Experimental Studies and Modeling of Mineral Precipitation in Mixing Zones Controlled by Parallel Flow and Double Diffusion

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The theme for the Idaho National Laboratory (INL) Scientific Focus Area (SFA) is "Understanding and Controlling Precipitation Reaction Fronts in Subsurface Environments." We are investigating how different modes of reactant mixing in porous media affects the spatial-temporal distribution of reaction products in porous media with a special focus on mineral precipitation reactions. The objective is to understand how the nature of mixing of reactants involved in multi-component precipitation reactions affects the rates of precipitation, and reductions in permeability or porosity, in order to predict and control these parameters in subsurface applications.

Precipitation of $CaCO_3$ in the mixing zone between two solutions flowing in parallel, one containing Ca^{2+} and one containing CO_3^{2-} (originally studied in a large flow cell [1]) has been studied using sand-packed flow cells. Reactant solutions were: A) $CaCl_2$, and B) $NaHCO_3$. Both solutions contained a pH indicator (cresol red), were pH adjusted to 9.2, and the densities were matched to less than 0.1% using NaCl. The objective was to use visible pH changes to determine how $CaCO_3$ precipitation reactions in the mixing zone affected changes in the local pH conditions as protons are released. A "pH wedge" appeared, as predicted by modeling, with one edge aligned with the centerline of the mixing zone with the other edge extending into the unbuffered $CaCl_2$ solution. As the reaction progresses, the pH wedge becomes narrow, or disappears, showing that small volume averaged amounts of $CaCO_3$ deposited in the mixing zone can inhibit further precipitation. The results have consequences for predicting volume averaged rates of reactions and changes in transverse permeability.

Double diffusion experiments were conducted in polyacrylamide gels and in fine sand media. The goal is to compare precipitation behavior and reductions in porosity or permeability between the two types of media, and between two chemical systems; calcium carbonate and calcium phosphate. In gel media with zero effective permeability, dramatic differences in precipitation patterns show the system-specific nature of mixing/precipitation patterns. Carbonate precipitation in the gel media initiates with a wide distribution of growing crystals that are widely spaced. In contrast, the phosphate system commences with multiple bands of fine material that evolve in position and width, and that appear to cause a more rapid reduction in porosity. In fine sand media density differences between solutions create mixing patterns that are not orthogonal to the diffusion boundaries. Density effects, which include local changes in density caused by precipitation reactions, can exert additional influences on reactant mixing. It is also likely that the presence of heterogeneous nucleation sites stimulate more rapid nucleation that leads to much finer zones of precipitation.

The ReActive Transport (RAT) code developed at INL has been used to capture the general features of the observed precipitation patterns in the experiments. Cross-platform comparison between RAT and PFLOTRAN has been conducted to confirm that the implementation of the model is accurate.

1. Tartakovsky, A. M., G. Redden, et al. (2008). "Mixing-induced precipitation: Experimental study and multiscale numerical analysis." Water Resources Research 44(6).