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## **Geometry-coupled reactive fluid transport at the fracture scale -Application to CO<sub>2</sub> geologic storage-**

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**Abstract:** Water acidification follows CO<sub>2</sub> injection and leads to reactive fluid transport through pores and rock fractures, with potential implications to reservoirs and wells in CO<sub>2</sub> geologic storage and enhanced oil recovery. Kinetic rate laws for dissolution reactions in calcite and anorthite are combined with Navier-Stokes law and advection-diffusion transport to perform geometry-coupled numerical simulations in order to study the evolution of chemical reactions, species concentration and fracture morphology. Results are summarized as a function of two dimensionless parameters: the Damköhler number  $Da$  which is the ratio between advection and reaction times, and the transverse Peclet number  $Pe$  defined as the ratio between the time for diffusion across the fracture and the time for advection along the fracture. Reactant species are

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readily consumed near the inlet in a carbonate reservoir when the flow velocity is low (low transverse Peclet number and  $Da > 10^{-1}$ ). At high flow velocities, diffusion fails to homogenize the concentration field across the fracture (high transverse Peclet number  $Pe > 10^{-1}$ ). When the reaction rate is low as in anorthite reservoirs ( $Da < 10^{-1}$ ) reactant species are more readily transported towards the outlet. At a given Peclet number, a lower Damköhler number causes the flow channel to experience a more uniform aperture enlargement along the length of the fracture. When the length-to-aperture ratio is sufficiently large, say  $l/d > 30$ , the system response resembles the solution for 1-D reactive fluid transport. A decreased length-to-aperture ratio slows the diffusive transport of reactant species to the mineral fracture surface, and analyses of fracture networks must take into consideration both the length and slenderness of individual fractures in addition to  $Pe$  and  $Da$  numbers.

Keywords:  $\text{CO}_2$  geologic storage; Mineral dissolution; Reactive fluid transport; Rock fracture; Navier-Stokes law

## 1. Introduction

Carbon dioxide  $\text{CO}_2$  injection into geological formations, either for enhanced oil recovery or  $\text{CO}_2$  geological storage, triggers a complex cascade of interconnected events that may include:  $\text{CO}_2$  advection (Saripalli and McGrail 2002; Nordbotten et al. 2005; Ennis-King and Paterson 2007), buoyancy (Bachu and Adams 2003; Bielinski et al. 2008; Okwen et al. 2010), convection of  $\text{CO}_2$ -dissolved water (Weir et al. 1996; Riaz et al. 2006; Hassanzadeh et al. 2007; Kneafsey and Pruess 2010), mutual diffusion and dissolution between  $\text{CO}_2$  and the water phase and salt precipitation (Gaus et al. 2005; Berne et al. 2010; Espinoza and Santamarina 2010; Li et al.

2011), viscous fingering of CO<sub>2</sub> (Homsy 1987; Fenghour et al. 1998; Cinar et al. 2009), and capillary trapping of the CO<sub>2</sub> phase by the water-saturated porous formation (Juanes et al. 2006; Kopp et al. 2009; Saadatpoor et al. 2009; Kim 2012). Furthermore, water acidification follows CO<sub>2</sub> dissolution and triggers reactions with minerals in the formation as well as with the cement around wells (Li et al. 2008; Solomon et al. 2008; Szymczak and Ladd 2009; Espinoza et al. 2011).

Reactive fluid transport generates positive feedbacks through hydro-chemo-mechanical couplings that may lead to emergent phenomena such as the formation of dissolution wormholes (Golfier et al. 2002; Berrezueta et al. 2013; Elkhoury et al. 2013; Hao et al. 2013; Mangane et al. 2013) and shear fractures in compression (Shin et al. 2008; Shin and Santamarina 2009). The mineral dissolution rate is scale dependent, and pseudo-kinetics issues must be considered when upscaling geochemical equilibrium (Li et al. 2008; Binning and Celia 2008). Studies of reactive fluid transport in the context of CO<sub>2</sub> injection have addressed the geological formation (Flukiger and Bernard 2009; Molins et al. 2012; Hao et al. 2013; Ovaysi and Piri 2013; Steefel et al. 2013; Ovaysi and Piri 2014), consequences on wellbores (Raouf et al. 2012; Brunet et al. 2013; Cao et al. 2013; Patel et al. 2014), and changes in fracture properties and injectivity (Wang and Gu 2011; Jafari Behbahani et al. 2012; Smith et al. 2012; Deng et al. 2013).

This study develops a geometry-coupled numerical model to study reactive fluid transport at the fracture scale, including the ensuing interactions between reactions, transport, and pore enlargement (Note: previous coupled models have explored hydro-chemical conditions but have not captured geometric changes, e.g., Li et al. 2008 and Binning and Celia 2008; pore enlargement is a precursor for fully coupled hydro-chemo-mechanical coupling). In particular, we implement all reactions needed to analyze CO<sub>2</sub>-rich water transport under conditions that

would develop in the context of CO<sub>2</sub> geologic storage and enhanced oil recovery in fractured media. The goal is to advance our understanding of the flow of CO<sub>2</sub>-dissolved water at the fracture-scale as water rich in total carbonic acid  $H_2CO_3^*$  and hydrogen ions  $H^+$  traverses the fracture. We summarize transport patterns in terms of key dimensionless numbers to facilitate the analyses of fracture networks subjected to reactive fluid transport and ensuing pore enlargements. Kinetic rates are analyzed first followed by a 2-D numerical simulation study of CO<sub>2</sub>-dissolved water injection.

## 2. Kinetic Rates

### 2.1 CO<sub>2</sub> Dissolution in Water

Injected carbon dioxide  $CO_2$  dissolves in the formation water or brine to sequentially form aqueous carbon dioxide  $CO_{2(aq)}$  and carbonic acid  $H_2CO_3$ , which eventually dissociates into bicarbonate ions  $HCO_3^-$  and hydrogen ions  $H^+$  (Details in Appendix). Assuming that the reaction rate is linearly proportional to the concentration of reactants (Equations A.1-to-A.3 in Appendix), the following kinetic laws are obtained:

$$\frac{d[CO_{2(g)}]}{dt} = -k_g [CO_{2(g)}] + k_{aq} [CO_{2(aq)}] \quad (1)$$

$$\frac{d[CO_{2(aq)}]}{dt} = k_g [CO_{2(g)}] - k_{aq} [CO_{2(aq)}] - k_{CO_2} [CO_{2(aq)}] + k_{H_2CO_3} [H_2CO_3] \quad (2)$$

$$\frac{d[H_2CO_3]}{dt} = k_{CO_2} [CO_{2(aq)}] - k_{H_2CO_3} [H_2CO_3] - k_{12} [H_2CO_3] + k_{21} [HCO_3^-] [H^+] \quad (3)$$

$$\frac{d[H^+]}{dt} = \frac{d[HCO_3^-]}{dt} = k_{12} [H_2CO_3] - k_{21} [HCO_3^-] [H^+] \quad (4)$$

where square brackets around species indicate species concentrations. Rate constants  $k_i$  in Equations 1-to-4 are summarized in Table 1.

We can numerically examine the evolution of species concentrations with these kinetic rate laws. For instance, the solution of differential Equations 1 to 4 (using 4<sup>th</sup> order Runge-Kutta method) shows that the concentration of hydrogen ions in water [ $H^+$ ] converges to  $10^{-3.28}$  mol/L and the acidity level drops to  $pH \approx 3.28$  at steady state (under a partial pressure of  $P_{CO_2} = 10$  MPa and temperature  $T = 40^\circ C$ ).

## 2.2 Mineral Dissolutions

Geological formations typically considered for  $CO_2$  storage are sandstones and carbonates (Bachu et al. 1994). Then, we analyze two representative minerals: calcite  $CaCO_3$  (fast dissolution), and anorthite  $CaAl_2Si_2O_8$  (slow dissolution). Dissolution rates in the presence of  $CO_2$  dissolved water are analyzed next.

*Calcite Dissolution.* Three concurrent chemical reactions take place when calcite is in contact with  $CO_2$  acidified water, each with its own rate constant  $k_i$  and equilibrium constant  $K_{eq}$  (Plummer et al. 1978):

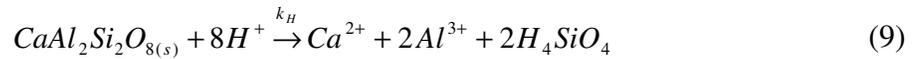


The first reaction consumes one mole of  $H^+$  and produces one mole of  $Ca^{2+}$  and one mole of  $HCO_3^-$  (Equation 5). The second reaction consumes one mole of  $CO_{2(aq)}$  in exchange for one mole of  $Ca^{2+}$  and two moles of  $HCO_3^-$  (Equation 6). The last reaction (Equation 7) has much smaller rate and equilibrium constants and it is ignored in the numerical simulation (Note: rate constants are listed in Table 1). The overall dissolution rate  $R_d$  is estimated as follows (Transition State Theory - Lasaga 1984; Li et al. 2008):

$$R_d = (k_1[H^+] + k_2[CO_{2(aq)}]) \left(1 - \frac{\Omega}{K_{tot}}\right) \text{ where } \Omega = \frac{[Ca^{2+}]^2[HCO_3^-]^3}{[H^+][CO_{2(aq)}]} \quad (8)$$

Note that  $\Omega$  at equilibrium is equal to the overall equilibrium constant;  $\log K_{tot} = 1.85 - 4.50 = -2.65$  (refer to Equations 5 and 6; Table 1).

*Anorthite Dissolution.* We adopt the model by Li et al. (Li et al. 2006) to represent the dissolution of anorthite. The reaction consumes eight moles of  $H^+$  to produce one mole of  $Ca^{2+}$ , two moles of  $Al^{3+}$ , and two moles of  $H_4SiO_4$ :



Again, the overall dissolution rate is described as a function of rate constants, concentrations of reactant species and saturation:

$$R_d = (k_H[H^+]^{1.5} + k_{H_2O} + k_{OH}[OH^-]^{0.33}) \left(1 - \frac{\Omega}{K_{tot}}\right) \text{ where } \Omega = \frac{[Ca^{2+}][Al^{3+}]^2[H_4SiO_4]^2}{[H^+]^8} \quad (10)$$

Rate constants and equilibrium constant are compiled in Table 1. We disregard the term  $k_{OH}[OH^-]^{0.33}$  during the numerical simulation because both the rate constant and the concentration of hydroxide  $[OH^-]$  are negligible.

Figure 1 compares the overall “local” mineral dissolution rates  $R_d$  for a fixed concentration of the total carbonic acid  $H_2CO_3^*$  at  $[H_2CO_3^*]=1\text{mol/L}$ . Results show that the concentration of hydrogen ions  $[H^+]$  controls the reaction rate of calcite when  $\text{pH} \leq \sim 4$  (thereafter, the high concentration of total carbonic acid  $[H_2CO_3^*]$  takes control), and the reaction rate of anorthite when  $\text{pH} \leq \sim 6$ . The reaction rate of calcite is several orders of magnitude higher than that of anorthite when  $2 < \text{pH} < 7$  (Figure 1).

### 3. Numerical Simulation of Reactive Fluid Flow

The coupling between hydro-chemical phenomena during the transport of reactive CO<sub>2</sub>-acidified water through a pore or fracture in a mineral system is investigated next. We start by identifying the governing dimensionless ratios.

#### 3.1 Dimensionless Ratios

Consider a reactive fluid advecting with velocity  $v$  [m/s] through a rock fracture driven by a pressure difference between inlet and outlet boundaries at a distance  $l$  [m] from each other. Reactant species are transported towards the mineral surface by molecular diffusion so that the fracture aperture  $d$  [m] and the diffusion coefficient  $D$  [m<sup>2</sup>/s] determine the characteristic time for transverse diffusion. Mineral dissolution at the fracture surface produces species that are carried away by both advection (downstream) and diffusion (in all directions).

Three dimensionless ratios capture the interplay between governing processes. The Damköhler number  $Da$  is the ratio between the advection time and the chemical reaction time (Fredd and Fogler 1998).

$$Da = \frac{t_{advection}}{t_{reaction}} = \frac{\kappa l}{v} \quad (11)$$

where the kinetic rate  $\kappa$  [1/s] =  $k_r \cdot S_s \cdot M_m$  is a function of the rate constant for mineral dissolution  $k_r$  [mol/m<sup>2</sup>/s], the mineral specific surface  $S_s$  [m<sup>2</sup>/g], and the mineral molar mass  $M_m$  [g/mol]. The Peclet number compares the time for either transverse  $Pe^\perp$  or longitudinal  $Pe^\parallel$  diffusion to the time for longitudinal advection (Golfier et al. 2002):

$$Pe^\perp = \frac{t_{diffusion}^\perp}{t_{advection}} = \frac{d^2 v}{4lD} \quad \text{and} \quad Pe^\parallel = \frac{t_{diffusion}^\parallel}{t_{advection}} = \frac{lv}{D} \quad (12)$$

#### 3.2 Simulation Method - Environment

Consider the plane across a rock fracture with length  $l$  much longer than the aperture  $d$ , i.e.,  $l \gg d$ , subjected to reactive fluid transport by the forced advection of  $\text{CO}_2$ -acidified water. The problem is simulated using the moving mesh function in COMSOL to reproduce the fracture enlargement due to chemical reaction (COMSOL 2008). Figure 2 summarizes the simulation scheme. Flow satisfies the Navier-Stokes' law (Equation A in Figure 2); species experience both advective and diffusive transport (Equation B in Figure 2). Mineral dissolution occurs at the interface between the fluid and the fracture walls with dissolution rate  $R_d$  as predicted by Equation 8 (calcite) or Equation 10 (anorthite). In the fracture, species undergo homogeneous reactions as predicted by Equations 1-to-4. The moving mesh function adjusts the mesh outwards according to the volume of dissolved mineral  $R_d \cdot (v_s/v) \cdot V_m$  [m/s], where  $(v_s/v)$  denotes the stoichiometric ratio of dissolved mineral to reactant species and  $V_m$  [m<sup>3</sup>/mol] is the molar volume of the mineral (Equation C in Figure 2).

Equations A, B and C in Figure 2 are fully coupled within the finite-element formulation (linear system solver: Direct-PARDISO - COMSOL 2008). The model consists of 1,608 triangular elements with maximum resolution around the inlet. A constant fluid injection velocity  $v_0$  is imposed at the inlet of the fracture plane (Figure 2). Note that Reynolds number  $Re = \rho v_0 l / \eta$  needs to be checked to ensure that laminar flow conditions apply (values remain within  $10^2 \leq Re \leq 10^1$  in this study). The non-pervious rock blocks that define the fracture are fixed in the far field, i.e., zero-strain boundaries, and the fracture planes move out in accordance with mineral dissolution. Species concentrations at the inlet remain constant and correspond to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in thermodynamic-equilibrium. The initial concentration of all species in the fracture plane corresponds to the system in thermodynamic-equilibrium and satisfies electro-neutrality at  $\text{pH}=8$ . Numerical computations continue until the total simulation time equals 10 times the advection

time  $10 \cdot l/v_0$  and involve more than 1,000 time steps. All parameters used for numerical simulations are summarized in Table 1.

### 3.3 Validation

There is no analytical solution for reactive fluid transport in a two-dimensional pore. Instead, we compare the analytical solution for one-dimensional geometry with 1-D numerical results obtained using the formulation described above. The governing equation for the one-dimensional transport of a reactive fluid is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \kappa c \quad (13)$$

For a single reactant species at an initial concentration  $c(x,0)=0$  for  $x>0$  and boundary conditions  $c(0,t)=c_0$  and  $c(\infty,t)=0$  for  $t \geq 0$ , the solution for the variation of the species concentration in space and time is (Boudreau 1997):

$$\frac{c}{c_0} = \frac{1}{2} \exp(\xi_2) \left[ \exp(-\xi_1) \operatorname{erfc}\left(\frac{2\xi_1 - \tau}{2\sqrt{\tau}}\right) + \exp(\xi_1) \operatorname{erfc}\left(\frac{2\xi_1 + \tau}{2\sqrt{\tau}}\right) \right]$$

where  $\beta^2 = \left(\frac{v^2}{4D^2} + \frac{\kappa}{D}\right)$   $\xi_1 = \beta x$ ,  $\xi_2 = \frac{vx}{2D}$ ,  $\tau = \frac{(v^2 + 4\kappa D)t}{D}$  (14)

Figure 3 shows that the 1-D numerically computed concentrations are in agreement with analytical results with minor deviations near the outlet. Two outlet boundary conditions are simulated to compare the finite-length numerical system with the infinite length analytical solution: 1) free flux, and 2) fixed outlet concentration  $c(l,t)=0$ . Numerical results bound the theoretical solution (Figure 3-b). Electro-neutrality is maintained during the numerical simulation.

## 4. Results and Discussion

Numerical simulation results for the 2-D fracture case relevant to CO<sub>2</sub> geological storage are presented herein in terms of species concentrations in space and time, the enlargement of the rock fracture and the morphing of the fracture geometry. Results are obtained for different regimes represented by dimensionless numbers  $Da$  and  $Pe^\perp$ .

### 4.1 Species Concentration

For both mineralogies, a higher advection velocity (lower  $Da$ ) yields higher concentrations of residual reactant species at the outlet due to the lower residence time. Thus, inlet species concentrations will influence deeper into the reservoir in anorthite. In particular:

- *High  $Da$  ( $>10^{-1}$ ) and Low  $Pe^\perp$  - Calcite.* Mineral dissolution couples with advection and diffusion to generate a concentration gradient across and along the pore/fracture aperture (for comparison, see Li et al. 2006). Figure 4 shows a snap-shot of instantaneous concentrations for all relevant species along a fracture in calcite. Slow transverse diffusion and homogenization across the aperture develops at low advection velocity (low  $Pe^\perp$ ) and leads to the large consumption of reactant species near the inlet (Figure 4-a). Clearly,  $H^+$  is readily consumed, the system reaches chemical equilibrium, and  $H_2CO_3^*$  passes through the rest of the fracture plane unconsumed in this calcite-dominant environment. The residual  $H_2CO_3^*$  at the outlet may react with other minerals and induce additional mineral dissolution in successive flow channels.
- *High  $Da$  ( $>10^{-1}$ ) and high  $Pe^\perp$  - Calcite.* When the advection velocity is high, diffusion fails to homogenize the concentration field across the fracture (high  $Pe^\perp$ ), and mineral dissolution is more uniform along the fracture length (Figure 4-b).
- *Low  $Da$  ( $<10^{-1}$ ) - Anorthite.* The longitudinal drop in reactant species is much lower in the

less reactive anorthite for the same advection regimes (Figure 5). The low reaction rate of  $H^+$  with anorthite allows more than two-thirds of  $H^+$  to reach the outlet unconsumed. The fluid acidity evolves as the numerical simulation proceeds. During the early stages of acidified fluid flow along the rock fracture, the pH drops near the inlet and remains at the initial pH~8 towards the outlet. The entire pore space acidifies and the area near the outlet converges to an asymptotic value pH~5 as advection continues and the system becomes saturated in terms of mineral dissolution (Figure 6).

Variations in reactant species concentrations along the fracture length are plotted in Figure 7-a at different normalized times  $t/(l/v_0)$ . The evolution of unconsumed reactants at the outlet are specifically explored in Figure 7-b for different  $Pe^\perp$  values. Results show the evolution towards "steady state" reactive fluid flow.

## 4.2 Enlargement

The rock fracture aperture increases as the reactive fluid passes through the fracture plane (Figures 4 and 5). The effect of advective velocity and reactivity are explored in Figures 8 and 9. Results show that pore enlargement decreases along the flow path as reactants become consumed (primarily next to the fluid-rock interface) and aqueous species concentration approaches equilibrium. In all cases, the normalized enlargement  $\Delta d/d$  in anorthite is three orders of magnitude smaller than that of calcite at comparable times and flow regimes (Figure 8 - Note: steady state conditions were reached with less than 2 pore volumes of flow through in all these cases).

Figure 9 compiles the observed evolving morphology in terms of dimensionless numbers,  $Da$  and  $Pe^\perp$ . At a given  $Pe^\perp$ , a lower  $Da$  causes the flow channel to experience a more uniform enlargement of the aperture along the fracture.

### 4.3 Time to Reach Quasi Steady-State Condition

The time to reach quasi steady-state concentration at the outlet  $t_{qc}$  is determined when species concentrations at the outlet  $c$  reach 95% of the equilibrium values  $c_{\infty}$  at  $t=\infty$  (refer to Figure 7-b). Figures 10-a and b indicate that the time to reach quasi steady-state  $t_{qc}$  for a fracture  $l/d=10$  is related to the advection time  $l/v_0$  through  $Da$  and  $Pe^{\perp}$  numbers.

The dimensionless time  $t/(l/v_0)$  equals the number of pore volumes that have traversed the fracture. At  $Pe \ll 1$  homogenization is diffusion-controlled and can be reached without flow, hence  $t/(l/v_0) \rightarrow 0$ . Near  $Pe \approx 1$  (depends on  $Da$ ), counter-flow diffusion delays the time to reach quasi steady-state, and the largest number of pore volumes is required to steady state:  $t/(l/v_0)$  approaches  $\approx 2$  (Figures 10-a and b). Finally, mineral dissolution and channel enlargement combine to extend the time to quasi steady-state conditions beyond the advection time when  $Pe \gg 1$ , and the number of pore volumes required exceeds  $t/(l/v_0)=1$ .

### 4.4 Initial Fracture Slenderness

Finally, let's examine the effect of fracture slenderness by varying the length-to-aperture ratio  $l/d$ ; we keep  $Da$  constant by changing the initial aperture  $d$ . When the ratio  $l/d$  is large  $l/d \geq 30$ , transverse diffusive transport homogenizes species concentrations across the fracture, and centerline concentrations resemble the 1-dimensional theoretical solution for the same advection velocity (Figure 11). For the same length  $l$ , a wider aperture  $d$  slows the transverse diffusive transport of reactant species to the mineral surface ( $t_{diff} \approx d^2/D$ ), and higher reactant concentrations remain along the centerline (Figure 11). Therefore, scaling must take into consideration both the fracture length and its slenderness (see also Li et al. 2008).

Let's examine a fracture network subjected to reactive fluid transport. If the length-to-aperture ratio of single fractures is large (i.e.,  $l/d \geq 30$ ), species concentration resembles a 1D

problem in each fracture. Then, if  $Pe \gg 1$  and  $Da \ll 1$ , fracture morphology evolves uniformly within each fracture (Figure 9), and can be modeled with a uniform aperture evolution during reactive transport. Single fracture morphology would evolve with a pyramidal shape outside these conditions. In all cases, steady state conditions are reached with less than 2 pore volumes of flow through each fracture when constant inlet chemistry is involved; clearly this is not the case in a fracture network. The situation is aggravated when highly reactive minerals are involved, such as in calcite as compared to anorthite, as much larger fracture enlargements will develop, other conditions being the same. In summary, fracture network analyses must consider both the length and slenderness of fractures, in addition to flow conditions captured in  $Pe$  and  $Da$ .

## 5. Conclusions

Reactive fluid transport through a rock fracture was simulated taking into consideration kinetic rate laws relevant to  $\text{CO}_2$  injection for geological storage and enhanced oil recovery in calcite and anorthite, which affect both reservoirs and wells. The geometry-coupled numerical simulation combines laminar flow, advective and diffusive mass transport of species, mineral dissolution and pore enlargement. Salient results follow.

Reactive fluid transport in a rock pore or fracture can be described in terms of two dimensionless parameters Damköhler  $Da$  and Peclet  $Pe$  numbers to take into consideration reactivity, advection and diffusion.

In highly-reactive low-advection conditions ( $Da > 10^{-1}$  and low  $Pe^\perp$  - e.g., low advection velocity in calcite), hydrogen ions  $H^+$  are readily consumed near the inlet, the fluid becomes saturated with reaction products, and  $H_2\text{CO}_3^*$  traverses the rest of the fracture length unconsumed. When the advection velocity increases and  $Pe^\perp > 10^{-1}$ , diffusion fails to homogenize the concentration field across the fracture, and mineral dissolution takes place more uniformly

along the fracture length.

In low reactivity cases ( $Da < 10^{-1}$  - anorthite),  $H^+$  is further transported along the fracture.

Low reactivity and  $Da$  values lead to a more uniform aperture enlargement along the length of the fracture at a given  $Pe^\perp$ . Therefore, the evolving morphology of the fracture depends on  $Da$  and  $Pe^\perp$ .

In general, mineral dissolution couples with pore enlargement to extend the time to reach quasi steady-state. In all cases tested in this study, steady state conditions for a single fracture subjected to constant inlet conditions are reached with less than 2 pore volumes of flow through.

Reactive fluid transport along a fracture resembles the 1-D problem when the length-to-aperture ratio is large, say  $l/d \geq 30$ . For a given length  $l$ , an increased fracture aperture  $d$  slows the diffusive transport of reactant species to the mineral fracture surface, and higher reactant concentrations remain along the centerline. Therefore, fracture network analyses must take into consideration both the length and slenderness of individual fractures in addition to flow conditions captured in  $Pe$  and  $Da$ .

The numerical approach developed in this study can be extended to 3-D fracture networks. Then, this mass-conserving model can be coupled with mechanical equilibrium and deformation compatibility to explore the response of fractured rock in the subsurface.

## **Appendix A: Kinetics - CO<sub>2</sub> Dissolution in Water**

Injected carbon dioxide  $CO_2$  dissolves in the formation water or brine to sequentially form aqueous carbon dioxide  $CO_{2(aq)}$  and carbonic acid  $H_2CO_3$ , which consequently dissociates into bicarbonate ions  $HCO_3^-$  and hydrogen ions  $H^+$  (Stumm et al. 1996; IPCC 2005):



The equilibrium constant  $K$  [-] for each chemical reaction defines the ratio of produced to reactant species concentrations at equilibrium and can be expressed as a ratio of forward to backward kinetic rates. All rate constants estimated at  $T \sim 40^\circ\text{C}$  are summarized in Table 1; details follow.

*Equation A.1.* The rate constant for the dissolution of gaseous carbon dioxide is  $k_g \approx 5 \cdot 10^{-3} \text{s}^{-1}$  at  $T \sim 25^\circ\text{C}$  (Sposito 1994). The rate constant for the reversed direction can be obtained from  $k_{aq} = k_g / K_H$  where  $K_H$  is Henry's constant.

*Equation A.2.* The reaction rate constant for hydration is  $k_{CO_2} \approx 0.04 \text{s}^{-1}$  at  $25^\circ\text{C}$  with activation energy  $E_a = 15 \text{kcal/mol}$ , and for dehydration is  $k_{H_2CO_3} \approx 20 \text{s}^{-1}$  at  $25^\circ\text{C}$  with  $E_a = 16 \text{kcal/mol}$  (Stumm et al. 1996). The rate constant at a given temperature can be computed using Arrhenius law:

$$k(T) = k_{25} \exp\left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad (A.4)$$

where  $k_{25}$  is the rate constant at  $T = 25^\circ\text{C} (= 298.15\text{K})$  and  $R$  is the gas constant. Rate constants  $k_{CO_2}$  and  $k_{H_2CO_3}$  are also used to calculate the equilibrium constant  $K$  in Equation A.2.

*Equation A.3.* Carbonic acid dissociation is very fast compared to reactions in Equations A.1 and A.2; we selected  $k_{12} \approx 10^7 \text{s}^{-1}$  at  $T \sim 40^\circ\text{C}$  (Zhang 2008). The rate constant for the reversed reaction is obtained from  $k_{21} = k_{12} / K_{H_2CO_3}$  where the equilibrium constant  $K_{H_2CO_3}$  is computed from  $K$  (Stumm et al. 1996):

$$K_{H_2CO_3} = K_1(1 + K) \quad (\text{A.5})$$

where  $K_1$  denotes the first acidity constant for the reaction in which  $H_2CO_3^*$  dissociates to bicarbonate and hydrogen ion (the asterisk denotes the combination of both aqueous carbon dioxide and carbonic acid). The value of the acidity constant is  $K_1 \approx 10^{-6.35}$  under standard conditions.

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Table 1 Parameters used in simulations

CO <sub>2</sub> kinetics			
$k_g$	$5 \times 10^{-3} \text{ s}^{-1}$ <sup>(1)</sup>	Rate constant of $\text{CO}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{aq})}$	
$k_{aq}$	$k_g / K_H$ <sup>(1)</sup>	Rate constant of $\text{CO}_{2(\text{g})} \leftarrow \text{CO}_{2(\text{aq})}$	
$k_{\text{CO}_2}$	$0.135 \text{ s}^{-1}$ <sup>(2)</sup>	Rate constant of $\text{CO}_{2(\text{aq})} \rightarrow \text{H}_2\text{CO}_3$	
$k_{\text{H}_2\text{CO}_3}$	$72.982 \text{ s}^{-1}$ <sup>(2)</sup>	Rate constant of $\text{CO}_{2(\text{aq})} \leftarrow \text{H}_2\text{CO}_3$	
$k_{12}$	$10^7 \text{ s}^{-1}$ <sup>(3)</sup>	Rate constant of $\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$	
$k_{21}$	$4.1 \times 10^{10} \text{ s}^{-1}$ <sup>(3)</sup>	Rate constant of $\text{H}_2\text{CO}_3 \leftarrow \text{H}^+ + \text{HCO}_3^-$	
$K_H$	$10^{-1.64}$ <sup>(2)</sup>	Henry's constant at 40°C	
Calcite fracture plane		Anorthite fracture plane	
$[\text{H}^+]_{\text{inlet}}$	$10^{-6} \text{ mol/L}$ to $10^{-3} \text{ mol/L}$	$[\text{H}^+]_{\text{inlet}}$	$10^{-6} \text{ mol/L}$ to $10^{-3} \text{ mol/L}$
$[\text{H}_2\text{CO}_3^*]_{\text{inlet}}$	$10^{-3} \text{ mol/L}$ to $1 \text{ mol/L}$	$[\text{H}_2\text{CO}_3^*]_{\text{inlet}}$	$10^{-3} \text{ mol/L}$ to $1 \text{ mol/L}$
$[\text{Ca}^{2+}]_{\text{inlet}}$	$1.36 \times 10^{-3} \text{ mol/L}$ <sup>(4)</sup>	$[\text{HCO}_3^-]_{\text{inlet}}$	$6.68 \times 10^{-4} \text{ mol/L}$ <sup>(4)</sup>
$[\text{HCO}_3^-]_{\text{inlet}}$	$6.68 \times 10^{-4} \text{ mol/L}$ <sup>(4)</sup>	$[\text{OH}^-]_{\text{inlet}}$	$1.50 \times 10^{-11} \text{ mol/L}$ <sup>(4)</sup>
$[\text{OH}^-]_{\text{inlet}}$	$1.50 \times 10^{-11} \text{ mol/L}$ <sup>(4)</sup>	$[\text{Ca}^{2+}]_{\text{inlet}}$	$2.11 \times 10^{-4} \text{ mol/L}$ <sup>(4)</sup>
$[\text{Cl}^-]_{\text{inlet}}$	$2.72 \times 10^{-3} \text{ mol/L}$ <sup>(4)</sup>	$[\text{Al}^{3+}]_{\text{inlet}}$	$3.51 \times 10^{-8} \text{ mol/L}$ <sup>(4)</sup>
		$[\text{H}_4\text{SiO}_4]_{\text{inlet}}$	$9.67 \times 10^{-13} \text{ mol/L}$ <sup>(4)</sup>
		$[\text{Cl}^-]_{\text{inlet}}$	$4.22 \times 10^{-4} \text{ mol/L}$ <sup>(4)</sup>
$[\text{H}^+]_{\text{initial}}$	$1.0 \times 10^{-8} \text{ mol/L}$ <sup>(5)</sup>	$[\text{H}^+]_{\text{initial}}$	$1.0 \times 10^{-8} \text{ mol/L}$ <sup>(6)</sup>
$[\text{H}_2\text{CO}_3^*]_{\text{initial}}$	$1.0 \times 10^{-5} \text{ mol/L}$ <sup>(5)</sup>	$[\text{H}_2\text{CO}_3^*]_{\text{initial}}$	$1.0 \times 10^{-5} \text{ mol/L}$ <sup>(6)</sup>
$[\text{Ca}^{2+}]_{\text{initial}}$	$1.59 \times 10^{-3} \text{ mol/L}$ <sup>(5)</sup>	$[\text{HCO}_3^-]_{\text{initial}}$	$4.47 \times 10^{-4} \text{ mol/L}$ <sup>(6)</sup>
$[\text{HCO}_3^-]_{\text{initial}}$	$4.47 \times 10^{-4} \text{ mol/L}$ <sup>(5)</sup>	$[\text{OH}^-]_{\text{initial}}$	$1.0 \times 10^{-6} \text{ mol/L}$ <sup>(6)</sup>
$[\text{OH}^-]_{\text{initial}}$	$1.0 \times 10^{-6} \text{ mol/L}$ <sup>(5)</sup>	$[\text{Ca}^{2+}]_{\text{initial}}$	$4.35 \times 10^{-4} \text{ mol/L}$ <sup>(6)</sup>
$[\text{Cl}^-]_{\text{initial}}$	$2.72 \times 10^{-3} \text{ mol/L}$ <sup>(5)</sup>	$[\text{Al}^{3+}]_{\text{initial}}$	$3.51 \times 10^{-8} \text{ mol/L}$ <sup>(6)</sup>
		$[\text{H}_4\text{SiO}_4]_{\text{initial}}$	$9.67 \times 10^{-13} \text{ mol/L}$ <sup>(6)</sup>
		$[\text{Cl}^-]_{\text{initial}}$	$4.22 \times 10^{-4} \text{ mol/L}$ <sup>(6)</sup>
$k_1$	$0.745 \text{ mol/m}^2/\text{s}$ <sup>(7)</sup>	$k_H$	$3.4 \times 10^{-4} \text{ mol/m}^2/\text{s}$ <sup>(8)</sup>
$k_2$	$8.6 \times 10^{-4} \text{ mol/m}^2/\text{s}$ <sup>(7)</sup>	$k_{\text{H}_2\text{O}}$	$1.8 \times 10^{-12} \text{ mol/m}^2/\text{s}$ <sup>(8)</sup>
$K_{\text{tot}}$	$10^{-2.65}$ <sup>(7)</sup>	$K_{\text{tot}}$	$10^{21.7}$ <sup>(8)</sup>
$v_0$	$10^{-3} \text{ cm/s}$ to $1 \text{ cm/s}$	Inlet velocity	
$\eta$	$10^{-3} \text{ Pa} \cdot \text{s}$	Viscosity of fluid	
$\rho_f$	$1,100 \text{ kg/m}^3$	Density of fluid	
$S_s$	$0.06 \text{ m}^2/\text{g}$ <sup>(9)</sup>	Specific surface of calcite and anorthite	
$M_m$	$100 \text{ g/mol}$	Molar mass of calcite	
	$277 \text{ g/mol}$	Molar mass of anorthite	
$V_m$	$3.7 \times 10^{-5} \text{ m}^3/\text{mol}$	Molar volume of calcite	
	$10.1 \times 10^{-5} \text{ m}^3/\text{mol}$	Molar volume of anorthite	
$D$	$2.0 \times 10^{-9} \text{ m}^2/\text{s}$	Average diffusion coefficient for all species	

Note: rate constants are computed for temperature  $T=40^\circ\text{C}$ . References are from: <sup>(1)</sup> Sposito 1994, <sup>(2)</sup> Stumm et al. 1996, <sup>(3)</sup> Zhang 2008; Species concentrations are examples computed for <sup>(4)</sup> pH=3.18, <sup>(5)</sup> pH=8 and  $K_{\text{tot}}=10^{-2.65}$ , <sup>(6)</sup> pH=8 and  $K_{\text{tot}}=10^{21.7}$ ; <sup>(7)</sup> Renard et al. 2005; Wigand et al. 2008; Algive et al.

2009, <sup>(8)</sup> Li et al. 2006, <sup>(9)</sup> Gaus et al. 2005.

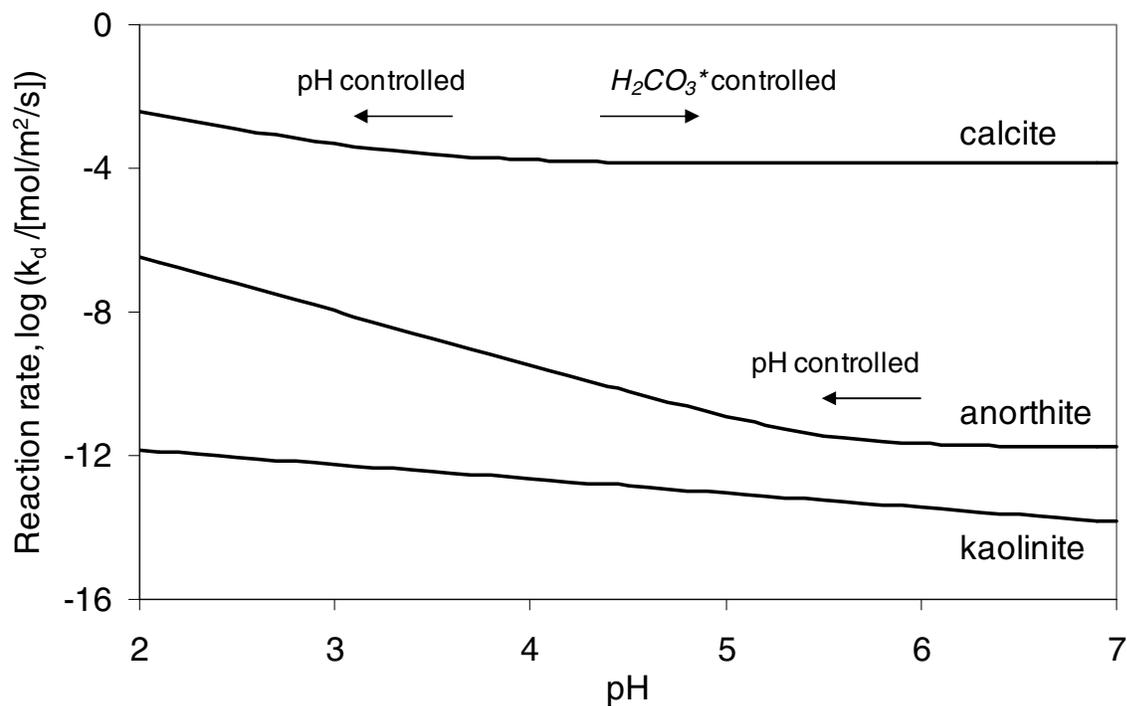


Figure 1 Reaction rate  $\log(k_d/[\text{mol}/\text{m}^2/\text{s}])$  for the dissolution of calcite  $\text{CaCO}_3$  and anorthite  $\text{CaAl}_2\text{Si}_2\text{O}_8$  at a temperature  $T=40^\circ\text{C}$  and for a fixed concentration of total dissolved carbon dioxide  $[\text{H}_2\text{CO}_3^*]=1\text{mol/L}$ . For comparison, the reaction rate is also plotted for kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  as a representative clay mineral of low reactivity; in this case,  $k_d=k_H[\text{H}^+]^{0.4}+k_{\text{OH}}[\text{OH}]^{0.3}$  where  $k_H=2.79\times 10^{-11}\text{mol}/\text{m}^2/\text{s}$  and  $k_{\text{OH}}=3.51\times 10^{-16}\text{mol}/\text{m}^2/\text{s}$  at  $T=40^\circ\text{C}$  (Li et al. 2006).

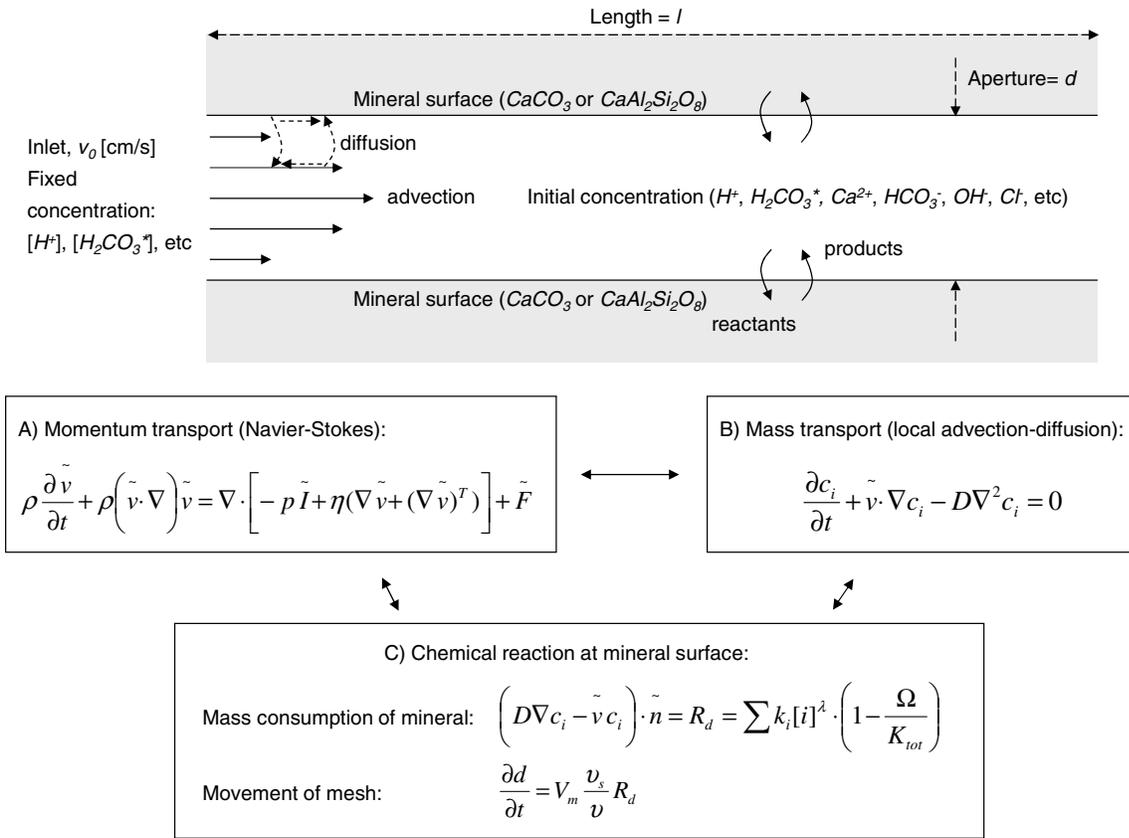


Figure 2 Numerical simulation scheme and governing equations for reactive fluid flow through a rock pore/fracture. Physics models used in COMSOL: (A) Incompressible Navier-Stokes ( $\eta$ : dynamic viscosity of fluid,  $\rho$ : density of fluid,  $\tilde{\mathbf{v}}$ : velocity field,  $p$ : pressure,  $\tilde{\mathbf{F}}$ : volume force field such as gravity; gravity is disregarded in the simulation), (B) Advection and diffusion ( $c_i$ : concentration of species  $i$ ,  $D$ : coefficient of molecular diffusion), and (C) Moving mesh ( $R_d$ : overall dissolution rate of mineral at the wall,  $k_i$ : reaction rate of reactant species  $i$ ,  $[i]$ : concentration of reactant species  $i$ ,  $\Omega$ : ionic concentration product,  $K_{tot}$ : equilibrium constant,  $d$ : fracture aperture,  $V_m$ : mineral molar volume,  $v_s/v$ : stoichiometric ratio between reactant species and dissolved mineral).

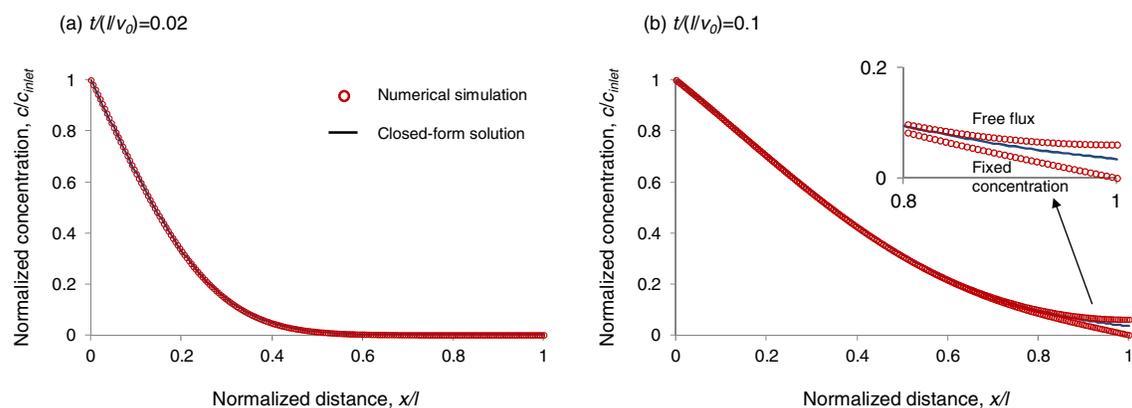


Figure 3 Code validation: Comparison between numerical simulation results and values predicted using the closed-form solution for 1-D reactive solute transport problem.

Assumptions: homogeneous reaction of single species  $c_A$  for reaction  $c_A \xrightarrow{k_{AB}} c_B$  where

$k_{AB}=0.1s^{-1}$ . The insert in pane-b shows the discrepancy between the closed-form solution for the infinitely long tube and the numerical solution for a finite tube with two boundary conditions: free flux and fixed initial concentration at the outlet. Fixed inlet concentration of  $c_A$   $[c_A]_{(0,t)}=1\text{mol/L}$ , initial concentration of  $c_A$   $[c_A]_{(x>0)}=0$ , fixed inlet velocity  $v_0=0.01\text{cm/s}$ , diffusion coefficient  $D=2\times 10^{-9}\text{m}^2/\text{s}$ .

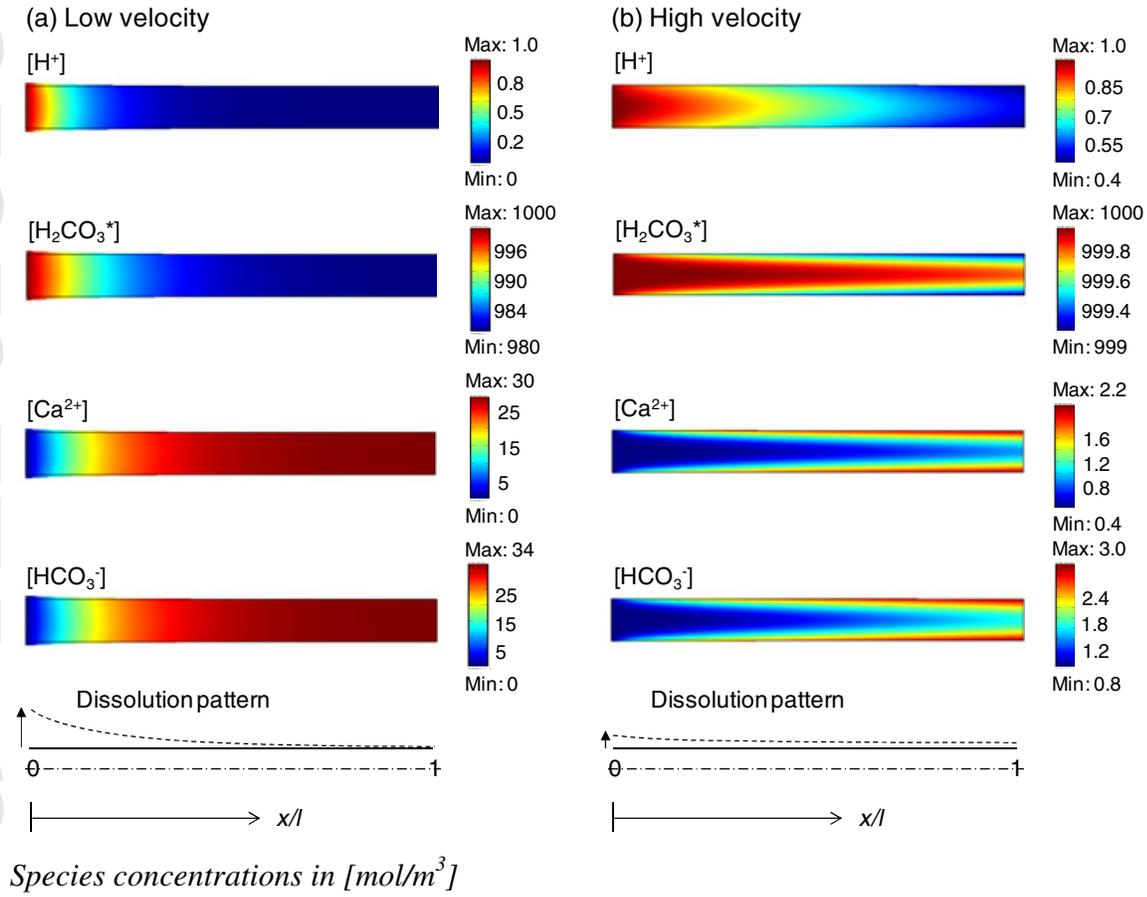


Figure 4 Reactive fluid transport along a fracture in calcite. Concentration of reactants  $[H^+]$  and  $[H_2CO_3^*]$ , and produced species  $[Ca^{2+}]$  and  $[HCO_3^-]$ . Dimensionless numbers are: (a)  $Da \approx 10^2$  and  $Pe^\perp \approx 3 \times 10^{-4}$ , and (b)  $Da \approx 10^{-1}$  and  $Pe^\perp \approx 3 \times 10^{-1}$ . Concentration results are shown at dimensionless times: (a)  $t = 5 \times (l/v_0)$  and (b)  $t = 1000 \times (l/v_0)$ . Species concentrations are in  $[mol/m^3]$ . All parameters are summarized in Table 1.

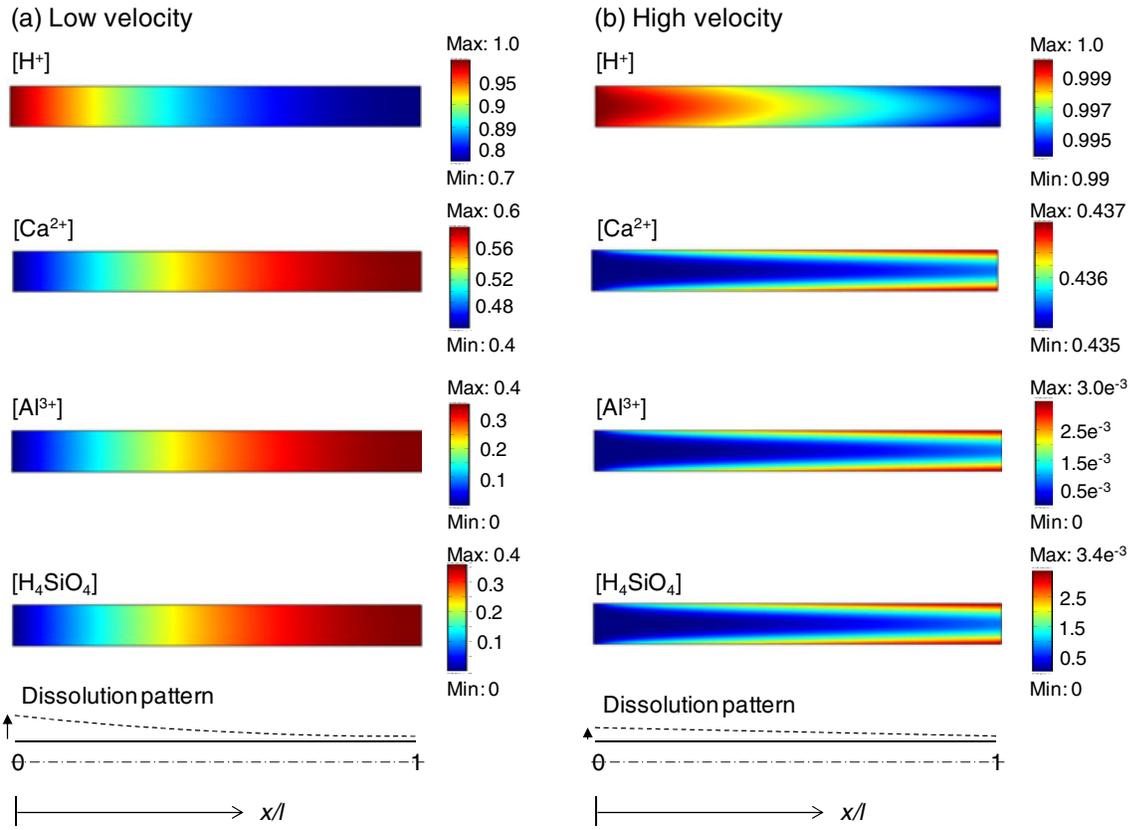


Figure 5 Reactive fluid transport along a fracture in anorthite. Concentration of reactant  $[H^+]$ , and produced species  $[Ca^{2+}]$ ,  $[Al^{3+}]$  and  $[H_4SiO_4]$ . Dimensionless numbers are: (a)  $Da \approx 6 \times 10^{-2}$  and  $Pe^\perp \approx 3 \times 10^{-4}$ , and (b)  $Da \approx 6 \times 10^{-5}$  and  $Pe^\perp \approx 3 \times 10^{-1}$ . Concentrations are shown at dimensionless times: (a)  $t = 0.5 \times (l/v_0)$  and (b)  $t = 100 \times (l/v_0)$ . Species concentrations are in  $[\text{mol}/\text{m}^3]$ . All parameters are summarized in Table 1.

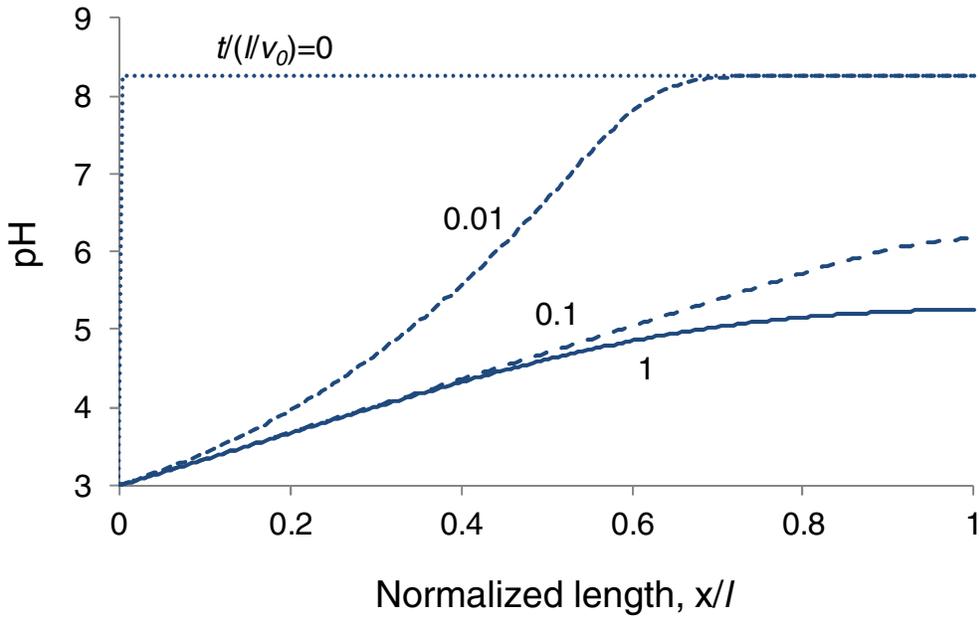


Figure 6 Evolution of pH in time and space - anorthite. Values of pH along the length of fracture plane at selected normalized times  $t/(lv_0)$ . Note:  $Da \approx 6 \times 10^{-3}$  and  $Pe^\perp \approx 3 \times 10^{-3}$ . The pH distribution reaches quasi-steady state when  $t/(lv_0) > 1$ .

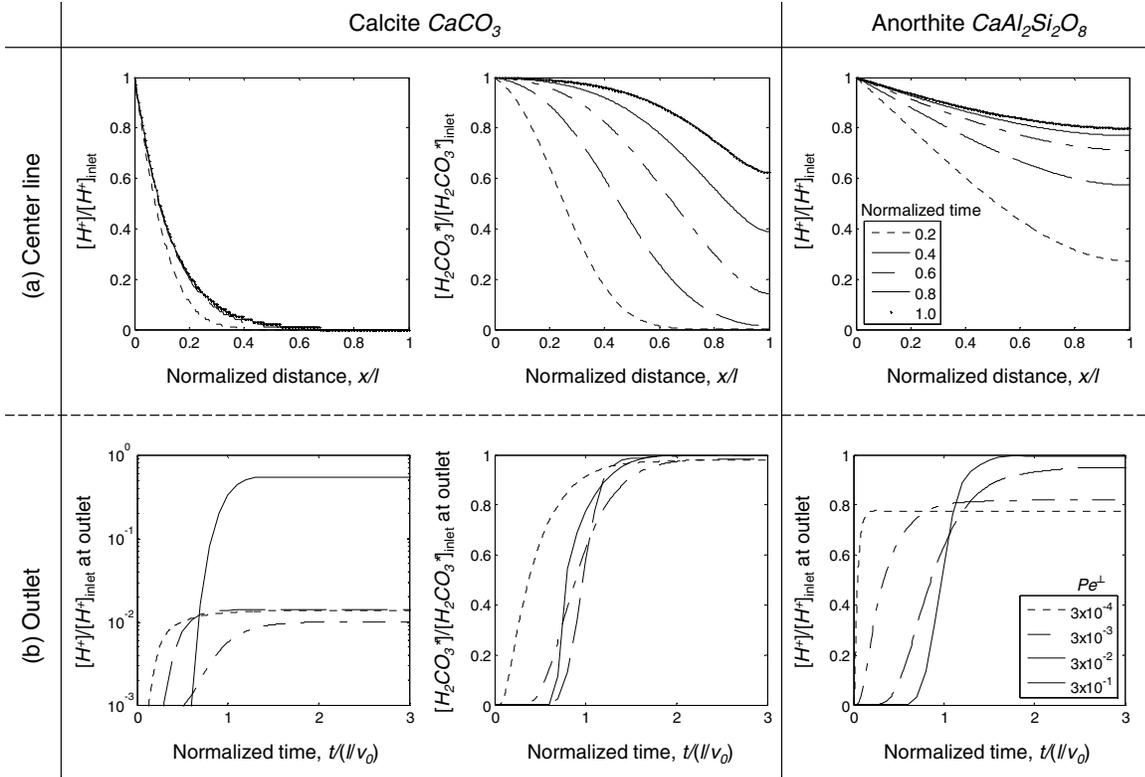


Figure 7 Variation of reactant species concentration: (a) along the centerline for different normalized times ( $Da \approx 10$  for calcite and  $Da \approx 6 \times 10^{-3}$  for anorthite) and (b) at the outlet for different transverse Peclet numbers  $Pe^\perp$ . All parameters are summarized in Table 1.

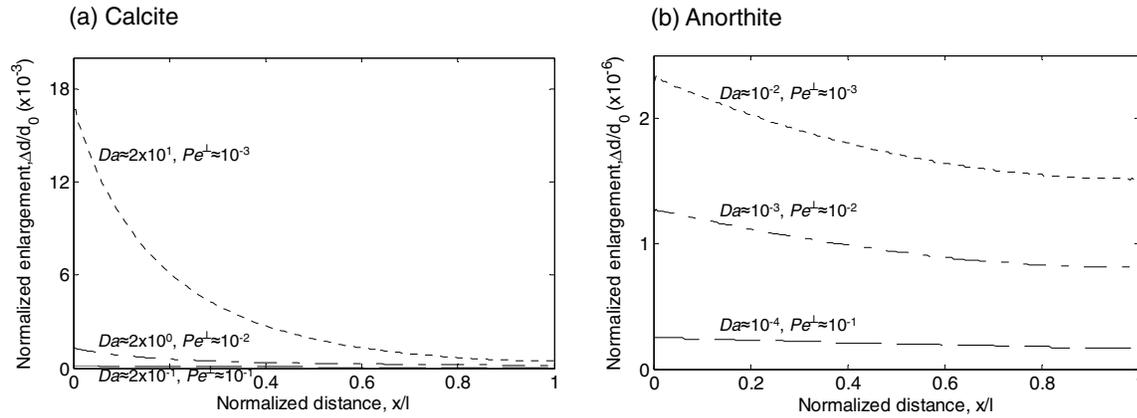


Figure 8 Normalized aperture enlargement  $\Delta d/d_0$  due to mineral dissolution along the fracture wall at the moment of quasi steady-state concentration conditions for different  $Da$  and  $Pe^\perp$  values and for a fracture slenderness  $l/d=10$ . (a) Calcite. (b) Anorthite. Note: orders of enlargement are different between the results for the two minerals. In all cases shown, steady state conditions were reached with less than 2 pore volumes of flow through (refer to Figure 10).

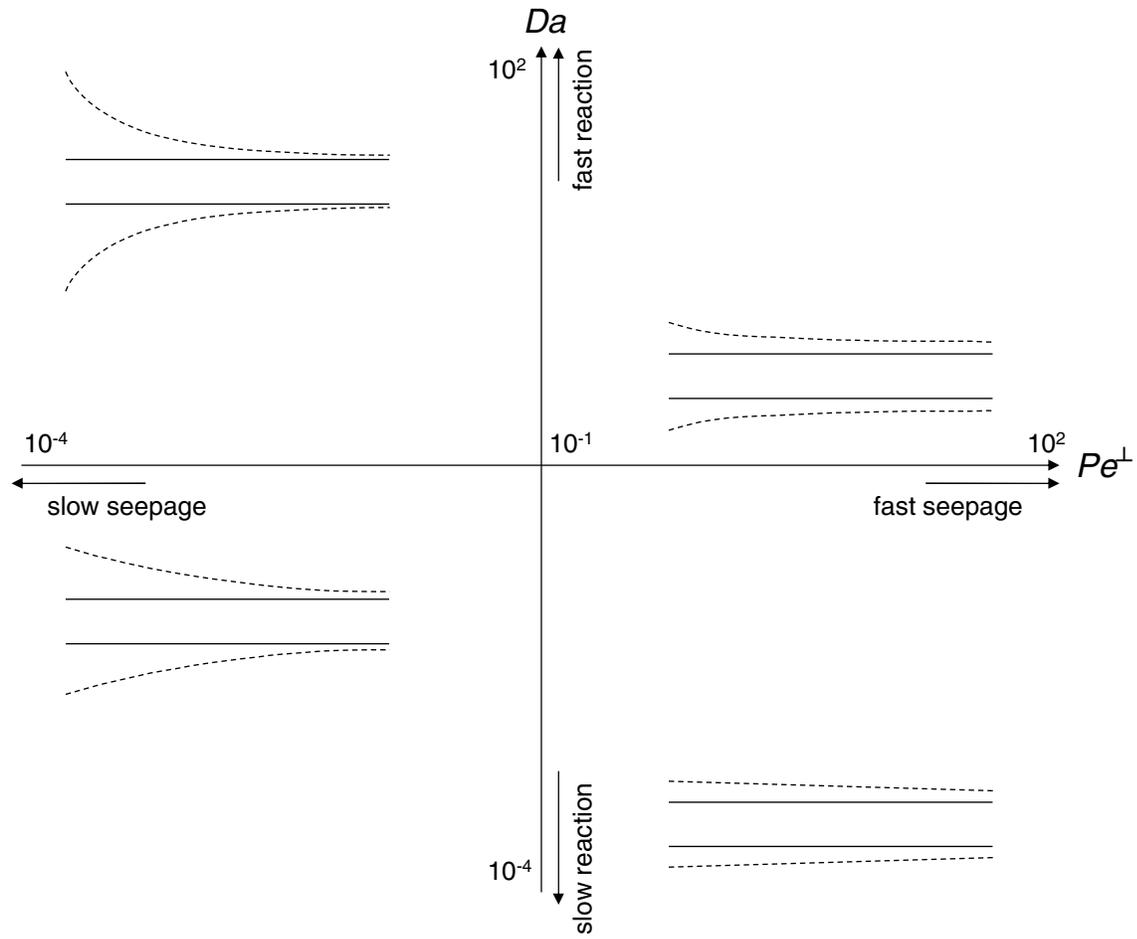


Figure 9 Evolving fracture morphology in the  $Da - Pe^\perp$  space. Sketches show dissolution patterns observed in numerical simulations of fractures with initially parallel planes. Trends shown in this dimensionless plot apply to both calcite and anorthite.

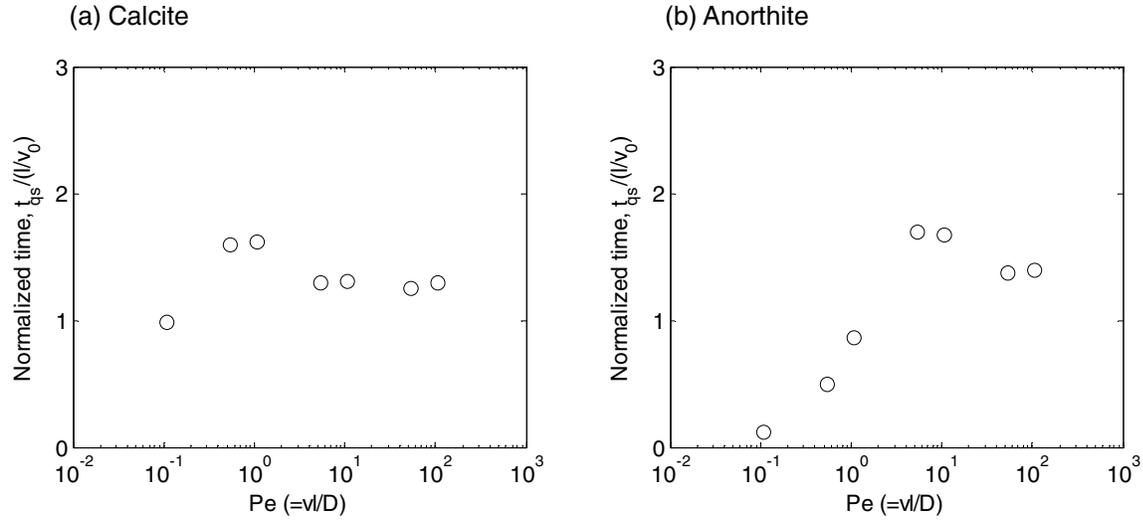


Figure 10 Time to reach quasi steady-state concentration  $t_{qs}$  at the outlet (95% of  $c/c_\infty$ , where the equilibrium value  $c_\infty$  is at  $t=\infty$ ). (a) Calcite ( $Da=10^{-1}\sim 10^2$ ) and (b) Anorthite ( $Da=6\times 10^{-5}\sim 6\times 10^{-2}$ ). Note: The time  $t_{qs}$  is normalized by the advection time  $l/v_0$  based on the fracture length  $l$  and the initial velocity  $v_0$ ; for an alternative interpretation, consider the normalized time  $t_{qs}/(l/v_0)$  as the number of pore volumes flushed through the fracture to reach steady state.

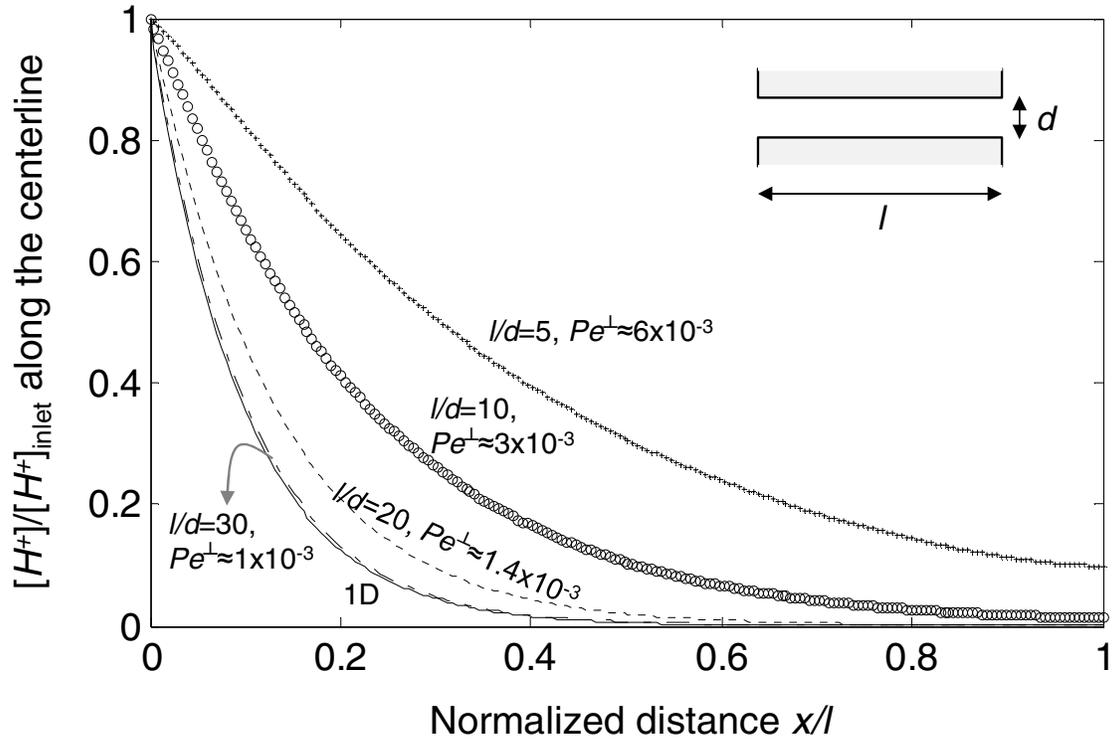


Figure 11 Effect of the length-to-aperture ratio  $l/d$  for the same  $Da \approx 10$ . Variation of the normalized concentration of hydrogen ions  $[H^+]/[H^+]_{\text{inlet}}$  at quasi steady-state for fractures in calcite with different slenderness. The theoretical 1-D solution is shown for comparison. All parameters are summarized in Table 1.