X-ray Microdiffraction Study of Uranium Speciation in Contaminated Vadose Zone Sediments from the Hanford Site, Washington

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Introduction

The Hanford Site in Washington State was the location of much of the Pu production for nuclear weapons during the Cold War. These production activities generated vast quantities of high-level nuclear waste. Much of this waste was in the form of aqueous-based sludge and was stored in large (hundreds of thousands of gallons) underground storage tanks. Unfortunately, a number of these tanks leaked, releasing large amounts of waste to the vadose zone. Subsequent transport of this waste has led to plume development in the underlying groundwater.

One area of particular concern is the spill associated with tank BX-102. The leak event associated with this tank released 91,600 gal of waste containing 7-8 metric tons of uranium. The waste was caustic (pH 10) and contained high concentrations of sodium, nitrate, carbonate, and phosphate. The result of this leak was a large uranium plume in the vadose zone [1].

Characterization studies have been underway for the past year to understand the distribution, molecular-scale speciation, and transport mechanisms of uranium in the vadose zone sediments. Knowledge of these variables and processes is essential for predicting the future transport of uranium in this plume, including its potential impact on groundwater. We have conducted extended x-ray absorption fine structure (EXAFS) spectroscopic studies of a number of samples from a borehole into the vadose zone beneath tank BX-102 and have found that uranium associated with the solid phase is a precipitate from the uranophane group of minerals [2]. These precipitates are quite small (0.1-1 μm) and are distributed heterogeneously throughout the grains in the vadose zone sediments [3]. Minerals from this group are silicates that contain U(VI) and structural alkaline or alkaline earth cations for charge balance. Unfortunately, the local structures of the minerals in this group are very similar, and their EXAFS spectra are effectively identical. Because their x-ray diffraction patterns differ substantially, micro x-ray diffraction (μXRD) can be used to identify which mineral or minerals from this group occur in these sediments. We have used μXRD to identify the specific uranophane group mineral present in two samples of contaminated sediments from the Hanford site.

Methods and Materials

Two samples of contaminated vadose zone sediments from beneath tank BX-102, Nos. 61A and 67A, were obtained for analysis. Thin sections of the samples were prepared as described in Ref. 4. Micro-scanning x-ray fluorescence (μSXRF) mapping was performed on these thin sections by using a focused x-ray beam at PNC-CAT beamline ID-20 at the APS. The x-ray beam was focused to a spot size of 20 × 20 μm by using a pair of Kirkpatrick-Baez mirrors, and the incident beam was monochromatized by using a Si(111) double-crystal monochromator. X-ray fluorescence was monitored with both a 13-element solid-state Ge energy-dispersive spectrometer and a log spiral bent Laue analyzer. Micro-EXAFS (μEXAFS) spectra were collected at select areas of high U concentration.

μXRD patterns were collected on select areas in transmission geometry by using phosphor image plates, which were read by a Fuji BAS2000 scanner. The resulting images were processed using FIT2D [5]. The sample-to-detector distance and geometric corrections were calculated from the pattern of Si. After these corrections were applied, the 2-D images were integrated radially to yield 1-D powder diffraction patterns that could then be analyzed by means of standard techniques. Background subtraction, including removal of the scattering from the glass slide, and phase identification were performed in JADE 6.5 (Materials Data Inc., Livermore, CA); some peak assignments were done manually.

Results

μSXRF mapping demonstrated that U was distributed heterogeneously throughout the samples and was not significantly correlated with other elements. An example map is shown in Fig. 1. μEXAFS spectra collected on select areas of high U concentration agreed well with the bulk spectra (Fig. 2), especially considering the numerous errors inherent in μEXAFS due to beam motion, sample vibration, and self-absorption of concentrated particles.

μXRD patterns were collected on six hot spots identified by μSXRF (six per thin section). The radially

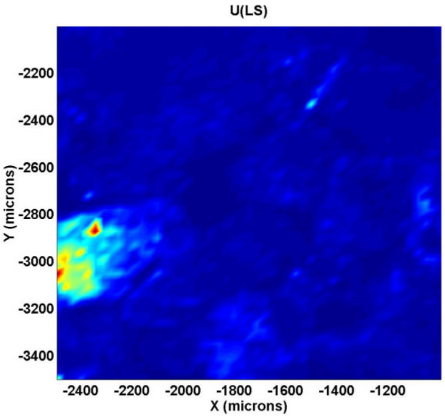

FIG. 1. Example μSXRF map of the uranium distribution in sample 61A. The U L_a fluorescence was measured with a log spiral bent Laue analyzer. Red corresponds to the highest U concentration.

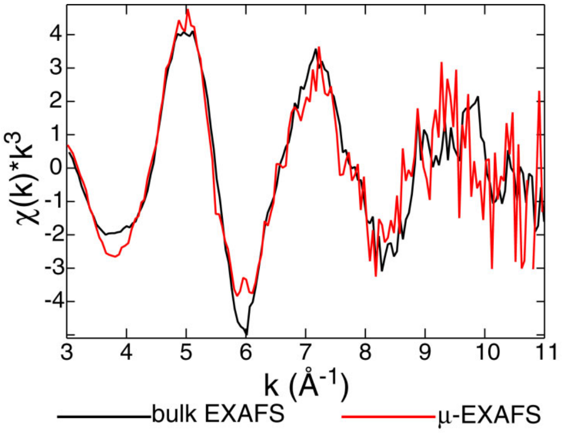

FIG. 2. Comparison of μEXAFS spectrum of a 20 × 20 μm area of high U concentration in sample 61A to the bulk EXAFS spectrum from the same sample [2].

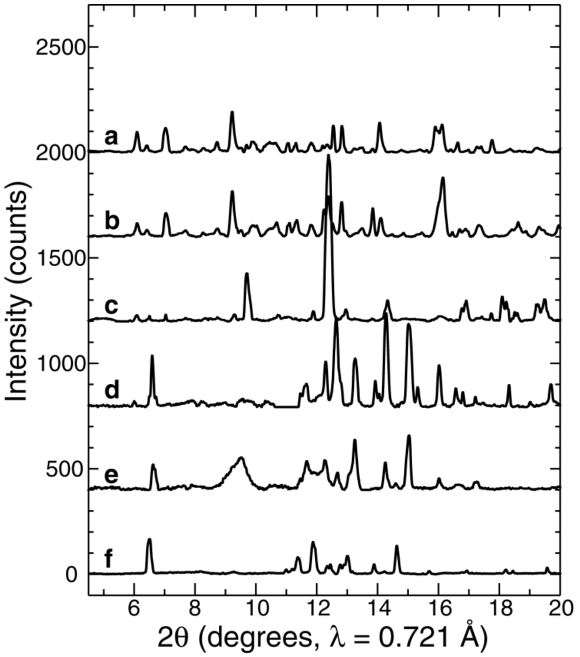

FIG. 3. Radially integrated and background-subtracted μXRD patterns from areas of high U concentration in samples 61A (a-c) and 67A (d-f).

integrated and background-subtracted patterns are shown in Fig. 3. Because all of the raw, 2-D patterns contained numerous sharp spots and few powder rings, the relative intensity of the peaks in the processed patterns are not accurate, and quantitative modeling of the patterns, such as use of Rietveld refinement methods to determine the relative percentages on individual phases, is not possible. While too numerous to label individually, most reflections in the patterns with d-spacings less than 6.5 Å (2θ larger than ~6.2°) are due to feldspar and quartz grains that make up the majority of these samples.

Although many of the strongest diffraction lines for the uranophane group minerals occur in the same region as the multiple feldspar and quartz lines, the most intense reflection for each mineral in this group occurs in the relatively "clean" 6.5-8.5 Å region. Examination of this region shows that strongest reflection of sodium-boltwoodite was present in four hot spots, three from 61A and one from 67A (Fig. 4). Reflections from other uranophane group minerals were not observed. The lack of reflections from any uranophane group minerals in two of the patterns is likely due to diffraction from only a small number of uranium-bearing particles. Because the uranium-bearing precipitates occur as crystallites that are 0.1 to 3 μm in size [3], the use of a 20-μm-diameter x-ray beam for diffraction may prevent illumination of enough particles to create a powder pattern. Since some patterns may be from areas containing 10 or fewer crystals, it can be expected that some reflections (e.g., the strongest lines of the uranophane group minerals) will not be observed. Even if reflections in the <6.5-Å region from an uranophane group mineral were present, the significant overlap of these reflections with those from other phases (e.g., quartz and feldspar) in the sample would make identification ambiguous. Additionally, the experimental setup necessary for these experiments requires transmission of the direct and diffracted beams through ~80 μm of minerals and epoxy as well as ~1 mm of glass. These phases induced a large background and intense point reflections, both of which lead to noise and detector saturation that make it difficult to observe reflections

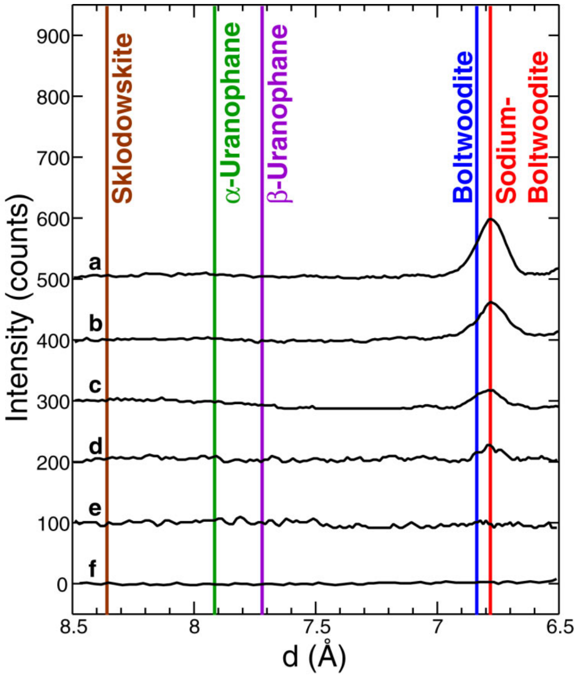

FIG. 4. μXRD patterns from areas of high U concentration in samples 61A (a-c) and 67A (d-f) plotted versus d-spacing for the region of the most intense lines of uranophane group minerals.

from phases in low concentration. Although only observed in four patterns, the presence of the primary reflection of sodium-boltwoodite and the lack of evidence for other uranophane group minerals suggest that sodium boltwoodite is the primary uranium species present in these samples.

Conclusions

μXRD confirmed the presence of sodium-boltwoodite in the vadose samples from below tank BX-102; no other uranophane group minerals were observed. Since this phase is moderately soluble, future dissolution will likely provide a continuous source of dissolved uranium to porewater and the groundwater below.

Acknowledgments

This research was supported by the U.S. Department of Energy (DOE) Environmental Management Science Program Grant No. FG07-ER0263495 and Battelle Contract No. 409089-A9E-P3623. We thank J. Serne, P. Gassman, S. Smith, and Z. Wang (PNNL) for preparing and shipping the thin sections to the APS. We also thank J. Cross and D. Brewe (PNC-CAT) for assistance with data collection at the APS, and thank P. Eng, S. Sutton, and V. Prakapenka (GSECARS) for providing the detector for the microdiffraction experiments. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. PNC-CAT is supported by funding from DOE BES, the National Science Foundation, the University of Washington, the Natural Sciences and Engineering Research Council in Canada, and Simon Fraser University.

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