Effects of Pore Structure Change and Multiscale Heterogeneity on Contaminant Transport and Reaction Rate Upscaling

University-Led Research

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Mineral dissolution and precipitation in porous media alters pore network structure and subsequent flow velocities, creating complex interactions between reaction and transport. This project investigates mineral reactions and alterations in flow permeability in a multi-scale, multi-dimensional study that combines experimentation, modeling and imaging. Primarily, we are targeting the reaction of highly caustic, radioactive waste solutions with subsurface Hanford sediments, and the immobilization of radionuclides.

(1) Reactive flow experiments. We are conducting experiments using reactive flow-through columns of several sizes. The most recent experiments performed at PNNL used 7.6-cm-long x 1.9-cm-diameter columns. Separate columns were packed with quartz sand and with Hanford sand to evaluate the influence of mineralogy on transport and reaction rates and changes in pore-structure resulting from contact with a synthetic tank waste liquid (STWL). Another column was flown through using STWL without Al, in which only dissolution is occurring, which results in porosity increases. Experiments have shown porosity changes ranging from 0.04 to 0.11, resulting in calculated permeability reductions on the order of 2 to 3 times. Also observed were changes in pore structure that would affect the unsaturated hydraulic properties of the sediments (moisture retention characteristics and relative permeability).

(2) Multiscale Imaging and Analysis. To examine the reaction-induced alterations of pore structure, we are using 3D X-ray computed microtomography, and 2D backscattered electron and energy-dispersive X-ray imagery. In our early work, columns reacted at PNNL were imaged using X-ray computed microtomography at BNL, but recently we are using an XMT system at EMSL (PNNL). The 3D images are analyzed in novel ways to quantify pore structure, mineral distribution, structural changes and fluid-air and fluid-grain interfaces. This informs pore network models for calculating expected changes in permeability and reactive surface area. At Princeton, using the method we have developed for sectioning the columns and using SEM and EDX for 2D imaging, sub-pore scale structural alterations have been observed. For example, secondary cancrinite precipitates were observed in reacted columns as a relatively uniform coating on all grain surfaces. 2D imaging also revealed that Hanford sediments have a large amount of intragranular porosity and that secondary precipitates were observed in intragranular space.

(3) Multiscale Modeling and Up-Scaling. This project involves modeling at several spatial scales. The column experiments are being modeled using the STOMP simulator to evaluate ways of representing effective reaction rates and feedback between changes in pore structure and the permeability relations needed for the continuum-scale. The column experiments have also been modeled using a custom reactive transport model to investigate the capacity for intragranular pore space in Hanford sediments to sequester and release radionuclides. Long-term leaching of Cs from intragranular pores is predicted to prolong the period of secondary contamination at the site. Finally, a specific application of our pore-network reactive transport modeling was aimed at understanding how CO_2-rich brines alter rocks containing fast-reacting minerals such as calcite and dolomite. These simulations of porosity and permeability evolution reveal the importance of considering different flow regimes (advection-controlled vs diffusion-controlled) and inlet fluid mixing scenarios. We have shown that there is not a unique continuum-scale permeability relationship that describes all reactive flow scenarios for even the same porous medium and that the spatial and temporal evolution of the network dictates the unique relationship between porosity and permeability.