Development of a Self-Consistent Model of Plutonium Sorption: Quantification of Sorption Enthalpy and Ligand-Promoted Dissolution

University-Led Research

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The overarching objective of this work is to develop a thermochemical model of Pu sorption to minerals and sediments that incorporates aqueous and solid phase speciation, redox reactions, and the influence of organic ligands. This has been done using a suite of techniques including variable temperature batch sorption, x-ray absorption spectroscopy, quantum mechanical modeling, and isothermal titration calorimetry.

This work has taken a detailed approach to understanding the reactivity of Pu and other actinides with goethite, hematite, and kaolinite surfaces and describe the data using a surface complexation modeling approach. The specific surface complexes in these models have been constrained to the extent possible by direct (x-ray absorption spectroscopy, XAS) and indirect (solvent extraction) methods of determining the Pu oxidation state and chemical species. For example, batch sorption and x-ray absorption near edge spectroscopy (XANES) starting with either Pu(III), Pu(IV), or Pu(V/VI) have demonstrated that Pu(IV) becomes the dominant oxidation state on quartz and hematite surfaces regardless of the initial oxidation state. Furthermore, variable temperature batch sorption experiments have demonstrated sorption of Eu(III), Th(IV), Pu(IV), Pu(V), and Np(V) to goethite (and hematite for Eu) increases with increasing pH and increasing temperature. The data indicate sorption is endothermic and that the increase in sorption with temperature is driven by a positive entropy. These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. This behavior has been supported using XAS and quantum mechanical modeling.

The surface complexation models described above have been used to describe Pu sorption and redox reactions with soils from the Savannah River Site and the Hanford 200 Area using a component additivity approach which accounts for specific mineral phases within each soil. The models are capable of predicting the degree of sorption observed on relatively short time scales. However, observations of Pu desorption from a SRS soil which has been contaminated with Pu for 30+ years indicate that desorption is either drastically kinetically hindered or irreversible. Thus, there appears to be an aging effect that is not currently accounted for in our thermochemically based modeling approach. The results from these experimental measurements are being compared with quantum mechanical calculations of actinide interactions with pure mineral phases. Current experimental efforts are focused on characterizing changes in Pu(IV) and Pu(V) source materials used in a new set of field lysimeter experiments called the Radiological Field Lysimeter Experiment (RadFLEx) at the SRS.