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Publication Date

2001-10-04

This abstract was prepared for an invited oral presentation at NUCEF 2001 (Nuclear Fuel Cycle Safety Engineering Research Facility Conference) to be held in Tokai-Mura, Japan, October 31 – November 2, 2001.

prepared: October 4, 2001

MOLECULAR INTERFACIAL REACTIONS BETWEEN PLUTONIUM AND MANGANESE OXIDE HYDROXIDE SURFACES

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Actinides can migrate in the environment mostly via aqueous media such as groundwater and surface, river, lake and seawater. Models predicting the hydrological transport through the environment require as input an actinide concentration, the true amount that is actually available for transport. Three major processes define the actinide source term: (1) solubility, (2) organic interaction, and (3) sorption. They are dependent on each other and each individual process is the result of several sub-processes. Also, colloid formation plays a major role in the actinide source term, and it is common to each of the three main processes. The current state of knowledge of several of these processes will be discussed and emphasis will be given to the interfacial reactions of plutonium with manganese oxides and oxyhydroxides surfaces.

Manganese oxides, present as minor phases in the vadose zone and other subsurface environments, may preferentially sequester actinides and transition metals over iron oxide/hydroxide minerals present in much larger amounts. Key thermodynamic and kinetic parameters governing the sorption of aqueous plutonium species in defined oxidation states on characterized mineral surfaces as a function of pH, actinide concentration, and ionic strength were determined on manganese oxyhydroxide minerals.

The minerals were characterized using X-ray diffraction, X-ray absorption spectroscopy (XAS), and potentiometric titration, and the oxidation state of the sorbed plutonium was determined using XAS and optical absorption spectroscopy. The results indicate that manganese oxide hydroxides, which show a variety of structure and manganese valence states, have large sorption capacities for Pu(VI) and Pu(V). Sorption increases as a function of mineral surface area and pH, especially at pH values above the pH_{PZC} where the mineral has a net negative surface charge. In addition, manganite and hausmannite (both predominantly Mn(III) minerals) reduce Pu(VI) and Pu(V) to Pu(IV), which then sorbs to the mineral. Redox reactions occur between the plutonium and the manganese, both in solution and on the minerals. XAS measurements show that plutonium is bound to these minerals in an inner sphere configuration, and that there is no evidence of PuO_2 precipitation on the surface. Based on these initial results, if plutonium contaminants in the environment contact manganese oxide hydroxide minerals, the plutonium can be sequestered through sorption at the mineral surface under specific conditions.