FINAL PROJECT SUMMARY REPORT

<u>Project title:</u> Understanding the Subsurface Reactive Transport of Transuranic Contaminants at DOE Sites

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Research Objectives

Our primary hypothesis is that actinides can interact with surfaces in fundamentally different ways than other metals, metalloids, and oxyanions and that this fundamental difference requires new approaches to studying and modeling transuranic sorption to minerals and geomedia. This project supports a key mission of the SBR program to develop sufficient scientific understanding such that DOE sites will be able to incorporate coupled physical, chemical, and biological processes into decision making for environmental management and long-term stewardship, while also supporting DOE's commitment to education, training, and collaboration with DOE user facilities.

The Project Team

Overall, the project has supported fifteen researchers. At Auburn, the project, in part, supported the work of one faculty member, one Ph.D. student, and three M.S. students. At Yale the project, in part, supported one faculty member and one postdoctoral research associate. At Notre Dame, the project, in part, supported one faculty, one postdoctoral research associate, and three Ph.D. students. At LBNL the project, in part, supported one senior scientist, one scientific engineering associate, and one postdoctoral research associate. The project, so far, has resulted in eight peer-reviewed journal articles (with approximately seven more anticipated), one published technical report, four Ph.D. dissertations, three M.S. theses, and several posters and presentations. Many of the postdoctoral, Ph.D., and M.S. students supported by this research have gone onto permanent positions in academia, DOE facilities, and the cleanup industry.

Summary of Research Outcomes

The sections below provides a brief summary of various accomplished made in this project. For more technical details, please refer to the cited journal publications related to the work.

1. Processing of nuclear fuels and materials has resulted in groundwater contamination by radionuclides. These actinide-contaminated waters may threaten human health upon entry into drinking-water aquifers or surface-water bodies. We systematically studied the dissolution, reduction and transport of uranium and transuranium elements in geological media.

Dissolution of actinide-bearing minerals is a source for radionuclides in groundwaters and the stability of synthetic crystals substantially influences their application to sequestrate and recycle actinides. We investigated the dissolution kinetics of two uranyl borates and one plutonyl borate,

 $UO_2B_2O_4$ (UBO), Na[(UO₂)B₆O₁₀(OH)]·2H₂O (NaUBO), and PuO₂[B₈O₁₁(OH)₄] (PuBO), with three different ligands, i.e., bicarbonate, phosphate, and natural humic acid (HA) (Yang et al., 2013a). These actinide borates were chosen because they possess different topologies that may influence dissolution. In the presence of bicarbonate, the apparent steady-state concentration of dissolved U(VI) and surface area-normalized dissolution rates were much higher for UBO compared to NaUBO. Uranyl phosphate, most likely in the form of (UO₂)₃(PO₄)₂(H₂O)₄, was precipitated on the surface of residual particles of UBO and NaUBO with phosphate. The dissolution rate of PuBO in NaNO₃ solution was much higher than UBO or NaUBO. This study revealed that actinide borate crystal dissolution was substantially influenced by crystalline structures of actinide borates and aqueous ligands.

We also analyzed the dissolution and reduction of U(VI) in three synthesized uranyl(VI) borate boronate crystals, i.e. $UO_2(CH_3BO_2)(H_2O)$ (UCBO), $UO_2B_2O_4$ (UBO) and and Na[(UO₂)B₆O₁₀(OH)]:2H₂O (NaUBO), by the bacteria Shewanella oneidensis MR-1 (Yang et al., to be submitted). Comparisons between the dissolved U(VI) concentrations for samples with bacteria and without bacteria indicate that MR-1 may be able to facilitate the dissolution of UCBO and UBO. Calculations based on the measurement for the dissolution of crystals imply the bacteria can directly acquire U(VI) within the crystals of UCBO and NaUBO. Laser ablationinductively coupled plasma mass spectrometry (LA-ICP-MS) analysis revealed that the interactions between C/P ligands in biomass and uranyl crystals are important for the dissolution and reduction of U(VI). The present study uncovered that the DMRB S. oneidensis can directly utilize crystalline phase U(VI), and the bioavailability of actinides in crystals are greatly influenced by the crystalline structures. These results are important for evaluating the environmental fate of solid-phase U and remediating the U-contaminated sites.

The fate of dissolved actinides is mainly governed by their association with colloids, and interactions between different types of colloids potentially regulate the kinetic and thermodynamic properties for radionuclides sorption to and desorption from the heterogeneous colloids. The interactions between colloidal metal oxide and HAs decreased the equilibrium partition coefficient of U on mixed colloids of metal oxide and HAs by up to 75%, and also greatly decreased the desorption rate of U from the heterogeneous colloids (Yang et al., 2013b). The influencing extent of interactions between different colloids depended on how the organic matter interacted with metal oxides; specifically, the inner-sphere complexation between metal and carboxyl moieties of HAs strongly inhibited the sorption of actinides. HAs also substantially facilitated both the microbial reduction of aqueous U(VI) and the re-oxidation of U(IV) nanoparticles. Direct measurement for the electronic conductivity of micrometer-scaled HA films revealed that HAs had similar electronic conductivity to those nano-wires produced by the metal-reduction bacteria. Direct electrical conduction by the HA macromolecular can play an important role in the reduction-oxidation recycle of actinides.

Association with colloidal HA may largely regulate the transport of U in geological media. Maximum relative breakthrough concentrations of U(VI) in our column experiments increased from undetectable levels (less than 0.001) in the absence of HAs to 0.17 to 0.54 with HAs (Yang et al., 2012). The strength of the HA effect on U mobility was positively correlated with the NMR-detected content of paraffinic carbon and the hydrophobicity of HAs, which indicates the importance of hydrophobic organic matter in facilitating U transport. Consistently, near-edge X-

ray absorption fine structure (NEXAFS) spectra coupled with scanning transmission X-ray microscopy (STXM) show that bound U was concentrated in micro areas of the HA that were composed of more hydrophobic carbon. Advection-diffusion model simulations for U and HA transport indicate that colloidal HAs played a more important role than dissolved HAs in mobilizing and co-transporting U.

Based on these studies, it is clear that natural organic matters greatly influence the dissolution, sorption-desorption, reduction, and transport of U and transuranium actinides in subsurface environments, and the effects are sensitive to the molecular structure of organic matter. We recommend that remediation of actinide contaminated sites carefully consider the impact of natural organic matter on the fate of radionuclides in the geologic media.

2. Novel crystalline actinide materials can be used to immobilize uranium and transuranium elements at radioactive waste disposal sites. The molten boric acid flux reaction of PuBr₃ with °C results in the formation of large light-yellow crystals of KBO₂ at 200 $K[B_5O_7(OH)_2] \cdot H_2O:Pu^{4+}$. Single crystal X-ray diffraction experiments on the Pu-doped $K[B_5O_7(OH)_2] \cdot H_2O$ demonstrate two features: (1) $K[B_5O_7(OH)_2] \cdot H_2O:Pu^{4+}$ adopts a onedimensional borate chain structure with void spaces between the chains; (2) The doping plutonium atoms do not reside on the potassium sites. The latter are not fully occupied. Both laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectrometer (EDS) analyses indicate that plutonium atoms are uniformly distributed in crystals of K[B₅O₇(OH)₂]·H₂O with an atomic K:Pu ratio of approximately 65:1 measured by LA-ICP-MS. UV-vis-NIR spectra taken from both freshly-made and one-day old crystals show that the plutonium present within the crystals is predominantly characterized by Pu(IV). A small amount of Pu(III) is also present initially, but slowly oxidized to Pu(IV) via interaction with X-ray absorption near-edge structure (XANES) and extended X-ray oxygen in the air. absorption fine structure (EXAFS) spectroscopic measurements confirm that plutonium is mainly present as a form similar to that of a PuO₂ cluster. The combined results suggest that the clusters containing Pu(VI) ions are uniformly distributed in the void spaces between the borate chains.

Neptunium incorporation in the torbernite/meta-torbernite $[Cu(UO_2)_2(PO_4)_2 \bullet nH_2O]$ system has been investigated in this study under both hydrothermal and slow diffusion conditions (at room temperature and 90°C) to examine the role synthetic conditions play on neptunium uptake by uranyl phases and whether hydrothermal incorporation studies feasibly model environmental incorporation. The hydrothermally prepared crystals contained approximately 19±2 and 73±3 times more neptunium on average than crystals grown during slow diffusion at room temperature and elevated temperature, respectively. UV-visible spectroscopy on the mother solution showed that on average 51.53(±0.04)% of the original neptunium(V) remains in solution following hydrothermal synthesis versus 37.24(±0.04)% following slow diffusion at room temperature and 73.62(±0.07)% at 90°C. Additionally, solid-state UV-vis-NIR indicated that the incorporated neptunium was predominantly present in the +6 oxidation state in the hydrothermal samples despite the fact that the initial oxidation state of neptunium in solution was +5 and no oxidizing species were present in the reactions. The oxidation state of neptunium in the slow diffusion samples was not able to be determined due to the low incorporation levels. These results suggest that neptunium(VI) may play a more significant role than previously expected in the environment.

During the solvothermal synthesis of a low-dimensional borate – KB₅O₇(OH)₂•2H₂O – in the presence of Pu(III), single crystals of plutonium dioxide unexpectedly formed. Single crystals of PuO₂ also formed during the hydrothermal synthesis of another borate – Na₂B₅O₈(OH)•2H₂O – in the presence of Pu(III). The reactions were conducted at 170°C and 150°C, respectively, which are much lower temperature than previously reported preparations of crystalline PuO₂. The yellow-green plate crystals were characterized by single crystal X-ray diffraction and solid state UV-Visible-NIR absorption spectroscopy. The crystal structure was solved by direct methods with R₁ = 1.26% for nineteen unique observed reflections. PuO₂ is cubic, space group $Fm\bar{3}m$, and adopts the fluorite structure type. The lattice parameter was determined to be a = 5.421(5)Å giving a volume of 159.3(2)Å³. The absorption spectrum is consistent with Pu(IV).

3. Colloids play an important role in governing the transport of radionuclides in geologic environments. As naturally occurring colloidal suspensions are compositionally heterogeneous, the subsurface fate of radionuclides may be sensitive to interactions among different kinds of colloids. Therefore, we investigated the adsorption equilibrium and desorption kinetics of uranium (U(VI)) in experiments conducted with compositionally homogeneous suspensions of colloidal SiO₂, ZnO, hydrous ferric oxide (HFO) or humic acids (HAs) as well as heterogeneous suspensions consisting of a colloidal metal oxide and HA. We found that the interactions between HAs and ZnO or HFO greatly inhibited the sorption of U onto colloids in the heterogeneous suspensions. HA-ZnO interactions enhanced the desorption of U from the heterogeneous colloidal suspensions, while the association between HA and SiO₂ or HFO inhibited U desorption. Molecular-level characterizations reveal that HFO interacted with HAs by electrostatic interactions, association with aliphatic/aromatic carbon and inner-sphere complexation with carboxyl functional groups, while SiO₂ and ZnO mainly associated with hydrophobic domains of HAs by weak interactions (e.g., van der Waals interactions). The present findings indicate that interactions between HA and metal-oxide colloids can substantially influence the desorption of U(VI) from these particles, thereby potentially affecting the mobility of uranium and transuranium elements in groundwater.

Reduction and oxidation reactions of metals are greatly influenced by natural organic matter (NOM), however, no previous studies have examined electrical conduction through NOM and the role of NOM resistivity in the reduction and oxidation of metals. We measured the electrical resistivity of model NOM (i.e., humic substances (HS)), by making micrometer-scaled HS wires from aqueous-phase HS. Our results indicate that the electrical resistivity of HS wires, which ranged from 0.26 to 26 Ω cm, overlapped with that of bacterial nanowires. These results imply that HS may be effective in conducting electrons between metals and metal-reducing bacteria. Furthermore, we found the fraction of freely-dissolved U(VI) was a key factor for U(VI) reduction, while electrical conduction through HS played an important role in U(IV) oxidation. Our results suggest that electrical conduction through NOM macromolecules may influence aqueous oxidation-reduction reactions and thus be important for the biogeochemical cycles of redox-sensitive metals.

4. The risk stemming from human exposure to actinides via the groundwater track has motivated numerous studies on the transport of radionuclides within geologic environments; however, the effects of waterborne organic matter on radionuclide mobility are still poorly understood. In this

study (Yang et al. 2012), we compared the abilities of three humic acids (HAs) (obtained through sequential extraction of a peat soil) to co-transport hexavalent uranium (U) within watersaturated sand columns. The strength of the HA effect on U mobility was positively correlated with the hydrophobicity of organic matter and NMR-detected content of alkyl carbon, which indicates the possible importance of hydrophobic organic matter in facilitating U transport. Consistently, initial near-edge X-ray absorption fine structure (NEXAFS) spectra collected with a scanning transmission X-ray microscope (STXM) show that U was enriched in micro areas of the HA that were composed of more aliphatic carbon. Such molecular- to column-scale evidence indicates the importance of considering hydrophobic organic matter in associating and co-transporting U. Evaluations of radionuclide transport within subsurface environments should additionally consider the chemical characteristics of waterborne organic substances, especially hydrophobic organic matter. This result has garnered a great deal of interest, especially from scientists involved in studies at the Rifle Site.

The morphology, composition, and heterogeneity of the dried Savannah River Site colloids obtained from soil columns have been examined by soft X-ray spectromicroscopy that is comprised of NEXAFS spectroscopy obtained with ~25 nm spatial resolution obtained by the use of a STXM at the Advanced Light Source. Near-edge spectroscopy measurements were performed at the C K-, O K-, Fe L-, Al K-, and Si K-edge to identify various minerals and organic compounds contained within the colloids. The STXM measurements of the colloidal material, combined with complementary lab-based characterization, are being interpreted to correlate and to understand the observed chemical behavior of the soils (Haliena et al. in preparation). The capabilities of the STXM to probe soil materials was greatly improved by staff on this project.

Both hard X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectra have been collected from a series of sands and clays exposed to U, Np, and Pu. Complementing the determination of the bulk speciation of actinides has been the investigation of the sub-micron speciation of the light element constituents by STXM soft X-ray spectromicroscopy in the same geomaterials. However, the concentration of the actinides in the geomaterials, the failure of the actinides to agglomerate to a sufficient detectable level, and the finite amount of beamtime precludes the direct correlation to the light atom speciation but still provides baseline chemical characterization of the geomaterials (Wang et al. in preparation).

5. We measured the pH-dependent adsorption of Th(IV), an analogue for Pu(IV) and other tetravalent actinides, to two geomedia: goethite (α -FeOOH(s)) and a heterogeneous Fecontaining sand from the southeastern U.S. (Melson et al. 2012) The goal was to examine whether or not the Th(IV)-goethite adsorption data could be used to predict the adsorption of Th(IV) by the heterogeneous sand. In the absence of either geomedia, after forty-eight hours the measured pH-dependent "adsorption" was consistent with the solubility of solid amorphous ThO₂(am, aged), despite the fact that ThO₂(am, aged) is generally not formed until approximately seventy days. We concluded that ThO₂(am, aged) was stabilized by precipitating on the walls of the reaction vessels. Ignoring this phenomenon could lead to experimental artifacts in Th(IV) adsorption studies. Thorium adsorption by both goethite and the sand was strongly pH dependent, with adsorption increasing sharply from pH~2 to pH~4. Two methods were utilized to predict the pH-dependent adsorption of Th(IV) by the sand using the Th(IV)-

goethite adsorption data. Using the Fe content of the sand and the Th(IV)-goethite adsorption data, we were able to predict the maximum amount of Th(IV) adsorption by the sand within 78% of the actual value (i.e., an error of 22%). In contrast, on a surface-area-normalized basis, we were only able to predict the maximum adsorption of Th(IV) by the sand within a factor of two. These results have important implications to scaling and extrapolating the results of batch-scale tetravalent actinide adsorption studies with pure minerals to predict their field-scale adsorption by and transport in heterogeneous subsurface media.

Post-doctoral Fellow

Dr. Yu Yang, Oct 2010-June 2012. He is currently a tenure-track assistant professor at University of Nevada, Reno.

Dr. Stefan Minasian supported in part is now a Project Scientist at LBNL.

Dr. Per-Anders Glans-Suzuki supported in part is now an Associate Beamline Scientist at LBNL.

PhD Dissertations Partly Funded by this Project

Dr. V. A. Loganathan, "An Assessment of U(VI) adsorption at Multiple Scales" Department of Civil Engineering, Auburn University, 2011.

Dr. Shuao Wang, "New Insights in Actinide Borate Chemistry" Civil Engineering and Geological Sciences, University of Notre Dame, 2012.

Dr. Juan Diwu, "Comparison of Transuranium Elements and their Proposed Surrogates" Civil Engineering and Geological Sciences, University of Notre Dame, 2013.

Nathan Meredith, "Incorporation of Neptunium and Plutonium into Subsurface Media" Department of Chemistry and Biochemistry, University of Notre Dame, 2014 (expected).

MS Theses Partly Funded by this Project

N. H. Melson, "Sorption of Thorium onto Subsurface Geomedia" Department of Civil Engineering, Auburn University, 2011.

B. P. Haliena, "Chemical Factors Influencing Colloid Mobilization and Th(IV) Transport through Saturated Subsurface Sediment" Department of Civil Engineering, Auburn University, 2012.

H. Zheng. "The Influence of Colloidal Kaolinite on Th(IV) Transport in Saturated Porous Media" Department of Civil Engineering, Auburn University, 2013.

Submitted/draft journal manuscripts

Yang Y, Wang S, Albrecht-Schmitt TE. Bioavailability of crystalline-phase uranium to the microbial reduction by *Shewanella oneidensis* MR-1. To be submitted to Applied Geochemistry

N. A. Meredith, S. Wang, J. Diwu, T. E. Albrecht-Schmitt, "Two Convenient Low-Temperature Routes to Single Crystals of Plutonium Dioxide," *Journal of Nuclear Materials*, **2013**, *submitted*.

Yang Y., X. Duan, J.E. Saiers and M.O. O. Barnett. Electronic conductivity of humic substances and its impact on uranium oxidation-reduction reactions. Planned Submission to *Geophysical Research Letters*.

Haliena, B., Minasian, S.G., D.K. Shuh, M.O. Barnett, Light atom speciation and correlations in Savannah River soils, to be submitted, draft in preparation.

Wang, S., S.G. Minasian, T. Albrecht-Schmitt, M.O. Barnett, D.K. Shuh, Spatially-resolved light atom and overall actinide speciation in a series of actinide-containing (U, Np, Pu) sands and clays, to be submitted to *Environmental Science & Technology*, draft in preparation.

Glasauer, S., S. Fakra, P. Wielder, T. Tyliszczak, D.K. Shuh, Solid phase transformation of uranium via bacterial reduction, to be submitted to *Environmental Science & Technology*, draft in preparation.

Haliena, B.P., D.K. Shuh, D.I. Kaplan, and M.O. Barnett. "Chemical Factors Influencing Colloid Mobilization and Th(IV) Transport through Saturated Subsurface Sediment." to be submitted to *Environmental Science & Technology*. Draft in preparation.

Published Journal Articles in 2013

Yang, Y., S. Wang, M.J. Polinski, Y. Liu, M.O. Barnett, and T.E. Albrecht-Schmitt (2013a). "Dissolution of uranyl and plutonyl borates: Influences of crystalline structures and aqueous ligands." *Chemical Geology*. **357**: 67-74.

Yang, Y., J.E. Saiers, and M.O. Barnett (2013b). "Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions." *Environmental Science & Technology*. **47**(6): 2661-2669.

N. A. Meredith, M. J. Polinski, J. N. Cross, E. M. Villa, A. Simonetti, T. E. Albrecht-Schmitt, "Synthetic Influences on Neptunium Incorporation in Naturally Occurring Copper Uranyl Phosphates," *Crystal Growth and Design*, **2013**, *13*, 386-392.

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Yang, Y., J. E. Saiers, N. Xu, S. G. Minasian, T. Tyliszczak, S. A. Kozimor, D. K. Shuh, M. O. Barnett (2012). "Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to Column Scale." *Environmental Science & Technology* **46**(11): 5931-5938.

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S. Wang, J. Diwu, A. Simonetti, C. H. Booth, T. E. Albrecht-Schmitt, "Interstitial Incorporation of Plutonium into a Low-Dimensional Potassium Borate," *Environmental Science & Technology*, **2011**, *45*, 9457-9463.

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Posters and Presentations

Yang Y. 2013. New Insights into organic matter-mediated fate of critical pollutants: Important for protecting water resources under global climate change. Department of Civil and Environmental Engineering, *University of Nevada*, Reno, NV, USA

Yang Y. 2013. Heterogeneous organic matter mediated fate of critical pollutants: Reactions and transport. Glenn T. Seaborg Institute, *Lawrence Livermore National Laboratory*, Livermore CA, USA.

Yang Y. 2012. Coupling microscale processes with macroscale migration for actinides: From dissolution and reduction of crystals to column transport. *Gordon Research Seminar Environmental Sciences: Water.* Holderness, NH, USA.

Yang Y. 2012. Coupling microscale processes with macroscale migration for actinides: From dissolution and reduction of crystals to column transport. *Department of Energy-Subsurface Biogeochemical Research (SBR) Contractor-Grantee Workshop*. Washington D.C., USA.

Yang, Y., J.E. Saiers, N. Xu, T. Tyliszczak, D. Shuh, and M.O. Barnett (2011). <u>Impact of Natural Organic Matter on Uranium Transport through Saturated Geologic Materials: From Molecular to Column Scale</u>. American Geophysical Union Fall Meeting, December 5-9, San Francisco, CA.

Yang Y. 2012. Fate of uranium and transuranium actinides in groundwaters: Dissolution, interaction with colloids and transport. *Gordon Research Conference Environmental Sciences: Water*. Holderness, NH, USA.

Yang Y, Saiers JE, Xu N, Shuh DK, Tyliszczak T, Barnett MO. 2011. Impact of natural organic matter on uranium transport through saturated geologic materials: From molecular to column scale. *American Geophysical Union Fall Conference*. San Francisco, CA, USA.

Loganathan, V. A., M. O. Barnett and T. P. Clement (2010). <u>An Assessment of U(VI)</u> <u>Adsorption at Multiple Scales</u>. 239th American Chemical Society Conference, March 21-25, San Francisco, CA.