxn} \sqrt{K_{SP}} \left[1 - C_{Ca^{2+}}^S C_{CO_3^{2-}}^S / K_{SP} \right] \quad (A.1)$$

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 of the main text. 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

$$r_1 = k_m (C_{Ca^{2+}}^S - C_{Ca^{2+}}) \quad (A.2)$$

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

$$r_1 = k_m (1 + K) (C_{\text{CO}_3^{2-}}^S - C_{\text{CO}_3^{2-}}) \quad (\text{A.3})$$

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

$$\begin{aligned} \tilde{C}_{\text{Ca}^{2+}}^S = & \frac{1}{2} [\tilde{C}_{\text{Ca}^{2+}} - (1 + K)(\beta + \tilde{C}_{\text{CO}_3^{2-}}^S)] \\ & + \frac{1}{2} \sqrt{[\tilde{C}_{\text{Ca}^{2+}} - (1 + K)(\beta + \tilde{C}_{\text{CO}_3^{2-}}^S)]^2 - 4(1 + K)(\beta \tilde{C}_{\text{Ca}^{2+}} + 1)} \end{aligned} \quad (\text{A.4})$$

and

$$\tilde{C}_{\text{CO}_3^{2-}}^S = \frac{1}{(1 + K)[\tilde{C}_{\text{Ca}^{2+}}^S - \tilde{C}_{\text{Ca}^{2+}} + (1 + K)\tilde{C}_{\text{CO}_3^{2-}}]} \quad (\text{A.5})$$

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,

$$\tilde{C}_{\text{Ca}^{2+}}^S = \frac{(1 + \beta)\tilde{C}_{\text{Ca}^{2+}}}{\tilde{C}_{\text{CO}_3^{2-}} + \beta} \quad \text{and} \quad \tilde{C}_{\text{CO}_3^{2-}}^S = \tilde{C}_{\text{CO}_3^{2-}} \quad \text{large } K \quad (\text{A.6})$$

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 summarize 120 experimental observations for mass-transfer coefficients in packed beds at different Péclet numbers. In our work for moderately high flow rates, $Pe_m = uL/D_m = 6 \times 10^4$. 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

$$Sh = \frac{k_m D_g}{D_m} \equiv 100 \quad (\text{A.7})$$

where D_g is the average particle diameter in m, and D_m is the molecular diffusion coefficient (10^{-9} m s^{-1}). D_g is obtained from a_V , as $D_g = 6/a_V$. We set a_V to 10^6 m^{-1} . Such a value is typical of mid-range (25 mD) permeability Indiana limestone. For example, according to Carman-Kozeny relation ($a_V[\text{m}^{-1}] = \sqrt{36\phi^3/K_l 10^{-12} 150(1 - \phi)^2}$, where K_l is permeability in Darcy units and ϕ is porosity). For a 25 mD Limestone with porosity 15%, $a_V \approx 2 \times 10^6 \text{ m}^{-1}$ (Kozeny 1927a; Carman 1956, 1997). Number substitution gives k_m of the order of 10^{-2} m s^{-1} . Having characteristic grain size, we estimate Reynolds number in our simulations ($Re = \rho u D_g / \mu$, where ρ is mass density in kg m^{-3} , u is flow linear velocity in m s^{-1} , and μ is dynamic viscosity in $\text{kg m}^{-1} \text{ s}^{-1}$) to be of the order of 1. Schmidt number ($Sc = \mu / \rho D_m$) is of the order of 1000.

Figures 4 and 5 of the text show the effect of various k_{rxn} and k_m on calcite concentration profiles and histories using Equations A.3 and 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



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

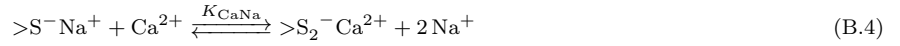
For calcium ion, there are two choices of surface complexation half-reactions:



or



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



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

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

and

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

where the parentheses enclosing species indicate surface concentrations in mole per unit area, the brackets enclosing species indicate bulk solution concentrations in mole per aqueous unit volume, F is Faraday's constant, φ_β 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

$$K_{CaNa} = \frac{K_{Ca}}{K_{Na}^2} = \frac{(>S_2^-Ca^{2+})[Na^+]^2}{(>S^-Na^+)^2[Ca^{2+}]} \quad (B.7)$$

In this expression, the β -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

$$\varphi \frac{\partial C_{Ca^{2+}}}{\partial t} + u \frac{\partial C_{Ca^{2+}}}{\partial x} = \varphi_1 a_{V_1} k_{rxn} \sqrt{K_{SP}} [1 - C_{Ca^{2+}}^2/K_{SP}] \quad (C.1)$$

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

$$u \left(\frac{\partial C_{\text{Ca}^{2+}}}{\partial x} \right)_{\hat{t}} = \varphi_1 a_{V_1} k_{rxn} \sqrt{K_{SP}} [1 - C_{\text{Ca}^{2+}}^2 / K_{SP}] \quad (\text{C.2})$$

To simplify notation, let $\tilde{C} = C_{\text{Ca}^{2+}} / \sqrt{K_{SP}}$; and $\tilde{x} = x/L$, where L is the core length. Accordingly, Equations C.1 and C.2 reduce to

$$\left(\frac{\partial \tilde{C}}{\partial \tilde{x}} \right)_{\hat{t}} = 2Da_{rxn} (1 - \tilde{C}^2) \quad (\text{C.3})$$

where $Da_{rxn} = \varphi_1 a_{V_1} k_{rxn} L / u$ is the reaction Damköhler number. For a uniform initial calcium concentration in the core, $\tilde{C}(0, x) = \tilde{C}_0$, and a fixed injected concentration, $\tilde{C}(t, 0) = \tilde{C}_\infty$, Equation C.3 integrates directly to the concentration profile behind a tracer front

$$\frac{C_{\text{Ca}^{2+}}(t, x)}{\sqrt{K_{SP}}} = \frac{\chi \exp[2Da_{rxn}(x/L)] - (-1)^n}{\chi \exp[2Da_{rxn}(x/L)] + (-1)^n} \quad \text{for } \hat{t} > 0; \quad n = \begin{cases} 0 & C_\infty < \sqrt{K_{SP}} \\ 1 & C_\infty > \sqrt{K_{SP}} \end{cases} \quad (\text{C.4})$$

where $\chi = (1 + C_\infty / \sqrt{K_{SP}}) / [1 - C_\infty / \sqrt{K_{SP}}]$. 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 χ is positive for both values of n .

Ahead of a water tracer, the solution is

$$C_L = C_0 \quad \hat{t} < 0 \quad (\text{C.5})$$

Calcium concentration ahead of a water tracer is that of the initial fluid in the core, C_0 , 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 the 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_{rxn} , m s^{-1}), the specific surface area (a_{V_1} , 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
-start
1 REM
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
```

```

Calcite2
-formula Calcite 1
-m 10
-m0 10
-tol 1e-10
-bad_stepmax 1000
-parms 1e-7 1e5 0.1

```

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 set $a_{V_1} = 10^5 \text{ m}^{-1}$. According to Carman-Kozeny equation (see above), this surface area corresponds to a 30 mD permeability, given all other parameters, which is a reasonable value (Carman 1997; Kozeny 1927b). We assumed a literature value of k_{rxn} of 10^{-5} ms^{-1} from Morse and Arvidson (2002). To match the Da_{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_{res}/N , where t_{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

```

Da_{rxn} values are established by setting column dimensions and volumetric flow rate through the column. It is convenient to vary Da_{rxn} on a logarithmic scale. We chose the following Da_{rxn} numbers: 0.1, 1, and 10. To achieve Da_{rxn} of 1 with the above settings, volumetric flow rate should be set to 8.5 mL min^{-1} or $1.413 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The higher or lower Da_{rxn} values are achieved by varying k_{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 $ut/\varphi L = 0.5 \text{ PV}$. Very good matches are observed for all Da_{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

$$\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{\partial n}{\partial C}\right] \frac{\partial C}{\partial t} + \frac{u}{\varphi} \frac{\partial C}{\partial x} = 0 \quad (\text{C.6})$$

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

$$\left[\frac{\partial C/\partial t}{\partial C/\partial x}\right]_C = \left[\frac{\partial x}{\partial t}\right]_C = \frac{u/\varphi}{\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{\partial n}{\partial C}\right]} \quad (\text{C.7})$$

The derivative $[\partial x/\partial t]_C$ 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

$$x = \frac{ut/\varphi}{\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{\partial n}{\partial C}\right]} \quad (\text{C.8})$$

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)

$$x = \frac{ut/\varphi}{\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{\Delta n}{\Delta C}\right]} \quad (\text{C.9})$$

where the symbol Δ 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 9 of the main text 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. Nevertheless, Equation C.9 remains valid, demanding that the calcium concentration directly behind the salinity shock obeys the constraint that

$$\Delta n = n(C_S, C_{Cl_\infty}) - n(C_0, C_{Cl_0}) = 0 \quad \text{at} \quad x = ut/\varphi L \quad (\text{C.10})$$

where $n(C_0, C_{Cl_0})$ is the amount of calcium adsorbed at the initial calcium and chloride concentrations on the porous exchanger surface, and $n(C_S, C_{Cl_\infty})$ is the amount of calcium adsorbed at the injected chloride concentration C_{Cl_∞} 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., $C_\infty > C_0$ or adsorption), or whether calcium ion elutes from the exchanger surfaces (i.e., $C_\infty < C_0$ 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_∞ , the calcium concentration in the injected solution (Pope et al. 1978).

$$x = \frac{ut/\varphi}{\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{[n(C_S, C_{Cl_\infty}) - n(C_\infty, C_{Cl_\infty})]}{[C_S - C_\infty]}\right]} \quad C_S \leq C \leq C_\infty \quad \text{loading} \quad (\text{C.11})$$

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_0 , followed by a salinity-wave zone with the concentration C_S , and finally a zone of injected concentration C_∞ .

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_∞ and C_S

$$x = \frac{ut/\varphi}{\left[1 + \frac{\varphi_2 a_{V_2}}{\varphi} \frac{\partial n}{\partial C}\right]}; \quad C_\infty \leq C \leq C_S \quad \text{unloading} \quad (\text{C.12})$$

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

The calcium concentration profile in the elution mode consists of four zones: initial calcium concentration in the column C_0 , followed by a salinity-wave zone with constant concentration C_S , a spreading ion-exchange zone between C_S and C_∞ , and finally a zone of constant injected concentration C_∞ . 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-/EXCHANGE_MASTER_SPECIES and the main reactions in which they participate.

For this particular simulation, we set $K_{CaNa} = 6600 \text{ m}^{-1}$. 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 $K_{CaNa} = 6600 \text{ m}^{-1}$ can be converted correctly into PHREEQC units, as shown below.

Assume that we have 0.0345 (note, it is different capacity from the main text, just for demonstration purpose) mol of exchanger in 1 L of pore liquid. Ca^{2+} and Na^{+} concentrations are $5 \cdot 10^{-3}$ and $50 \cdot 10^{-3} \text{ mol L}^{-1}$, respectively. Chloride concentration is charge balanced. By solving for equilibrium values of exchange species, we obtain the corresponding surface concentrations

$n_{S_2-Ca^{2+}} = 1.5 \cdot 10^{-2}$ mol/L and $n_{S-Na^+} = 4.5 \cdot 10^{-3}$ mol/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, $ut/\varphi L = 0.5$ PV, $CEC = 0.0345$ mol L⁻¹, and $K_{CaNa} = 6600$ 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 $C_\infty > C_0$, the term “unloading” means $C_\infty < C_0$, 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
density   1
-water    1
Na        0.03
Ca        0.005
Cl        0.04

SOLUTION 1-1000 Initial solution for column
units     mol/L
temp      25.0
pH        7 charge
-water    1
Na        0.05
Ca        0.005
Cl        0.06

```

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 Danckwerts 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)

$$\tilde{C}(\tilde{t}, \tilde{x}) = \frac{1}{2} \operatorname{erfc} \left[\frac{(\tilde{x} - \tilde{t}) \sqrt{Pe_L}}{\sqrt{\tilde{t}}} \right] + \frac{1}{2} \exp(Pe_L) \operatorname{erfc} \left[\frac{(\tilde{x} + \tilde{t}) \sqrt{Pe_L}}{\sqrt{\tilde{t}}} \right] \quad (C.13)$$

where $\tilde{C} = (C - C_0)/(C_\infty - C_0)$ with the subscript 0 and ∞ denoting initial and injected solute concentrations; $\tilde{t} = ut/\varphi L$, $\tilde{x} = x/L$, and $Pe_L = uL/D_L$ is the longitudinal Péclet number.

C.8 Numerical Solution of Dispersion

Tracer flow implementation in 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 ($\alpha = L/Pe_L$), 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 s
```

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

$$C(x, t) = C_\infty, \quad \text{at } x = 0 \quad (\text{C.14})$$

and

$$C(x, t) = C^* + \frac{D_L}{u} \frac{\partial C(x, t)}{\partial x}, \quad \text{at } x = 0, C^* = C_\infty, \text{ or at } x = L, C^* = C_0 \quad (\text{C.15})$$

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 boundary conditions at the outlet that would correspond to Equation 7. According to van Genuchten and Parker (1984), we assume negligible dispersion in the porous-medium exit line and write

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

where L^- means that the concentration is evaluated inside the column, just before the exit. We next impose continuity of concentration at the medium exit so that $C_{iE}(t, L^-) = C_{iE_L}$. With the fine-enough grid, such an assumption is fulfilled. Then, we can rewrite Equation C.17 as

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

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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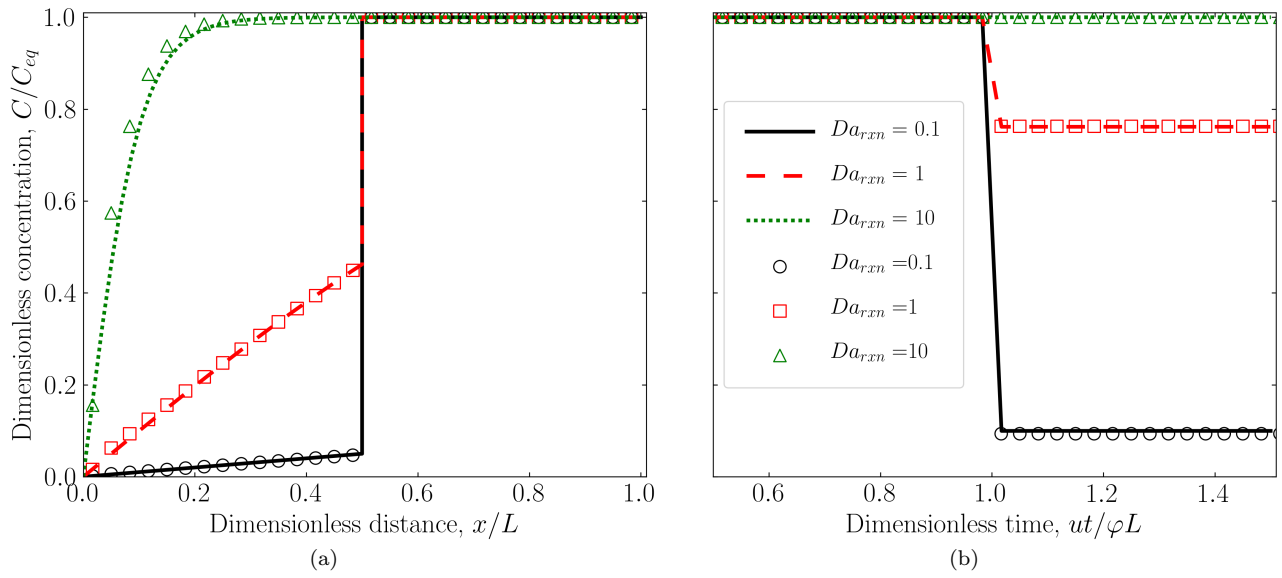


Fig. C.1 Dimensionless Ca^{2+} dissolution concentration (a) profiles at $ut/\varphi L = 0.5$ injected pore volumes and (b) effluent history with no ion exchange, no mass transfer resistance, and no aqueous speciation equilibrium reactions. Reaction Damköhler numbers are 0.1, 1, and 10. Injected calcium 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.

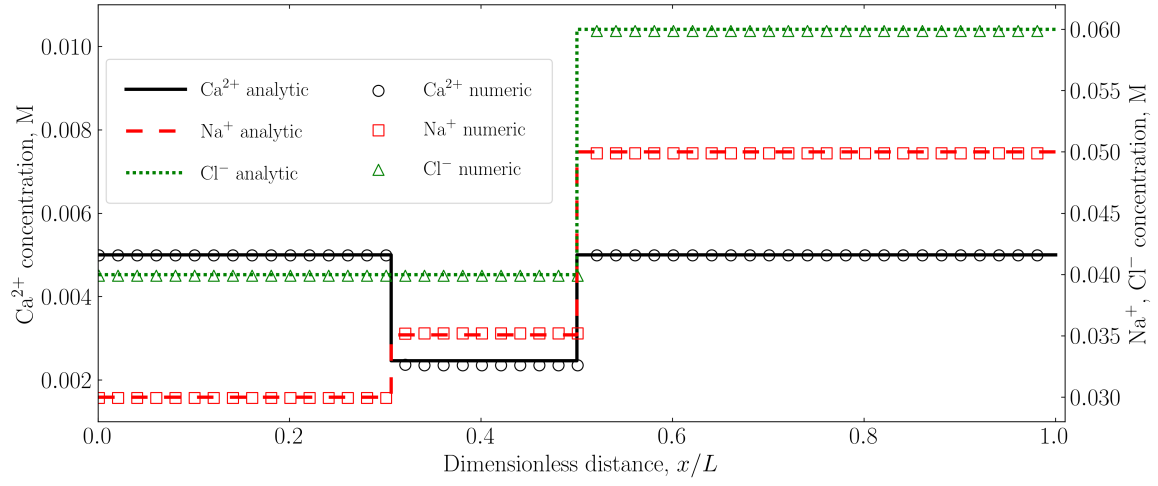


Fig. C.2 Comparison of the numeric (symbols) and analytic (lines) binary ion-exchange concentration profile at $ut/\varphi L = 0.5$ PV. Case 1, equal-calcium loading. The initial column concentrations are calcium = 5 mM; sodium = 50 mM, chloride = 60 mM. The injected concentrations are calcium = 5 mM;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

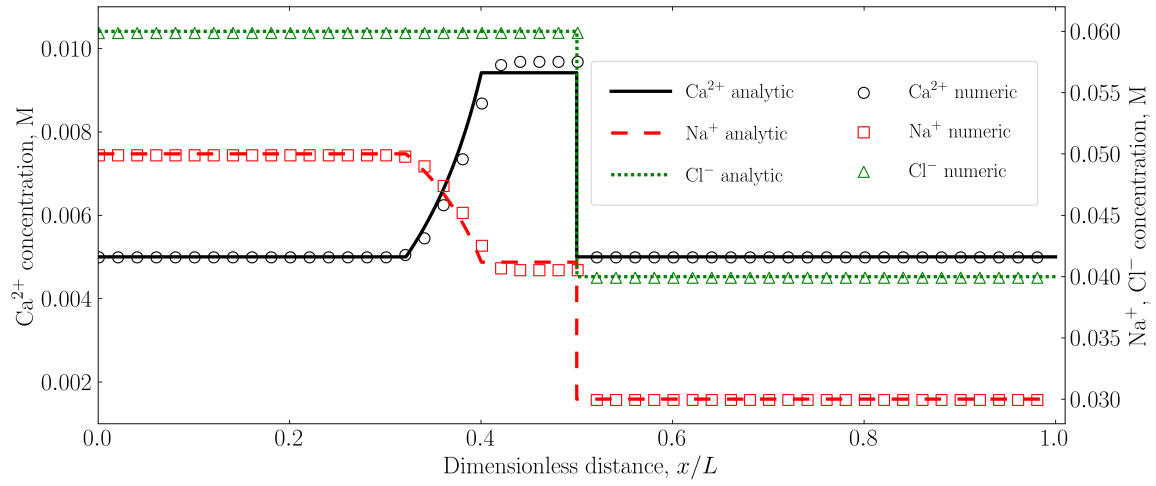


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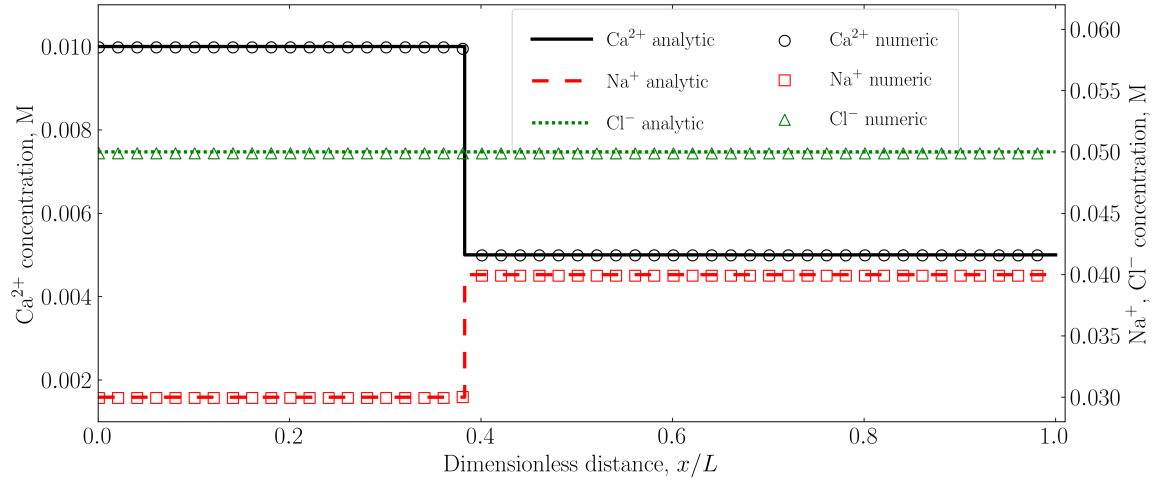


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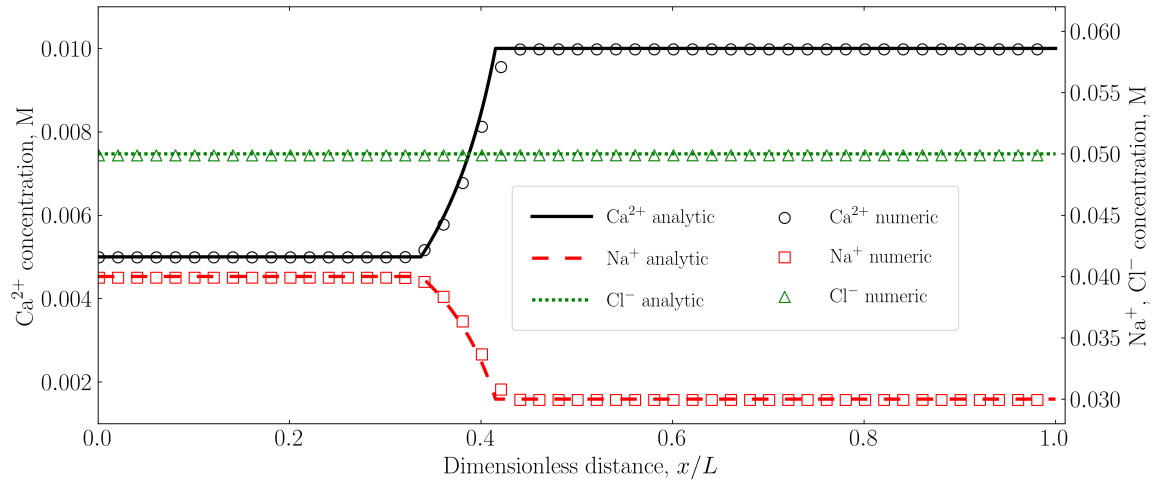


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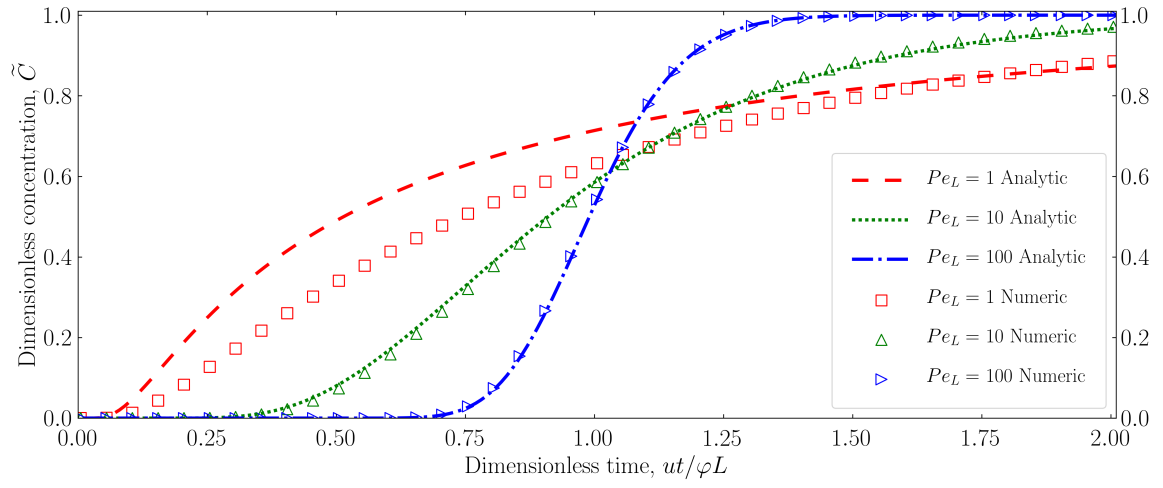


Fig. C.6 Comparison of the analytic (lines) and numeric (symbols) solutions for tracer concentration history over a range of Péclet numbers (log-spaced from 1 to 100). The boundary conditions for PHREEQC model are “flux” with continuous dispersion coefficient.

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Table C.1 Summary of concentrations used in each calculation

Calculation	Ion	C_∞ , M	C_0 , 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