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

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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 μSXRF to determine the microscopic distribution and element associations of Cu and U. These samples were also analyzed by U L_{3,2} 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.

μSXRF 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 µm × 20 µm was accomplished using a pair of Kirkpatrick-Baez mirrors, and the incident beam was monochromatized using a Si (111) double-crystal monochromator.

U L_{3,2} 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_{3,2}) 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 (χ(k)) were extracted and k^2-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.

Results and Discussion
μSXRF 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 μSXRF (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).

<table>
<thead>
<tr>
<th>300 Area Samples</th>
<th>U Conc.(ppm)*</th>
<th>Cu Conc. (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP1-4.5</td>
<td>1600</td>
<td>32400</td>
</tr>
<tr>
<td>NP1-6</td>
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<td>5540</td>
</tr>
<tr>
<td>NP4-1</td>
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<tr>
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<td>4940</td>
</tr>
<tr>
<td>B11494</td>
<td>540</td>
<td>5530</td>
</tr>
</tbody>
</table>

*As determined by XRF. *Sample data from Serne et al. [4]

XAFS Results
U L_{3,2}-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 Å⁻¹ in the EXAFS spectrum, and the hump at R=3.7 Å 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.

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References