Project Title: Center for Environmental Kinetic Synthesis (CEKA)
Project Number: 1024948
Science Category: EMSI
Principal Investigator: Peter C. Lichtner (LANL)

1. Research Objective

CEKA, as an Environmental Molecular Science Institute, is a joint research initiative of the National Science Foundation and U.S. Department of Energy, Biological and Environmental Research (BER). DOE collaborators are from DOE facilities at Los Alamos National Lab, Lawrence Berkeley National Lab and Pacific Northwest National Lab. The chief goals for CEKA are to 1) collect and synthesize molecular-level kinetic data into a coherent framework that can be used to predict time evolution of environmental processes over a range of temporal and spatial scales; 2) train a cohort of talented and diverse students to work on kinetic problems at multiple scales; 3) develop and promote the use of new experimental techniques in environmental kinetics; 4) develop and promote the use of new modeling tools to conceptualize reaction kinetics in environmental systems; and 5) communicate our understanding of issues related to environmental kinetics and issues of scale to the broader scientific community and to the public.

2. Research Progress and Implications

This report summarizes work after the first 2 years of a 5 year project. Kang et al. (2004, 2006a, 2006b) and Lichtner and Kang (2006) have developed the first pore-scale LB model for single phase multi-component reactive transport in porous media. Similar chemical complexity as found in conventional continuum models is now possible with the LB model. The model takes into account advection, diffusion, homogeneous reactions among multiple aqueous species, heterogeneous reactions between the aqueous solution and minerals, as well as changes in solid and pore geometry. Homogeneous reactions are described through local equilibrium mass action relations. Mineral reactions are treated kinetically through boundary conditions at the mineral surface, and not volume averaged as is done in continnum formulations and early applications of the LB method. This enables a more realistic treatment of the precipitation rate in the case of diffusion limited reaction. The LB model has been applied to the simulation of reactive transport for various geometric and chemical systems at the pore scale. It is currently being applied to upscaling from the pore scale to the continuum scale to investigate the influence of pore scale heterogeneity on continuum-based multi-scale reactive transport models, including radionuclide migration.

Using the multi-component Lattice Boltzmann model, Lichtner and Kang have simulated crystal growth from a single-component supersaturated solution. They have found that as the process changes from diffusion-controlled to surface reaction-controlled, the crystal transforms from open cluster-type structure, via compact coral-type structure, to compact circular structure, and correspondingly, the fractal dimension of the crystal structure increases from a value close to that of a diffusion-limited aggregation (DLA) structure to the Euclidian value for a circle. At a high Damkohler number, crystal

formed from a single nucleus becomes more compact as the saturation increases. At a low Damkohler number, the crystal has a fairly round shape for different saturation values and the effect of saturation is insignificant (Figure 1).

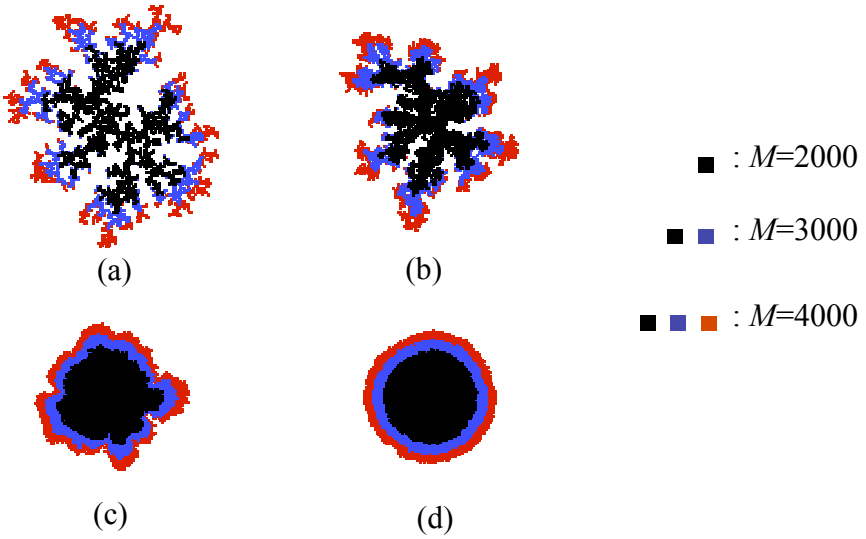

Figure 1. Multi-component Lattice Boltzmann model for simulating reactive transport in porous media at the pore scale (Kang & Lichtner, Los Alamos National Lab). Crystal structures at different masses and *Da* numbers: (a) *Da*=600, (b) *Da*=150, (c) *Da*=48, (d) *Da*=2.

They have also simulated injection of CO_2 into a 2D limestone rock at the pore scale based on photographic images of rock thin sections (Figure 2). Calculations are performed for the chemical system: Na^+-Ca^{2+}-Mg^{2+}-H^+-SO_4^{2-}-Cl^--CO_2 with the reaction of calcite to form dolomite and gypsum. Secondary species included in the simulation are: OH^-, HSO_4^-, H_2SO_4(aq), CO_3^{2-}, HCO_3^-, $CaCO_3$(aq), $CaHCO_3^+$, $CaOH^+$, $CaSO_4$(aq), $MgCO_3$(aq), $MgHCO_3^+$, $MgSO_4$(aq), $MgOH^+$, NaCl(aq), $NaHCO_3$(aq), NaOH(aq). Initial rock composition is calcite. Secondary minerals include dolomite and gypsum. Resulting geometry, volume fraction of calcite, dolomite, and gypsum, concentration of total Ca^{2+}, Mg^{2+}, and SO_4^{2-}, and pH are plotted. The results show that as the reaction rate constants decrease, the deposition of dolomite becomes more uniform surrounding the dissolving calcite grains. Only a small amount of gypsum forms near the inlet. At some point in the simulation, the major pores for flow become blocked halting further fluid flow through the medium.

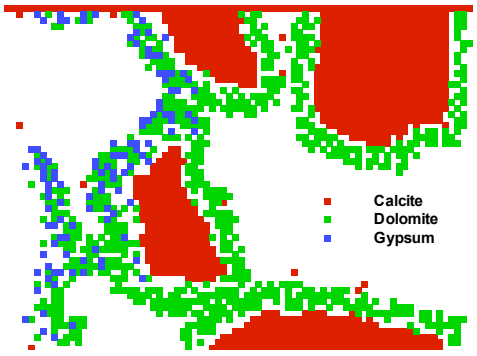

Figure 2: Resulting geometry for mineral reaction rate constants 10^{-8} mol/cm^2/s for calcite and gypsum, and 10^{-9} mol/cm^2/s for dolomite.

Finally, they have simulated reactive transport in a well-defined structured porous medium and upscaled the results to dual and single continuum formulations (Figure 3). Through upscaling pore-scale processes to the continuum scale it is possible to identify key parameters and physicochemical processes that control macroscopic phenomena and simultaneously provide constitutive relations needed in continuum models. By comparing the pore-scale results averaged over a REV to continuum-scale models the validity of volume averaging can be ascertained for complex pore geometries. They hypothesized that pore-scale simulations will enable the most appropriate continuum model—single, dual or multiple continua—to be determined, or they will demonstrate that upscaling is in fact not possible, for example, as is expected in the presence of reaction instabilities resulting in wormhole formation. In cases where upscaling is shown to be valid, pore-scale simulations can provide appropriate values for macro-scale properties of the porous medium such as primary and secondary flow domains and interfacial area, permeability, tortuosity, dispersivity, and reactive surface area.

Upscaling pore scale simulations of reactive transport in a porous medium to a single continuum formulation indicates that it is generally necessary to use effective parameters in the continuum description that may have no obvious relation to their measurable counterparts. By identifying a multi-scale continuum formulation, however, it should be possible to base the model on parameters that are more closely related to physical properties. Although computationally it is much more desirable to use a single continuum model with effective properties than it is to use a multi-scale model with more realistic, measurable properties, the main difficulty is obtaining appropriate effective medium properties needed for the single continuum model. Shown in Figure 4 is a comparison with the breakthrough curves for leaching a tracer from the secondary porosity. The only fit parameter is the tortuosity of the secondary continuum. Using the value for the tortuosity obtained from the non-reactive case, it is possible to predict the stationary state reactive solution with linear kinetics without introducing any additional fit parameters and using only the geometric properties of the medium. By introducing an effective surface area it is possible to exactly match the dual continuum results with a single continuum model. The formula for the effective surface in this case can be obtained exactly with the result

$$a_{eff} = a_b + a_{mb}\sqrt{\frac{a_m \phi_m D_m}{k}}\left(\frac{1-\exp\left[-2l_m\sqrt{ka_m/\phi_m D_m}\right]}{1+\exp\left[-2l_m\sqrt{ka_m/\phi_m D_m}\right]}\right)$$

where a_{eff} denotes the effective surface area for the single continuum model, a_b and a_m denote the primary secondary continuum specific surface area, respectively, a_{mb} denotes the interfacial area separating the two continua, k denotes the mineral kinetic rate constant, and ϕ_m, D_m, and l_m denote the secondary continuum porosity, effective diffusivity, and domain length (assuming a 1D linear matrix domain—this assumption is not essential).

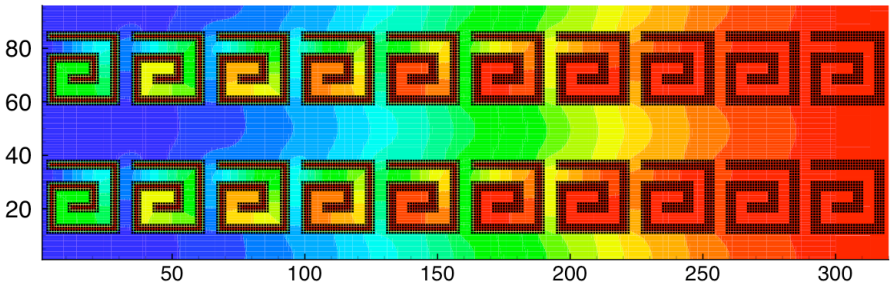

Figure 3: LB result for flow of a tracer through a structured porous medium with primary and secondary porosity.

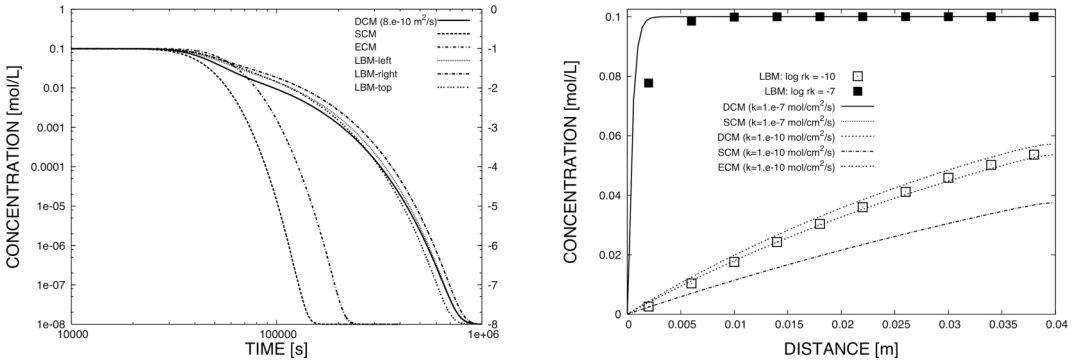

Figure 4: Single, equivalent and dual continuum model fits to the tracer LB breakthrough curve (left), to the LB volume averaged spatial concentration profile for linear reaction kinetics (right).

In addition to the work described above, Lichtner and Carey (2006) have developed a new approach for incorporating solid solutions into reactive transport equations. The approach makes use of discretization of the solid solution composition space and a kinetic formulation of stoichiometric end-member mineral reaction rates to find the most stable solid solution composition. This new approach should be useful for modeling co-precipitation of radionuclides. Carey and Lichtner (2006) have applied the model to the CSH phase in concrete degradation to model well-bore integrity during CO_2 sequestration.

3. **Planned Activities for FY07-FY09**

- Upscaling pore scale (lattice Boltzmann model) simulations of real 3D images to a multi-scale continuum model in collaboration with Kang and CEKA-PSU. We have demonstrated that it is possible to upscale lattice Boltzmann simulations involving well-defined structured porous media to multi-scale continuum formulations. The next step is to apply the method to real 3D porous media using images obtained from microtomography, including

reactive and non-reactive species. In collaboration with others at CEKA-PSU microfluidic experiments will be carried out to validate the model calculations. (Years 3-5)

- Develop massively parallel model for Shale Hills field site in collaboration with Lu, Duffy, and CEKA-PSU. Shale Hills field site has been extensively monitored and modeled on a coarse grid. This work will use parallel computing to increase the fidelity of the simulations and improve understanding of the weathering processes taking place in the watershed. (Years 3-5)

- Preliminary results of modeling the Merced chronosequence with a single continuum formulation has demonstrated the need to use much smaller surface areas compared to measured BET values by several orders of magnitude to account for the observed weathering profile. We plan to model the Merced chronosequence weathering profiles using the dual continuum FLOTRAN model to incorporate preferential pathways in collaboration with CEKA-PSU. A goal of this effort is to determine if it is possible to describe the observed profiles with measured surface areas in a dual continuum framework. (Year 3-4)

- Add isotopic exchange to FLOTRAN for modeling supergene enrichment of porphyry copper deposit in collaboration with Kang and CEKA-PSU. (Year 3)

- Apply FLOTRAN and lattice Boltzmann model to modeling induced polarization with CEKA-PSU. (Year 3)

4. **Information Access**

Peer Reviewed Publications

Kang, Q., D. Zhang, P.C. Lichtner, and I.N. Tsimpanogiannis (2004) Lattice Boltzmann model for crystal growth from supersaturated solution, Geophysical Research Letters, vol. 31, p. 1029.

Kang, Q., P.C. Lichtner, and D. Zhang (2006a) Lattice Boltzmann pore-scale model for multi-component reactive transport in porous media, Journal of Geophysical Research, 111, B05203 (1-12).

Lichtner, P.C. and W.J. Carey (2006) Incorporating solid solutions in geochemical reactive transport equations using a kinetic discrete composition approach, Geochimica Cosmochimica Acta, 70, 1356-1378.

Lichtner, P.C. and Q. Kang (2006) Comment on: Upscaling geochemical reaction rates using pore-scale network modeling, by Li, Peters and Celia, Adv. Water Res., in press.

Carey, J.W. and P.C. Lichtner (2006) Calcium Silicate Hydrate (C-S-H) Solid Solution Model Applied To Cement Degradation Using The Continuum Reactive Transport Model

FLOTRAN, Proceedings of the Transport Properties and Concrete Quality Workshop, Arizona State University, Tempe, Arizona, October 10-12, 2006, in press.

Papers Submitted for Publication

Lichtner, P.C. and Q. Kang (2006) Upscaling Pore-Scale Reactive Transport Equations using a Multi-Scale Continuum Formulation, submitted to special issue on multi-scale processes in Water Resources Research.

Kang, Q., P.C. Lichtner, and D. Zhang (2006b) An improved lattice Boltzmann model for multi-component reactive transport in porous media at the pore scale, submitted to special issue on multi-scale processes in Water Resources Research.

Presentations

Kang, Q., and P.C. Lichtner (2005) Pore-scale studies of CO_2 sequestration in geologic formations, 4th Annual Conference on Carbon Capture & Sequestration, May 2-6, 2005, Alexandria, Virginia.

Kang Q., and P.C. Lichtner (2005) Lattice Boltzmann pore-scale model for coupled multi-component flow, diffusion, and reaction, 15th Annual Goldschmidt Conference May 20-25, 2005 in Moscow, Idaho, USA, SS-18, Diffusion-reaction systems in the earth sciences: new characterizations and modeling approaches.

Kang, Q., and P.C. Lichtner (2005) Pore-scale model for multi-component reactive transport in porous media. 230th ACS National Meeting in Washington, D.C., August 28-Sept 1, 2005.

Kang, Q. and P.C. Lichtner (2005) Upscaling of reactive-transport processes in porous media: from pore to continuum scales, AGU 2005 Fall Meeting, Dec. 5-9, 2005.

Kang, Q., P.C. Lichtner, and D. Zhang (2006) Recent Progresses in Lattice Boltzmann Simulations of Flow and Multi-Component Reactive Transport in Porous Media, June 19-22, 2006, Computational Methods in Water Resources XVI International Conference, Copenhagen, Denmark (invited).

Lichtner, P.C. and Q. Kang (2006) Upscaling Reactive Transport Processes from Pore to Continuum Scales in Porous and Fracture Media. Department of Energy's Environmental Remediation Sciences Program (ERSP) annual PI meeting, April 3-5, 2006, Airlie Conference Center in Warrenton, VA (invited).

Lichtner, P.C. and Q. Kang (2006) Role of pore-scale heterogeneity on reactive flows in porous materials: validity of the continuum representation of reactive transport, June 19-22, 2006, Computational Methods in Water Resources XVI International Conference, Copenhagen, Denmark.