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# Upscaling calcite dissolution rates using network model simulations

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**ABSTRACT:** This paper presents a method to examine upscaling of geochemical reaction rates in porous media. Focusing on a CO<sub>2</sub>-brine-rock system, we simulate calcite dissolution using two representations of the porous medium. Using a continuum model, the porous medium is characterized by its spatially-averaged properties. Using a network model, the porous medium is constrained to have the same spatially-averaged hydrodynamic properties, but heterogeneities in mass transport and reaction kinetics at the pore scale are taken into account. Simulation results show that reaction rates in the two models evolve in disparate ways, resulting in different pH conditions and amounts of calcite dissolved. The continuum model overestimates rates at early stages leading to underestimation of rates at steady state. This methodology can be used to investigate length-scale dependencies of geochemical reaction rates and examine the conditions under which reaction rates can be linearly upscaled.

## 1 INTRODUCTION

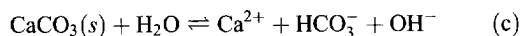
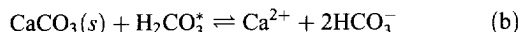
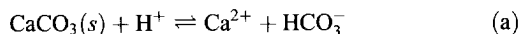
Reactive transport simulations generally employ a continuum approach, which involves discretizing the domain of interest into a number of grid blocks (Lichtner 1985; Steefel and MacQuarrie 1996). Each grid block is described by spatially-averaged properties, with detailed information at the pore scale ignored. Reaction rates are estimated via simple linear upscaling, where geochemical reaction rate constants measured in well-mixed laboratory systems are applied with total reactive surface area. Lab-measured reaction rate constants generally reflect mineral surface reactivity. At the scale of a grid block, reaction rates depend not only on mineral reactivity, but also on factors that control mass transport of reactive species, such as hydrodynamic conditions (Berner 1978) and pore property heterogeneities. Therefore, simple linear upscaling may introduce inaccuracies. Appropriate use of the continuum approach for reactive transport modeling requires an awareness of the conditions under which reaction rates can and cannot be linearly upscaled.

This paper introduces a method of examining considerations in upscaling geochemical reaction rates by comparing the calcite dissolution rates using a continuum model and a network model. The work is focused on a CO<sub>2</sub>-brine-rock system, a porous medium of one grid block size, in which dissolved CO<sub>2</sub>

reacts with the solid phase consisting of 10% calcite as the reactive mineral and 90% sandstone as the non-reactive mineral. Simulation results are presented for a single set of system conditions.

## 2 THE REACTION RATE LAW

Calcite dissolution can be represented as three parallel reactions occurring simultaneously (Plummer et al. 1978).



While all three are reversible reactions, this work is focused on conditions where dissolution is the net reaction. The respective reaction rates  $r_a$ ,  $r_b$  and  $r_c$  ( $\text{mmol cm}^{-2} \text{sec}^{-1}$ ) have the following forms:

$$r_a = k_a \{\text{H}^+\} (1 - \Omega_a) \quad (1)$$

$$\text{where } \Omega_a = \frac{\{\text{Ca}^{2+}\} \{\text{HCO}_3^-\}}{\{\text{H}^+\} K_{eq,a}}, \quad (2)$$

$$r_b = k_b \{\text{H}_2\text{CO}_3^*\} (1 - \Omega_b)$$

$$\text{where } \Omega_b = \frac{\{\text{Ca}^{2+}\}\{\text{HCO}_3^-\}^2}{\{\text{H}_2\text{CO}_3^*\}K_{eq,b}}, \quad (3)$$

$$r_c = k_c\{\text{H}_2\text{O}\}(1 - \Omega_c)$$

$$\text{where } \Omega_c = \frac{\{\text{Ca}^{2+}\}\{\text{HCO}_3^-\}\{\text{OH}^-\}}{\{\text{H}_2\text{O}\}K_{eq,c}}.$$

Here, the species activity,  $\{\}$  ( $\text{mmol}/\text{cm}^3$ ), is the product of the activity coefficient and the species concentration,  $[\ ]$  ( $\text{mmol}/\text{cm}^3$ ). Activity coefficients are calculated using the Davies equation and are considered constant during simulation because the increase in the ionic strength due to the dissolution reactions is not significant. Each  $\Omega$  is the reaction saturation ratio. The equilibrium constants  $K'_{eq}$  are obtained by combining the equilibrium constant of calcite dissolution and the dissociation constants of carbonic acid and bicarbonate at  $25^\circ\text{C}$ . Values of reaction rate constants  $k_a$ ,  $k_b$ ,  $k_c$  ( $\text{cm}/\text{sec}$ ) are from Plummer et al. (1978).

Equations 1 through 3 are the reaction rate laws that describe heterogeneous reaction kinetics at solid surfaces. As such, they do not account for any mass transfer kinetic limitations. In this work, aqueous phase reactions, such as carbonic acid dissociation, are assumed to be instantaneous.

### 3 CONCEPTUAL MODELS

#### 3.1 The continuum model

One way to represent the  $\text{CO}_2$ -brine-rock system is using a "continuum model", which ignores the details at the pore scale and is characterized by bulk properties. No spatial concentration gradient is assumed in the aqueous phase. Following Lichtner's work (1985), the mass balance equations are written for three basic "components",  $\text{Ca}^{2+}$ ,  $C_T$ , and  $\text{H}_T$ , with  $C_T$  being the summation of the carbon-bearing species, and  $\text{H}_T$  the total aqueous proton, defined as  $[\text{H}_T] = [\text{H}^+] + [\text{H}_2\text{CO}_3^*] - [\text{CO}_3^{2-}] - [\text{OH}^-]$ .

$$V_{con} \frac{d[\text{Ca}^{2+}]}{dt} = Q_{con}[\text{Ca}^{2+}]_{in} - Q_{con}[\text{Ca}^{2+}] + R_{con}A_{con} \quad (4)$$

$$V_{con} \frac{d[C_T]}{dt} = Q_{con}[C_T]_{in} - Q_{con}[C_T] + R_{con}A_{con} \quad (5)$$

$$V_{con} \frac{d[\text{H}_T]}{dt} = Q_{con}[\text{H}_T]_{in} - Q_{con}[\text{H}_T] - R_{con}A_{con} \quad (6)$$

Here  $V_{con}$ ,  $Q_{con}$ , and  $A_{con}$  are the total void volume, volumetric flow rate and total reactive surface area, respectively. The concentration  $[\ ]_{in}$  corresponds to the solute concentration at the incoming boundary. The reaction rate at the continuum scale is denoted  $R_{con}$ , with  $R_{con} = R_{con,a} + R_{con,b} + R_{con,c}$ , calculated by using the reaction rate laws and applying the labmeasured reaction rate constants directly. Concentrations of other species ( $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{CO}_3^*$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) are calculated by using their aqueous equilibrium relationships and the definitions of  $C_T$  and  $\text{H}_T$ .

#### 3.2 The network model

An alternative way of representing the  $\text{CO}_2$ -brinerock system is with the pore-scale network model, which discretizes the pore space into a collection of pores within a connected network. Each pore distinguishes itself by its volume, surface area, reactive surface area, and conductances with its neighbors. The network model is constrained to have the same volumetric flow rate, total void volume, total reactive surface area as the continuum model. The pores are assumed to have irregular shapes and to be arranged on a cubic lattice. Pore throats are conceptually represented by conductances between pores. Based on literature data for Fontainebleau sandstones (Lindquist et al. 2000), pore volume is assumed to have a lognormal distribution. As conductivity normally has a lognormal distribution (Freeze 1975), conductance is assumed to have a lognormal distribution too, but local values are conditioned on volumes of connected pores. Surface area is assumed to follow an exponential distribution. Within each pore, 10% of the surface area is modeled as reactive. Assuming Poiseuille flow between pores and an incompressible fluid, the flow field is solved.

We assume that at the pore scale, the reaction rate is surface-controlled. That is, a uniform aqueous concentration is assumed for each species within each pore, and the reaction rate laws are represented using equations 1 through 3. Using a Damkohler number analysis, this assumption was found to be valid when  $\text{pH} > 3$ . Mass balance equations for the three basic components within each pore  $i$  are formulated in the same way as in the continuum model:

$$V_i \frac{d[\text{Ca}^{2+}]_i}{dt} = \sum_{Q_j > 0} Q_j [\text{Ca}^{2+}]_j + \sum_{Q_j < 0} Q_j [\text{Ca}^{2+}]_i + r_i A_i \quad (7)$$

$$V_i \frac{d[C_T]_i}{dt} = \sum_{Q_j > 0} Q_j [C_T]_j + \sum_{Q_j < 0} Q_j [C_T]_i + r_i A_i \quad (8)$$

$$V_i \frac{d[H_T]_i}{dt} = \sum_{Q_j > 0} Q_j [H_T]_j + \sum_{Q_j < 0} Q_j [H_T]_i - r_i A_i \quad (9)$$

where the subscript  $j$  designates the index for the neighbors of pore  $i$ , varying from 1 to the coordination number of pore  $i$ . The pore volume  $V_i$ , reactive surface area  $A_i$ , and  $Q_j$ 's pertain to pore  $i$ . On the right side of these equations, the first term takes into account the rate of mass incoming from the neighbor pores, the second term accounts for the rate of mass outgoing from pore  $i$ , and the third term represents the mass change rate due to reaction, with total reaction rate  $r_i = r_{a,i} + r_{b,i} + r_{c,i}$ . Concentrations of other species within each pore  $i$  are calculated as in the continuum model. Notice that in this model, the equilibrium relationships hold within each pore, but are not constrained to hold across the network.

#### 4 UPSCALING METHODS

In the network model,  $r_i$  depends on the local aqueous concentrations. The upscaled reaction rate for the network is a function of  $r_i$ 's, as well as local reactive surface areas  $A_i$ 's. In the network model, the upscaled reaction rate for reaction  $a$   $R_{N,a}$  is computed as follows:

$$R_{N,a} = \frac{\sum_{i=1}^n r_{a,i} A_i}{\sum_{i=1}^n A_i} \quad (10)$$

where  $n$  is the total number of pores. Values of  $R_{N,b}$  and  $R_{N,c}$  are computed in a similar manner. The total upscaled reaction rate in the network model is thus:

$$R_N = R_{N,a} + R_{N,b} + R_{N,c} \quad (11)$$

and is equivalent to the mass change rate in the network per unit total reactive surface area ( $\text{mmol cm}^{-2} \text{sec}^{-1}$ ).

To compare the steady state dissolution rates in these two models, we define an upscaling coefficient,  $\eta$ , as follows:

$$\eta = \frac{R_N}{R_{con}} \quad (12)$$

For each reaction, we define:

$$\eta_a = \frac{R_{N,a}}{R_{con,a}}, \eta_b = \frac{R_{N,b}}{R_{con,b}}, \eta_c = \frac{R_{N,c}}{R_{con,c}} \quad (13)$$

The upscaling coefficients reflect the effect of factors controlling mass transport of reactive species, such as hydrodynamic conditions. As such, they are correction factors accounting for the scaling effect. If  $\eta$  is close to unity, the direct use of reaction rate constants ( $k_a$ ,  $k_b$  and  $k_c$ ) in the continuum model does

not cause significant inaccuracy and reaction rates can be linearly upscaled.

#### 5 SIMULATION CONDITIONS

The regular-latticed network is composed of a total of 2000 pores, corresponding to the physical size of  $0.67 \times 0.67 \times 1.33 \text{ cm}^3$ , 12% of which is pore space. The total reactive surface area is  $3.52 \text{ cm}^2$ . The coordination number of each non-boundary pore is 6. A pressure difference is imposed at opposite boundaries, with no flow boundaries applied in the other two directions, resulting in one dimensional flow. It is assumed that the pore structure and the availability of reactive surface area are unchanged over time, so that a steady state of calcite dissolution is established. The mass balance equations were solved using the adaptive Runge-Kutta algorithm. The brine at the boundary is at equilibrium with  $P_{\text{CO}_2} = 1 \text{ atm}$ , with  $[\text{Ca}^{2+}]$  being zero, entering the system with the flow rate  $8.33 \times 10^{-4} \text{ cm}^3/\text{sec}$ . Initially the brine within pores has  $\text{pH} = 7$ , with zero  $[\text{Ca}^{2+}]$ .

#### 6 RESULTS AND DISCUSSION

##### 6.1 Results

Figure 1 shows the predicted reaction rates for the individual and total reactions from each of the two models. The high  $[\text{H}_2\text{CO}_3^*]$  from the boundary leads to the dominance of reaction  $b$ ; reactions  $a$  and  $c$  have only a small contribution to the total reaction rate. The rates of each of the three reactions are determined by the extent to which the system is near to or far from reaction equilibrium, and for reactions  $a$  and  $b$ , the reaction rates are also directly affected by the  $\text{pH}$  and dissolved carbonic acid concentration, respectively. The initial condition of zero dissolved calcium maximizes the deviation from equilibrium. Over time, values of  $\Omega$  remain orders of magnitude smaller than unity, but the dissolution rates of reactions  $a$  and  $b$  are subsequently enhanced due to the influx of dissolved carbonic acid and the associated low  $\text{pH}$ . Since reaction rate  $c$  depends only on the value of  $1 - \Omega$ , its value remains almost constant over time.

With the exception of reaction rate  $c$ , the reaction rates predicted from the two models evolve in disparate ways. Initially  $R_{con}$  is larger than  $R_N$ , but the steady state value of  $R_{con}$  is smaller than  $R_N$ . Comparison of Figure 1 and Figure 2 shows that the evolution of rates  $a$  and  $b$  follows the same shape as the evolution of  $[\text{H}^+]$  and  $[\text{H}_2\text{CO}_3^*]$ , respectively, which explains the difference between the rates predicted by the two models. In the continuum model,

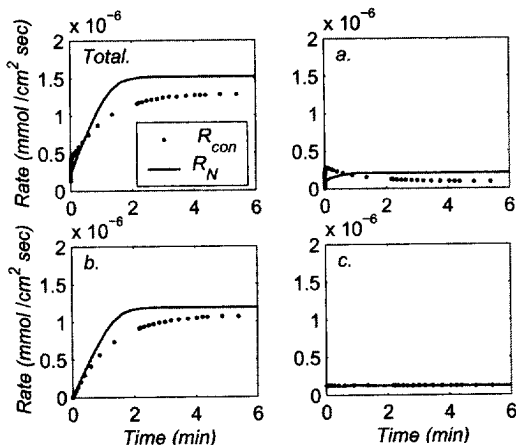


Figure 1. Evolution of the total reaction rates and reaction rates *a*, *b*, and *c*.

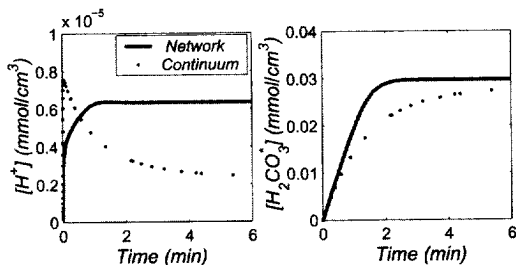


Figure 2. Evolution of  $[H^+]$  and  $[H_2CO_3]$ .

the initial fast release of calcium, and the associated increase in pH and consumption of  $H_2CO_3$ , creates conditions that ultimately reduce the rate of calcite dissolution. Consequently, at steady state the continuum model underestimates  $[H^+]$  and  $[H_2CO_3]$ , resulting in an underestimation of the individual and total reaction rates.

Values of  $\eta_{tot}$ ,  $\eta_a$ ,  $\eta_b$  and  $\eta_c$  are 1:18, 2:50, 1:10, 1:03, respectively. The magnitude of  $\eta_a$  is especially large, due to the direct dependence of the rate *a* on  $[H^+]$ , which is sensitive to the predicted amount of dissolved calcite by each model. The value of  $\eta_{tot}$  depends largely on the  $\eta$  value of the dominant reaction, which is reaction *b* here.

The continuum model's inability to describe the temporal trends of important solute concentrations is explained through examination of the role of spatial heterogeneities in the concentration field of the network. Figure 3 shows the distribution of calcium concentrations and pH values as predicted by the network model at steady state. Also shown are the network model's volume-averaged values and the

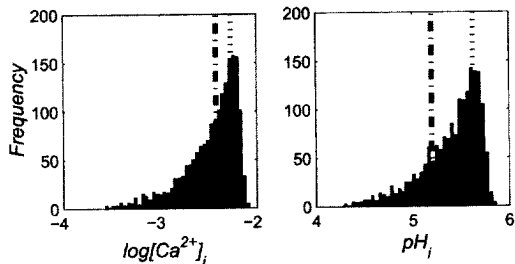


Figure 3. Distributions of  $\log[Ca^{2+}]_i$  and  $pH_i$  at steady state. The dashed and dotted lines represent  $[Ca^{2+}]_N$  and  $[Ca^{2+}]_{con}$ , respectively.

continuum model's uniform values (the volume-averaged pH was computed by volume averaging values of  $[H^+]$  and translating this into pH). The distributions of  $[Ca^{2+}]$  and  $[H^+]$  span almost two orders of magnitude and are highly skewed which leads to nonlinear upscaling. As expected,  $[Ca^{2+}]_{con}$  is larger than  $[Ca^{2+}]_N$ . This further explains why  $R_{con}$  is smaller than  $R_N$  in Figure 1. The big difference between  $pH_{con}$  and  $pH_N$  indicates the sensitivity of pH to the amount of calcite dissolved. Moreover, calculation shows that solution equilibrium relationships do not hold across the network. For example,  $[H^+]_N \times [OH^-]_N = 1.8 \times K_w$ . The continuum model imposes equilibrium conditions that do not really exist at the continuum scale.

## 6.2 Discussion

The difference in the simulation results of these two models illustrates the error that can be produced when using lab-measured reaction rate constants in continuum modeling. Spatial heterogeneities produce skewed solute concentration distributions and non-equilibrium conditions that may not be captured in the grid-block approach. The methodology presented in this paper can be used to examine how processes controlling reaction rates at the pore scale transfer to the continuum scale. It can be used to explore how  $\eta$  changes with factors such as hydrodynamic condition and spatial distribution of reactive surface area. Such exploration will elucidate the conditions under which lab-measured reaction rate constants can or cannot be used directly at the continuum scale. In conclusion, this method presents itself as a powerful tool for investigating the upscaling of geochemical reaction rates.

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