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ENVIROSUITE: USING STATE-OF-THE-ART SYNCHROTRON TECHNIQUES TO UNDERSTAND ENVIRONMENTAL REMEDIATION SCIENCE ISSUES AT THE MOLECULAR LEVEL

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ABSTRACT

Although DOE’s Environmental Management program has made steady progress in cleaning up environmental legacies throughout the DOE complex, there are still significant remediation issues that remain to be solved. For example, DOE faces difficult challenges related to potential mobilization of radionuclides (e.g., actinides) and other hazardous contaminants in soils, removal and final treatment of high-level waste and residuals from leaking tanks, and the long-term stewardship of remediated sites and engineered disposal facilities, to name just a few. In some cases, new technologies and technology applications will be required based on current engineering expertise. In others, however, basic scientific research is needed to understand the mechanisms of how contaminants behave under specific conditions and how they interact with the environment, from which new engineering solutions can emerge.

At Brookhaven National Laboratory (BNL) and Stony Brook University, scientists have teamed to use state-of-the-art synchrotron techniques to help understand the basic interactions of contaminants in the environment. Much of this work is conducted at the BNL National Synchrotron Light Source (NSLS), which is a user facility that provides high energy X-ray and ultraviolet photon beams to facilitate the examination of contaminants and materials at the molecular level. These studies allow us to determine how chemical speciation and structure control important parameters such as solubility, which in turn drive critical performance characteristics such as leaching.

In one study for example, we are examining the effects of microbial activity on actinide contaminants under conditions anticipated at the Waste Isolation Pilot Plant. One possible outcome of this research is the identification of specific microbes that can trap uranium or other contaminants within the intracellular structure and help mitigate mobility. In another study, we are exploring the interaction of contaminants with soil and plant roots to better understand the mechanisms responsible for uptake. This effort will lead to improvements in phytoremediation, an innovative and cost-effective approach to the cleanup of large volumes of soil with low concentrations of contaminants. In a third effort, we are investigating molecular interactions of contaminants in high-level waste tanks with potential grouting materials for remediation of the West Valley, NY site to assess their suitability and long-term performance.
INTRODUCTION

The behavior of environmental contaminants including speciation, distribution, reactivity, transformations, mobility, biogeochemical cycling, and bioavailability ultimately depends on molecular-scale structure and properties. The intense x-ray beams produced by synchrotron radiation sources provide a variety of spectroscopic techniques that are ideally suited for studying contaminant behavior at the molecular level. Synchrotron-based methods have enabled this new level of characterization by offering element and chemical state specificity, high spatial and energy resolution, excellent detection sensitivity, and the ability to work with wet samples safely sequestered within environmental cells. The high level of expertise for synchrotron-based studies of contaminant behavior was developed by a multidisciplinary community which draws scientists from soil and agricultural sciences, geochemistry, chemistry, physics, biology, microbiology, hydrology, ocean sciences, climatology and atmospheric sciences. One of the most significant challenges continues to be how best to incorporate results from molecular-level studies into the environmental management decision-making process.

Synchrotron-based molecular environmental science research will continue to make critical contributions to DOE's mission of protecting the environment by providing, among other things, the fundamental understanding required to develop and deploy cost-effective remediation strategies for the nation's most pressing contamination issues. The National Synchrotron Light Source at BNL, which is a national user research facility funded by the DOE's Office of Basic Energy Science, operates two electron storage rings which provide intense light spanning the electromagnetic spectrum from the infrared through x-rays. The experimental tools available at the NSLS, which is one of four DOE synchrotron facilities, are unique within the Eastern United States and approximately 15% of the 2,500 users that visit the NSLS each year conduct environmental science research. The breadth of this research is reflected in the wide range of experimental methods and beamlines used by the environmental science community at the NSLS. As this user community has grown dramatically over the past decade, researcher demand for state-of-the-art synchrotron-based tools optimized for environmental research has also grown. BNL's EnviroSuite Strategic Initiative aims to establish a unified voice for this diverse community and take the lead in developing resources at the NSLS required to conduct world-class molecular environmental science research.

In addition, BNL recently teamed with researchers at Stony Brook, Temple, and Penn State universities in a collaboration known as the Center for Environmental Molecular Science (CEMS). CEMS, which is supported by the National Science Foundation and DOE, brings together an even broader group of scientists from a wide range of disciplines, to conduct fundamental environmental science research and provide outreach to new users and students interested in exploring state-of-the-art synchrotron-based techniques. In addition to cutting edge molecular environmental science, the objectives of EnviroSuite and CEMS include the development of state-of-the-art methods and facilities that will be available to the scientific community at large. For example, as part of this initiative, NSLS at BNL is upgrading a beam line with appropriate end-station equipment that will be dedicated to the study of molecular environmental science with at least 50% of the available time reserved to the general users.

This paper will provide a brief introduction to the synchrotron-based methods available to EnviroSuite users at the NSLS. A description of the basic workings and capabilities of individual techniques will be followed by three examples of how basic molecular-level information derived from synchrotron-based studies can contribute to solving complex environmental management issues.
SYNCHROTRON-BASED METHODS

While the following section provides a very brief overview of a number of the methods most commonly employed by EnviroSuite scientists at the NSLS, we recommend a number of excellent reviews for additional information. [1, 2]

X-ray Absorption Fine Structure (XAFS) Spectroscopy

XAFS spectroscopy has gained widespread use within the environmental sciences because of its unique ability to determine the chemical speciation (oxidation state and structure of the local bonding environment) of metals and radionuclides in complex heterogeneous samples at environmentally-relevant concentrations in environments that reflect real-world conditions (e.g., water-saturated environments). An XAFS spectrum is the measure of a material’s x-ray absorbance as a function of incident x-ray energy. Each element has a characteristic peak in absorbance (absorption edge), which occurs when exposed to a specific incident x-ray energy. As the incident x-ray energy is scanned beyond an element’s absorption edge, the absorption intensity decays and the oscillations in the decaying signal define the XAFS spectrum. The XAFS spectrum is sub-divided into the X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectral regions. The low kinetic energies of ejected electrons near the absorption edge facilitate interactions with electronic states closely associated with the central atom, and therefore, XANES spectral features are sensitive to changes in the oxidation state and bonding geometry of the central atom. In contrast, electrons in the EXAFS region possess additional kinetic energy which promotes interactions with more distant neighboring atoms. The oscillations produced by these interactions in the EXAFS spectral region can be used to determine the atomic number, distance and coordination number of the surrounding atoms within a 5Å radius of the element of interest.

XAFS spectroscopy can be used as a chemical fingerprinting technique in which case unknown spectra are compared with spectra of reference compounds for which the speciation is known. A second approach compares unknown spectra with model-derived spectra to extract structural parameters including coordination numbers and bond lengths to neighboring atoms. Although many factors including the x-ray source characteristics, detection system and sample matrix can affect the quality of an XAFS spectrum, the limitations of applying XAFS spectroscopy to determine chemical speciation chiefly depend on element concentration. The low concentration limits are highly case dependent but a reasonable rule of thumb is >10 ppm yields acceptable XANES spectra and >500-1000 ppm yields acceptable EXAFS spectra. The ability to conduct XAFS studies of water-saturated samples is critical for environmental sciences research because it avoids sample alteration caused by drying (required for other analytical methods) and enables flow-through experiments for real-time studies of contaminant transformations. XAFS beamlines at the NSLS are suited for measurements of water-saturated samples in an ambient atmosphere for elements in the periodic table with core electron absorption energies from V to Cd (5.5 to 27.1 keV) for K-shell electrons and from Cs to Pu (5.7 to 23.1 keV) for L-shell electrons. In addition, experimental cells capable of operating at elevated pressure and temperature enable studies of contaminants during waste-form processing and storage in underground waste repositories.

As XAFS spectroscopy is often used to examine contaminant behavior in heterogeneous media such as soils, sediments and waste-forms, it is critical to consider that the information represents the average taken over all chemical environments of a given contaminant present in the area illuminated by the x-ray beam (typically 10-20 mm²). Two common methods used for spectral deconvolution include principle component analysis[3] and least-squares linear combination.
The success of these approaches is highly system-dependent. In the best case, where a set of different species for the contaminant of interest have distinct spectral signatures, a component can be identified only if it comprises more than 10% of the total contaminant concentration. This can have significant consequences when a release of just a fraction of the total amount of a contaminant associated with the solid matrix results in unacceptably high dissolved contaminant concentrations. Significant progress toward being able to account for microscopic heterogeneity, however, has been made using the following synchrotron-based micro-analytical techniques.

Microprobe and microspectroscopy

When the x-rays generated by a synchrotron facility are focused onto a sample mounted so that it can raster through the fixed incident beam, the spectroscopic information previously discussed in the XAFS section is made available with a spatial resolution that is limited by the focusing optics. The micro-focusing mirrors currently installed at the micro-analytical x-ray beamline (X26A) at the NSLS, which is managed and operated by the University of Chicago, are capable of achieving an incident x-ray beam with a full width half maximum spot of 2x10 μm. A second micro-analytical beamline dedicated to EnviroSuite users currently under construction at the NSLS will have similar focusing characteristics with approximately five times the x-ray beam intensity. Several micro-analytical methods are currently available at beamline X26A including element mapping, microspectroscopy and microdiffraction.

Element mapping or x-ray fluorescence (XRF) spectroscopy entails rastering the sample through a micro-focused beam of fixed x-ray energy while measuring the fluorescence intensity of each element of interest by using an energy-discriminating solid-state detector. A properly calibrated element map reveals the spatial distribution of element concentrations within the sample. The XRF method at X26A has a nominal detection limit of 1 ppm. Microspectroscopy can be used to interrogate a contaminant's chemical speciation within areas of high concentration that are revealed by the element map. Microdiffraction analysis maps the spatial distribution of crystalline materials within a sample matrix such as minerals within a sediment sample. Used together, these tools can help determine phase associations and identify predominant contaminant transformation pathways. These micro-analytical methods have also shown great versatility in studying contaminants within the discrete structures of biological systems such as plants and microorganisms. The infrared micro-spectroscopy methods available at the NSLS beamline U10 allow micro-analytical studies of organic molecules in soils, sediments, wasteforms and biological systems.

While these micro-analytical methods provide unparalleled details about contaminant speciation within heterogeneous environments, one should always consider whether observations made within a 5 to 10 mm² area of a sample are representative of field-scale behavior. This limitation highlights the need for careful integration of field-scale observations and sampling procedures with sub-sampling procedures used for micro-analytical measurements.

Scanning Transmission X-ray Microscopy (STXM)

The STXM measures the x-ray absorbance of a material in the soft x-ray region (100-1200 eV) and like the micro-analytical methods discussed above it uses a micro-focused incident beam and sample rastering to produce spatially resolved maps. STXM also operates in both fixed and scanned incident beam energy modes. Scientists at the NSLS have been working at the forefront of STXM method development.[5] Beamline X1A currently uses micro-focusing zone plates to achieve a spatial resolution on the order of hundreds of nanometers. The strongest electronic
absorption edges within the soft x-ray region and thus the greatest spectral contrast is observed for C, N and O atoms within a sample. Significant data processing is required to produce meaningful images. Scientists at the NSLS, however, are actively working with environmental scientists to develop effective data analysis methods.[6]

X-ray Microtomography

Synchrotron-based microtomography also measures x-ray absorbance of a material with a micro-focused beam. This method, however, produces 3-D maps by combining multiple images collected along the arc of a sphere whose center is located within the sample. Advanced data processing methods can be used to determine 3-D density profiles and element distributions. Density profiles of sediments during active flow conditions have shown great promise to directly measure pore connectivity and monitor pore structure evolution under changing solution conditions.[7] By combining density profiles and element distributions, 3-D contaminant distributions can be monitored during transport conditions in sediments or within microorganisms.[8, 9]

EXAMPLES

The three examples presented in this section provide an introduction to the range of research projects underway as part of the EnviroSuite initiative at BNL.

Grout formulations for emplacement of residual metal and actinide contamination

As part of the DOE’s D&D efforts at West Valley, NY, grout formulations are being tested as possible backfill material for high level waste-tank heels and ancillary facilities. A viable grout for this site must effectively sorb and immobilize a wide range of residual actinide and heavy metal contaminants. Several grout formulations containing different constituents including blast furnace slag, zeolite, apatite, portland cement, and fly ash are being considered. At BNL we are contributing to this effort by investigating the sorption of all RCRA elements as well as 10 radionuclides onto grout formulations and the individual constituent materials.

The relatively high residual Cr concentrations (=160 mg/kg) present in the tank heels have received special attention by managers because of the risk posed by the toxic, carcinogenic and highly mobile Cr(VI) oxyanion species.[10] Results from Cr sorption isotherms for two grout formulations are linear below 500±100 mg/kg of sorbed Cr and only exhibit non-linear sorption at the higher concentrations of sorbed Cr measured (500-1200 mg/kg). For the linear range of these isotherms the slope (i.e., $K_d$ or $[\text{Cr on solid}] / [\text{Cr remaining in liquid}]$) ranges between 6 and 7 mL/g. The maximum Cr sorption capacity of the two grouts, which was determined by extrapolating the curvature of the slope in the non-linear region to the apparent isotherm plateau, is approximately 1200 mg/kg. Results from Cr sorption isotherms conducted with the individual grout components reveal a number of important results. For example, the Cr sorption capacity of the cement component was substantially greater than any of the other individual component materials. The $K_d$ for the cement was approximately 18 mL/g and Cr uptake was linear up to 7500 mg/kg suggesting that this component likely accounts for the greatest proportion of Cr uptake by the two grout formulations. The blast furnace slag, which because of its high Fe(II) content was expected to show the greatest capacity to sequester Cr by reduction to Cr(III), showed slightly lower Cr sorption capacity than the cement with a non-linear isotherm throughout the measured concentration range (0.5-100 mg/kg) that reached a plateau at approximately 2000 mg/kg of sorbed Cr.
X-ray absorption near edge structure (XANES) spectra were recorded at the Cr Kα absorption edge using beamline X-23A2 for the two grouts, cement, slag, and zeolite samples after equilibrating for 100 days in aqueous solutions that initially contained only Cr(VI) species. The goal of these experiments was to determine if Cr sorption coincides with the reduction of Cr(VI) to Cr(III) species. The abiotic reduction of Cr(VI) to Cr(III) at mineral surfaces has been demonstrated as an effective method for detoxifying and immobilizing Cr contamination as Cr(III) species are relatively non-toxic and highly insoluble.[11] The XANES spectra shown in Figure 1 compare reference materials for Cr (VI), Cr(III) and a Cr(VI)/Cr(III) mixture with Cr-entrained cement, slag and one of the two grout formulations. Based on inspection, the Cr(VI) standard spectrum contains a sharp peak at ~5994 eV that is not present in the Cr(III) std spectrum. This peak which is often referred to as a pre-edge feature is indicative of a Cr atom in the +6 oxidation state that is bonded to four oxygen atoms, whereas a spectrum without this peak is characteristic of a Cr atom in the +3 oxidation state that is bonded to six oxygen atoms.

By calibrating the intensity of this peak with spectra containing known Cr(VI)/Cr(III) ratios, the peak intensity can be used in conjunction with bulk sorption measurements to determine the absolute concentration of Cr(VI) and Cr(III) in an unknown sample.[12] Here we use the peak intensity as a relative gauge of the Cr(VI)/Cr(III) ratio and find that while the cement has the highest Cr sorption capacity it does not reduce Cr(VI) species. In contrast, while the slag has a slightly lower Cr sorption capacity, it effectively reduces the vast majority of the sorbed species to Cr(III). The spectrum for the grout formulation indicates that approximately half of the sorbed Cr is reduced to Cr(III) when the grout is exposed to a Cr(VI)-containing solution.

This study demonstrates both how synchrotron-based spectroscopic investigations complement classic bulk measurements and the need to base decisions on results acquired using both approaches. Based on these results, it may be necessary to design grout formulations with higher capacities for Cr(VI) sorption and reduction.
Phytoremediation of radionuclides and heavy metals

The use of plants to remove metal and radionuclide contaminants from soils has been investigated at several sites at BNL that contain low concentrations of radionuclides (<200 pCi/g) including $^{137}$Cs and heavy metals (<1000 mg/kg) including Pb, Cr and Ag. Field tests were used to evaluate the uptake capacity of different plant species. Of the many plant species tested, *Amaranthus aureus* L. (*A. aureus*) provided concentration ratios (CR = [plant] / [soil]) for $^{137}$Cs and Sr that made it, and related species, suitable candidates for phytoextraction of radionuclides. The relationship between bulk elemental concentrations in *A. aureus* and in the soil in which it was grown varied widely among the soil contaminants tested (Sr, Mn, Fe, Cr, Zn, Cu, Ag, Pb, Ni, Cd, $^{137}$Cs) with Sr uptake at CR=48 and Pb uptake at CR=0.3.

One aspect of this remediation method that is important to understand is the distribution of a contaminant between the roots and the above-ground shoots. Ideally, for phytoextraction, the contaminant should be translocated to the shoots, leaving relatively little in the roots. Harvesting above ground portions of the plant will, therefore, remove most of the contaminant without leaving much in the roots where it will return to the soil. If, on the other hand, a large portion of the contaminant is sequestered and remains in the roots, then a plant species could negatively impact the soil by creating local zones of high contaminant concentrations. To accurately determine contaminant distributions and begin to investigate promising sequestration and translocation mechanisms, samples of *A. aureus* were grown on the BNL filter-beds where the plants were started from seed. Mature plants were then pulled from the soil, washed and brought to beamline X-26A at the NSLS for synchrotron-based x-ray microprobe analysis. Samples were sliced to ~0.5 mm thickness and placed on Kapton tape. No other processing, such as drying, was required. The x-ray beam (16.3 keV) was focused to a 20 μm spot diameter and element concentrations (Fe, Ni, Zn, Cu, Pb, Rb, and Sr) were mapped by rastering the sample at 50 μm steps. The fluorescence signal was recorded for 15 seconds at each pixel. Rb, which exhibits similar chemistry to Cs in soils, is used as a proxy for Cs because the Cs fluorescence emission lines are not readily accessible with the experiment configuration. Figure 2 shows that Rb is

![Fig. 2. Optical photograph (lower left) and synchrotron-based micro-XRF element maps of Pb, Rb and Sr distributions in *A. aureus* roots and stems of plants grown from seed in contaminated filter-bed sediments located at BNL. Element maps were collected at the NSLS beamline X26A.](image-url)
quite evenly distributed throughout the plant, with the highest concentrations in vascular bundles of the stem. In contrast, Pb is concentrated in the root while only small quantities are translocated to the stem and Sr concentrates in the stem while only low concentrations remain in the root. Sr distribution in the stem is less diffuse than Rb. Both the high CR and the ready translocation from the roots to the stems of Sr suggests that plants of the genus *A. aureus* may be useful for extracting $^{90}$Sr from contaminated soils. Similarly a high CR observed for Rb suggests that $^{137}$Cs may also be moved to the stems although the significant Rb remaining in the roots would be left in the soil after harvest.

Studies are currently underway that combine detailed XAFS spectroscopy studies of metal-organic complexes with both x-ray and infrared spectromicroscopy studies of metals contained in plant tissues grown in controlled laboratory environments. This series of studies conducted in greatly simplified experimental systems, which were designed based on the field-scale studies discussed above, is aimed at understanding the mechanisms controlling both the metal and radionuclide uptake at the plant-root/soil interface (i.e., rhizosphere) and the subsequent translocation from the root to the shoots. A better understanding of these fundamental mechanisms will in turn produce new and enhanced phytoremediation methods.

**Microbial mobilization of uranium in a waste repository**

In the Waste Isolation Pilot Plant (WIPP) repository, actinides in the transuranic waste will be present in various chemical forms; these forms will be determined both by the pH, Eh, ionic composition and bacterial community of the natural groundwaters at the WIPP site and the waste constituents (metal oxides, nitrates, phosphates, organic ligands, and biodegradable organic constituents) placed in the repository. In order to assess the future performance of the repository, a detailed understanding of the complex interactions between all of these constituents is required to identify and ultimately control the predominant mechanisms governing waste stability. Microorganisms can substantially alter actinide speciation both directly by using an actinide species in its metabolic processes and indirectly by creating Eh, pH and chemical gradients that result from chemical consumption and production. In order to investigate these complex interactions, we characterized uranium speciation in the presence of a bacterium (*Halomonas* sp.) that had been isolated from the WIPP repository environment.[13]

The disposal environment within WIPP was simulated by adding uranyl-citrate (1mM) to a growth-medium (nitrate, phosphate and succinate) containing brine (3.4 M NaCl). Uranium solid and solution-state chemistry were determined using EXAFS and UV-vis spectroscopies, respectively (see Fig. 3). Uranyl-citrate was not stable in the brine mixture and the liberated uranium was consumed in a precipitate. Figure 3B shows the EXAFS spectra for the experimental data and the corresponding theoretical fits which indicate that the unknown uranium-containing precipitate has a similar local structure to a uranyl-hydrogen-phosphate reference compound. Growth of *Halomonas* sp., as indicated by denitrification and citrate metabolism (1.2 mmol h$^{-1}$), resulted in solubilization of the uranium-containing precipitate. The UV-vis spectra of the filtered culture solution showed the appearance of an aqueous uranyl-dicarbonate species during bacterial growth. This observation suggests that bacterial metabolism and resulting carbonate evolution controlled uranyl-hydrogen-phosphate dissolution.
Fig. 3. (A) Citrate (determined by HPLC) and uranyl-dicarbonate concentrations (determined by UV-vis spectroscopy) as a function of time in aqueous growth medium containing 1 mM uranyl-citrate, *Halomonas* sp. and 3.4 M sodium chloride. (B) EXAFS spectra (solid lines) and theoretical fits (dashed lines) of a uranyl-hydrogen-phosphate reference compound and the unknown uranium-containing precipitate observed prior to significant bacterial growth. EXAFS spectra were collected at the NSLS beamline X18B.

These results show how X-ray absorption spectroscopy can be used to provide insight into actinide chemical speciation in complex environments such as the simulated WIPP repository. Moreover, the results demonstrate that actinide transformations induced by microbial activity can have profound effects on actinide stability even in the most caustic environments.

**SUMMARY**

The molecular-level information provided by synchrotron-based methods will provide a scientific basis to allow the development of cost-effective remediation strategies, and more importantly will validate and build confidence in long-term stewardship strategies within DOE's environmental management program. To this end the NSLS offers a variety of tools for researchers to acquire the unique information necessary to begin to understand the molecular-level structures and mechanisms that govern contaminant transformations and waste-form stability. The complex nature of bringing molecular-level information to bear on environmental management issues requires a collaborative multi-disciplinary approach to environmental science research and technology development and implementation. The effective communication between researchers working in the laboratory, engineers implementing strategies in the field, and program managers deciding how to fund research and technology development, ultimately requires close collaboration to ensure that everyone understands the benefits and limitations of molecular-level information. The EnviroSuite program at BNL intends to bring together the people and resources necessary to implement this approach and make significant contributions to solving waste management and long-term stewardship challenges.

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