

Discussion

# Reply to “Comment on upscaling geochemical reaction rates using pore-scale network modeling” by Peter C. Lichtner and Qinjun Kang

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Our paper “Upscaling geochemical reaction rates using pore-scale network modeling” [1] presents a novel application of pore-scale network modeling to upscale mineral dissolution and precipitation reaction rates from the pore scale to the continuum scale, and demonstrates the methodology by analyzing the scaling behavior of anorthite and kaolinite reaction kinetics under conditions related to CO<sub>2</sub> sequestration. We conclude that under highly acidic conditions relevant to CO<sub>2</sub> sequestration, the traditional continuum-based methodology may not capture the spatial variation in concentrations from pore to pore, and scaling tools may be important in correctly modeling reactive transport processes in such systems.

This work addresses the important but difficult question of scaling mineral dissolution and precipitation reaction kinetics, which is often ignored in fields such as geochemistry, water resources, and contaminant hydrology. Although scaling of physical processes has been studied for almost three decades [2–5], very few studies have examined the scaling issues related to chemical processes [6–8], despite their importance in governing the transport and fate of contaminants in subsurface systems.

Lichtner and Kang correctly point out that under conditions of relatively slow reaction rates and fast diffusion, the continuum approach should apply. However, they failed to note that in our model, such “benign” conditions only apply at the single pore level. The relative importance of reaction and diffusion rates is determined by the spatial scale. At the network scale, the larger spatial length requires longer times for the diffusion process to homogenize the concentration field, while reaction rates are faster

due to the presence of a larger amount of mineral surface area when the larger spatial domain is considered (see our time scale analysis in the discussion section of our paper). As a result, the diffusion process becomes the relatively slower process, and therefore, conditions at the network scale are not easily treated as a continuum, as we demonstrate in our paper.

Although it was our purpose to understand the mechanisms of the scaling behavior and to identify conditions under which the continuum approach may not be sufficient, we do not mean to suggest that the continuum approach is not applicable under all circumstances. Based on our study, the continuum approach fails under conditions where reaction rates are fast enough to develop concentration gradients at the network scale. However, it is still an appropriate approach to use under many circumstances. For example, with a much higher boundary pH in the case of minerals with a pH dependent rate like anorthite, or in the case of minerals with much slower dissolution rates (e.g., quartz), reaction rates will be commensurately smaller, thus eliminating the development of significant concentration gradients at the network scale. But in other cases, the traditional continuum approach fails and requires modification to correctly model the reactive transport processes, as pointed out in our contribution.

Lichtner and Kang pointed out three main concerns with our work. In the following, we address these three concerns one by one.

## 1. Species-dependent diffusion coefficient and violation of charge balance

Lichtner and Kang pointed out that the problem of charge balance was ignored in our work. It is true that

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we did not consider charge balance, and a full treatment of the Nernst–Planck equation, with incorporation of electrochemical migration that occurs as a result of the development of a diffusion potential when charged species diffuse at different rates, has not been used here [9]. However, the approach we took is one of the two methods that have been used to simplify species-dependent diffusion. One method, as pointed out by Lichtner, is to use a fixed diffusion coefficient for all species to avoid the violation of charge balance [10,11]. The other method is to use species-dependent diffusion coefficients, but to neglect the charge balance and electrochemical migration. The second simplification method is standard in ocean modeling and early diagenesis [12,13], with the justification that the effect of charge balance, or electrochemical migration, is mostly negligible due to the high background electrolyte concentration, present without significant gradients themselves, used in such modeling. In fact, in a recent paper that does fully consider the species-dependent diffusion and charge balance in seawater, Giambalvo et al. [14] found that adding the electrochemical migration term only “introduces a slight curvature into what would otherwise be a linear profile for a conservative ion undergoing pure diffusive transport at steady state.” In our situation, such electrochemical migration should also be negligible, because the background brine salinity (0.45 mol/L) is sufficiently high (close to the salinity of the sea water).

To evaluate the effect of these two simplification methods on reactive transport processes, we set up a relatively simple scenario, with the model system being a cylinder, and anorthite and kaolinite present as reactive phases along the cylinder wall. Highly acidic brine (pH = 3.0, with a representative NaCl concentration of 0.45 mol/L) flows through the cylinder, at a constant flow velocity of  $5.0 \times 10^{-3}$  cm/s. Anorthite and kaolinite dissolve or precipitate at the cylinder wall, and eventually the system reaches steady state. The steady-state  $\text{Ca}^{2+}$  spatial profile in the cylinder at the flow direction is an indicator of the extent of the reactive transport processes that occur. We use a numerical model Crunch [15,16] that has the option of considering or neglecting the electrochemical migration that occurs as a result of charge imbalances when charged species diffuse at different rates.

Fig. 1 compares the steady-state  $\text{Ca}^{2+}$  profile under five different conditions: (1) a saline aqueous phase with electrochemical migration (charge balance), (2) a saline aqueous phase without electrochemical migration, (3) a saline aqueous phase with the same diffusion coefficients for all the aqueous species (no species-dependent diffusion, with the fixed diffusion coefficient being  $0.8 \times 10^{-5}$  cm<sup>2</sup>/s), (4) a dilute aqueous phase with electrochemical migration and (5) a dilute aqueous phase without electrochemical migration. From the figure, it is obvious that neglecting electrochemical migration (charge balance) in the saline solution has almost no effect. It is in dilute solutions, however, that the neglect of electrochemical migration makes a significant difference. Another interesting observation is that large

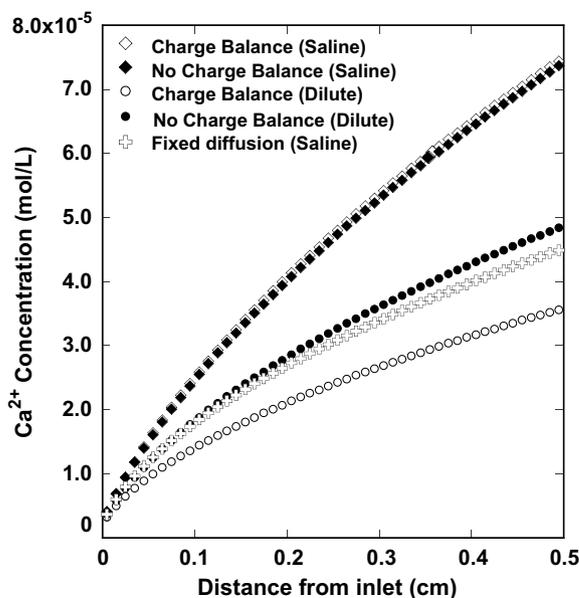


Fig. 1. Steady-state  $\text{Ca}^{2+}$  spatial profiles in a cylinder with anorthite and kaolinite as the reactive minerals at the cylinder wall. This figure compares the effect of considering charge balance in species-dependent diffusion in saline and dilute aqueous phase, as well as the effect of using a fixed diffusion coefficient ( $0.8 \times 10^{-5}$  cm<sup>2</sup>/s).

errors can be introduced in saline solution by using a fixed diffusion coefficient, although charge is conserved in such cases. In the study of reactions in deep sea sediments discussed by Giambalvo et al. [14], the error in using the same value for all of the diffusing species was significantly greater than the error associated with the neglect of electrochemical migration (Steeffel, pers. commun., 2006).

## 2. Network (pore) scale heterogeneity

Lichtner and Kang argue that the main cause of the large spatial variation in concentration obtained in the network model is the large variation in mineral surface area used in the simulation, and that therefore the continuum calculation is not based on a REV. They question the extent of the spatial variation of mineral surface area at the pore scale, and the size of REV. To address these points, first of all we want to point out that the REV size is around 6000 pores for the network. As shown in Fig. 2, both the porosity and the mineral-surface-area-to-volume ratio stabilize when the number of pores exceeds 6000. In our simulation the network contains 9000 pores, larger than the REV size. As such, the control volume for the continuum model, which is the same as the total volume of the network model, is large enough for the continuum calculation.

Secondly, Lichtner and Kang appear to misunderstand how we chose the values of surface area at the pore scale. We chose  $1.3 \times 10^4$  cm<sup>-1</sup> to be the average of surface-area-to-volume ratio for the network, justified as being an intermediate value based on the Sen data [17]. The range of surface area variation was not based on the Sen data,

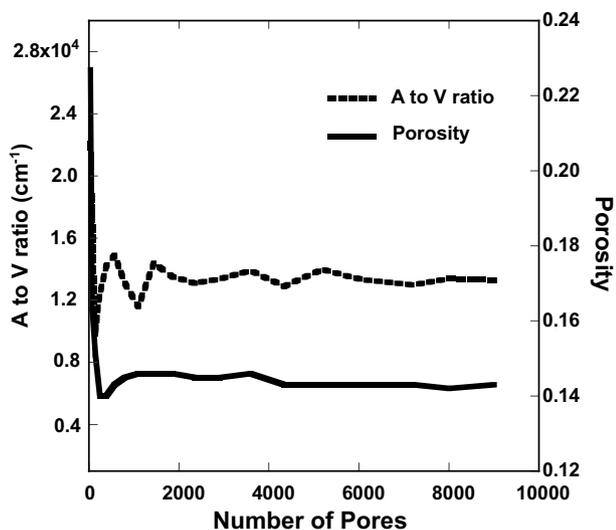


Fig. 2. The overall porosity and mineral area over volume ratio of the network model as a function of the pore number included in the network model. The network model reaches the size of REV at around 6000 pores.

but rather, it is the result of the form of the distribution we used for surface area. Although we carefully searched through all of the available data in the literature, we could not find any information that documents the extent of variation in surface area at the individual pore scale. We assumed the form of the distribution to be exponential, based on the fact that the surface area of a pore should be larger than the geometric surface area of the corresponding spherical pore. The exponential distribution is a single parameter distribution, with the variance equal to the inverse of the square of the mean. The resulting values of pore surface area do vary over several orders of magnitude, as a result of the large variation in pore volume.

However, the large spatial variation in mineral surface area is not the main cause of the large variation in concentrations from pore to pore. To illustrate this, we maintain the same total amount of surface area at the network scale as in the case simulated in our paper, and carry out the simulation for two other cases with much smaller variations of mineral surface area. One case is with a uniform distribution of pore surface area, so that the amount of surface area in each pore is the same; in the other case, we specify a constant ratio of area per pore volume for all pores (constant  $A-V$  ratio), as this ratio is a key factor that determines the reaction dynamics in a pore. The simulations were run under the same conditions as in case A in our paper, with a highly acidic aqueous phase at the boundary.

Simulation results show that with much smaller variations in mineral surface area, large spatial variations in concentration still occur. The steady state pH values span almost the same range as in case A in our paper. As a result, the rates calculated from the continuum model still fail to predict the overall reaction rate, as shown in Fig. 3. For anorthite dissolution, the distribution form and the spatial variation of mineral surface area have a minor effect. For kaolinite precipitation, the extent of variation has a relatively larger effect. However, the rate from the continuum model is still orders of magnitude smaller than the prediction of the network models, with the ratios from the continuum model to the network model being 0.083 and 0.051 for fixed area to volume ratio and uniform distribution respectively. Such values are similar to the ratio of 0.048 with the exponential distribution in our paper.

These results indicate that the large variation in mineral surface area is not the key factor that leads to the large discrepancy between rates from the two models. In fact, we found that the spatial pattern and the abundance of

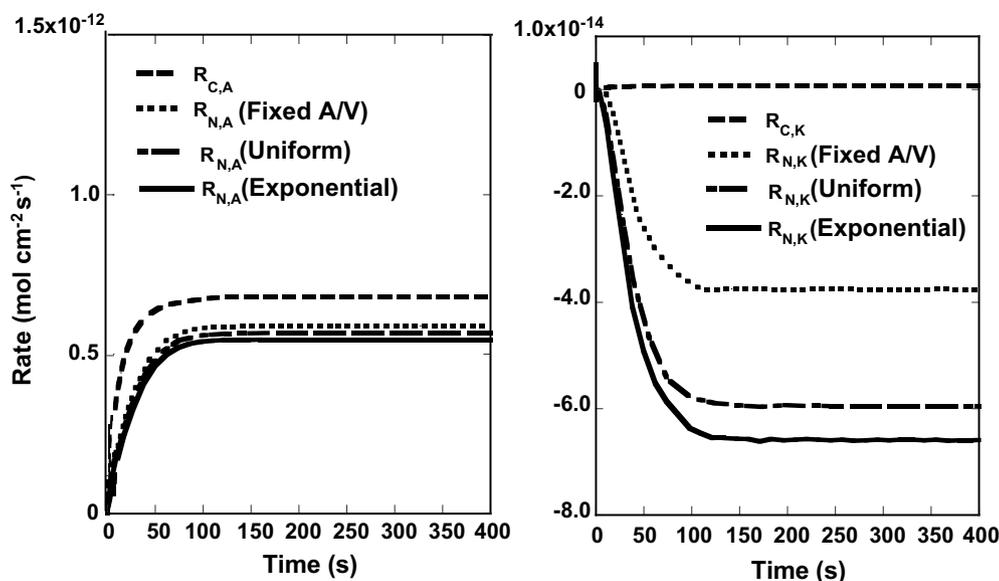


Fig. 3. The evolution of anorthite and kaolinite reaction rates from the continuum model ( $R_{C,A}$  and  $R_{C,K}$ ) and those from the network models with exponential distribution of surface area (as done in our paper), with fixed area over volume ratio, and with uniform distribution of pore surface area. The average surface area over volume ratio remains constant for all cases.

reactive minerals within the network play a much more important role. As detailed elsewhere [18], the discrepancy between the rates from the two models tends to be smaller when the reactive minerals (anorthite and kaolinite) are more evenly distributed throughout the network, and when the reactive minerals are abundantly present. Large clustered reactive mineral blocks, which may often be the case in reality, lead to larger discrepancies than is the case with a more homogeneous distribution, due to the inability of mass transport mechanisms to homogenize the concentration field across the whole network model.

### 3. Violation of homogeneous equilibria and volume averaging

Lichtner and Kang argued that the calculation of volume averaged reaction rates may be troublesome for two reasons. One is that the species concentrations should be flux averaged, instead of volume averaged. The second reason is that our calculation violated homogeneous equilibria. We believe that flux averaging would generate similar results to volume averaging, due to the correlation between pore conductance and the volumes of connected pores (see Section 3.2.2 in our paper for details). Such a correlation associates relatively large fluxes with large pores, and relatively small fluxes with small pores, which would lead to similar averaged concentrations, whether weighted by flux or volume.

Concerning the possible violation of homogeneous equilibria, one would expect that such equilibria apply in a well-mixed system with no spatial variation in concentration. In fact, this is the case at the individual pore scale, and is implemented in the calculation of species concentrations in individual pores. However, at the network scale, we

would argue that the violation of homogeneous equilibria is exactly the result of scaling effects, due to the large concentration gradients, as indicated in Fig. 10 in our paper.

Still, one may argue that since the volume-averaged reaction rates are intended to represent rates estimated from field sampling, which usually includes mixing of pore water from multiple pores, the homogeneous equilibria should apply for such calculations. Lichtner and Kang also suggested that we calculate the averaged reaction rates by calculating the concentrations of total species first, and then use laws of mass action to calculate concentrations of primary and secondary species. Such calculation uses the conservative quantities of the total species, and imposes the laws of mass action as an additional constraint. To see how large an effect this method would have in comparison to the approach we adopted in our paper, we carried out some additional calculations using their suggested method. Fig. 4 compares the reaction rates obtained from such calculations with those from the volume averaging method used in our paper. In this case, it appears that the approach of Lichtner and Kang does not make a significant difference. For kaolinite, the rates calculated using flux averaging and homogeneous equilibria still predict the wrong reaction direction. In general, however, we agree that where the averaging procedure is intended to present actual mixing processes (e.g., mixing in the wellbore), the total concentrations should be averaged first before applying the homogeneous equilibrium constraint.

As we discuss in our paper, the failure of the volume averaging method is attributed to the fact that it non-discriminantly averages the concentrations over all pores, while only the concentrations in reactive pores reflect the reaction progress. Similarly, the flux averaging method is also a non-discriminant averaging method. Although the

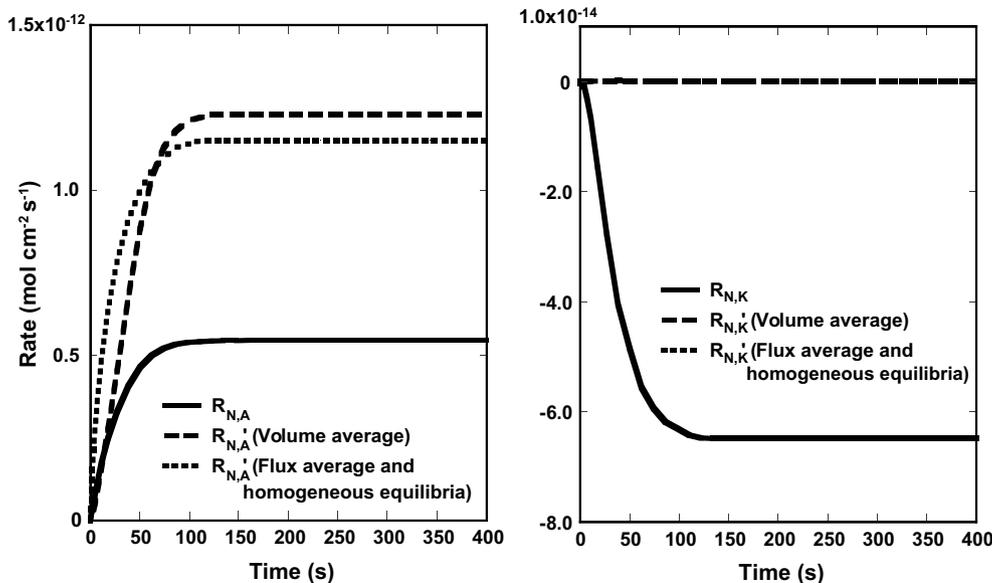


Fig. 4. Evolution of anorthite and kaolinite reaction rates calculated from the network model, from the volume averaging method, and from the flux averaging method with the application of homogeneous equilibria suggested by Lichtner and Kang (see text for details of calculation).

averaged total concentrations reflect the total mass change within the network, it does not accurately reflect the reaction progress in reactive pores, and the application of the homogeneous equilibria by itself does not improve the results significantly.

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