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

ABSTRACT: The overarching objective of this work is to examine Pu(IV) and Pu(V) sorption to pure metal (oxyhydr)oxide minerals and sediments using variable temperature batch sorption, X-ray absorption spectroscopy, electron microscopy, and quantum-mechanical and empirical-potential calculations. The data will be compiled into a self-consistent surface complexation model. The novelty of this effort lies largely in the manner in which the information from these measurements and calculations will be combined into a model that will be used to evaluate the thermodynamics of Pu sorption reactions as well as to predict sorption of Pu to sediments from DOE sites using a component additivity approach. This study has demonstrated that sorption of Pu cannot be simply described by interactions between a single oxidation state. Rather the complex, redox sensitive nature of Pu must be fully constrained in order to obtain a sorption model which accurately predicts the observed species. This presentation will focus on the progress made in the past year examining 1) quantification of actinide sorption enthalpies, 2) examination of the mechanisms underlying surface mediated redox reactions, and 3) aging of Pu surface complexes resulting in irreversible or hysteretic sorption.

Quantification of actinide sorption enthalpies: The sorption of Eu(III), Np(V), Pu(IV), and Pu(V) to the iron oxide minerals hematite and goethite has been examined as a function of temperature. Quantifying the sorption constants allows for evaluation of the sorption enthalpy and entropy through the use of a van't Hoff plot. Both Eu(III) sorption to hematite and Pu(IV) sorption to goethite had positive enthalpy values and entropy values. These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. The entropy of Eu(III) and Pu(IV) were 439 ± 26 $J \cdot K^{-1} \cdot mol^{-1}$ and 187 ± 25 $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The higher value for Eu(III) indicates the importance of the loss of at least 5 of the initial 9 hydrating water molecules upon sorption. This loss of water upon sorption and formation of a bidentate surface complex was verified using quantum mechanical modeling, extended x-ray absorption fine structure spectroscopy (EXAFS), and electron microscopy. The surface complexation models generated as part of this task have been used to successfully predict successfully sorption of Np(V) and Pu(IV/V) to Hanford 200 Area sediments.

Examination of surface mediated reduction: Using quantum mechanical modeling and dual isotope batch sorption experiments, a series of experiments has examined the reduction of Pu(V) to Pu(IV) on mineral surfaces. These experiments are vital to understanding the frequent observations of surface mediated Pu(V) reduction on non-redox active mineral surfaces such as quartz (which was verified in this work using X-ray absorption near edge structure spectroscopy, XANES). Dual isotope batch sorption tests using ^{242}Pu and ^{238}Pu demonstrated that processes such as generation of radiolytic byproducts of water and disproportionation of Pu at the surface were unlikely to be the cause of Pu(V) reduction. These results were supported by quantum mechanical modeling which examined the influence of various radiolytic byproducts which were co-adsorbed with Pu.

Aging of Pu surface complexes: Desorption of $^{239/240}$Pu was examined on a subsurface sediment from the Savannah River Site which had been aged 32 years. To compare the aged Pu with "fresh" Pu, ^{242}Pu was

reacted with the aged Pu-contaminated soils for three days. Batch sorption/desorption experiments and selective extractions for total and amorphous iron demonstrated that the reversibility of sorption of Pu decreases significantly with aging time. This may be due to the transfer of Pu from amorphous to crystalline iron phases within the soil matrix or stronger binding of Pu to the solid surface based on the dehydration of the surface complex as described above.