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

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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.

Quantification of actinide sorption enthalpies: Ongoing experiments have demonstrated that 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 Gibbs free energy increases with temperature. Thus, in all cases the endothermic reaction must be balanced by a positive entropy to yield a negative Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. The increase in sorption as a function of temperature follows the trend, Th(IV) > U(VI) > Eu(III) > Np(V) which also corresponds to the effective ion charges and hydration energies of the given actinide oxidation states.

Examination of Pu redox speciation at solid water interfaces: 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. These experiments have been coupled with quantum mechanical calculations investigating the potential role of alpha radiolysis products, such as hydrogen peroxide (H_2O_2) and hydroxyl radical (•OH), in the reduction of Pu(V/VI) to Pu(IV). Preliminary results indicate that the OH radical readily reacts with water in the first hydration sphere instead of proceeding toward the electron density of the plutonyl. We have inferred that this reaction with a hydrating water transfers a hydrogen, creating a new •OH closer to the plutonyl. Ongoing work is examining the potential role of surface catalysis.

Examination of Pu aging and mineral incorporation: Desorption of $^{239/240}$Pu aged 30+ years on SRS sediment was examined and found to be essentially irreversible. A "fresh" ^{242}Pu tracer added during the desorption step did not exhibit the same behavior. Electron microscope and microprobe studies are examining the spatial distribution of Pu within these samples. The results from these experimental measurements are being compared with quantum mechanical calculations of actinide incorporation into pure mineral phases.