

An XAFS and μ SXRF Study of Uranium and Copper Speciation in Contaminated Sediments from the 300 Area, Hanford, WA

J. G. Catalano,¹ G. E. Brown, Jr.,^{1,2} J. M. Zachara³

¹Surface & Aqueous Geochemistry Group, Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115; ²Stanford Synchrotron Radiation Laboratory, SLAC, MS 99, 2575 Sand Hill Road, Menlo Park, CA 94025; ³Pacific Northwest National Laboratory, P.O. Box 999, MSIN K3-61, Richland, WA 99352

Introduction

The Hanford Site in Washington State was the location of much of the plutonium production for nuclear weapons during the Cold War. As part of these operations, the Hanford 300 Area was the site of fuel fabrication and other research and development activities. Approximately 25 separate locations in the 300 Area were used to dispose of radioactive and hazardous waste. Numerous areas of soil contamination are also present. Over 25 million cubic yards of solid and liquid waste were disposed of in ponds, trenches, and landfills. As no drains were provided, the liquid waste has percolated through the soil into the underlying groundwater, which flows into the nearby Columbia River. The groundwater is currently contaminated with uranium, and the soils and sediments contain high-levels of both uranium and copper.

It is essential to understand the speciation of uranium and copper in the contaminated soils and sediments of the 300 Area if predictive transport models are to be developed. This information is also essential to developing effective remediation strategies. In this study, we have used synchrotron-based X-ray spectroscopic methods to study the speciation of U and Cu in contaminated soil and sediment samples from the Hanford Site. Samples from the 300 Area were examined by μ SXRF to determine the microscopic distribution and element associations of Cu and U. These samples were also analyzed by U L_{III}- and Cu K-edge XAFS spectroscopy to determine the chemical speciation of these elements.

Methods and Materials

Four sediment and soil samples from the 300 Area were obtained for analysis (Table 1). Thin sections of samples NP4-1 and NP1-6 were prepared as described by Liu et al. [1]. Sample NP4-1, NP4-2, NP1-4.5, and NP1-6 were prepared for XAFS analysis by packing 250 to 300 mg of each sample in a Teflon® sample holder, which was then sealed with 10 mil Kapton® tape and heat-sealed in polyethylene bags.

μ SXRF mapping was performed on these thin sections using a focused X-ray beam on beamline ID-20 (PNC-CAT) at the Advanced Photon Source (APS). Focusing of the X-ray beam to a spot size of 20 μ m \times 20 μ m was accomplished using a pair of Kirkpatrick-Baez mirrors, and the incident beam was monochromatized using a Si (111) double-crystal monochromator.

U L_{III}- and Cu K-edge XAFS spectra were measured at room temperature on beamline BM-13 (GSECARS) at the APS using a Si (111) double-crystal monochromator. Data were collected in fluorescence-yield mode using a 13-element energy-dispersive solid-state Ge detector. The monochromator was detuned 40-60% to reduce the harmonic content of the incident X-ray beam. A yttrium (U L_{III}-edge) or copper (Cu K-edge) metal foil was mounted between two ionization chambers downstream of the sample for energy calibration, which was monitored continuously during each XAFS scan and was found

to vary by not more than ± 0.25 eV. All such variations were corrected for in the final spectra so that all spectra are referenced to the same energy scale. The first inflection point in the yttrium foil K-edge was set to 17038 eV, and in the copper foil K-edge to 8979 eV. XAFS data were processed using the SixPACK [2] interface to IFEFFIT [3]. XANES data were background-subtracted and normalized to an edge-step of 1. After background-subtraction, the EXAFS data ($\chi[k]$) were extracted and k^3 -weighted. The EXAFS spectrum of sample B11494 from a previous study [4] of the 300 Area North Process Ponds was also included in the analyses.

Table 1. Description of samples examined in this study.

300 Area Samples	U Conc.(ppm) ^a	Cu Conc. (ppm) ^a
NP1-4.5	1600	32400
NP1-6	400	5540
NP4-1	3000	14000
NP4-2	2400	4940
B11494 ^b	540	5530

^aAs determined by XRF. ^bSample data from Serne et al. [4]

Results and Discussion

μ SXRF Analysis of U and Cu Distribution

The microscopic distribution of U and Cu in thin sections of sample NP4-1 and NP1-6 was analyzed using μ SXRF (Fig. 1). Both U and Cu are distributed heterogeneously throughout the samples. In some locations, U and Cu appear highly correlated (Fig. 1A), while in other locations (Fig. 1B), they occur adjacent to one another, possibly in separate phases. Cu and Fe are generally uncorrelated (Fig. 1C).

XAFS Results

U L_{III}-edge XAS spectra were collected for samples NP4-1, NP4-2, NP1-4.5, NP1-6, and all contained only U(VI), based on the XANES spectra (data not shown). The EXAFS spectra of the four NP samples were similar (Fig. 2), suggesting there is little variability in the speciation of U in these samples. A comparison of these spectra to a library of EXAFS spectra of U(VI) mineral standards demonstrates a close match to uranyl tricarbonate phases (Fig. 3). The feature at $k=6.8 \text{ \AA}^{-1}$ in the EXAFS spectrum, and the hump at $R=3.7 \text{ \AA}$ in the Fourier Transform, generally identifies the presence of carbonate groups bound bidentate to U(VI), as occurs in the uranyl tricarbonates. However, there are some slight difference in the NP sample spectra and those of U(VI) tricarbonates (Fig. 4). These spectra are also similar to those reported for U(VI)-substituted CaCO₃ phases [5-7], and the sediment samples contain as much as 45 wt.% CaCO₃ (J.M. Zachara, personal communication). The Cu K-edge XAS spectra (Fig. 5) are generally consistent with aqueous Cu(II), as they lack a signal from a 2nd-shell neighbor. They also may be indicative of a poorly ordered phase.

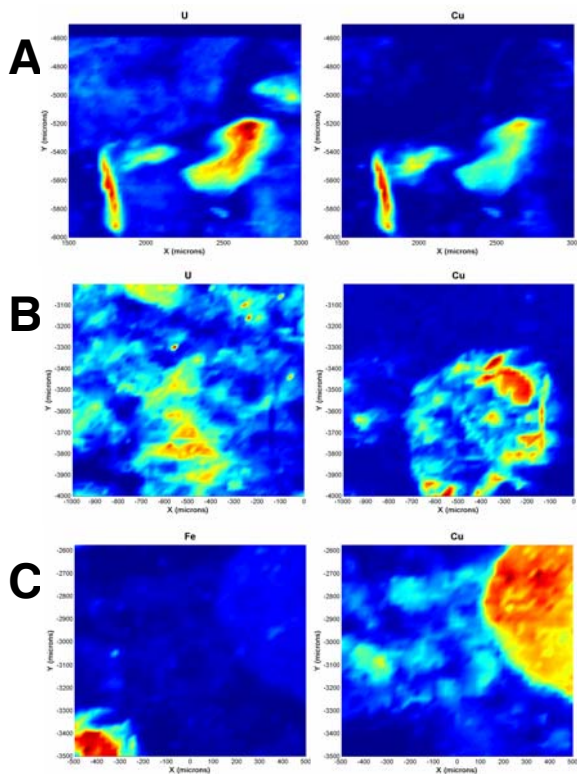


Fig. 1. (a) Area of sample NP1-6 showing overlapping distributions of U and Cu; (b) area of sample NP4-1 showing adjacent but non-overlapping distributions of U and Cu; and (c) area of sample NP4-1 showing distinct Fe-rich and Cu-rich regions.

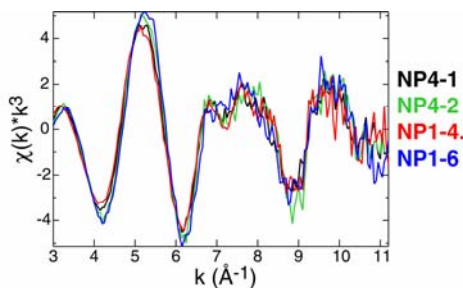


Fig. 2. Comparison plot of the k^3 -weighted EXAFS spectra of the four 300 Area samples.

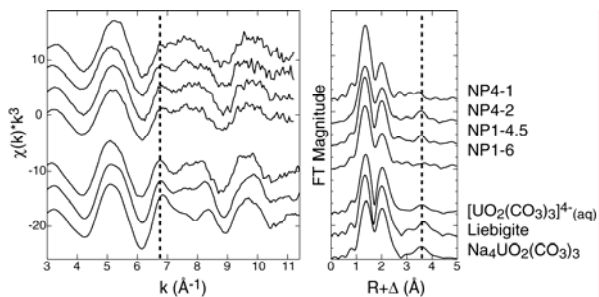


Fig. 3. Comparison of the EXAFS (left) and Fourier Transform (right) spectra of the four 300 Area samples to those of common uranyl tricarbonate phases.

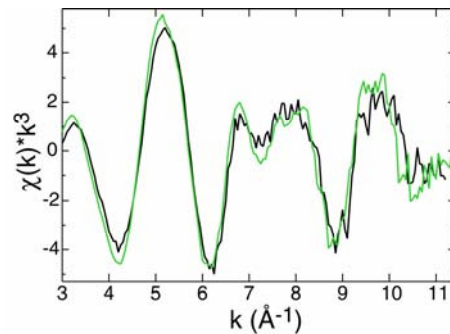


Fig. 4. Comparison of the EXAFS spectrum of sample NP4-2 (black) to that of aqueous $[UO_2(CO_3)_3]^{4-}$ (green).

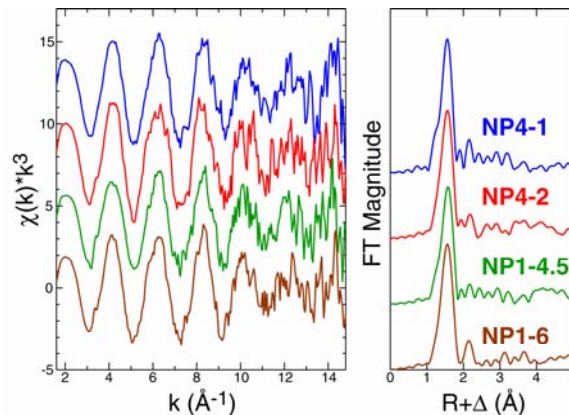


Fig. 5. Comparison of the Cu K-edge EXAFS (left) and Fourier Transform (right) spectra of the 300 Area samples.

Comparison of the EXAFS Spectra of 300 Area Samples to Previous Studies

The EXAFS spectra of the four 300 Area samples (Fig. 6) show little variability, and are similar to the spectra of U-substituted aragonite from [5] and U-substituted Method II calcite from Reeder et al. [6]. The EXAFS spectrum of sample B11494 (Fig. 10) is similar to the spectrum of U-substituted calcite sample of [7]. All the spectra considered in this study are consistent with U(VI) associated with $CaCO_3$ phases. While the presence of U contained in or associated with other phases cannot be ruled out, the majority of U appears associated with $CaCO_3$ in all samples. The variability in the NP sample spectra are possibly due to a variation in the amount of U contained in the Method I-type and Method II-type form of calcite substitution, or a variation in the amount of U contained in calcite and aragonite. As the Cu spectra lack distinguishing features beyond a 1st oxygen shell, it is not clear with what phase(s) Cu is associated. However, the EXAFS spectra of Cu(II) adsorption complexes on calcite surfaces are reported to also show a lack of significant structure [8].

Conclusions

- In the 300 Area soils and sediments, uranium occurs as U(VI) and copper as Cu(II).
- U and Cu are often found together or adjacent to one another; these always appear separate from Fe.
- U appears bound to carbonate groups, and is likely contained in a $CaCO_3$ mineral (calcite or aragonite).

- It is unclear what phase(s) Cu is bound to or associated with, although the data are consistent with an association to CaCO_3 minerals.
- Future U release in the 300 Area will be controlled by the dissolution of CaCO_3 minerals.

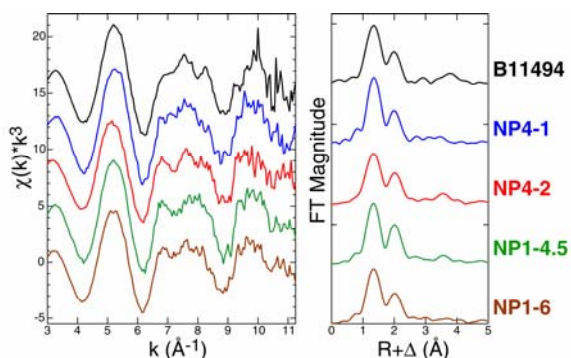


Fig. 6. Comparison of the U L_{III} -edge EXAFS (left) and Fourier Transform (right) spectra of samples from the 300 Area.

Acknowledgements

This research was supported by DOE-EMSP grant FG07-ER0263495 and Battelle contract 409089-A9E-P3623. We thank Sam Webb (SSRL) for insights on using SixPACK, Matt Newville (GSECARS) for support in collecting the XAFS spectra, and Julie Cross and Dale Brewé for assistance in collecting the μXRF data. Use of the Advanced Photon

Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. PNC-CAT is supported by funding from the U.S. Department of Energy-Basic Energy Sciences, the National Science Foundation, the University of Washington, the Natural Sciences and Engineering Research Council in Canada, and Simon Fraser University. GSECARS is supported by the National Science Foundation - Earth Sciences (EAR-0217473), Department of Energy - Geosciences (DE-FG02-94ER14466) and the State of Illinois.

References

- [1] C. Liu, J.M. Zachara, O. Quafoku, et al., *Geochim. Cosmochim. Acta.*, in press (2004).
- [2] S.M. Webb, *Phys. Scr.*, in press (2004).
- [3] M. Newville, *J. Synch. Rad.* **8**, 322-324 (2001).
- [4] R.J. Serne, C.F. Brown, H.T. Schaefer, E.P. Pierce, M.J. Lindberg, Z. Wang, P. Gassman, J.G. Catalano, 300 Area Uranium Leach and Adsorption Project Report. ERC FY01-02 Final Report. United States Department of Energy, Richland Operations, Richland, WA 99352 (2002).
- [5] R.J. Reeder, M. Nugent, G.M. Lamb, et al., *Environ. Sci. Technol.* **34**, 638 (2000).
- [6] R.J. Reeder, M. Nugent, C.D. Tait, et al., *Geochim. Cosmochim. Acta* **65**, 3491 (2001).
- [7] S.D. Kelly, M.G. Newville, L. Cheng, et al., *Environ. Sci. Technol.* **37**, 1284 (2003).
- [8] E.J. Elzinga, R.J. Reeder, *Geochim. Cosmochim. Acta* **66**, 3943-3954 (2002).