U(VI) Mobility in Acidic Waste Plumes: Laboratory Experiments and Surface Complexation Modeling using F-Area Savannah River Site Sediments

Wenming Dong, Jiamin Wan (PI), Tetsu K.Tokunaga, Hua Guo, Patricia M. Fox, James A. Davis

Earth Sciences Division, Lawrence Berkeley National Laboratory

The mobility of uranium (U) plumes is of great concern under acidic geochemical conditions in many contaminated DOE sites. The mechanisms controlling U mobility under acidic conditions in aquifer sediments are not well understood. Our objective is to understand the mechanisms and factors controlling U adsorption behavior, and predict its mobility under acidic conditions. The acidic U plume (pH < 5) at the F-Area of Savannah River Site (SRS) was selected as the study site. The F-Area sediments were characterized to identify grain size distribution, mineralogy, surface area, and secondary phases present in grain coatings. Laboratory batch equilibrium experiments for U(VI) adsorption onto sediments of different grain sizes (bulk, coarse, fine) and onto reference minerals (goethite, kaolinite) were performed over a range of pH conditions (pH 3.0 – 8.5). To understand the mechanisms of U(VI) adsorption within the grain coatings, a combination of synchrotron and microscopic techniques were used. A component-additivity (CA) based surface complexation model (SCM) was developed to predict U(VI) adsorption under variable geochemical conditions.

Our experimental and modeling results indicate that: (i) the fine fractions (≤ 45 μm) in sediments control U(VI) adsorption due to their large surface areas (relative to the coarse quartz sand); (ii) goethite and kaolinite were identified as the major reactive phases in the fine fractions of sediments. Kaolinite is a more important sorbent for U(VI) at pH < 4.0, while goethite plays a major role at pH > 4.0; (iii) our CA model combines an existing U(VI) SCM for goethite and a modified U(VI) SCM for kaolinite along with estimated relative surface area abundances of these component minerals. The modeling approach successfully predicts U(VI) adsorption behavior on the background F-Area sediments. The model suggests that exchange sites on kaolinite dominate U(VI) adsorption at pH < 4.0, goethite and kaolinite edge sites co-contribute to U(VI) adsorption at pH 4.0 - 6.0, and goethite dominates U(VI) adsorption at pH > 6.0. The coarse fraction (> 45 μm) showed stronger adsorption per unit surface area than goethite and kaolinite under acidic conditions (pH < 5.0). The synchrotron and microscopic studies show that the coatings on quartz grains ranged in size from 1 to 20 microns in thickness and contained a complex mixture of iron oxides and aluminosilicates. Although goethite is the predominant Fe oxide in fine-grained sediments of the F-area, the predominant Fe oxide in the quartz coatings was hematite. Concentration gradients in adsorbed U(VI) within coatings appeared to be only related to the spatial abundance of hematite, not to reaction time (≥2 hr). This implies that U(VI) adsorption by the coatings differs from that of the fines, which may impact U(VI) transport within the sand-dominated, beach barrier reactive facies.

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