Journal of Radioanalytical and Nuclear Chemistry, Vol. 234, Nos 1–2 (1998) 237–242

In situ examination of uranium contaminated soil particles by micro-X-ray absorption and micro-fluorescence spectroscopies

D. B. Hunter,* P. M. Bertsch

Advanced Analytical Center for Environmental Sciences, University of Georgia, Savannah River Ecology Laboratory, Aiken, SC 29801, USA

(Received February 5, 1998)

Two complimentary spectroscopic techniques, X-ray absorption and fluorescence spectroscopy have been conducted at spatial scales of 1 to 25 μm on uranium contaminated soil sediments collected from two former nuclear materials processing facilities of the DOE: Fernald, OH and Savannah River Site, SC. A method of imbedding particles in a non-reactive Si polymer was developed such that individual particles could be examined before and after extraction with a wide range of chemicals typically used in sequential extraction techniques and others proposed for *ex situ* chemical intervention technologies. Using both the micro-X-ray fluorescence (XRF) and micro-X-ray Absorption Near Edge Structure (XANES) techniques, both elemental and oxidation state distribution maps were generated on individual particles before and following chemical extraction. XANES can determine the relative proportion of U(VI) and U(IV) in phases comprising individual particles before and after extraction and showed that greater than 85% of the uranium existed as hexavalent U(VI). Fluorescence spectra of contaminated particles containing mainly U(VI) revealed populations of uranyl hydroxide phases and demonstrated the relative efficacy and specificity of each extraction method. Correlation of XAS and fluorescence data at micron scales provides information of U oxidation state as well as chemical form in heterogeneous samples.

Introduction*

Uranium is a widespread contaminant introduced into the environment as a result of mining and manufacturing activities related to the nuclear power industry, detonation of U-containing munitions at DoD facilities, and as a result of nuclear weapons materials production and processing at DOE facilities.[1] At DOE facilities, U is the most common radionuclide contaminant in groundwater/sediment systems and is often found associated with other metals such as Ni, Cr, and Cu. Oxidation state is a fundamental property of U speciation that greatly influences U solubility and mobility. Under many environmentally relevant redox conditions U will be present in the hexavalent state as the uranyl moiety (UO_2^{2+}) and/or uranyl species derived from hydrolysis and complexation of this moiety with carbonate, fluoride, sulfate and phosphate ligands.[2] In contrast, U(IV) forms highly insoluble solid phases such as uraninite ($UO_2(c)$).[3–5] There are reports of direct microbial reduction of U(VI) to U(IV) and this process could potentially be used as an in situ biological remediation strategy. Other U remediation methods under consideration include chemical extraction technologies. Considerable knowledge of chemical speciation of the U contamination is needed for such technologies to be effective.

Several studies have characterized U contamination at the former U processing facility at Cincinnati, OH (Fernald Environmental Management Project or FEMP) and some have employed advanced spectroscopic techniques.[3,6–8] By comparison, much less characterization and very little advanced spectroscopic analysis has been conducted on U contaminated sediments at the DOE's Savannah River Site, another former U processing facility near Aiken, SC. The soils from the FEMP site were contaminated with U from both aqueous and airborne particles,[7] whereas, the U in sediments collected at the SRS was discharged primarily as aqueous waste. This paper describes a characterization strategy similar to that developed by MORRIS' group at Los Alamos National Laboratory.[9] Specifically, this includes characterizing U binding environments classed according to bulk physical and chemical soil characteristics such as soil particle size, particle density, and extractability by various chemical extraction methods and then applying spectroscopic techniques to refine and complement speciation information through direct measurement. Bulk-scale analyses are important for determining major chemical phases and the average speciation within a sample. However, the information gained from such analyses can be difficult to interpret in samples containing complex mixtures of chemical phases present in heterogeneous, contaminated sediments. In contrast, spatially resolved analyses can probe homogeneous or less heterogeneous domains representing distinct chemical phases present in heterogeneous samples at a micro-scale. Spatially resolved data can help deconvolve information generated at a bulk scale, but provides chemical speciation data relevant to small sampling populations within the bulk sample.

---

* E-mail: hunter@srel.edu

0236–5731/98/USD 17.00

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

This paper describes preliminary applications of two spatially resolved, advanced spectroscopic techniques to complement bulk physical and chemical measurements of U contaminated soils. X-ray absorption spectroscopy (XAS) utilizing synchrotron radiation is a non-invasive, in situ method that can be used do distinguish U(VI) and U(IV) oxidation states. The energy of an X-ray absorption edge increases with increasing valence, resulting from the reduced shielding of the core electrons from the nucleus. This increase in the binding energy of the core levels is often manifested by shifts in pre-edge and bound-state edge features in an X-ray Absorption Near Edge Structure (XANES) spectrum that can be correlated to differences in the oxidation state of a cationic center.[10] Such shifts in the position of the L_{III} edge for U in glasses have been previously reported,[11,12] and BERTSCH et al.[3] systematically evaluated the method for providing U oxidation states within U-bearing mineral phases based on the L_{III} edge position. Utilizing the dedicated X-ray microprobe beamline, X26-A, at the National Synchrotron Light Source, XANES measurements can be made on spatial scales as small as 25 μm under ideal conditions. The other spectroscopic technique applied was optical luminescence conducted on a microscope platform capable of spatial resolution of luminescence spectra down to 1 μm. The emissive electronic transitions in uranyl species are best described as ligand (axial oxygen p orbital)-to-metal (f-orbital) charge transfer in nature.[13] Shifts in emission spectra are indicative of distortions in the vibrational energy levels of the uranyl stretching modes. Whereas XANES can elucidate oxidation state, fluorescence micro-spectroscopy can provide information on bonding environments about U(VI) emissive species.

Experimental

Synchrotron XRF micro-probe

The synchrotron X-ray fluorescence microprobe on beamline X-26A at the National Synchrotron Light Source (Brookhaven National Laboratory, NY) was used in its normal configuration[14,15] with the addition of a silicon, channel-cut (111) monochromator on the incident radiation. The beam size was adjusted to between 50×50 and 300×300 μm with tantalum shutters operated via a computer controlled motorized stepping micrometer. XANES spectra were collected at 0.3 eV step increments over a 120 eV energy range (relative to 17163 eV) extending from about 50 eV below to approximately 100 eV above the U L_{III} absorption edge. The count rate at each incident step ranged between 2 and 20 live seconds such that the total counts at the absorption maximum were ~10,000. The U L_{III} fluorescence X-rays were measured under ambient atmospheric conditions with a Si(Li) energy dispersive detector having an area of 30 mm^2 mounted at 90 degrees to the incident beam and 1 cm from the sample. Soil and sediment samples were mounted on ~200 μm thick Kapton adhesive windows within cardboard sample holders that were attached to 5×5 cm^2 slide mounts. An exception was for the sand fraction samples which were deposited as a single layer on a silicone adhesive substrate such that single (100–300 μm) or small clusters (50–100 μm) of grains could be examined. A uraninite UO_2 (c) sample was the U(IV) and a UO_3 and reagent grade uranyl acetate was the U(VI) reference materials for these investigations. Edge positions are expressed relative to edge of the pure UO_2 (c) sample which was arbitrarily set to 0 eV. Standards used to generate the admixture calibration curve were prepared by mixing appropriate proportional amounts by weight of each phase and then homogenizing them in a grinding mill prior to mounting. The absorption edge was defined as the half-height (determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. The absorption edge positions of all standards and samples were referenced against the edge position of the UO_2 (c) standard which was rerun before and after each sample. The edge position could be determined to within 0.2 eV representing an uncertainty of ~5% in oxidation state determination.

UV-VIS fluorescence micro-probe

Spatially resolved fluorescence spectroscopy was conducted on a Nikon Diaphot 200 inverted fluorescence microscope. A high voltage mercury lamp provided ultra-violet irradiation with a standard microscope fluorescence cube providing excitation wavelengths from 330–380 nm and emission wavelengths >420 nm. An Acton Arc-150 spectrometer equipped with a 300 and a 1200 groove·mm^{-1} grating was interfaced on the microscope's camera port. Light dispersed from the spectrometer was focused on a Princeton Instrument's 1024 pixel LN_2 cooled CCD camera system. Typically, 40 pixels were binned in the Y array for each of the 1024 pixels in the X array. Spectral resolution as limited by the gratings in the spectrometer was 0.5 nm for the 300 groove·mm^{-1} grating and 0.1 nm for the 1200 groove·mm^{-1} grating. Spatial illumination spot sizes of <5 μm were achieved by aperturing down the illumination spot and using a 20X or 40X fluorescence objective. To assist in qualitative interpretation of emission spectra, a library of spectra of mineral standards (courtesy of the National Museum of Natural History) was generated for: becquerelite-$Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$; schoepite-$(UO_2)(OH)_2 \cdot H_2O$; rutherfordine-$UO_2CO_3$; bassetite-

$Fe(UO_2)_2(PO_4)_2$; meta-autunite-$Ca(UO_2)_2(PO_4)_2$; uranophane-$Ca(UO_2)_2(SiO_3OH)_2$; and coffinite-$USiO_4$.

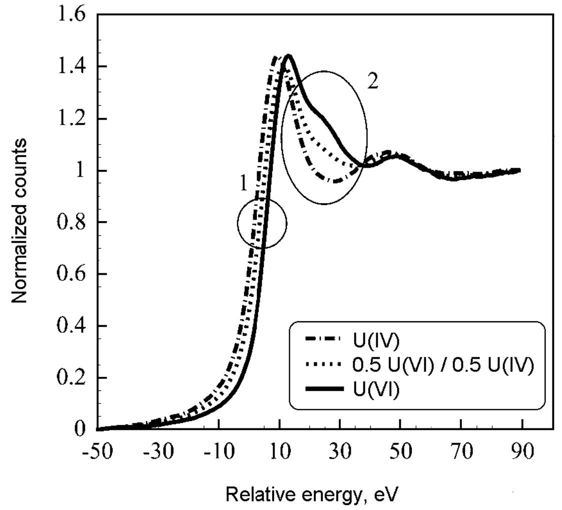

Fig. 1. Uranium L_{III} XANES Spectrum of U(IV) (—— UO_2(c)), U(VI) (-.- UO_3(c)) and an equal mixture of U(IV) and U(VI) (...). A linear relationship exists between the edge shift and the proportion of U(IV)/(U(VI) (circle labeled as 1). There are also differences observable in the post-edge region (circle labeled as 2)

Extraction methods

Much of the U associated with the SRS sediments is found in chemically labile fractions, according to sequential extraction techniques (≥90% as specifically sorbed + organic + oxide bound).[16] As is typical of many wetland systems in the Upper South Eastern Coastal Plain, the sediments display significant stratification or layering, with alternating organic-rich (ca. 8–12% OC, L1) and organic-poor (ca. <2% OC, L2)/oxide-rich sand layers. Sediment and soil samples were separated by sieving and centrifugation into three fractions: sand fraction defined as <300 µm but >50 µm; silt fraction defined as <50 µm but >2 µm ; and clay fraction defined as <2 µm. A four step sequential extraction technique was performed on suspended clay fractions or mounted sands by using a modified procedure from MILLER et al.[17] The extractants used and the phase affected by each were (listed in order from least to most aggressive): 0.01M NH_2OH-HCl + 0.1M HNO_3 – Mn oxide bound; 0.1M $Na_4P_2O_7$ – organically bound; 0.175M $(NH_4)_2C_2O_4$ + 0.1M $H_2C_2O_4$ – amorphous Fe oxides; 0.015M Na citrate + 0.05M citric acid+ 0.5 g Na-dithionite - crystalline Fe oxides. Sand particles were partially embedded in either an epoxy or silicone adhesive on silica disks to permit XRF and fluorescence measurements to be conducted before and after treatment.

Results and discussion

A linear relationship ($r^2 = 0.987$) exists between the proportional amounts of U(IV) and U(VI) in the physical admixtures and the central location of the edge position (defined by the "half-height" energy) (Fig. 1).[3] The ~3.75 to 4.3 eV shift to lower energy in the edge position of tetravalent U containing UO_2 (c) relative to the U(VI) phases, is accompanied by the absence of the shoulder (multiple scattering resonance [MSR]) on the high energy side of the main absorption feature (the maximum above edge intensity) characteristic and diagnostic of U(VI) containing phases[11,12] (Fig. 1). This latter region of the XANES spectrum for uranyl compounds is related to multiple scattering events in the direction of the linear U-O-U group involving electrons excited into the continuum.[12] Variation in bonding environments are manifested as subtle differences in the above-edge region of the XANES spectrum arising from multiple scattering events.

The XANES spectra for various regions within the clay, silt, and sand fractions from a FEMP soil sample (SP2) provided evidence for zones of varying U concentration and oxidation state. The bulk U concentration of the FEMP sand fraction,[7] for example, was reported to be 1070 $\mu g \cdot g^{-1}$, which is close to or at the detection limit often reported for adsorbed metals on many conventional XAS beam lines and was the highest U concentration examined in this study. It is possible to generate high quality XANES spectra utilizing the X-ray microprobe capability at bulk sample concentrations at least two orders-of -magnitude below this level within a reasonable collection time because the U is localized within the sample. The clay sized fraction had absorption edges indicative of primarily a U(VI) phase (Fig. 2a). However, as particle size approached the size of the probe beam, a greater spread in edge energies was observed, indicating that some measurements contained up to 20% reduced U(IV) in the silt fraction (Fig. 2b). Finally, for particle sizes equal to, or greater than the probe beam size, XANES measurements indicated the presence of isolated pure U(IV) phases (Fig. 2c). This is consistent with the previous SEM/EDX analyses of these samples, where the discrete U phases were found to exist as 10–100 µm particles.[6,7] It appears that the regions identified in the FEMP soil sample with intermediate edge positions may represent areas having finely divided discrete phases of U(IV) surrounded by a larger number of U(VI) containing particles or surface associated U(VI) phases.

Similar to Fernald samples, sediment samples from the Savannah River Site also exhibited particle-to-particle variability in U concentration for silt and sand particles. After collection of more than 50 XANES spectra on different sand, silt, and clay sized samples, there was no evidence for any discrete contaminated particles of primarily U(IV). There was some evidence for subtle differences in post-edge region but these will not be discussed here.

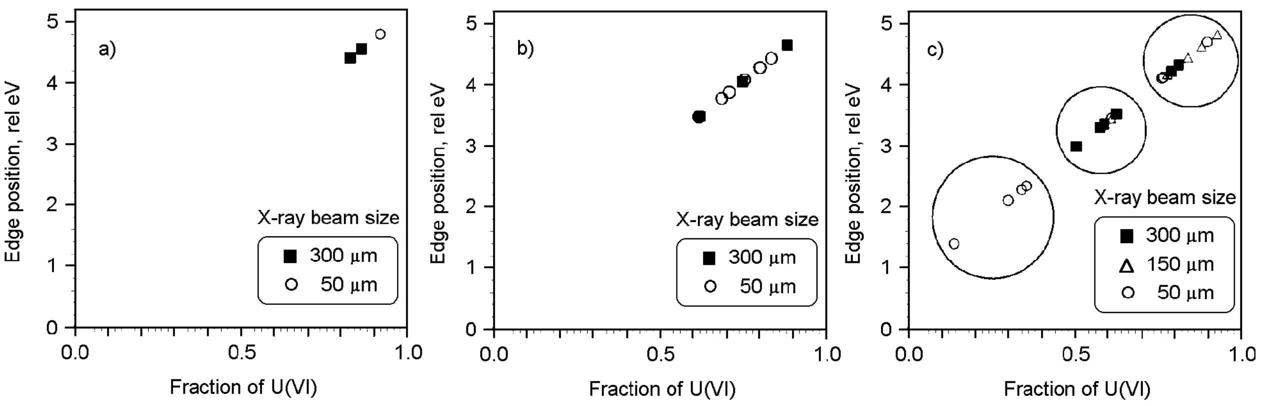

Fig. 2. Uranium XANES edge positions measured on Fernald sample SP2-2-ABC isolated into clay (a), silt (b), and sand (c)

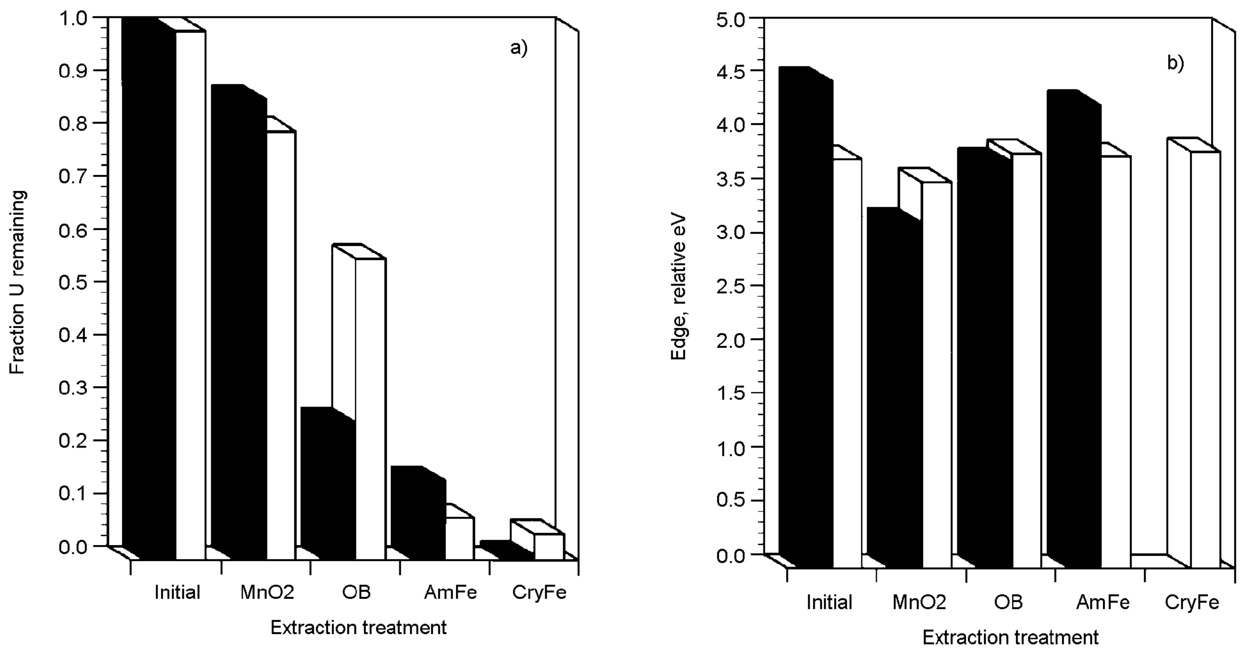

Fig. 3. Sequentially extracted clays from the Savannah River Site for an organic rich sediment (solid bars) and an organic poor sediment (open bars). Left chart (a) shows the residual U remaining after extraction. The chart on the right (b)shows the measured XANES edge position at each extraction step. Extraction steps were Mn oxide bound (MnO_2), organically bound (OB), amorphous Fe (AmFe), and crystalline Fe (CryFe)

The next step was the application of sequential extraction techniques to the clay fraction of SRS sediment samples and to collect XANES spectra after each extraction step. This provided essentially a bulk measurement approach to investigate whether residual U(IV) would become measurable after extraction of specific U(VI) phases. Figure 3a shows the proportion of residual U remaining in the sample after each extraction step as determined by X-ray fluorescence intensity. In the organic rich sample, about 60% of U was extracted from the 'organically bound' fraction whereas 10% of U was extracted from the amorphous Fe fraction. The organic poor sediment showed no evidence for an enrichment of extractable U(IV) from shifts in the XANES edge energy. However, in the organic rich fraction, the XANES indicated a small shift of the edge following the MnO_2 occluded extraction. This ~1 eV shift is interpreted as the presence of ~20% U(IV) in the residual U after this extraction. Since only 80% of the original U remained this would represent the presence of ~15% U(IV) in the original sample. A >±5% error is associated with this method for determination of relative U(IV)/U(VI) fractions and the edge shift should have been detectable prior to extraction. Hence, it is possible that the presence of this reduced U may be an artifact of the extraction.

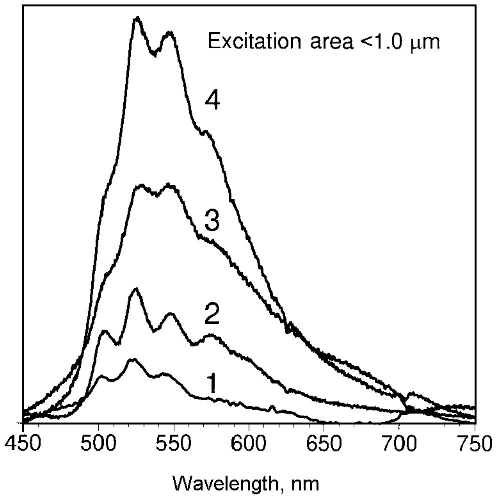

Fig. 4. Four representative emission spectra from U contaminated SRS sands

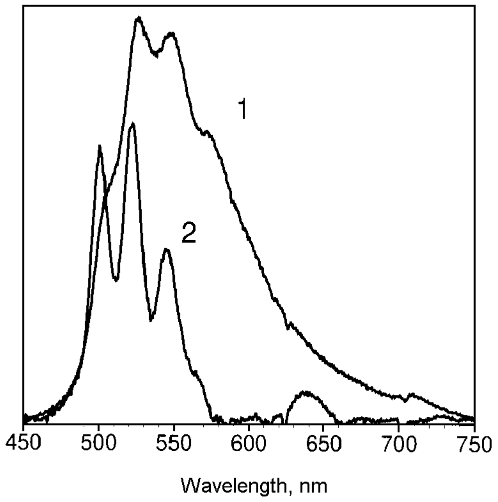

Fig. 5. Emission spectra of the same sand particle before (1) and after (2) 'amorphous Fe' extraction

Bulk samples of SRS sediments readily demonstrated distinctive fluorescence of uranyl species. Despite the implication that U is primarily associated with the organic phase (Fig. 3a), this association appears not to substantially quench fluorescence. The structure in these emission spectra derives from the resolution of the ground state electronic potential along the total symmetric stretching coordinate.[13] Under the microscope, fluorescence was intense enough to only require between 1 to 30 second acquisition times at 1 μm illumination sizes. In contrast to MORRIS et al.,[18] who isolated particles by fluorescence color for bulk emission measurements, we could rapidly investigate emission on a particle to particle basis, without bias of selection and bulk averaging of emission from many particles. Figure 4 illustrates the four primary classes of emission spectra collected. Generally, it was found that at 1 μm illumination scale, the background fluorescence from the sediment particles was minimal. The primary differences between spectra in Fig. 4 are line widths of the vibronic spacings and a 5 nm shift from emission spectra 2, 3 and 4 relative to spectra 1. In general, these spectra differ substantially to emission patterns seen for Fernald soils,[18] suggesting fundamental speciation differences between SRS and Fernald U contaminated soils.

The emission spectra in Fig. 4 are red shifted from UO_2^{2+} and most resembled uranyl hydroxide complexes.[13,19] Deconvolution techniques were attempted by scaling individual spectra and subtracting from other spectra. These attempts were rarely successful and when they were, resultant spectra fell into one of the four classes shown in Fig. 4. This is an indication that heterogeneous chemical environments, although complex, can be resolved into more homogeneous units at small spatial sampling areas. Importantly, this implies distinct speciation differences between these four classes of emission rather than linear combinations of slightly shifted spectra.

The first extraction step (MnO_2 occluded) resulted in quenching the U emission for all following extractions. It is important to realize that the residual U can chemically interact with the extractant without necessarily being extracted. The 'Organically Bound' fraction, when conducted by single versus a sequential extraction, showed only a diminished emission intensity. The 'Amorphous Fe' extraction, when conducted individually, resulted in a blue shift of the vibronic spacings as well as an overall improvement in linewidth resolution (Fig. 5). This blue shift is consistent with acid hydrolysis or complexation into a less distorted environment about the totally symmetric axial oxygens. In general, extractants used to dissolve specific phases suffer from a lack of selectivity and may not prevent readsorption . Our results provide evidence that U in contaminated sediments is redistributed between complex phases or precipitates as a secondary phase during sequential extraction. In either case, the speciation of residual U has been altered during extraction and this must be considered important to the efficacy or evaluation of remediation technologies that rely on chemical extraction or enhanced solubilization technologies.

Conclusions

Uranium contaminated sediments at the SRS differ substantially in U chemistry when compared to Fernald (work by Dave MORRIS' group at LANL). There is little evidence for substantial of reduction of U in sediments at the SRS (<10%) as investigated by XANES spectroscopy. Sequential extraction procedures suggest that most U is associated with organics and amorphous iron oxides. Fluorescence spectra suggest amorphous hydroxy-uranyl phases which are not quenched due to a primary association with organics. Future work involves the application of micro-FT-Raman and micro-FTIR spectroscopies and time resolved laser induced micro-fluorescence spectroscopy to further elucidate micro-chemical U environments, *in situ* in contaminated sediments located on the SRS and other DOE sites.

*

This research was supported by Financial Assistance Award Number DE-FC09-96SR18546 from the U.S. Department of Energy to the University of Georgia Research Foundation and by ERDA/WSRC subcontract AA46420T.

References

1. R. G. RILEY, J. M. ZACHARA, E. J. WOBBER, USDOE Report DOE/ER-0547T, 1992.
2. F. WIEGEL, Uranium, in: The Chemistry of the Actinide Elements, 2nd ed., J. J. KATZ et al. (Eds), Vol. 1, Chapman and Hall, 1986, Chap. 5, p. 169.
3. P. M. BERTSCH, D. B. HUNTER, S. R. SUTTON, S. BAJT, M. L. RIVERS, Environ. Sci. Technol., 28 (1994) 980.
4. D. LANMUIR, Geochim. Cosmochim. Acta, 42 (1978) 547.
5. B. NAGY, F. GAUTHIER-LAFAYE, P. HOLLIGER, D. W. DAVIS, D. J. MOSSMAN, J. S. LEVENTHAL, M. J. RIGALI, J. PARNELL, Nature, 354 (1991) 472.
6. E. C. BUCK, N. R. BROWN, N. L. DIETZ, Environ. Sci. Technol., 30 (1996) 81.
7. S. Y. LEE, J. D. MARSH, Oak Ridge National Lab. Publ. ORNL/TM-11980 ESD 3786, Oak Ridge National Laboratory, Oak Ridge, TN, 1992.
8. C. V. TIDWELL, D. E. MORRIS, D. E. CUNNANE, S. Y. LEE, Remediation, Spring, 1996, p. 81.
9. D. E. MORRIS, C. J. CHISOLM-BRAUSE, M. E. BARR, S. D. CONRADSON, P. G. ELLER, Geochim. Cosmochim. Acta, 17 (1994) 3613.
10. G. S. BROWN, S. DONIACH, in: Synchrotron Radiation Research, H. WINICH, S. DONIACH (Eds), Plenum, New York, 1980, p. 353.
11. D. PETIT-MAIRE, J. PETIAU, G. CALAS, N. JACQUET-FRANCILLON, J. Physique, C8 (1986) 849.
12. G. KALKOWSKI, G. KAINDL, W. D. BREWER, W. KRONE, J. Physique, C8 (1986) 943.
13. D. E. MORRIS, D. D. THORNTON, B. PADILLA, Los Alamos National Lab. Report LALP-94-19, 1994.
14. B. M. GORDON, K. W. JONES, Nucl. Instrum. Methods, B10/11 (1985) 293.
15. A. L. HANSON, K. W. JONES, B. M. GORDON, J. G. POUNDS, W. KWIATEK, M. L. RIVERS, G. SCHIKLOVSKY, S. R. SUTTON, Nucl. Instrum. Methods, B24/25 (1987) 400.
16. V. L. BATSON, P. M. BERTSCH, B. E. HERBERT, J. Environ. Quality, 25 (1996) 1129.
17. W. P. MILLER, D. C. MARTENS, L. W. ZELAZNY, Soil Sci. Soc. Am. J., 50 (1986) 598.
18. D. E. MORRIS, P. G. ALLEN, C. J. CHISOLM-BRAUSE, S. D. CONRADSON, R. J. DONOHOE, N. J. HESS, J. A. MUSGRAVE, C. D. TAIT, Environ. Sci. Technol., 30 (1996) 2322.
19. C. MOULIN, P. DECAMBOX, V. MOULIN, J. G. DECAILLON, Anal. Chem., 67 (1995) 348.