Fluid Flow, Solute Mixing, and Precipitation in Porous Media

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Abstract

Nucleation and growth of minerals and colloids in porous media often depend on molecular-level diffusive mixing of solutes. Solute mixing at the interface between two solutions can be particularly important in engineering applications that involve the injection of solutions. Alternatively, solute mixing can occur adjacent to reactant sources such as cell/solution and mineral/solution interfaces. Furthermore, engineering applications often involve rapid change where conditions may be far from equilibrium, which can present challenges for how reactants are delivered and how results are predicted using models. Although many of the fundamental component processes (e.g., precipitation equilibrium and kinetics, fluid flow and solute transport) are reasonably well understood, the deposition of solids in porous media is coupled to flow. Characterizing this coupling and predicting its effects on contaminant transport are the objectives of this project.
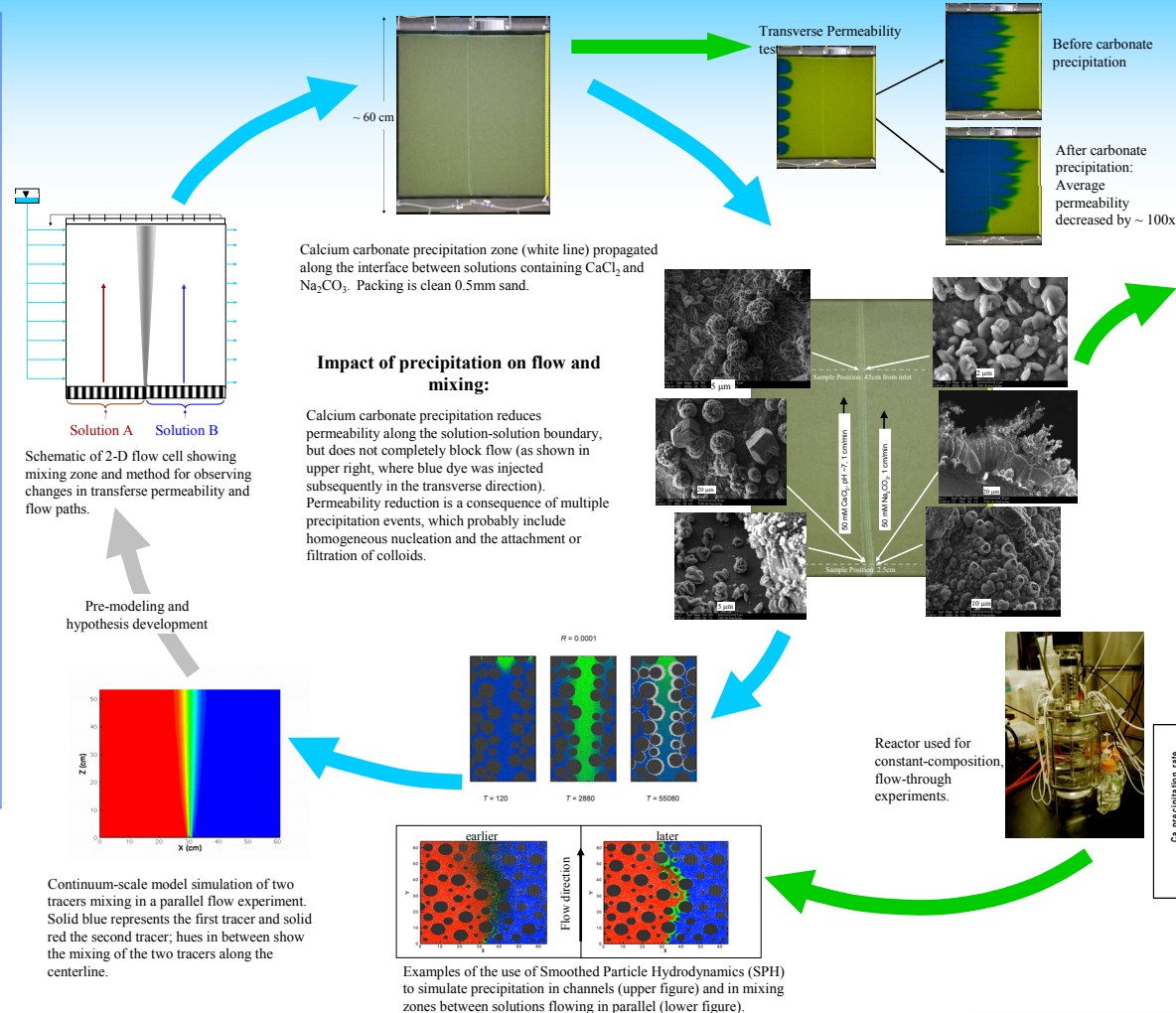
Thus far we have focused on systems with parallel flow of calcium and carbonate solutions. Calcium carbonate precipitates are propagated along the solution-solution boundary in the direction of flow. The spatial distribution of carbonate phases depends on the interactions between precipitation and dissolution kinetics, which are in turn functions of pore-scale saturation indices and solute ratios, nucleation mechanisms, crystal growth conditions, and changes in porosity and flow.

At the pore scale, we have simulated precipitation and porosity and mixing changes using the Smooth Particle Hydrodynamics (SPH) method. Macroscopic simulations have been performed using a finite-element multicomponent reactive transport simulator with various degrees of grid refinement and multiple alternative parameterizations. A goal is to use SPH simulations as the basis for parameterization of the macroscopic model by comparing results from the two scales with our experimental results.

Ongoing and planned activities include: characterization of carbonate precipitation products and kinetics under variable ion ratios and including co-precipitation with Sr; 2-D experiments with physical and chemical heterogeneity, and continued development of pore-scale and continuum scale modeling simulations with linking between pore-scale to continuum-scale representations of experimental data.
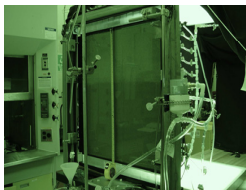
2-D Flow Cell. Flow is vertical for precipitation experiments. Horizontal flow is used for visualization of changes in permeability.

Schematic of 2-D flow cell showing mixing zone and method for observing changes in transferse permeability and flow paths.

Pre-modeling and hypothesis development

Continuum-scale model simulation of two tracers mixing in a parallel flow experiment. Solid blue represents the first tracer and solid red the second tracer; hues in between show the mixing of the two tracers along the centerline.

Transverse Permeability test

Before carbonate precipitation

After carbonate precipitation: Average permeability decreased by ~ 100x

Calcium carbonate precipitation zone (white line) propagated along the interface between solutions containing $CaCl_2$ and Na_2CO_3. Packing is clean 0.5mm sand.

Impact of precipitation on flow and mixing:

Calcium carbonate precipitation reduces permeability along the solution-solution boundary, but does not completely block flow (as shown in upper right, where blue dye was injected subsequently in the transverse direction). Permeability reduction is a consequence of multiple precipitation events, which probably include homogeneous nucleation and the attachment or filtration of colloids.

Reactor used for constant-composition, flow-through experiments.

Examples of the use of Smoothed Particle Hydrodynamics (SPH) to simulate precipitation in channels (upper figure) and in mixing zones between solutions flowing in parallel (lower figure).

Supporting experiments for conceptual models and numerical simulations

Relationships between solution compositions and the kinetics of mineral precipitation have been well studied. Although there exist many unresolved questions, useful functional relationships along with plausible mechanistic explanations have been established. However, experimental data usually comes from systems that:

- are well-stirred in order to isolate the role of diffusion
- have low to moderate saturation ratios, and
- have stoichiometric or constant ion ratios.

Conditions in porous media can fall outside these conditions (Note the concentration gradients shown in the SPH simulations.) Therefore, studies of precipitation and Sr co-precipitation kinetics will include:

→Extending conditions to high saturation ratios (IAP/K$_{sp}$ >> 100) that can favor metastable polymorphs such as amorphous or cryptocrystalline $CaCO_3$, vaterite and aragonite. Analytical methods will include XRD, SEM and XAS analyses.

→Conducting flow-through precipitation rate experiments in which the flow rate is adjusted to replenish solutes at different rates in order to understand precipitation events that are surface- or transport-controlled (or both).

→Extend the range of ion ratios in precipitation experiments in order to understand systems where reactants are being generated (e.g., by urea hydrolysis) or consumed at different rates. Calcite precipitation rate data are frequently fit using the expression

$$R = k(IAP/K_{sp} - 1)^n.$$

However, Lin and Singer (2005) among others have shown that rates measured at the same IAP/K$_{sp}$, but different CO_3^{2-}/Ca^{2+} ratios are not equivalent and that rate can be expressed by:

$$R = k(Ca^{2+})^p(CO_3^{2-})^q.$$

We have designed calcite-seeded, "constant-composition" experiments with varying CO_3^{2-}/Ca^{2+} ratios to span the range of expected solute concentrations across the mixing zone of the 2D experiments. The derived rate expression and the Sr distribution coefficients calculated from the experimental results will be applied in the pore scale modeling.
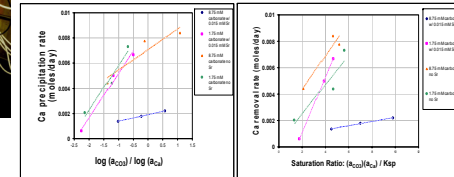
Preliminary data from C. Corriveau and R. Smith (unpublished data) from flow-through experiments relating ion ratios to calcite precipitation rate.

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