

## **FY 2006 Annual Report**

### **Environmental Remediation Sciences Program at the Stanford Synchrotron Radiation Laboratory**

**ERSP Project Number 95709**

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#### **1. Objectives**

Synchrotron radiation (SR)-based techniques provide unique capabilities to address scientific issues underpinning environmental remediation science and have emerged as major research tools in this field. The high intensity of SR sources and x-ray photon-in/photon-out detection allow noninvasive *in-situ* analysis of dilute, hydrated, and chemically/structurally complex natural samples. SR x-rays can be focused to beams of micron and sub-micron dimension, which allows the study of microstructures, chemical microgradients, and microenvironments such as in biofilms, pore spaces, and around plant roots, that may control the transformation of contaminants in the environment. The utilization of SR techniques in environmental remediation sciences is often frustrated, however, by an “activation energy barrier”, which is associated with the need to become familiar with an array of data acquisition and analysis techniques, a new technical vocabulary, beam lines, experimental instrumentation, and user facility administrative procedures. Many investigators find it challenging to become sufficiently expert in all of these areas or to maintain their training as techniques evolve. Another challenge is the dearth of facilities for hard x-ray micro-spectroscopy, particularly in the 15 to 23 KeV range, which includes x-ray absorption edges of the priority DOE contaminants Sr, U, Np, Pu, and Tc. Prior to the current program, there were only two (heavily oversubscribed) microprobe facilities in the U.S. that could fully address this energy range (one at each of APS and NSLS); none existed in the Western U.S., in spite of the relatively large number of DOE laboratories in this region.

The goal of this DOE BER ERSP-funded program is to lower access barriers for ERSP users at SSRL by providing expert hands-on scientific and technical support tailored to the needs of ERSP investigators. This objective is accomplished programmatically by funding a scientific staff member at SSRL (Dr. Sam Webb), who provides assistance to ERSP users in the following critical areas: (a) technical advice in writing beam time proposals and planning experiments, (b) training and support in data acquisition at SSRL beam lines and (c) in data analysis procedures, and importantly, (d) development of new software tools for data analysis, with emphasis on environmental studies. Techniques supported by this program include x-ray absorption spectroscopy (XAS), *in-situ* synchrotron x-ray diffraction (SR-XRD), microbeam x-ray fluorescence chemical imaging ( $\mu$ -XRF), and  $\mu$ -XAS/XRD. Another major goal of this program is to develop innovative techniques for environmental remediation sciences. Currently, we are implementing a hard-x-ray microprobe facility at SSRL for  $\mu$ -SXRF/ $\mu$ -XAFS/ $\mu$ -XRD measurements on priority DOE contaminants, with emphasis on the 10 – 23 KeV range. Another important area of innovation has been the development of a program to support user

investigations of the chemical dynamics of reactions (bio-)mineral transformations using *in-situ* SR-XRD. Engineering and management for this project are supported by DOE-BES.

## 2. Progress and Implications

This report summarizes work after year 2 of a 4 year project.

### 2.1 ERSP user support program

*ERSP User Research at SSRL.* At least 17 ERSP-funded projects received direct support from this program in FY 2006. ERSP project numbers for these grants are: 86748, 90163, 94878, 95018, 1021814, 1022978, 1024775, 1025143, 1027601, 1027699, 1027705, 1027869, 1027833, 1027834, 1027837, 1027897, 1027957. These projects were supported at 3 XAS beam lines (BL2-3, 10-2, and 11-2) and 3 x-ray scattering beam lines (2-1, 10-2, and 11-3). ERSP activity at these beam lines is estimated to have been 423 shifts, which represents about 16% of all beam time available to users at these beam lines during FY06. This represents a significant increase over the comparable value from FY 2005 (11%), which was the first full year of this grant, suggesting that this BER-funded project is achieving its primary goal of increasing user access for ERSP researchers.

*Highlights from ERSP-funded user research programs at SSRL.* Two brief selected highlights from ERSP-funded research that has been conducted at SSRL are given here.

***In Situ Biological U(VI) Remediation within a Highly Contaminated Aquifer at the FRC Site*** (M. Ginder-Vogel, W.-M. Wu, S. Fendorf, and C. Criddle, Stanford University; J. Carley and P. Jardine, ORNL). Pilot-scale tests of *in-situ* uranium bioremediation have been conducted at the Y-12 facility (Area 3) at the Oak Ridge, TN, Field Research Center (FRC). This site provides a controlled subsurface environment in which the complex interplay of soil and sediment mineralogy, aqueous geochemistry, microbial activity, and potential U(IV) oxidants can be investigated as they impact U(VI) bioreduction. Over the course of 31 years, millions of gallons of plating wastes containing high concentrations of uranium and nitric acid were generated at this location and discharged into unlined ponds (the S-3 ponds). In 1983, the ponds were capped and converted into a parking lot; however, uranium contamination remains and continues to migrate through subsurface fractures to surface discharge points. Prior to our remediation efforts, the uranium concentration in groundwater at Area 3 was ~210  $\mu\text{M}$ , far in excess of the maximum allowable concentrations defined by the US EPA (0.126  $\mu\text{M}$ ). Sediment samples from the inner treatment zone wells and a sampling well were analyzed using XANES spectroscopy at SSRL Beam Line 11-2. Prior to biostimulation, U(IV) was not detectable in the subsurface of Area 3. Partial reduction of U(IV) was first observed in the inner zone injection well on day 258, and U(IV) continued to accumulate in this well for the duration of the experiment (Wu *et al*, *ES&T* **40**, 3986, 2006). By day 535, U(IV) was present throughout the bioremediation zone. These results demonstrate that microbial activity has produced low dissolved uranium concentrations and high proportions of solid-phase U(IV) throughout the subsurface remediation system. Continued biostimulation has resulted in groundwater uranium concentrations below the US EPA drinking water standards. The long-term goal of this project is to decrease the flux of uranium leaving the site to the point that it is harmless.

***Structural Sequestration of U(VI) in Bacteriogenic Manganese Oxides*** (S.M. Webb, and J.R. Bargar, SSRL; and B. Tebo, OHSU). Manganese oxides are formed in soils and watersheds *via* bacterial catalysis of the oxidation of dissolved Mn(II) to Mn(IV). Bacteriogenic Mn oxides are

among the most aggressive scavengers of metal ions and are known to drive the natural attenuation of heavy metal contaminants such as zinc in acid mine drainage-contaminated watersheds. Interactions of U(VI) with Mn biooxides have not been previously investigated, but are of interest because Mn(II) and Mn-oxidizing bacteria are common in U(VI)-contaminated soils. EXAFS and *in-situ* SR-XRD measurements were performed at SSRL to investigate the molecular-scale mechanisms of U(VI) binding in the presence of actively forming Mn biooxides. These results indicate that at U(VI) concentrations of 1 to 10  $\mu\text{M}$ , U(VI) may be bound within tunnels in bacteriogenic Mn oxides (Webb *et al*, *ES&T* **40**, 771, 2006). These findings are significant in the context of uranium transport in aquifers because structural binding mechanisms provide a relatively high capacity to sorb the contaminant and simultaneously allow for slow release kinetics as compared to other modes of binding such as sorption at particle surfaces. These results indicate that bacteriogenic Mn oxides may be suitable for the long-term stabilization of subsurface U(VI) in *in-situ* engineered remediation technologies.

*Software for Environmental Remediation Science at Synchrotron Sources.* In FY 2006, this grant supported the development of significant new software tools, authored by Dr. Webb, for environmental remediation investigations *at all U.S. synchrotron facilities*. A major new analysis package for microprobe image processing, the Microanalysis Toolkit, was created and released, which allows viewing of image data and sophisticated manipulation and analysis of spectral data, including mathematical and image processing functions, principal component analysis, and linear combination fitting of XANES imaging data. The Toolkit is designed to be very portable and can be used on most file formats generated at US synchrotron sources. A graphical interface for XRD background subtractions has also been developed by Dr. Webb, which allows the rapid removal of window and solution scattering from data and is very useful when processing large amounts of diffraction data from area detectors. Several upgrades were released for the XAS data analysis interface, *SixPACK*, which is widely used around the U.S. and on 4 other continents. All of the programs above are provided free to the public and are available for download from <http://www-ssrl.slac.stanford.edu/~swebb>.

*Outreach and Education.* A web site has been created (<http://www-ssrl.slac.stanford.edu/mes/remedi/index.html>) to provide key information and links to SSRL resources for ERSP users. A two-day workshop on Synchrotron X-ray Scattering Techniques in Materials and Environmental Sciences was held on May 15-17, 2006 and was focused in part on the needs of ERSP users.

## **2.2 Innovative techniques for environmental remediation sciences at SSRL**

*Hard x-ray microprobe for study of priority DOE contaminants* FY 2006 activities were focused on the initial testing of an x-ray microprobe for  $\mu\text{-XAS}$ ,  $\mu\text{-XRD}$ , and  $\mu\text{-XRF}$  measurements, installed at BL 2-3 on a shared-time basis, and optimized for experiments on radionuclides of interest to ERSP researchers including Sr, U, Np, Pu, Am, and Tc. It also provides experimental capability for priority heavy metal contaminants, including Cr, As, Se, Hg, and Pb. The microprobe was found to produce a focused beam of 2  $\mu\text{m}$  diameter, which is close to the theoretical limit. User commissioning was initiated on schedule in the summer of 2006. Preliminary measurements demonstrate that the microprobe will provide the capability for routine chemical imaging and  $\mu\text{-XANES}$  measurements on natural samples, and will provide  $\mu\text{-EXAFS}$  capability for sample spots that are locally relatively concentrated, such as small mineral grains, pore fillings, and grain coatings.

*In-situ chemical dynamics of (bio-)mineral transformations.* The study of chemical dynamics of environmental reactions by *in-situ* XRD is a powerful technique for quantifying kinetic relationships, but requires a detector that can record a full diffraction pattern quickly. We have implemented a large area MAR345 detector to study reactions in flow-through capillaries to record high-quality time-resolved XRD patterns of mineral transformations in wet mineral-bacteria mixtures. The viability of this technique to quantify reaction kinetics has been demonstrated in studies of the transformations of biogenic manganese oxides in the presence of added metal reactants (Co(II)). This technique can be used to examine many biological and environmental systems and has raised a significant interest among ESRP users.

### 3. Planned Activities

We will continue to grow the user support program and integrate it more tightly into the overall ESRP program in FY 2007 by working with our existing ESRP collaborators to develop new tools for ESRP research (such as epifluorescence microscopy at the hard x-ray microprobe) and by establishing new relationships with other ESRP researchers. With the hard x-ray microprobe facility, we will complete user commissioning of the imaging and XAS data collection systems, and subsequently begin commissioning an area CCD detector (purchased in FY 2006) for  $\mu$ -XRD measurements. We will subsequently begin to develop data analysis tools for  $\mu$ -XRD data processing, which will continue as a major effort in 2008. Two ancillary projects for the microprobe will be to develop the capability to simultaneously perform epifluorescence and x-ray microscopy and the installation of a cold stage to preserve samples during beam exposure.

### 4. Information Access

Information developed as a result of this grant is represented by publications produced by ESRP projects active at SSRL and supported by this project. These publications are listed below.

#### FY 2006 Publications and Dissertations

B. Cancès, F. Juillot, G. Morin, V. Laperche, L. Alvarez, O. Proux, J.-L. Hazemann, G. E. Brown, Jr. and G. Calas, "XAS Evidence of As(V) Association with Iron Oxyhydroxides in a Contaminated Soil at a Former Arsenical Pesticide Processing Plant", *Environ. Sci. Technol.* **39**, 9398 (2005).

J. G. Catalano, J. P. McKinley, J. M. Zachara, S. M. Heald, S. C. Smith and G. E. Brown, Jr., "Changes in Uranium Speciation through a Depth Sequence of Contaminated Hanford Sediments", *Environ. Sci. Technol.* **40**, 2517 (2006)

J. G. Catalano, "Molecular Scale Studies of Uranium Speciation in Contaminated Hanford, Washington Sediments and Related Model Systems", *Stanford University*, 2005; Advisor: G. E. Brown, Jr.

M. Ginder-Vogel, C. S. Criddle and S. Fendorf, "Thermodynamic Constraints on the Oxidation of Biogenic  $\text{UO}_2$  by Fe(III) (Hydr)oxides", *Environ. Sci. Technol.* **40**, 3544 (2006)

W. W. Lukens, J. J. Bucher, D. K. Shuh and N. M. Edelstein, "Evolution of Technetium Speciation in Reducing Grout", *Environ. Sci. Technol.* **39**, 8064 (2005)

G. Ona-Nguema, G. Morin, F. Juillot, G. Calas and G. E. Brown, Jr., "EXAFS Analysis of Arsenite Adsorption onto Two-Line Ferrihydrite, Hematite, Goethite, and Lepidocrocite: Influence of Surface Structure", *Environ. Sci. Technol.* **39**, 9147 (2005).

E. M. Pierce, J. P. Icenhower, R. J. Serne and J. G. Catalano, "Experimental Determination of  $\text{UO}_2(\text{cr})$  Dissolution Kinetics: Effects of Solution Saturation State and pH", *J. Nucl. Mater.* **345**, 206 (2005)

J. H. Priester, S. G. Olson, S. M. Webb, M. P. Neu, L. E. Hersman and P. A. Holden, "Enhanced Exopolymer Production and Chromium Stabilization in *Pseudomonas putida* Unsaturated Biofilms", *Appl. Environ. Microb.* **72**, 1988 (2006)

S. M. Webb, C. C. Fuller, B. M. Tebo and J. R. Bargar, "Determination of Uranyl Incorporation into Biogenic Manganese Oxides Using X-ray Absorption Spectroscopy and Scattering", *Environ. Sci. Technol.* **40**, 771 (2006)

D. M. Wellman, J. G. Catalano, J. P. Icenhower and A. P. Gamerdinger, "Synthesis and Characterization of Sodium Meta-Autunite,  $\text{Na}[\text{UO}_2\text{PO}_4] \cdot 3\text{H}_2\text{O}$ ", *Radiochim. Acta* **93**, 393 (2005)

W.-M. Wu, J. Carley, T. Gentry, M. A. Ginder-Vogel, M. Fienen, T. Mehlhorn, H. Yan, S. Carroll, M. N. Pace, J. Nyman, J. Luo, M. E. Gentile, M. W. Fields, R. F. Hickey, B. Gu, D. Watson, O. A. Cirpka, J. Zhou, S. Fendorf, P. K. Kitanidis, P. M. Jardine and C. S. Criddle, "Pilot-Scale *in Situ* Bioremediation of Uranium in a Highly Contaminated Aquifer. 2. Reduction of U (VI) and Geochemical Control of U(VI) Bioavailability", *Environ. Sci. Technol.* **40**, 3986-3995 (2006)

### **FY 2005 Publications**

G. E. Brown, Jr., J. G. Catalano, A. S. Templeton, T. P. Trainor, F. Farges, B. C. Bostick, T. Kendelewicz, C. S. Doyle, A. M. Spormann, K. Revill, G. Morin, F. Juillot and G. Calas, "Environmental Interfaces, Heavy Metals, Microbes, and Plants: Applications of XAFS Spectroscopy and Related Synchrotron Radiation Methods to Environmental Science", in *Proceedings 12th International Conference on X-ray Absorption Fine Structure (XAFS XII)*; Malmo, Sweden, June 22-27, 2003. *Phys. Scr. T* **115**, 80 (2005)

J. G. Catalano and G. E. Brown, Jr, "Uranyl Adsorption onto Montmorillonite: Evaluation of Binding Sites and Carbonate Complexation", *Geochim. Cosmochim. Acta* **69**, 2995 (2005)

J. G. Catalano, T. P. Trainor, P. J. Eng, G. A. Waychunas and G. E. Brown, Jr, "CTR Diffraction and Grazing-incidence EXAFS Study of U(VI) Adsorption onto  $\alpha\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  (1102) Surfaces", *Geochim. Cosmochim. Acta* **69**, 3555 (2005)

J. G. Catalano, J. A. Warner and G. E. Brown, Jr., "Sorption and Precipitation of Co(II) in Hanford Sediments and Alkaline Aluminate Solutions", *Appl. Geochem.* **20**, 193 (2005)

C. M. Hansel, S. G. Benner and S. Fendorf, "Competing Fe(II)-induced Mineralization Pathways of Ferrihydrite", *Environ. Sci. Technol.* **39**, 7147 (2005)

M. Karabulut, E. Metwalli, A. K. Wittenauer, R. K. Brow, G. K. Marasinghe, C. H. Booth, J. J. Bucher and D. K. Shuh, "An EXAFS Investigation of Rare-Earth Local Environment in Ultraphosphate Glasses", *J. Non-Cryst. Solids* **351**, 795 (2005)

W. W. Lukens, J. J. Bucher, D. K. Shuh and N. M. Edelstein, "Evolution of Technetium Speciation in Reducing Grout", *Environ. Sci. Technol.* **39**, 8064 (2005)

Savage, K. S., Bird, D. K., and O'Day, P. A., "Arsenic speciation in synthetic jarosite" *Chemical Geology* **215**, 473-498 (2005)

Vlassopoulos, D., O'Day, P. A., Rivera, N., Rafferty, M. T., and Andrews, C. B. "Arsenic removal by granular iron: A field-based study of rates, mechanisms and long-term performance" in *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*, O'Day et al. (Eds.), American Chemical Society Symposium Series **915**, 344-360 (2005)

J.-K. Yang, M. O. Barnett, J. Zhuang, S. E. Fendorf and P. M. Jardine, "Adsorption, Oxidation, and Bioaccessibility of As(III) in Soils", *Environ. Sci. Technol.* **39**, 7102 (2005)