

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. In the final year of this project we have utilized the conceptual and quantitative models describing Np and Pu speciation in subsurface environments to describe the mobility of Pu in a series of field lysimeter experiments called the Radiological Field Lysimeter Experiment (RadFLEX) at the SRS. Analysis of effluent samples from field lysimeters after exposure to 3 years of natural rainfall showed no mobilization of Pu above detection limits. Furthermore, measureable concentrations of Np in the effluent were only found from lysimeters with Np(V) sources. Lysimeters containing Np(IV)O₂ did not have any measurable concentrations of neptunium in the effluent. These findings are supported by laboratory and computational investigations of the strong association of tetravalent actinide species with mineral surfaces. After coring several Pu bearing lysimeters, little transport of Pu had been observed and greater than 99% of the Pu appeared to have remained within the source. There was a greater downward migration of the Pu^VO₂(NH₄)(CO₃)(s) source after just 2 years in the field compared with previously observed transport from Pu(IV) and Pu(III) sources after 11 years in the field. This behavior is consistent with both the enhanced mobility of pentavalent actinides relative to other actinides as well as reduction of Pu(V) to Pu(IV) leading to formation of Pu(IV) surface complexes or Pu(IV) (hydr)oxide precipitates. However, as transport of Pu(V) sources was slightly greater than other oxidation states, it is likely that the slightly enhanced transport observed within the lysimeters is due to transport of Pu as Pu(V) prior to reduction to Pu(IV). In addition, the presence of organic matter decreased the mobility of Pu(V). Although further investigation is needed, this could be due to enhanced reduction of Pu in the presence of organic matter leading to increased sorption to minerals or complexation of Pu with organic matter associated with the bulk minerals. These field lysimeter observations highlight the importance of Pu reduction as a major factor limiting the environmental mobility of Pu in environmental systems.