

Upscaling Reaction Rate Laws In Geochemical Reactive Transport Using Pore-Scale Network Models

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Introduction

Reliable predictions of reactive transport in geological porous media are important in

*carbon geosequestration studies *aquifer remediation *nuclear waste disposal *other applications

Reactive processes occur at the pore-scale, with grain sizes $O(0.5\text{mm})$ (see Fig 1)

Given the size of geological systems to be used for CO_2 sequestration (in excess of 100's of km^2) and the long time horizon for predictions (10^2 - 10^3 years), explicit resolution of system heterogeneities at the micro-scale (i.e., the pore scale) is infeasible over the foreseeable future.

Consequently, practical geochemical reactive transport models operate at the continuum scale:

- require assumptions of homogeneity (uniform concentration over a numerical gridblock)
 - applied over averaging volumes far exceeding pore and grain sizes (eg. gridblocks 100's of m^3).
- However, sub-grid heterogeneities can undermine the macro-scale model accuracy, e.g., mineral weathering rates predicted from lab-scale data can overpredict observed field-scale rates by several orders of magnitude (eg. Steefel et al., 2005).

This work focuses on reaction rate laws describing acid-driven mineral dissolution and examines whether reaction rates applicable at the pore-scale, $O(10\text{-}100\mu\text{m})$, are realistic at larger continuum scales, $O(1\text{-}10\text{mm})$. We then consider the problem of developing upscaled reaction laws.

Motivation and Previous Work

Li et al (2006) considered a rectangular lattice pore-network model with sparse reactive clusters and found continuum-scale models over-predicted reaction rates compared to pore simulations

Differences especially large in acidic environments with reactive mineral heterogeneity, which may be typical of geosequestration of CO_2 (acidic) into brine aquifers

In this work we apply a similar methodology to a more realistic pore-scale network model with irregular connectivity and observation-based distribution of reactive minerals thru the network.

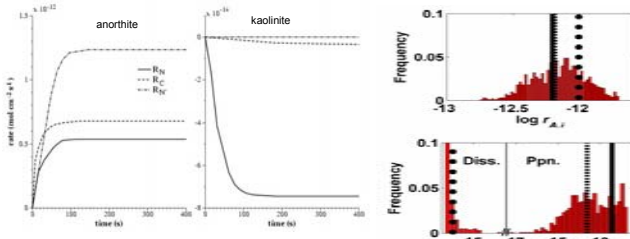


Fig 2: Pore-scale vs continuum reaction rates (Li Li'06)

System Description (Pore Geometry And Geochemistry)

Sandstone core 3W4 from the Viking formation in the Alberta sedimentary basin (Canada) – potential CO_2 sequestration site due to proximity to oil/gas extraction and power infrastructure
Geometry of pore network – pore volumes/areas and connectivity (analysed at SUNY Brook):

- Identified using X-ray computed tomography of the sandstone core
- $2.9 \times 2.9 \times 1.4 \text{ mm}^3$ core comprises 14,767 pores and 46,451 throats, porosity is 0.24
- Pore volumes and pore surface areas ~ approximately log-Normal, distributions shown in Fig 3
- Pore surface area scaled using BET measurements (crushed/noncrushed samples)
- Statistical distribution of reactive minerals (analysed at Princeton University)
- Back-scatter electron imaging and energy-dispersive X-ray spectroscopy (Fig 1)
- All pores contain kaolinite (80% of surface area), 20% of pores contain anorthite (20% of area)

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Objectives

Bridge the gap between pore-scale geochemical reaction rates and effective reaction rates for modelling at core-scales

1. Construct a representative pore-scale reactive transport model for acid-driven mineral dissolution approximating likely CO_2 sequestration scenarios
2. Use the model to investigate the upscaling of kinetic reaction rates under various pH conditions

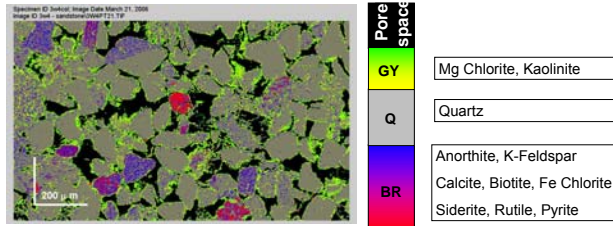


Fig 1: Distribution of reactive minerals in 3W4 (estimated from spectroscopy/BSE)

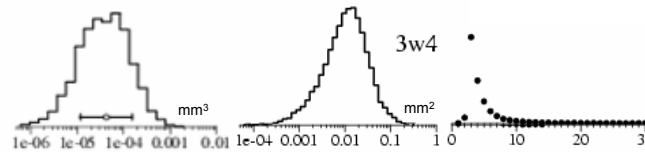


Fig 3: Distribution of pore volumes, surface areas and coordination numbers for core 3W4

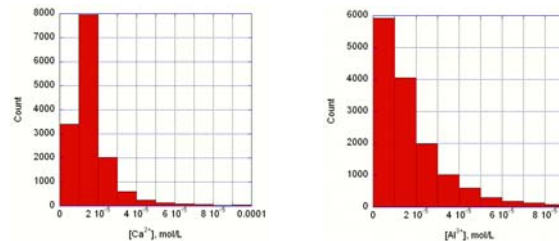


Fig 4: Distribution of Ca and Al concentrations in the network model after 100 sec of inflow

Numerical Model and Computational Scheme

Irregular pore network with reactive transport model described by large sparse ODE system

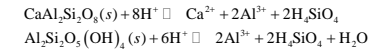
$$V_i \frac{dy_i}{dt} = \sum_{j=1}^{N(i)} q_{ji} y_j + \sum_{j=1}^{N(i)} q_{ij} y_j + \sum_{j=1}^{N(i)} D_{ji} a_{i,j} \frac{y_j - y_i}{l_{i,j}} + S_i$$

The pressure field is assumed at steady state after boundary conditions imposed

Reactive transport resolved using adaptive Runge-Kutta time stepping with embedded nonlinear solver for equilibrium reactions

Chemical Reactions and Kinetic Rate Laws

Primary interest: acid-driven kinetic dissolution of kaolinite and anorthite



In addition, 9 aqueous equilibrium eqns are considered, including



Kinetic rate laws of the form below (this may or may not need modification during upscaling!)

$$r_M = k_M \{ \text{H}^+ \}^{\Omega_M} (1 - \Omega)^n \quad r = \text{reaction rate per unit area; } k = \text{rate constant}$$

$$(\text{H}) = \text{activity of } \text{H}^+, \quad \Omega = \text{saturation state} = \frac{\text{Ionic Activity Product}}{\text{Equilibrium Constant}}$$

Reaction rate constants adapted from Li et al. (2006)

Methodology

- 1) Simulate inflow of CO_2 -rich fluid into initially carbon-free domain using
 - the pore-scale network model, individually resolving concentrations/reactions at each pore
 - a "continuum"-scale model that assumes the domain has uniform concentration of species
- 2) Compare averaged pore-scale vs "lumped" continuum simulations (same total reaction area)
- 3) Develop corrections to the continuum model to make it more consistent with pore-scale results
 - eg, simplest approach – adjust the area of reactive minerals in the continuum model

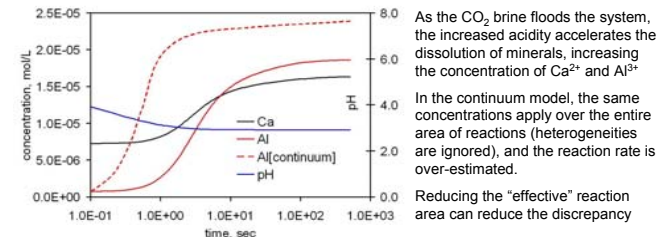


Fig 5: Representative evolution of concentrations of pH, Ca and Al as the network is flooded with CO_2 -rich brine. The distribution of species in the pores is shown in Figure 4.

Current Results and Conclusions

Pore-scale network modelling is a useful tool for investigating the upscaling of reaction rate laws

Approximating a distributed pore-scale network with a "bulk" continuum model becomes progressively inaccurate as the acidity of the system is increased (in both synthetic/real studies).

Simple corrections to reactive surface areas can work, but require "calibration" to pore-scale results. Their generality to other flow regimes and pH conditions needs analysis.

Current work is proceeding in 4 directions:

- 1) improving the estimates of the pore-scale areas of reactive minerals for use at the pore-scale
- 2) applying simple upscaling techniques (correcting the "effective" area of reactive minerals)
- 3) reducing the influence of the inflow boundary condition on the results of the analysis
 - * non-parametric techniques (inferring the shape of the upscaled reaction law relationship) and
 - * stochastic approximations (since replacing a nonlinear distributed system with lumped approximation may not be unique).

References

- Steefel, C.I., DePaolo, D.J., Lichtner, P.C. (2005) Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. Earth Planetary Sci. Letters, 240:539-558.
Li Li, Catherine A. Peters *, Michael A. Celia (2006) Upscaling geochemical reaction rates using pore-scale network modeling, Advances in Water Resources, 29:1351–1370.