

**Project 86748**  
**Characterization of U(VI) Sorption-Desorption Processes and Model**  
**Upscaling**  
**William P. Ball**  
**Johns Hopkins University**

**RESULTS TO DATE:** Introduction and Project Objectives

In order to apply predictive reactive transport models to the Hanford site, detailed knowledge of the speciation of contaminants is required. Important speciation parameters include: (1) oxidation state; (2) the local molecular structure surrounding contaminant elements; (3) the type and binding of a contaminant ion sorption complex (if adsorbed); (4) the type(s) of phase within which a contaminant is structurally incorporated [e.g., present in a three-dimensional precipitate(s)]; (5) the phase associations of a contaminant; (6) the microscopic distribution of a contaminant within sediments and soils.

In the present 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. To complement and complete our initial XAFS investigation of U speciation in contaminated vadose zone sediments below tank BX-102, we have also performed mXRD studies of two sediment samples to identify the specific U(VI)-silicate phase present. Samples from the 300 Area were examined by mSXRF to determine the microscopic distribution and element associations of Cu and U. These samples were also analyzed by U LIII- and Cu K-edge XAFS spectroscopy to determine the chemical speciation of these elements.

**Conclusions to Date**

- (1) Uranium occurs primarily as sodium-boltwoodite  $[\text{Na}_2(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 3\text{H}_2\text{O}]$  in the BX-102 sediment samples.
- (2) The dissolution kinetics of sodium-boltwoodite will be a major control on the future transport of U beneath tank BX-102.
- (3) In the 300 Area soils and sediments, uranium occurs as U(VI) and copper as Cu(II).
- (4) U and Cu are often found together or adjacent to one another; however, these elements don't appear to be spatially associated with Fe.
- (5) U appears to be bound to carbonate groups, and is likely contained in a  $\text{CaCO}_3$  mineral (calcite or aragonite).
- (6) It is unclear what phase(s) Cu is bound to or associated with, although the data are consistent with an association with  $\text{CaCO}_3$  minerals.
- (7) Future U release in the 300 Area will be controlled by the dissolution of  $\text{CaCO}_3$  minerals.

**DELIVERABLES:** (1) J.G. Catalano and G.E. Brown, Jr. (2004) Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences. *Am. Mineral.* (in press).

(2) G.E. Brown, Jr., J.G. Catalano, A.S. Templeton, T.P. Trainor, F. Farges, B.C. Bostick, T. Kendelewicz, C.S. Doyle, A.M. Spormann, K. Revill, G. Morin, F. Juillot, and G. Calas (2004) Environmental interfaces,

heavy metals, microbes, and plants: Applications of XAFS spectroscopy and related synchrotron radiation methods to environmental science. *Physica Scripta* (in press).

(3) J.G. Catalano and G.E. Brown, Jr., EXAFS study of uranyl adsorption on Wyoming montmorillonite. *Proceedings of Water-Rock Interactions XII*. (submitted).

(4) J.G. Catalano, S.M. Heald, J.M. Zachara, and G.E. Brown, Jr., Spectroscopic and diffraction study of uranium speciation in contaminated vadose zone sediments from the Hanford site, Washington State, USA. *Environ. Sci. Technol.* (submitted).