

Final Scientific/Technical Report

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Recipient: Princeton University

Project Title: **Up-Scaling Geochemical Reaction Rates for Carbon Dioxide (CO₂) in Deep Saline Aquifers**

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Executive Summary:

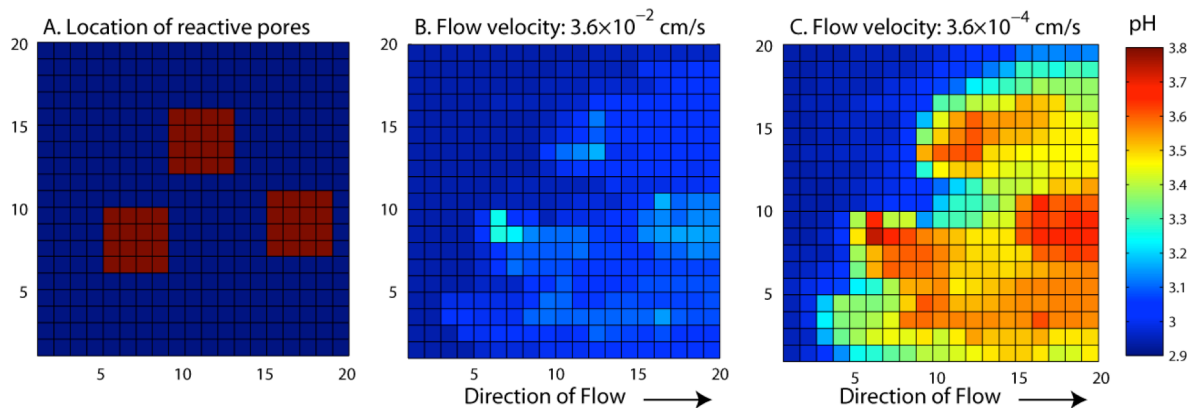
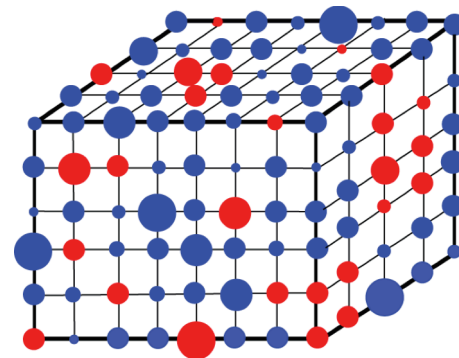
Geochemical reactions in deep subsurface environments are complicated by the consolidated nature and mineralogical complexity of sedimentary rocks. Understanding the kinetics of these reactions is critical to our ability to make long-term predictions about subsurface processes such as pH buffering, alteration in rock structure, permeability changes, and formation of secondary precipitates. In this project, we used a combination of experiments and numerical simulation to bridge the gap between our knowledge of these reactions at the lab scale and rates that are meaningful for modeling reactive transport at core scales. The focus is on acid-driven mineral dissolution, which is specifically relevant in the context of CO₂-water-rock interactions in geological sequestration of carbon dioxide. The project led to major findings in three areas. First, we modeled reactive transport in pore-network systems to investigate scaling effects in geochemical reaction rates. We found significant scaling effects when CO₂ concentrations are high and reaction rates are fast. These findings indicate that the increased acidity associated with geological sequestration can generate conditions for which proper scaling tools are yet to be developed. Second, we used mathematical modeling to investigate the extent to which SO₂, if co-injected with CO₂, would acidify formation brines. We found that there exist realistic conditions in which the impact on brine acidity will be limited due to diffusion rate-limited SO₂ dissolution from the CO₂ phase, and the subsequent pH shift may also be limited by the lack of availability of oxidants to produce sulfuric acid. Third, for three Viking sandstones (Alberta sedimentary basin, Canada), we employed backscattered electron microscopy and energy dispersive X-ray spectroscopy to statistically characterize mineral contact with pore space. We determined that for reactive minerals in sedimentary consolidated rocks, abundance alone is not a good predictor of mineral accessible surface area, and should not be used in reactive transport modeling. Our work showed that reaction rates would be overestimated by three to five times.

Project Accomplishments and Activities:

In this project, we used a combination of experiments and numerical simulation to bridge the gap between our knowledge of small-scale geochemical reaction rates and rates meaningful for modeling reactive transport at core scales. The focus was on CO₂-water-rock interactions in the context of geological sequestration of carbon dioxide – specifically acid-driven mineral dissolution and precipitation. Below we summarize the major activities and findings.

Upscaling reaction rate laws. Geochemical reaction rate laws are often measured using crushed minerals in well-mixed laboratory systems that are designed to eliminate mass transport limitations. Such rate laws are often used directly in reactive transport models to predict the reaction and transport of chemical species in consolidated porous media found in subsurface environments. Due to the inherent heterogeneities of porous media, such use of lab-measured rate laws may introduce errors, leading to a need to develop methods for upscaling reaction rates. We developed a methodology for using pore-scale network modeling to investigate scaling effects in geochemical reaction rates, as depicted in Figure 1. The reactive transport processes are simulated at the pore scale, accounting for heterogeneities of both physical and mineral properties. Mass balance principles are then used to calculate reaction rates at the continuum scale. To examine the scaling behavior of reaction kinetics, these continuum-scale rates from the network model are compared to the rates calculated by directly using laboratory-measured reaction rate laws and ignoring pore-scale heterogeneities. We demonstrated this by upscaling anorthite and kaolinite reaction rates under simulation conditions relevant to geological CO₂ sequestration. Simulation results show that under conditions with CO₂ present at high concentrations, pore-scale concentrations of reactive species and reaction rates vary spatially by orders of magnitude, and the scaling effect is significant. With a much smaller CO₂ concentration, the scaling effect is relatively small. These results indicate that the increased acidity associated with geological sequestration can generate conditions for which proper scaling tools are yet to be developed. These findings demonstrate the use of pore-scale network modeling as a valuable research tool for examining upscaling of geochemical kinetics. The pore-scale

Fig. 1. [RIGHT] A simplified conceptual representation of the pore-scale network model with pores of different volumes. The pores used in this work are actually of irregular shape, with no distinction between pore bodies and pore throats. The red color indicates reactive pores and the blue color represents non-reactive pores. [BELOW LEFT] An example distribution of reactive minerals (in red) in the middle layer of a network. [BELOW CENTER AND RIGHT] Steady-state pH fields for two different mean flow velocities.



model allows the effects of pore-scale heterogeneities to be integrated into system behavior at multiple scales, thereby identifying important factors that contribute to the scaling effect.

Limitations for brine acidification from SO₂ co-injection with CO₂. Co-injection of sulfur dioxide during geologic carbon sequestration can cause enhanced brine acidification. The magnitude and timescale of this acidification will depend, in part, on the reactions that control acid production and on the extent and rate of SO₂ dissolution from the injected CO₂ phase. Here, brine pH changes were predicted for three possible SO₂ reactions: hydrolysis, oxidation, or disproportionation. Also, three different model scenarios were considered (Fig. 2), including models that account for diffusion-limited release of SO₂ from the CO₂ phase. In order to predict the most extreme acidification potential, mineral buffering

reactions were not modeled. Predictions were compared to the case of CO₂ alone, which would cause a brine pH of 4.6 under typical pressure, temperature, and alkalinity conditions in an injection formation. In the unrealistic model scenario of SO₂ phase equilibrium between the CO₂ and brine phases, co-injection of 1% SO₂ is predicted to lead to a pH close to 1 with SO₂ oxidation or disproportionation, and close to 2 with SO₂ hydrolysis. For a scenario in which SO₂ dissolution is diffusion-limited and SO₂ is uniformly distributed in a slowly advecting brine phase, SO₂ oxidation would lead to pH values near 2.5 but not until almost 400 years after injection. In this scenario, SO₂ hydrolysis would lead to pH values only slightly less than those due to CO₂ alone. When SO₂ transport is limited by diffusion in both phases, enhanced brine acidification occurs in a zone extending only 5 m proximal to the CO₂ plume, and the effect is even less if the only possible reaction is SO₂ hydrolysis. In conclusion, the extent to which co-injected SO₂ can impact brine acidity is limited by diffusion-limited dissolution from the CO₂ phase, and may also be limited by the availability of oxidants to produce sulfuric acid.

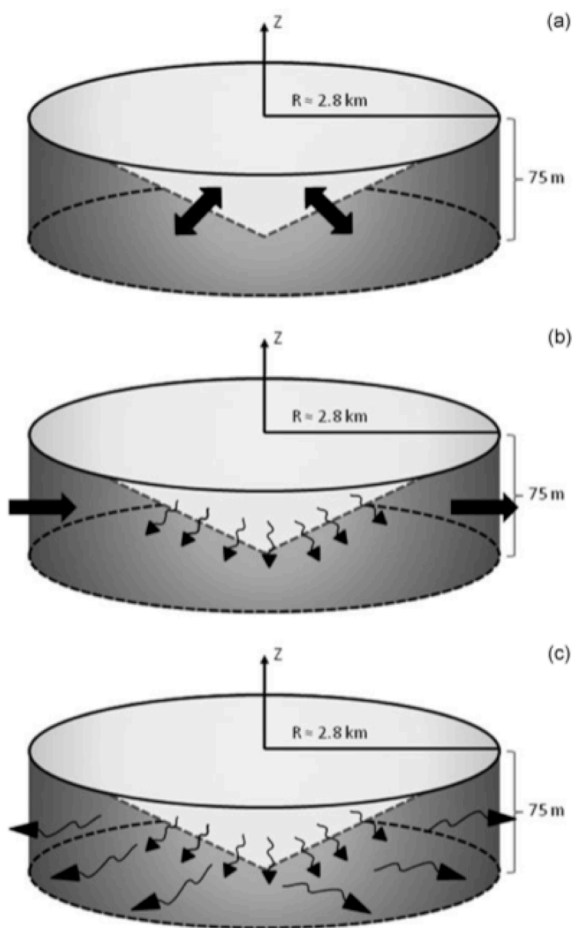


Fig. 2 - Schematic diagram of model system showing the scCO₂ plume (light gray) and brine volume (dark gray): (a) SO₂ phase equilibrium between the CO₂ and brine phases; (b) diffusion-limited SO₂ dissolution with uniform sulfur distribution in an advecting brine phase; (c) diffusion-limited SO₂ dissolution with diffusive transport of SO₂ in a stagnant brine phase.

Accessible surface areas of reactive minerals in consolidated rock. The major challenge with reactive transport modeling in consolidated media is accurate characterization of surface area, and the apportionment of this surface area to reactive minerals. Existing methods of quantifying mineral surface areas for consolidated media at best are imprecise and at worst are not valid because they do not account for obscured grain surfaces by clay minerals, inaccessibility of reactive minerals due to matrix cementation, and inaccessibility of reactive minerals due to presence as grain inclusions.

Through a combination of Backscattered Electron (BSE) scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of thin sections, we have developed a novel image analysis method to quantify the accessibility of minerals to formation fluids in sedimentary sandstones. The main goal was to determine the extent to which mineral accessibility is well represented by measures of mineral abundance, such as volume fraction. This provides insight on how uncertain are the estimates of surface areas that are often used in reactive transport and reaction path models in the context of deep sedimentary formations.

For three Viking sandstones (Alberta sedimentary basin, Canada), we employed backscattered electron microscopy and energy dispersive X-ray spectroscopy to examine mineral content and to statistically characterize mineral contact with pore space. BSE imaging was used and a segmentation algorithm was developed to study the relationships between mineral abundances and mineral accessibilities, as measured by the extent of pore-to-mineral contact. This allowed us to broadly classified minerals into three categories: kaolinite, quartz, and “reactive” minerals.

We concluded that if a mineral volume fraction is used in reactive transport modeling as a proportional measure of accessible surface area in consolidated sandstones, the reaction rates are likely to be overestimated by three to five times. In all three specimens, kaolinite is the primary authigenic clay mineral cementing quartz grains. It accounts for only 5% to 31% of mineral content, but 65% to 86% of pore-mineral contact boundaries. The sandstone specimen has 6% minerals in the “reactive” category, which in this study includes minerals other than kaolinite and quartz, such as K-feldspar, apatite and pyrite. For this specimen, only one third of the reactive minerals are accessible to pore fluids due to clay-mineral grain coatings. For the shaly sandstone, only one fifth of its 5% reactive minerals are accessible to pore fluids due to regions of cementation of fine detrital matrix. The conglomerate sandstone has only 1% of its mineral matter in this category, and these are often found as inclusions rather than grains.

We then extended this work by using high-resolution BSE images co-interpreted with EDX elemental maps, which have high accuracy in mineral identification (Figure 3). In this method, we are not limited to broad classification of minerals. We are able to quantify specific mineral types, and draw conclusions about accessibility for the particular minerals that are important in the context of interactions with acidic pore fluids as will occur in CO₂ geologic sequestration. One such image is shown below.

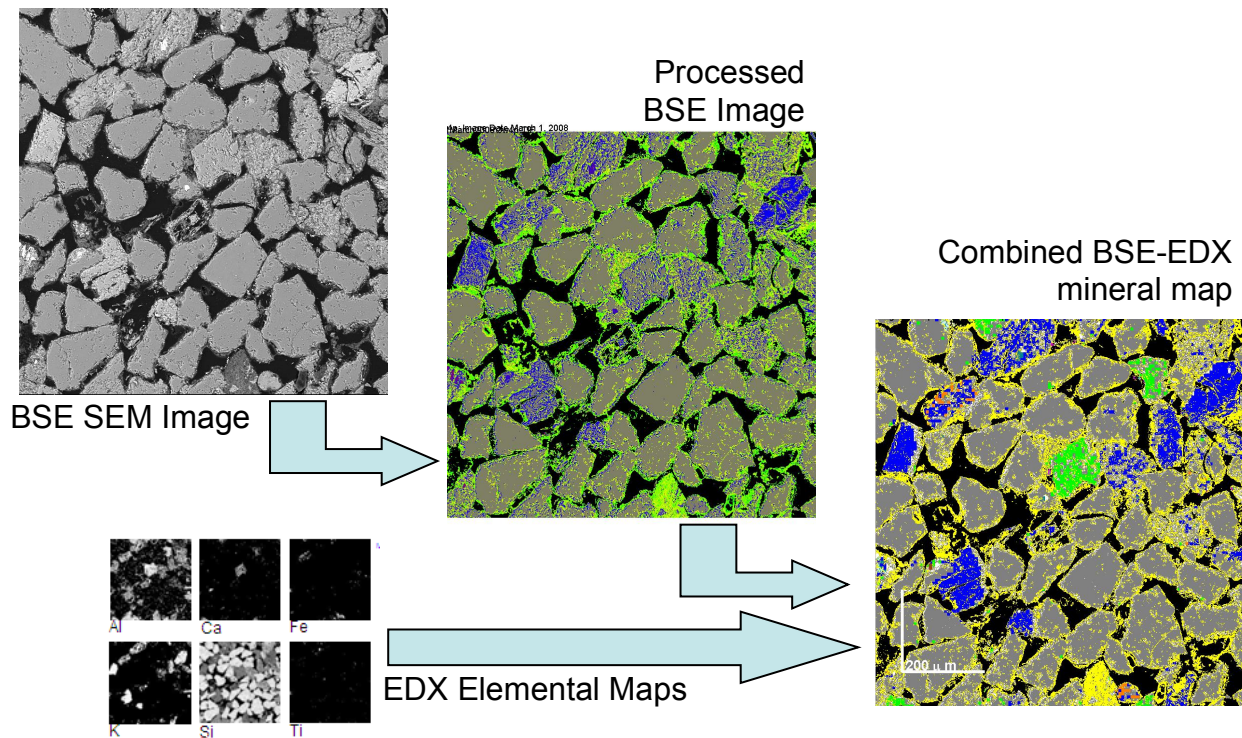


Figure 3. Novel method for combining backscattered electron microscopy with X-ray spectroscopy to make detailed maps of reactive minerals for consolidated sedimentary media.

Newly fostered collaborations:

This project was key in establishment of two new collaborations in the Peters' research group. First, the new means of mapping reactive minerals led to a new collaboration with researchers at the DOE National Energy Technology Lab in Morgantown WV (Grant Bromhal and others), for experimental work reacting caprocks with CO₂- saturated brines. Second, the collaboration between Brent Lindquist and Catherine Peters in this project led to interest from PNNL researchers (Um and Rockhold) in applying 2D and 3D mineral mapping capabilities to Hanford contaminated sediments.

Journal Publications:

Kim, D., C. A. Peters, and W. B. Lindquist (2011), Upscaling geochemical reaction rates accompanying acidic CO₂-saturated brine flow in sandstone aquifers, *Water Resour. Res.*, 47, W01505, doi:10.1029/2010WR009472.

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Crandell, L.E., Ellis, B.R., Peters, C.A. 2010. "Dissolution Potential of SO₂ Co-Injected with CO₂ in Geologic Sequestration." *Environmental Science & Technology*. 44 (1): 349–355. DOI 10.1021/es-2009-02612m.

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- Li, L.; C. A. Peters; M. A. Celia. 2006. "Upscaling Geochemical Reaction Rates Using Pore-Scale Network Modeling." *Advances in Water Resources*, 29:1351-1370.

Conference Papers and Presentations:

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- Peters, C. A.; W. B. Lindquist; M. A. Celia. 2008. "Up-Scaling Mineral Accessibility and Pore Networks for CO₂ Reactive Transport in Sandstones". *Geosciences Research Symposium: Basic Research Relevant to CO₂ Sequestration*, Gaithersburg, MD, March 2008. Organized by Nick Woodward, Office of BES, U.S. DOE.
- Ellis, B. R., Peters, C. A., Buschkuehle, M. 2007. "Formation Buffering Potential Pertaining to Geological Storage of Carbon Dioxide", *EOS Trans. AGU*, 88(52) Fall Meet. Suppl. Abstract U43C-1378.
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- Peters, C. A. and Maier, M. L. 2006, Backscattered Electron Imaging of Viking Sandstones for Mapping Reactive Minerals, Eos Trans. AGU, 87(52), Fall Meet. Suppl., Abstract H54D-07
- Peters, C. A., J. A. Lewandowski, M. L. Maier, M. A. Celia, L. Li. (2006). Mineral Grain Spatial Patterns and Reaction Rate Up-Scaling. CMWR-XVI = XVI International Conference on Computational Methods in Water Resources, edited by P. J. Binning, P. K. Engesgaard, H. K. Dahle, G. F. Pinder and W. G. Gray. Copenhagen, Denmark, June, 2006. DOI (Metadata): 10.4122/1.1000000299. DOI (Full text): 10.4122/1.1000000300.
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- Li, L., C. A. Peters and M. A. Celia. 2004. "Effects of pore-scale heterogeneities on

continuum-scale rates of reactions associated with anorthite dissolution." Geological Society of America Annual Meeting, Denver, November 7 - 10, 2004, Abstract 168-2.

Theses:

"A New BSE-EDX Method to Quantify Mineral Abundance and Accessibility in Sandstones", Kimberley M. Bowman, MS Thesis, Civil & Environmental Engineering, Princeton University, June 2008.

"Scaling of Geochemical Reaction Rates Using Pore-Scale Network Modeling: An Investigation of Anorthite and Kaolinite Reaction Kinetics", Li Li, Ph.D. Thesis, Civil & Environmental Engineering, Princeton University, September 2005.