The objective of the LLNL SFA Thrust 1 is the further development of a mechanistic understanding of the dominant processes controlling actinide migration in the environment. The research is primarily focused on plutonium. However, we have expanded some of the research to include Np so as to exploit the similarities and differences between these actinides and develop a deeper understanding of their behavior in the environment.

The overarching hypothesis for Thrust 1 is:

> Hypothesis: *The biogeochemical mechanisms controlling* ***redox transformations of actinides and their stabilization*** *as aqueous complexes, binary surface complexes, ternary surface complexes, precipitates, and co-precipitates will determine actinide migration in the environment.*

In order to test our hypothesis, we have divided this thrust into the following 6 focus areas:

A. *Identifying the Mechanisms Driving Surface-Mediated Reduction of Pu and Np*
B. *The Effect of Natural Organic Matter on Pu and Np Redox Transformations and Sorption Reactions*
C. *Characterizing the Structural and Chemical Behavior of Pu Nanocolloids*
D. *Probing the Role of Microbes in Manipulating Pu Behavior*
E. *Simulating the Molecular-Level Behavior of f-Elements*
F. *Characterizing Molecular Level Actinide Complexes and Redox Transformations*

In this presentation, we examine how natural organic matter affects the sorption behavior and reduction of Pu(V). First, we describe the role of extracellular polymeric substances in the reduction of Pu(V), the subsequent sorption of Pu as Pu(IV), and the inhibition of Pu(IV) intrinsic colloid formation as a result of Pu-EPS complexation. Second, the role of hydroxamate functional groups, prevalent in siderophore compounds, as reducing agents as well as Pu complexants is explored through a combination of UV-Vis spectroscopy and GC-MS characterization of hydroxamate hydrolysis rates and hydrolysis products. These experiments represent the start of a comprehensive investigation into the natural organic matter functional groups that control Pu redox transformations and complexation in the environment.

The objective of LLNL's SFA is to *identify and quantify the biogeochemical processes that control the fate and transport of actinides in the environment*. The research approach of our Science Plan is to combine (1) **Fundamental Mechanistic Studies** that identify and quantify biogeochemical processes that control actinide behavior in solution and on solids, (2) **Field Integration Studies** that investigate the transport characteristics of Pu and test our conceptual understanding of actinide transport, and (3) **Actinide Research Capabilities** that allow us to achieve the objectives of this SFA and provide new opportunities for advancing actinide environmental chemistry.

Research Thrusts 1 and 2 are guided by broad central hypotheses:

> *Thrust 1 Hypothesis: The biogeochemical mechanisms controlling* ***redox transformations of actinides and their stabilization*** *as aqueous complexes, binary surface complexes, ternary surface complexes, precipitates, and co-precipitates will determine actinide migration in the environment.*
>
> *Thrust 2 Hypothesis: The biogeochemical processes that ultimately control actinide subsurface mobility/immobility are driven by local variations in the geology, geochemical conditions, colloid composition and abundance, and* ***chemical characteristics of the initial actinide source****.*

Research Thrust 3 is not hypothesis driven. Instead, it is guided by the research efforts and capability development needs described in Research Thrusts 1 and 2.

Detailed descriptions of the Research Thrusts and associated Focus Areas will be presented in the poster. The new structure of our LLNL's SFA Science Plan reflects the research progress that we have made since the FY12 SFA review and an increased focus on Field Studies and Actinide Research Capabilities that we have chosen to implement in this Science Plan. Since its inception in FY10, our SFA research has made significant progress in identifying the mechanistic processes governing Pu sorption, desorption, complexation, redox transformations, precipitation, and the associated rates of reaction. While our mechanistic understanding of processes controlling Pu transport is far from complete, there is a compelling need to begin evaluating our conceptual and mechanistic understanding from the perspective of remediation and long-term stewardship of legacy sites. This is the focus of Research Thrust 2. The development of new Actinide Research Capabilities stems from our substantial investment in applying unique spectroscopic and numerical approaches to actinide environmental chemistry. These capabilities have led to a number of collaborations with the broader international actinide environmental science community. The intent is to develop these capabilities to achieve the scientific objectives of our SFA and provide unique research capabilities to the broader scientific community.

Our SFA is focused on improving our conceptual understanding of actinide transport in the environment by integrating molecular-scale and field scale observations. The intended goal is to provide the scientific basis for remediation and long-term stewardship of DOE's legacy sites and, more broadly, increase our understanding of and enable predictive control of phenomena in environmental systems sciences.

The success of our program relies on the development and use of state-of-the-art spectroscopic and computational capabilities that are unique to LLNL. Development of these spectroscopic and computational capabilities is intended to benefit the scientific community as a whole. Our intent is for our SFA to be a hub for world-class, U.S. and international radiochemistry research and education. The LLNL SFA has already led to a number of synergistic activities that take advantage of LLNL's unique capabilities and staff. They include i) the development of ultra-trace Np measurements to resolve NNSA-EM contamination questions at the NNSS (formerly NTS), ii) applying NMR and TEM capabilities to actinide separations (collaboration with the former H. Nitsche group), iii) applying Pu TEM capabilities to Nuclear Energy, Used Fuel Disposition, iv) development of NanoSIMS techniques for actinide detection at nanometer spatial scales and sub ppm levels of contamination, v) unprecedented femtomolar detection of Pu using the accelerator mass spectrometry facility at CAMS, and vi) providing LLNL's unique capabilities to visiting students and collaborators.

Research Thrust 3 of the LLNL SFA is focused on the development of state-of-the-art actinide research capabilities that are essential to the success of our SFA Science Program and provide new opportunities for the broader actinide and environmental systems science communities. We have highlighted five capabilities:

A. *NMR and EPR of Actinide Complexes*
B. *NanoSIMS of Actinides*
C. *Actinide TEM-EELS*
D. *Actinide Analysis at the Center for Accelerator Mass Spectrometry (CAMS)*
E. *f-Element Ab Initio Modeling*

In this presentation, we will highlight the progress made to date in Ab Initio modeling of Pu hydrolysis and water coordination for Pu(OH)x (x=1-4) and development of Auxiliary Field Quantum Monte Carlo (AFQMC) for the accurate calculation of redox potentials of aqueous actinide ions. In addition, we describe recent efforts to examine ligand exchange rates and mechanisms for a number of Np(VI) species.

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