
Effects of Mineral Impurities and Heat on Uranium(VI) Sorption onto Bentonite

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ABSTRACT:

Most nuclear waste disposal options include compacted bentonite, consisting of montmorillonite clay, as part of a barrier system to minimize contaminant mobility. Uranium (U) is the primary element in spent nuclear fuel, and from an environmental perspective, a potential contaminant of water resources. Furthermore, uranium may control nuclear fuel degradation rates and the consequent release of other radioactive contaminants based on its diffusive transport away from waste canisters. Uranium sorption onto clay and other mineral surfaces is expected to limit U(VI) mobility in these systems. However, at this point a prediction of U(VI) sorption and transport behavior in performance assessment (PA) models is complicated by a series of factors, such as: (1) the presence of various U(VI) solution species with different charges and sorption characteristics; (2) the complex microstructure of montmorillonite clay resulting in two types of clay porosities and multiple sorption sites; (3) the largely unknown effects of bentonite mineral impurities on pore water chemistry, U(VI) sorption and diffusion behavior; and (4) the potential impacts of heat, generated by the decay of spent fuel, on mineralogical and microstructural transformations, and any subsequent effects on radionuclide sorption and mobility.

In this project, we will investigate the effects of calcite impurities on U(VI) sorption and diffusion onto montmorillonite before and after mineral exposure to heat. Based on a combination of data from U(VI) batch sorption experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy, we will develop a new U(VI)-montmorillonite surface complexation model to determine under which conditions impurity effects are relevant for U(VI) sorption processes, and how they can be incorporated into PA models. In diffusion experiments, we will further test the relevance of changes in U(VI) sorption behavior for the diffusive transport of U(VI). Molecular dynamics (MD) calculations will support the simulation of diffusion results by evaluating steric effects associated with the size of U(VI) solution complexes (relative to the sub-nanometer width of montmorillonite nanopores).

This project will provide a comprehensive experimental data set of U(VI) sorption distribution coefficients (K_d values) for Na-montmorillonite/bentonite systems, in the presence of calcite impurities, over a wide range of chemical solution conditions, and before and after mineral exposure to heat. Our new U(VI) sorption model will allow us to (1) predict U(VI) sorption behavior under these complex system conditions, (2) determine the conditions under which calcite impurities are relevant, and (3) elucidate the most-likely, underlying mechanism(s) for these effects. At last, the integration of our surface complexation model into a state-of-the-art reactive diffusion model will allow us to characterize the impact of U(VI) speciation on U(VI) diffusion in bentonite barriers. All of these results will have direct implications for the development of PA models, since they can either help to justify a decrease in PA model complexity, or provide a scientific basis for the incorporation of these complex system behaviors.