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

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ACCOMPLISHMENTS

What are the major goals of the project?

This university lead SBR project is a collaboration lead by Dr. Brian Powell (Clemson University) with co-principal investigators Dan Kaplan (Savannah River National Laboratory), Yuji Arai (presently at the University of Illinois), Udo Becker (U of Michigan) and Rod Ewing (presently at Stanford University).

Hypothesis: The underlying hypothesis of this work is that strong interactions of plutonium with mineral surfaces are due to formation of inner sphere complexes with a limited number of high-energy surface sites, which results in sorption hysteresis where Pu(IV) is the predominant sorbed oxidation state. The energetic favorability of the Pu(IV) surface complex 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.

Objectives: 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 the information from these measurements and calculations will be combined into a model that will be used to evaluate the thermodynamics of plutonium sorption reactions as well as predict sorption of plutonium to sediments from DOE sites using a component additivity approach.

Project Organization: The project was originally organized around the first three tasks listed below. Then in 2014 when the original phase of the project was ending, a renewal request was sent to DOE program managers requesting an additional $50,000 to evaluate the behavior of Pu in a series of field lysimeter experiments. These were unique, time sensitive experiments so obtaining this renewal was critical for the long term experimental plan of the lysimeter facility and enabled our team to recover several lysimeters containing various Pu sources after 3 to 4 years of exposure in the field. The addition of a field component to this work enabled our team to apply the conceptual and quantitative models from the laboratory studies to field scale data.

Task 1: Mechanistic Description of Plutonium Sorption in Binary Plutonium-Mineral and Pu-Sediment Systems
Task 2: Computational Modeling of Actinide Sorption,
Task 3: Effects of Redox Reactions and Ligand Complexation on Plutonium Desorption
Task 4: Characterization of Plutonium Behavior in Field Lysimeter Experiments (Task added in 2014)

What was accomplished under these goals?

Key Task 1 Project Results:

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. Sorption of Eu(III), Th(IV), and Pu(IV) all increase with increasing temperature and have positive enthalpy values and entropy values. Thus the enthalpy is thermochemically unfavorable and the reactions are driven by the positive

entropy term. These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. Our recently published paper has combined surface complexation modeling, quantum mechanical modeling, x-ray absorption spectroscopy, and electron microscopy to produce a mechanistically based self-consistent model of Eu(III) sorption to hematite [1]. The data indicate the entropy of Eu(III) sorption was 439 ± 26 $J \cdot K^{-1} \cdot mol^{-1}$ and and that the coordination number for Eu(III) decreased from 9 to 5 upon sorption. Assuming a bidentate surface complex based on the XAS and QM data, this result indicates the loss of 5 of the initial 9 hydrating water molecules. These results and those from similar studies with Pu(IV), Th(IV), and Np(V) are indicating that our experimental hypothesis is correct.

We have generated surface complexation models of Pu and Np sorption to SRS and Hanford sediments based on the batch sorption data. Examples of these model fits are shown in Figure 2 [2]. Neptunium sorption to SRS soil can be predicted assuming only interactions with iron phases but aluminosilicate and iron phases were required to predict Np and Pu sorption to Hanford 200 Area sediments.

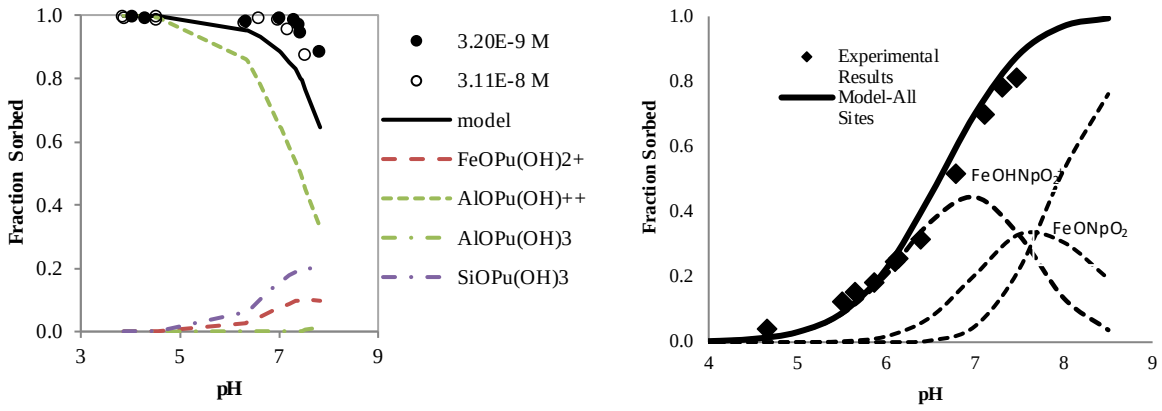

Figure 1: Component additivity surface complexation models of (left) Pu sorption to Hanford 200 area soil and (right) Np sorption to SRS soil. Two papers describing these results are currently in draft form.

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 [3]. 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 edges 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 that were co-adsorbed with Pu. We also recently published a paper demonstrating the influence of these surface mediated reduction reactions on Pu transport through SRS soils [4]. These data are currently being modeled using our surface complexation model.

The influence of Pu concentration on the reduction of Pu(V) on hematite was also examined [5]. Changes in aqueous- and solid-phase plutonium oxidation state were monitored as a function

of time and plutonium concentration in hematite (α-Fe_2O_3) suspensions containing initially Pu(V). Batch kinetic experiments were conducted at plutonium concentrations between 10^{-8} and 10^{-6} M at pH 5 and 0.3 g/L (9.3 m^2/L) hematite. Surface-mediated reduction of Pu(V) was observed under all conditions studied. However, differences in the reaction kinetics demonstrate that the mechanism of Pu(V) reduction changes as a function of plutonium concentration. Adsorption of Pu(V) was found to be the rate-limiting step at plutonium concentrations less than approximately 10^{-7} M Pu(V). Plutonium reduction in these systems was attributed to trace amounts of Fe(II) in the hematite structure. Reduction of Pu(V) was found to be the rate-limiting step at concentrations higher than approximately 10^{-6} M Pu(V) and is attributed to the formation of PuO_{2+x}•nH_2O nanoparticles and the Nernstian favorability of Pu(IV) surface complexes. The reaction order with respect to plutonium concentration was found to be -0.68 ± 0.09, indicating that there is a concentration dependence in these systems. This work strongly suggests that the kinetics of experiments carried out under high plutonium concentrations (*i.e.*, > 10^{-7} M Pu) cannot be directly extrapolated to environmental concentrations of plutonium.

Finally, a series of x-ray absorption spectroscopy measurements using multiple initial Pu oxidation states was performed. XANES data collected on mineral phases reacted with Pu(III), Pu(IV), Pu(V,VI), and Pu(VI) indicated that Pu(IV) is always the dominant oxidation state on the hematite and quartz surfaces, except after reaction with Pu(III). Plutonium precipitates were observed in all quartz samples, regardless of initial oxidation state, whereas, in the hematite samples, Pu precipitates were only observed after reaction with Pu(III), despite all reaction systems being oversaturated with respect to Pu(IV). Combined, the data suggest that Pu(IV) is the thermodynamically favored oxidation state in the presence of hematite and quartz, and that, under these experimental conditions, hematite may hinder Pu colloid formation. For plutonium, this has significant implications for environmental remediation, disposal of plutonium-bearing legacy wastes, and development of new solid phase-based actinide separations processes. A manuscript describing these data is in preparation and plans are to submit the manuscript to Geochimica et Cosmochimica Acta.

Key Task 2 Project Results

Computational modeling studies were completed to examine key processes which could either be compared directly with experimental data or for system for which experimental data could not be collected. For example, in our earlier study of Eu(III) sorption of hematite, computational modeling supported the finding of a bidentate surface complex with partial dehydration of the Eu(III) ion [1].

<u>PuO_2 colloid interactions with goethite:</u> The aim of this study is to elucidate how goethite influences the structure and energetics of sorbed Pu oxide as well as provide insight into the process by which Pu is sorbed at the goethite surface through using molecular-scale models. This may explain why experimental studies have indicated rare *bcc, Ia-3* Pu_4O_7 nanocolloids sorbed onto goethite (*Pnma,* α-FeOOH), rather than *fcc* PuO_2. *b initio* calculations conducted on bulk PuO_{2-x} phases demonstrate that the transformation of the bulk *fcc* PuO_2 to bulk PuO_{2-x} phases, such as a *bcc* Pu_2O_3, is thermodynamically unfavorable. The *bcc, Ia-3* Pu_4O_7 phase is 3.3 eV less favorable than the *fcc* PuO_2 phase in an oxygen-containing environment; the energetics associated with the transformation of *fcc* PuO_2 to a *bcc* phase is heavily influenced by the removal of O atoms. However, the distortion on the goethite surface and the gain in interfacial energy make the formation of hypostoichiometric PuO_{2-x} more thermodynamically feasible.

Empirical forcefield methods on a simple cubic model indicate that a lattice mismatch of <10% lead to a maximum adsorbate size of about 5 nm, in agreement with the experimental adsorbate size. This study was published in Radiochimica Acta.

An ab initio study of the adsorption of Eu^{3+}, Pu^{3+}, Am^{3+}, and Cm^{3+} complexes on hematite (001) surface: Role of magnetism on adsorption: Inner-sphere complexes of Eu^{3+}, Pu^{3+}, Am^{3+}, and Cm^{3+} adsorbed to the antiferromagnetic and ferromagnetic hematite (001) surface were modeled by using DFT (GGA + U) calculations in order to compare the spin configuration, atomic and electronic structures, and adsorption energies between the trivalent actinide analogue Eu^{3+} and the corresponding actinides An^{3+}. Eu^{3+} forms a tridentate-binuclear surface complex on hematite with a Eu-Fe distance of 3.4 to 3.8 Å. Adsorption of Eu^{3+} on the ferromagnetic hematite surface is energetically more favorable than on the antiferromagnetic surface, while the opposite is the case for all actinides An^{3+}. When retaining a similar adsorption configuration (e.g., coordination number = 6), An^{3+} cations are adsorbed ~0.2 Å closer to the surface compared to Eu^{3+}. Partial density of states analysis indicates the ionic bond properties of the Eu-$O_{surface}$ and An-$O_{surface}$ bonds. An increasing number of bands above the Fermi energy were found when Eu^{3+} and An^{3+} were adsorbed to the ferromagnetic surface but not on the antiferromagnetic surface, indicating the ferromagnetic substrate becomes more semiconducting upon the adsorption of these cations. The differences in the spin configurations of the hematite surfaces and the adsorbed cations have a weak but distinct influence on the adsorption energy. Although the antiferromagnetic spin configuration of hematite is dominant in nature, metastable ferromagnetic domains on hematite may influence the energetics of cation adsorption.

Theoretical study of PuO_2^+ redox reactions with radiolysis products of plutonium such as hydrogen peroxide: This study (in progress) addresses questions such as: What is the thermodynamics and activation energy of dehydration, outer to inner sphere conversion, electron and spin transfer when plutonyl reacts with radiolysis products of plutonium or typical environmental reductants. In addition, it describes what the electron and spin-density pathways are from a reductant to the plutonyl, especially if they are catalyzed by semiconducting minerals such as the goethite or insulators such as quartz. Solution calculations indicate reduction of Pu(V/VI) in the presence of H_2O_2 and OH radical is unlikely to occur; calculations indicate H_2S and Fe^{2+} are unlikely to participate in redox reactions with Pu(V) and Pu(VI) in solution. Calculations of PuO_2^+ sorption to the goethite surface indicate energetic favorability of a sorbed surface product, with a ΔE of -8.11 eV. These calculations show a net spin transfer from goethite iron to the plutonium, reducing it to the 4+ state; this is more favorable in the presence of Fe^{2+}, unfavorable in the presence of H_2S or radiolysis products H_2O_2 or OH radical. Calculations on the quartz surface do not exhibit change in plutonyl spin density, although energetic favorability of a sorbed surface product is predicted. This calculation confirms the thermodynamic favorability of a sorbed plutonium species on quartz, and further supports the suggestion that reduction of Pu to the 4+ state requires a substrate or surface (Sanchez, 1985, Hixon et al, 2013).

Key Task 3 Project Results

Aging of plutonium surface complexes: Desorption of ^{239}Pu was examined on a subsurface sediment from the Savannah River Site which had been aged 32 years. To compare the aged

plutonium with "fresh" plutonium, ^{242}Pu was added as a tracer to the aged Pu-contaminated soils. Batch sorption/desorption experiments and selective extractions demonstrated that sorption of plutonium increases significantly with aging time. This may be due to the transfer of plutonium from amorphous to crystalline iron phases within the soil matrix or stronger binding of plutonium to the solid surface based on the dehydration of the surface complex as described above. A manuscript describing these results is in preparation and will be submitted to Environmental Science and Technology.

Key Task 4 Project Results

Analysis of Field Lysimeter Samples: The United States Department of Energy (DOE) Savannah River Site (SRS), in collaboration with Clemson University scientists, is conducting field lysimeter experiments at the meso-scale dealing with the long-term fate and transport of radionuclides in the vadose zone. In this experiment, radionuclides are buried in 61 cm long x 10 cm diameter lysimeters packed with soil from the SRS and remain open to precipitation in order to mimic the conditions of the vadose zone. Effluent is collected from the lysimeters quarterly to provide a measure of radionuclide transport. Several Pu lysimeter sources were placed in triplicate to allow for destructive analysis of the source material and concentration profile within the soil after 2, 4, and 10 years. Several sources of Pu in varying oxidation states have been placed in lysimeters for these experiments. The results from destructive coring of the two-year Pu lysimeters are compared here with results from a previous set of Pu field lysimeter experiments conducted under similar conditions with 11 years in the field in the 1980's. In these experiments, soil is digested in concentrated HNO_3 and the liquid phase is analyzed by LSC for total alpha activity ($^{239/240}Pu$). Select samples were also analyzed by alpha spectroscopy to confirm that $^{239/240}Pu$ were the major alpha emissions in the samples. These two sets of experiments include various sources of Pu initially in the III, IV, V and VI oxidation states. The transport observed with variable oxidation states between the two sets of experiments qualitatively correlates with the theoretical expectations, IV < VI < III < V. After two years little transport of Pu(V) has been observed and greater than 99% of the Pu appears to have remained within the source. There was increased downward migration of the $Pu^{V}O_2(NH_4)(CO_3)(s)$ 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: (1) enhanced reduction of Pu in the presence of organic matter leading to increased sorption to minerals or (2) complexation of Pu with organic matter bound to 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.

Characterization of sediments associated with the Pu-doped lysimeter coupons: This project has examined the Pu sources deployed in the SRS RadFLEx facility. The lysimeters were deployed in 2012 and of the 48 lysimeters, 18 have Pu sources containing $Pu_2^{III}(C_2O_4)_3(s)$, $Pu^{IV}(C_2O_4)_2(s)$, $Pu^{IV}O_2$ nanocolloids and $NH_4Pu^{V}O_2CO_3(s)$. The source consists of a ~2 mg of a

solid sample placed between two glass fiber filters. Triplicate lysimeters for each of these sources are currently in the field with plans to remove them at three time intervals over the next 10 years. Additionally, a set of plutonium sources was archived in an inert atmosphere under controlled temperature and moisture laboratory conditions. These archived sources are designed to provide a comparison for evaluating the impact of environmental conditions on plutonium oxidation state transformations. In November 2014, two lysimeters containing $NH_4Pu^{V}O_2CO_3(s)$ sources (one with and without organic matter amendments) were removed from the field and analyzed. To date, the characterization has been performed using X-ray absorption spectroscopy (XAS) for 3 archived sources ($Pu^{IV}(C_2O_4)_2(s)$, $Pu^{IV}O_2$ nanocolloids and $NH_4Pu^{V}O_2CO_3(s)$) and 2 sources exposed in lysimeters ($NH_4PuO_2CO_3$ with and without organic matter respectively).

Even after storage in an inert atmosphere changes in the $Pu^{IV}(C_2O_4)_2(s)$ and $NH_4Pu^{V}O_2CO_3(s)$ sources were observed. Pu(IV)-oxalate is known to be susceptible to decomposition by alpha radiation with a half time of 64 days. However, nothing has been reported reagarding the stability of $NH_4PuO_2CO_3(s)$. The EXAFS spectra of $NH_4PuO_2CO_3(s)$ indicated that more than one species is present, including approximately 70% PuO_2. This same source, after exposure in the field lysimeter for 2.5 years with and without presence of organic matter, is mainly composed of PuO_2 (Table 1). However, there are notable differences in structure, mainly a shorting Pu-O distance in the sample containing no ameded OM. Moreover, linear combination fitting of the XANES spectra indicated >90% PuO2 in the OM amended lysimeter source which was higher than the OM free source. However, it is noteworthy that layering of the soil amended with organic matter could have had significant influence on the flow of water through the source. Potential artifacts from this are being examined. In order to evaluate and demonstrate the impact of the soil (with and without OM) on the source, a new $NH_4PuO_2CO_3(s)$ source will be synthesized. The degradation of this source will be followed over the time with and without the presence of the soil to determine if the soil accelerates the formation of PuO_2. Regarding the PuO2(s) nanocolloid source, the EXAFS results are consistent with previously observed colloidal particles with slightly shorter Pu-O and Pu-Pu distance compared to bulk PuO_2. (*Ekberg et al., Dalton transactions,2013).* In order to obtain more information, the morphology of plutonium particles in sources will be examined using TEM. Indeed, the distances are very similar for Lys41 and Pu(IV) colloids.

Table 1: EXAFS data on plutonium in sources archived and exposed in lysimeter (in green) compared with literature data.

	Pu-O	Pu…Pu
PuO_2	*7* O at 2.34 Å	9 Pu at 3.82 Å
Pu colloidal particles	8 O at 2.294 Å	3.9 Pu at 3.793 Å
Pu(IV) colloids	8 O at **2.30** Å σ^2 = 0.0123 Å^2	3.9 Pu at **3.77** Å σ^2 = 0.0048 Å^2
Lys22 : $NH_4Pu(CO_3)$ with OM	8 O at **2.31** Å σ^2 = 0.0086 Å^2	4.6 Pu at **3.81** Å σ^2 =0.0036 Å^2
Lys41 : $NH_4Pu(CO_3)$	8 O at **2.30** Å σ^2 = 0.0118 Å^2	4.0 Pu at **3.77** Å σ^2 =0.0043 Å^2

Desorption experiments using sediments from field lysimeters: Desorption experiments were conducted on soils which were in contact with the $NH_4PuO_2CO_3(s)$ sources (with and without OM amendment in the soil) after 2.5 years in the field. Three desorption periods of 3, 14 and 60 days

under aerobic and anaerobic conditions were performed in 10 mM NaCl. Select samples were also filtered (30k MWCO) to evaluate the potential impact of colloidal particles. Results obtained for one replica, after 3 and 14 days, in aerobic conditions are shown in Figure 2. Under anaerobic conditions, plutonium concentration in the aqueous phase is often below detection limits; Thus, oxidation of Pu(IV) to Pu(V) could be a controlling factor in the desorption of Pu. The data in Figure 2 have K_d values similar to our previous work and there appears to be a significant difference between 3 and 14 days. Desorption rate constants and potential aging effects will be examined in the coming months.

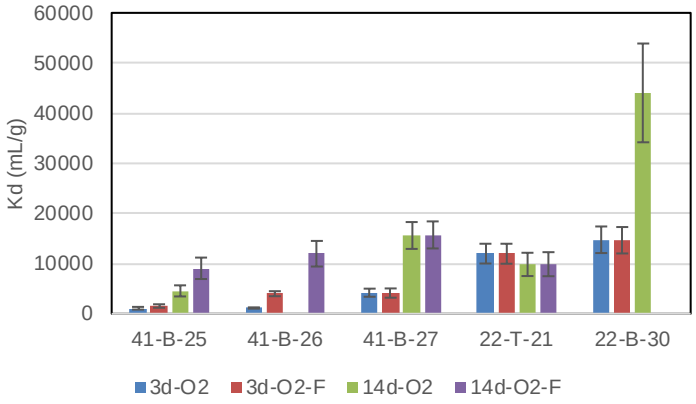

Figure 2: Desorption Kds (mL/g) for 239/240Pu for 3 day (blue), 3 day after filtration (orange), 14 day (gray) and 14 day after filtration (yellow) desorption experiments, in the presence of 10 mM ionic strength NaCl in oxygenated conditions. 41 = lysimeter 41 without OM amendment. 22= lysimeter 22 with OM amendment.

Savannah River Site: field lysimeter experiment: Currently the effluent at the RadFLEx facility, SRS, is being measured for Pu by using ICP-MS with a limit of detection of ~10^{-13} M. This is significantly higher than the groundwater Pu concentrations observed at field sites such as the NNSS. Therefore, we have begun sampling the effluent using a low-level technique which concentrates Pu from a larger initial sample volume and uses long alpha spectroscopy count times to measure the concentration. In a full suite of samples from lysimeters containing $Pu_2(C_2O_4)_3$, $Pu(C_2O_4)_2$, PuO_2, and $PuO_2NH_4CO_3$ sources, the range of measured Pu concentraions in the effluent is 3.3 x 10^{-15} to 9.0 x 10^{-13} M. These values are near solubility limits for Pu(IV). These measurements demonstrate that our method is capable of detecting these low levels of Pu and that more advanced methods such as MC-ICPMS and CAMS are needed only for select samples to test a particular hypothesis.

What opportunities for training and professional development has the project provided?

There were 10 graduate students and one postdoc involved over the course of the project. Each of these students is gaining an invaluable experience of working on a large multidisciplinary project. These students and postdocs come from a wide range of disciplines and all are leveraging their particular area of expertise to the study of radioactive waste disposal and gaining hands-on experience in the safe handling of radioisotopes. This is a critical need for the scientific community given the significant decreases in researchers with experience handling radioisotopes.

How have the results been disseminated to communities of interest?

We have published nine peer-reviewed journal manuscripts and one book chapter to date and have another four manuscripts in preparation. Each of these are listed in the "Products" section of this report.

What do you plan to do during the next reporting period to accomplish the goals?

This project has ended so there will be no activities in the next period.

PRODUCTS:

Publications

Published:

Taylor, S., Powell, B. A., Becker, U., "Influence of the goethite (a-FeOOH) surface on the stability of distorted fcc PuO_2 and PuO_{2-x} phases" *Radiochimica Acta,* 102(12), 821-841, 2016.

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Hixon, A. E., Hu, Y., Kaplan, D. I., Kukkadapu, R. K., Nitsche, H., Qafoku, O., Powell, B. A., "Influence of Iron Redox Transformations on Plutonium Sorption to Sediments" *Radiochimica Acta*, 98, 685-692, 2010.

In Preparation:

Estes, S. E., Hixon, A. E., Arai, Y., Conradson, S., Powell, B. A., "Spectroscopic Evidence of Pu(IV) Favorability on the Surfaces of Hematite and Quartz", In Preparation, To be submitted to *Geochimica et Cosmochimica Acta,* 2016

Yuan, K., Taylor, S. D., Powell, B. A., Becker, U., "An ab initio study of the adsorption of Eu^{3+}, Pu^{3+}, Am^{3+}, and Cm^{3+} complexes on hematite (001) surface: Role of magnetism on adsorption" In Preparation, To be submitted to *Radiochimica Acta,* 2016

Miller, T. Kaplan, D. I., Powell, B. A., "Surface component additivity modeling of neptunium sorption to Savannah River Site Sediments", In Preparation, To be submitted to *Geochimica et Cosmochimica Acta,* 2016

Emerson, H. P. and Powell, B. A., "Examination of the Effects of Aging on Desorption and Sorption of Plutonium from 32-year-old Plutonium Contaminated Sediments Using Multiple Isotopes", In Preparation, To be submitted to *Environmental Science and Technology,* 2016

Intellectual Property

No intellectual property has been developed on this project.

Technologies or Techniques

None

Other Products

None

PERSONNEL AND COLLABORATIONS

Project Personnel

All graduate students and postdocs involved with this work have been at Clemson University and University of Michigan. At the start of this project Brian Powell and Yuji Arai were both at Clemson and Rod Ewing and Udo Becker were at University of Michigan. However, during the renewal phase Yuji Arai transferred to University of Illinois Urbana-Champagne and Rod Ewing transferred to Stanford University.

Clemson University

Hilary Emerson - Graduate Student
Amy Hixon - Graduate Student
Sarah Herr – Graduate Student
Shanna Estes – Graduate Student
Kathryn Peruski – Graduate Student
Rachel Pope – Graduate Student
Erin Black – Graduate Student
Melody Maloubier – Postdoc

University of Michigan

Evan Killeen - Graduate Student
Ke Yuan - Graduate Student
Sandra Fernando - Graduate Student

IMPACT

What is the impact on the development of the principal discipline(s) of the project?

Through this project, we have developed self-consistent models of Pu sorption to mineral phases. These models are based on a thermochemical framework and the chemical reactions describing the sorption process are based upon species identified using spectroscopic and computational modeling techniques. Overall the work has demonstrated that strong association of Pu with mineral surfaces is energetically favorable and likely driven by the dehydration of both the Pu ion and the mineral surface upon sorption. This increased understanding of Pu sorption can help to explain observations of far-field transport of Pu at locations such as the Nevada National Security Site.

What is the impact on other disciplines?

This is a very broad scoping project and covers a wide range of disciplines already. So it is difficult to assess what impact, if any, we may be having on discipline outside our range.

What is the impact on the development of human resources?

As discussed above, we have had 10 graduate students and one postdoc involved with this project. All are gaining experience working on a large multidisciplinary team of researchers as well as gaining experience with the safe use of radionuclides. Thus, we are producing a team of scientists with expertise in expertise in geochemistry, radiochemistry, environmental science, hydrogeology, and computational modeling.

What is the impact on physical, institutional, and information resources that form infrastructure?

None

What is the impact on technology transfer?

None. No invention disclosures were submitted as part of this project.

What is the impact on society beyond science and technology?

This is a basic science proposal and we have no methods or metrics implemented in our work to make any statement regarding the impact of this work on society.

CHANGES-PROBLEMS

Actual or anticipated problems or delays and actions or plans to resolve them

Nothing to report at this time.

Changes in approach and reasons for change

Nothing to report at this time.

Changes that have a significant impact on expenditures

Nothing to report at this time.

Significant changes in use or care of human subjects, vertebrate animals, and/or biohazards

Nothing to report at this time.

Change of primary performance site location from that originally proposed

Nothing to report at this time.

BUDGET

The budget has been completely expended at this point in time.

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