# 2006 ERSD Annual Report

*DOE-BER Environmental Remediation Sciences Project # 1027871*

# Coupling Between Flow and Precipitation in Heterogeneous Subsurface Environments and Effects On Contaminant Fate and Transport

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## Research Objective

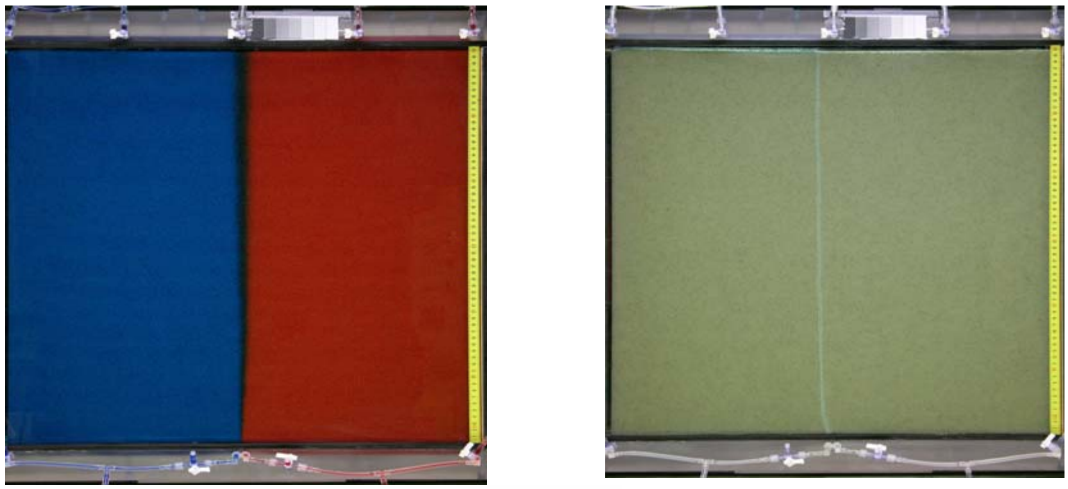
Reactive mixing fronts can occur at large scales, e.g. when chemical amendments are injected in wells, or at small scales (pore-scales) when reactive intermediates are being generated *in situ* at grain boundaries, cell surfaces and adjacent to biofilms. The product of the reactions such as mineral precipitates, biofilms or filtered colloids modifies permeability leading to the complex coupling between flow and reactions and precipitation. The objectives are to determine how precipitates are distributed within large and small scale mixing fronts, how permeability and flow is modified by precipitation, how the mobility of a representative contaminant, strontium, is affected by the precipitation of carbonates, and how subsequent dissolution of the carbonates result in mobilization of Sr and increased flow. The desired outcomes of the project are to help develop methods leading to sequestration of metal contaminants, and to determine how macroscopic field-scale modeling can be applied to predict the outcome of remediation activities.

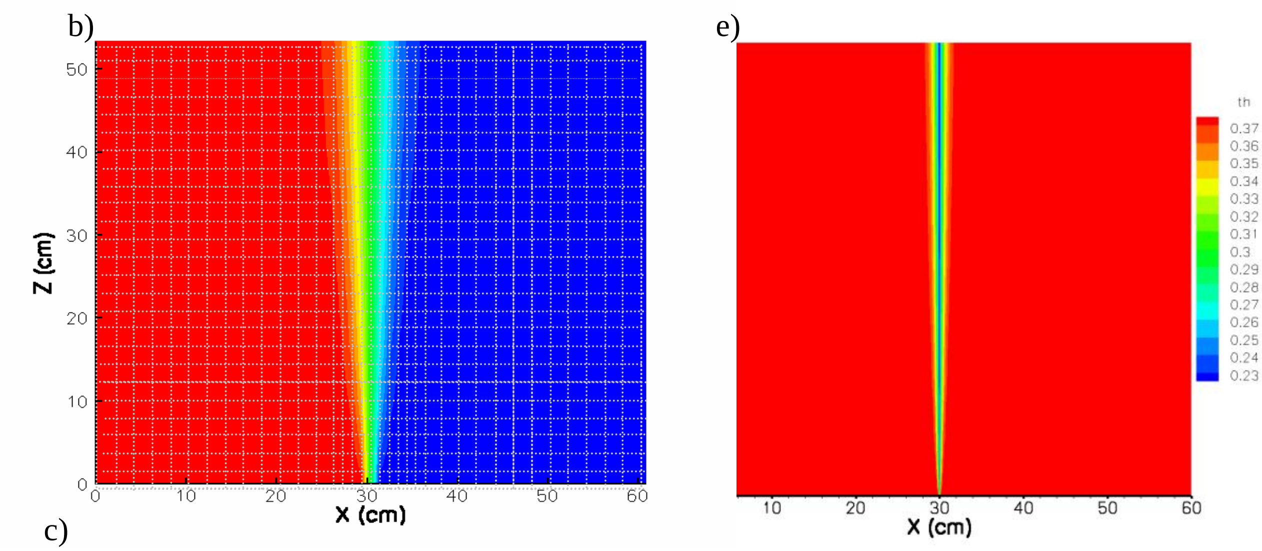
## Research progress at PNNL

In the first year the research efforts at PNNL were concentrated on multi-scale modeling of the mixing induced precipitation. A new numerical model based on Smoothed Particle Hydrodynamics method was developed and used to simulate pore-scale reactive transport and precipitation. A multi-grid resolution finite element model was used to study precipitation on macroscopic scale. The main outcomes and implications of these activities are summarized in the Section 3 of this report.

## Research Progress and Implications

During the first year of the project the experiments were conducted at **INL** using homogeneous sand-packed cells, dye tracers for observing mixing behavior between parallel flowing solutions, and the generation of calcium carbonate precipitates within the mixing zones (Figure 1). The numerical simulations were performed at PNNL. The most prominent results and implications are summarized as follows: 1) Macroscopic simulations using effective transport properties of experimental sediments predict mixing and precipitation zones that are much wider than observed in the experiment. Adjustment of the transverse dispersion coefficient to account for the difference in “true” mixing versus dispersion and using finer grids near the mixing zone can lead to better simulations of the reaction front (Figure 1); 2) Mineral precipitation has a pronounced anisotropic impact on media permeability. Longitudinal permeability is only minimally affected while transverse permeability is greatly reduced. 3) Pore-scale simulations have accurately simulated the thin reaction fronts and decreases in media permeability in both 2-dimensional and 3-dimensional simulations.





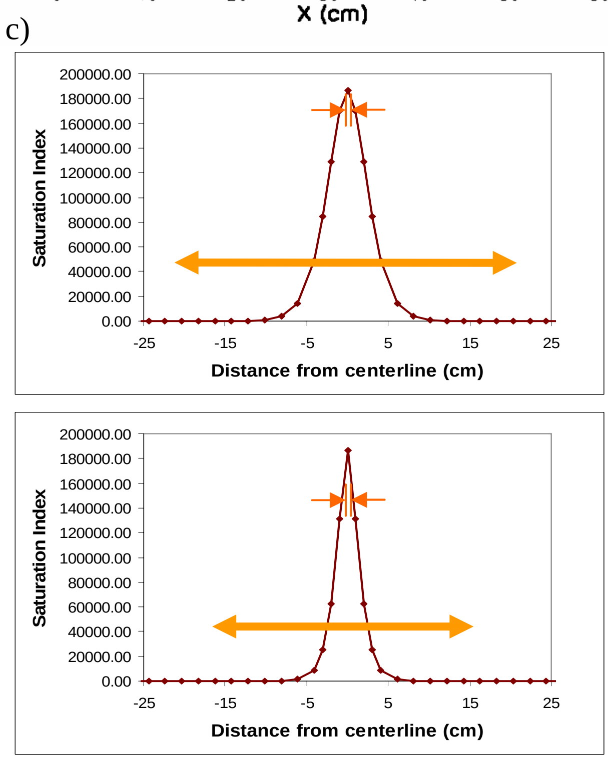




FIGURE 1. Comparisons between experimental and model simulations: a) Parallel flows (upward) of red and blue dyes showing the mixing front, b) Grid-based simulation of mixing, c) expectations for broad ranges of precipitation without considering changes in permeability, and based only on saturation indices for calcite (high, top, and low, bottom, dispersion cases), d) Experimental generation of a calcium carbonate precipitate within the mixing front between $Na_2CO_3$ and $CaCl_2$ solutions injected separately at the bottom of the different halves of a vertical 60cm x 60 cm flow cell (The white line in the middle of flow cell is a zone of calcium carbonate precipitation), and e) Coupled transport and precipitation continuum (Darcy) scale simulation. The maximum reduction in porosity is from the initial value of 38% to 23%.

The results of two-dimensional and three-dimensional simulations are shown in Figures 2 and 3 respectively.

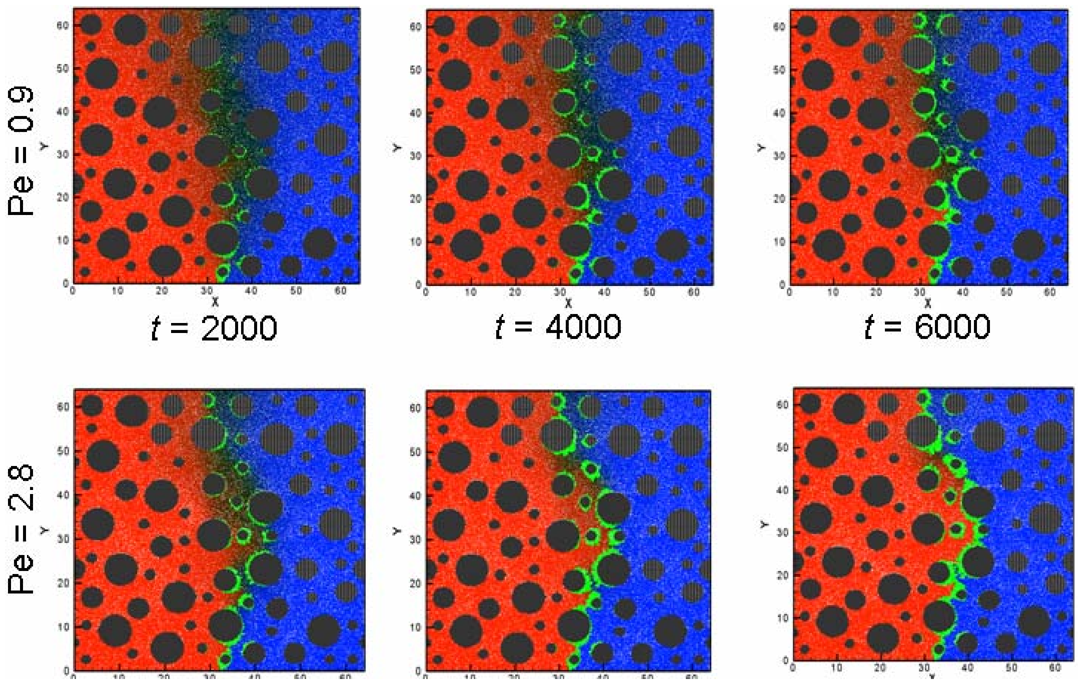



FIGURE 2. Flow and precipitation for Pe=0.91 and 2.81. The black particles represent soil grains, the green particles represent the precipitate and the color scale represents the concentrations of solutes *A*, *B* and *C* with red corresponding to $C^A = 1$, blue corresponding to $C^B = 1$ and black corresponding to the $C^C/C^C_{max} = 1$, where $C^C_{max}$ is the maximum concentration of solute *C*.

Pore-scale simulations demonstrate that precipitation greatly affects mixing of the two solutes, and this illustrates why a simple continuum-scale model does not properly predict the width of the reaction and precipitation zone. We proposed a new form of the homogeneous and heterogeneous reaction terms in the classical advection dispersion equation. These terms involve the transport and mixing indices that account for non-uniform concentration distribution and highly localized reaction. The preliminary results show that accurate prediction can be obtained using grids much larger that the size of the precipitation zone.

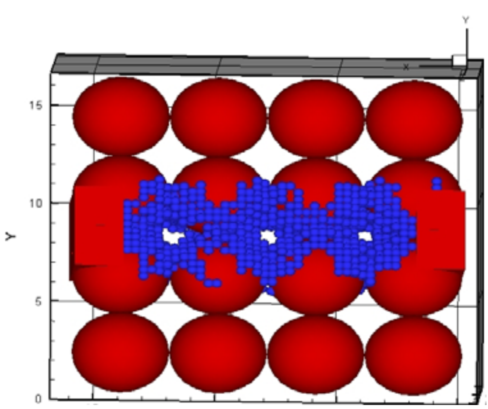



Figure 3. Three-dimensional pore scale simulations of the calcite (blue) particles on the surface of the soil grains (red particles). The pockets of trapped fluid are observed in the middle of precipitate layer. Our results show that the amount of trapped fluid strongly depends on Peclet number.

**Implications:** The consequences of precipitation events on flow and transport are being illustrated through the experimental and modeling work done to date in the project. Restricted communication between regions with reactants has consequences for the rates, spatial distributions, and evolution of processes in subsurface environments that are subject to engineered manipulations and, in some cases, natural events. We see how isotropic systems can develop anisotropic properties. We also see how the distributions of mass at small scales have meaningful implications for macroscopic system behavior. It is important to point out that, while this project is using a relatively simple chemical model for a process that modifies permeability, the principles apply to colloid filtration and biofilm growth. It is also important to point out that being able to intentionally manipulate subsurface flow and solute transport is as important as overcoming challenges to understanding differences between simple conceptual models and the behavior of real systems. We demonstrated that pore-scale models can be used to estimate effective transport properties and to develop better understanding of the coupled processes leading to improved conceptual models. We developed a new form of transport equation that may be able to accurately describe mixing and precipitation without explicitly resolving precipitation front. The numerical solution of the new equation will be computationally more efficient that the solution of the standard advection dispersion equation.

**Activities planned for year 2**

A) Calcium carbonate precipitation kinetics and products over a wide range of saturation indices and ion activity ratios will be characterized in batch and flow-through experiments. This activity will be conducted primarily at the University of Idaho under the direction of Dr. Robert Smith, and with assistance from Mike Reddy at the U.S. Geological Survey. The range of conditions will be those that are represented within the mixing zones of the porous media experiments. Investigations of the impact of ion ratios is important with respect to the *in situ* generation of one reactant, which mimics the microbially facilitated generation of carbonate ion, where concentration of the other reactant, $Ca^{2+}$, is constant. Precipitation experiments will include homogeneous reactions, and precipitation in the presence of seed minerals including calcite, a model ion exchanger, and natural material from the INL site where Sr contamination is a being addressed.

B) Impacts of calcium carbonate precipitation on Sr speciation will be conducted as part of the carbonate precipitation experiments in A) where Sr is present in solution and as an adsorbed species on ion-exchange minerals. The speciation of $Sr^{2+}$ will be analyzed by synchrotron-based spectroscopy at the Argonne National Laboratory Advanced Photon Source in collaboration with Dr. Shelly Kelly.

C) 2-dimensional flow-through precipitation experiments will be conducted as described in the original proposal. Initially, the experiments in homogeneous media will be replicated. This will be followed by experiments in media with constructed fast flow paths, heterogeneities with contrasting permeabilities, and chemical heterogeneities. Precipitation will be promoted at macroscopic mixing fronts between multiple solutions, and at the pore-scale where *in situ* generation of carbonate will be promoted via the enzyme catalyzed hydrolysis of urea.

D) Small-scale 2-D Hele-Shaw cells will be constructed where pore-scale precipitation events can be observed in greater detail for comparison against and validation of the SPH simulations.

E) The 3-dimensional SPH model simulations will be expanded to include larger domains where the impact of different precipitation mechanisms can be tested.

F) We will begin to develop the relationships between pore-scale and continuum scale model predictions with the intent of establishing the basis for macroscopic parameterization.

**Publications, Presentations**

**Journal Publications:**

1) A. M. Tartakovsky, T. Scheibe, G. Redden, P. Meakin, Pore-scale Smoothed particle hydrodynamics model of mixing induced precipitation, Water Resources Research (under review).

2) A.M. Tartakovsky, P. Meakin and T. Scheibe, A smoothed particle hydrodynamics model for reactive transport and mineral precipitation in porous and fractured porous media, Water Resources Research. (under review)

**Presentations:**

1)Fujita, Y., G. Redden, R. Smith, Y. Wu and R. Versteeg (2006). Microbially catalyzed calcite precipitation in porous media: potential for geophysical mapping of precipitate distribution. AGU Joint Assembly, Baltimore, MD.

2)Redden, G. D., Y. Fang, T. Scheibe, A. M. Tartakovsky, D. T. Fox and T. A. White (2006). Metal precipitation and mobility in systems with fluid flow and mixing: Illustrating coupling and scaling issues. American Chemical Society, 231st ACS National Meeting, Atlanta, GA, American Chemical Society.

3) Redden, G. D., Y. Fang, T. D. Scheibe, A. M. Tartakovsky, D. T. Fox, Y. Fujita and T. A. White (2006). FLUID FLOW, SOLUTE MIXING AND PRECIPITATION IN POROUS MEDIA. INRA 2006 Environmental Subsurface Science Symposium, Moscow, ID.

4)Scheibe, T. D., A. M. Tartakovsky, G. Redden, P. Meakin and Y. Fang (2006). Pore-scale simulations of reactive transport with smoothed particle hydrodynamics. Society for Industrial and Applied Mathematics Annual Meeting, Boston, MA.

5) Redden, G. D., Y. Fujita, T. D. Scheibe, A. M. Tartakovsky, R. W. Smith, M. M. Reddy, and S. D. Kelly. 2006. Coupling Between Flow and Precipitation In Heterogeneous Subsurface Environments and Effects on Contaminant Fate and Transport (Project no. 99272), Poster presented at the 2006 ERSP Principal Investigators Meeting, Warrenton, Virginia, April 2006.

6) Tartakovsky, A., T. Scheibe, G. Redden, P. Meakin, and Y. Fang, 2006. Smoothed particle hydrodynamics model for reactive transport and mineral precipitation, in Proceedings of the XVI International Conference on Computational Methods in Water Resources, edited by Philip J. Binning, Peter K. Engesgaard, Helge K. Dahle, George F. Pinder and William G. Gray. Copenhagen, Denmark, June, 2006.

7) Scheibe, T. D., Y. Fang, A. M. Tartakvovsky, and G. Redden, 2006. Hydrogeologic controls on subsurface biogeochemistry: Field-scale effects of heterogeneous coupled physical and biogeochemical processes. Geological Society of America Annual Meeting (Invited), October 22-25, Philadelphia, PA.