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

University-Led Research

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This project is focused on developing a fundamental understanding of the environmental behavior of plutonium through the development of a mechanistic model of plutonium speciation in subsurface environments. The speciation model will be a thermodynamic surface complexation model of plutonium sorption to mineral surfaces that is self-consistent with macroscopic batch sorption data, X-ray absorption spectroscopy (XAS) measurements, electron microscopy analyses, and quantum-mechanical calculations. The overarching hypothesis of the project that the strong interactions of actinides with mineral surfaces result from the formation of inner sphere complexes with a limited number of high-energy surface sites, and that displacement of solvating water molecules from the actinide and mineral surface during sorption is energetically favorable and results from a large increase in entropy.

In order to test the above hypothesis without involving the complex redox chemistry of plutonium, Eu(III) and Np(V) were selected as strongly and weakly hydrated, respectively, species. Sorption of Eu(III) to hematite increased strongly with temperature while Np(V) exhibited little change. This is consistent with our hypothesis showing that sorption of Eu(III) is entropically driven as hydrating waters are removed from the mineral surface and the Eu(III) ion upon sorption. A series of unique, high energy k-shell Eu EXAFS measurements were performed and confirmed at the coordination number of Eu(III) decreases upon sorption (consistent with the removal of hydrating waters) and that a bidentate, mononuclear surface species forms. Sorption enthalpy and entropy values were calculated using a surface complexation model and the van't Hoff equation. Consistent with the overarching hypothesis of this work, sorption of Eu(III) was entropically driven. This observation of the dominant entropy term is consistent with the experimental hypothesis that the energetic favorability of actinide surface complex formation is strongly influenced by positive sorption entropies, which are mechanistically driven by displacement of solvating water molecules from the actinide and mineral surface during sorption. These results are currently being compared with quantum mechanical models of Eu(III) sorption as both inner and outer sphere complexes.

Sorption of Pu(IV) and Pu(V) to goethite has exhibited a similar increase with increasing temperature. These experiments as well as many others in the literature, have observed surface mediated reduction of Pu(V) to Pu(IV) although the specific mechanism, including the reductant, is still unclear. Experiments are being performed to examine possible mechanisms. Experiments with multiple Pu isotopes (^{238}Pu and ^{242}Pu) have shown that alpha particle generated radiolysis does not appear to significantly influence the reduction rate. Attempts to remove trace Fe(II) during hematite nanoparticle synthesis by aeration did not influence the observed reduction rates. Furthermore, the reduction rate on the Pu(V) nanoparticles was significantly influenced by light, indicating that semiconducting properties of the mineral can influence the electron transfer reaction. It is possible that goethite may indirectly participate in Pu(V) reduction by acting as a catalyst or electron shuttling device to transfer charges between coadsorbates, as suggested by recent quantum mechanical modeling of uranyl reduction on goethite in the presence of hydrogen disulfide.

These Pu sorption studies will be used to develop thermochemically based surface complexation models as discussed above for the Eu(III)-hematite system. The surface complexation constants will be used to predict sorption of Pu to sediments from the Savannah River Site and the Hanford Site. Experiments quantifying sorption of Th(IV), Pu(IV), Pu(V), and Np(V) have been completed. Based on differences between systems with initially Np(V) and Pu(V), both sediments appear to facilitate surface mediated reduction of Pu(V) to Pu(IV).