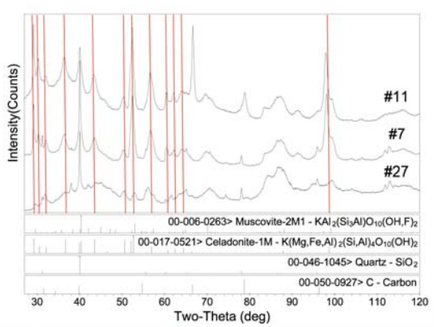
Detecting heavy metals: Micro XRD uncovers technetium that may resist remobilization

Researchers at EMSL are using micro x-ray analysis to gain insight into the biogeochemical processes that influence the fate and transport of subsurface contaminants, such as ^{99}Tc. Technetium contamination of groundwater is one concern at the Hanford Site in Richland, Washington and at the Field Research Center in Oak Ridge, Tennessee. Sediments that differed in mineralogy and aggregation were obtained from both contaminated areas and analyzed using capabilities including EMSL's micro XRD. These analyses revealed an oxidation-resistant Tc(IV) phase that exists with Fe(III) within iron-containing micas in the sediment from Oak Ridge. The mica flakes were a mineral phase called celadonite. Researchers concluded that ^{99}Tc found in natural subsurface sediments that has been reduced by Fe(II) associated with certain mineral phases may be increasingly resistant to oxidation and remobilization. This discovery may eventually aid remediation efforts to curb the hazardous health implications from ^{99}Tc.

Fredrickson JK, JM Zachara, AE Plymale, SC Heald, JP McKinley, DW Kennedy, C Lui, and P Nachimuthu. 2009. "Oxidative dissolution potential of biogenic and abiogenic TcO_2 in subsurface sediments." *Geochimica et Cosmochimica Acta* 73:2299-2313.

Micro XRD Quick Specs

- High spatial resolution of 10 µm
- Cu and Cr anodes available for use
- Curved image plate detectors allow collection of a larger section of Ewald sphere



Micro x-ray diffractograms of isolated Tc-containing sediment particles showing celadonite diffraction pattern (left).

About EMSL

EMSL, a U.S. Department of Energy national scientific user facility located at Pacific Northwest National Laboratory, provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.

EMSL's distinctive focus on integrating computational and experimental capabilities as well as collaborating among disciplines yields a strong, synergistic scientific environment. Bringing together experts and an unparalleled collection of state-of-the-art instruments under one roof, EMSL has helped thousands of researchers use a multidisciplinary, collaborative approach to solve some of the most important and complex national scientific challenges in energy and environmental sciences.

To learn more about EMSL, the science conducted at EMSL, as well as the instruments and expertise available to users, visit **www.emsl.pnl.gov**.

Become an EMSL user

Researchers are invited to access the world-class capabilities and collaborate with the internationally recognized experts at EMSL via its peer-reviewed proposal process. To submit a proposal, follow the five-steps outlined on the EMSL website (**www.emsl.pnl.gov**) under User Access. Current and potential EMSL users are encouraged to respond to Calls for Proposals, which are announced each spring. However, unique research proposals that fall outside the Calls for Proposal focus may be submitted at any time.

Applicants are encouraged to submit proposals for use of EMSL's capabilities in combination with each other with an emphasis on integrating computational and experimental instruments. In general, users whose open research proposals are accepted may use EMSL resources free of charge. Open research is loosely defined as science and engineering research for which the resulting information is published and shared broadly within the scientific community.

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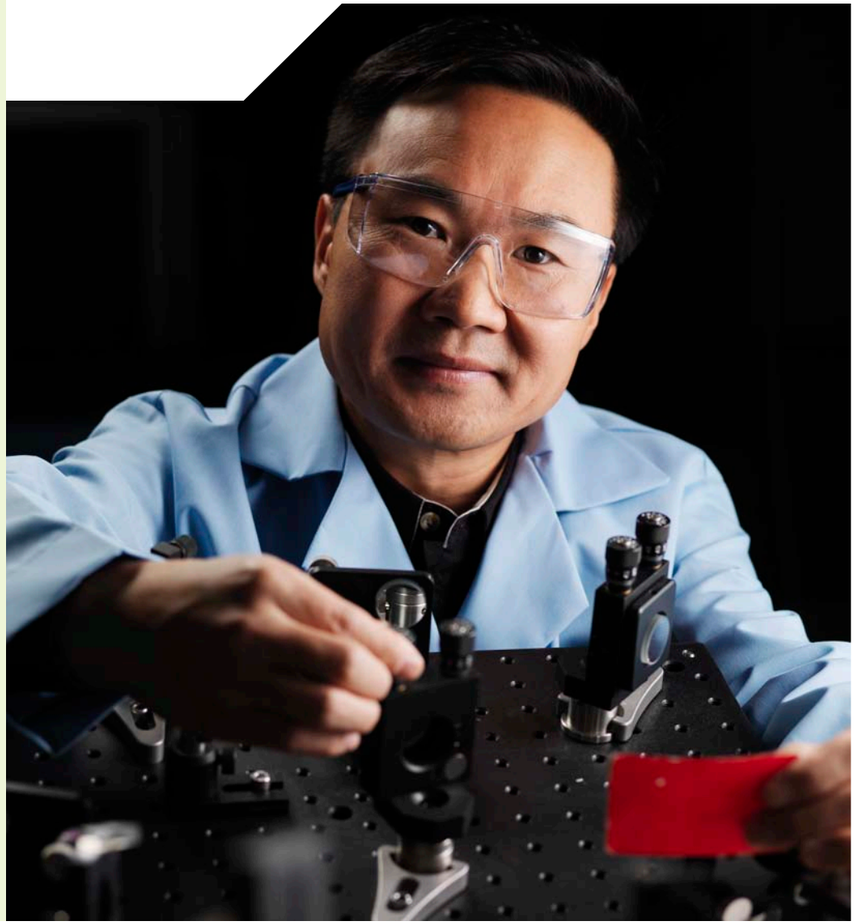
PNNL-SA-68534 September 2009

EMSL

Scientific Innovation Through Integration

Radiochemistry at EMSL:

Scientific Resources, Scientific Discoveries



www.emsl.pnl.gov

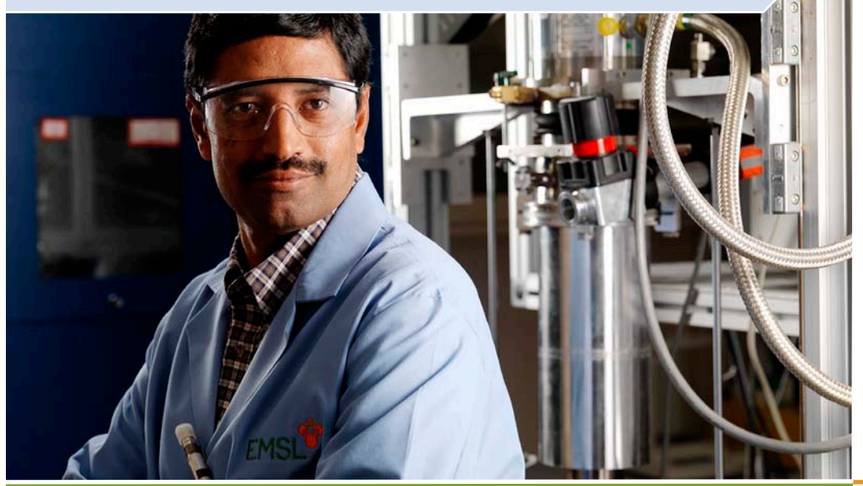
Recovery Act: Investing in innovation

The Department of Energy's Office of Science is investing in the Pacific Northwest National Laboratory through the American Recovery and Reinvestment Act. EMSL—the Environmental Molecular Sciences Laboratory, a national scientific user facility on the PNNL campus—is receiving $60 million of this funding. This investment will allow EMSL to obtain capabilities that deliver innovative scientific discoveries in support of DOE's mission.

EMSL's new actinide chemistry capabilities are expected to provide the scientific community with state-of-the-art capabilities in a unique, radiological research environment.

Several new instruments for EMSL's proposed radiological capability, purchased with a portion of the Recovery Act funding, will strengthen EMSL's problem-solving environment for radiochemistry research. The acquisition process for this capability is underway – a mission need statement has been approved by the Pacific Northwest Site Office, the statement is under review with DOE's Office of Biological and Environmental Research, and the following instruments are on order. Upon delivery and installation, they are expected to be housed in an environment designed to accommodate radiological studies.

- Electron microprobe systems capable of quantitative and qualitative elemental analysis, non-destructive x-ray microanalysis and imaging of solid materials, as well as secondary-electron, back-scattered electron, and cathode-luminescence imaging of both natural and synthetic solid materials
- High-field (700 MHz and above) nuclear magnetic resonance spectrometer system, with wide-bore, for conducting solid-state molecular structure determinations and studies
- Environmental scanning electron microscope, focused ion beam, electron backscatter diffraction and energy dispersive x-ray spectroscopy capabilities integrated into one system.



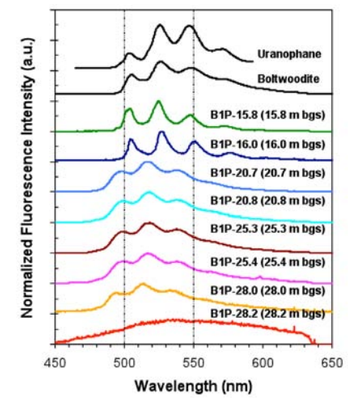
www.emsl.pnl.gov

Building upon a solid capability set

The Recovery Act will accelerate scientific discovery by building upon EMSL capabilities already available to researchers around the world. Examples of discoveries relevant to the field of actinide chemistry by EMSL users and staff that reflect use of current EMSL capabilities, including time-resolved laser-induced fluorescence spectroscopy (TRILFS), Mössbauer spectroscopy, and micro x-ray diffraction (micro XRD).

Biogeochemical breakthroughs: Using fluorescence spectroscopy to see how uranium travels through sediments

TRILFS is used to detect and characterize fluorescent radionuclides and heavy metal ions, including uranium, near their solubility limits and, in most cases, differentiates species of these ions and their complexes. Using EMSL's TRILFS, researchers from PNNL and Brookhaven National Laboratory conducted macroscopic and spectroscopic investigations on contaminated Hanford Site vadose zone sediments in shallow, medium, and deep depths. They discovered several different uranium surface phases in the contaminated sediments indicating that the uranium release mechanism could be complicated and that detailed characterization of the sediments would be needed to estimate uranium fate and transport in vadose zone. Understanding how environmental contaminants behave at a fundamental level and predicting their behavior with models based on experimental measurements is helping researchers devise remediation strategies.



Uranyl fluorescence spectra vary from boltwoodite/uranophane-type secondary precipitates to surface-adsorbed U(VI) phases with blue-shifted, less-resolved spectral features as the sediment depth increases.

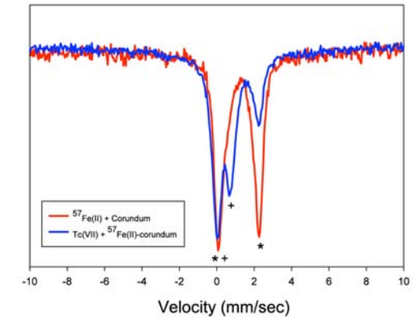
Um W, Z Wang, RJ Serne, BD Williams, CF Brown, CJ Dodge, and A Francis. 2009. "Uranium Phases in Contaminated Sediments Below Hanford's U Tank Farm." *Environmental Science & Technology* 43(12):4280-4286.

TRLIFS Quick Specs

- FDO-900 frequency doubler enables scanning from 220 to 1800 nm
- Time-gated intensified CCD camera and thermoelectrically cooled time-gated photomultiplier tube for luminescence analysis
- Oxford and Cryo Industries cryostats fitted with four sealed quartz optical windows and internal heating elements

Trapping technetium: Mössbauer spectroscopy reveals how adsorbed iron reduces technetium

Technetium-99, a fission product of ^{235}U and ^{239}Pu, is an important subsurface contaminant of study because it has a long half-life. It's migration in subsurface environments is strongly tied to its valence state, which influences its speciation, solubility, and sorption behavior. To better understand redox transformations in technetium upon its interaction with the common subsurface component iron, researchers from Pacific Northwest National Laboratory (PNNL) and Argonne National Laboratory (ANU) used ^{57}Fe-Mössbauer spectroscopy at EMSL and Tc-x-ray spectroscopy (XAS) at ANU to study the kinetics of Tc(VII) reduction by $^{57}Fe(II)$ sorbed on the aluminum (hydr)oxides diaspore (a-AlOOH) and corundum (a-Al_2O_3). Mössbauer and XAS analyses revealed that Tc(VII) was completely reduced by adsorbed Fe(II) within 11 days (diaspore suspension) and 4 days (corundum suspension). Mössbauer measurements showed that the adsorbed Fe(II) signal became less intense with Tc(VII) reduction and was accompanied by an increase in the intensity of the Fe(III). Using Tc-extended x-ray absorption fine structure (EXAFS) at ANU, the researchers found that the final heterogeneous redox product on corundum was similar to Tc(IV) oxyhydroxide (TcO_2nH_2O). Such knowledge about the reduction of Tc(VII) to Tc(IV) by adsorbed Fe(II) may lead to efficient approaches for Tc immobilization.



*Room temperature Mössbauer spectra: Sorbed $^{57}Fe(II)$ content decreases upon reaction with Tc(VII) [Fe(II) peaks indicated by * and Fe(III) peaks indicated by +].*

Peretyazhko, T, JM Zachara, SM Heald, RK Kukkadapu, C Liu, AE Plymale, and CT Resch. 2008. "Reduction of Tc(VII) by Fe(II) Sorbed on Al (hydr)oxides." *Environmental Science & Technology* 42(15): 5499-5507.

Mössbauer Quick Specs

- Isotope-specific technique
- ^{57}Fe (~95% studies)
- Actinide examples: ^{151}Eu, ^{237}Np (sources: ^{237}U, ^{237}Pu, ^{241}Am)
- Five ^{57}Fe-Mössbauer spectroscopy units
- Four cryogen-free closed-cycle refrigerant cryostats
- Two-chamber environmental chambers with -35°C freezer
- Remote monitor and control