

Uranium Speciation in Contaminated Sediments: XAFS Studies of Model and Natural Systems

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Statement of Problem and General Approach: Long-term sequestration of uranium at sites within the DOE complex is a significant problem that requires molecular-level information on the speciation, phase association, and spatial distribution of uranium. Designing remediation/sequestration strategies relevant to complex natural systems requires studies of uranium speciation and interactions in simplified model systems as well as in the natural systems. We have used this coupled approach to conduct molecular-level studies of the speciation and phase association of uranium in the vadose zones of Hanford Area 200 and Area 300 sites as well as in model systems designed to understand how U(VI) adsorbs to mineral surfaces.

Speciation of Uranium in the Hanford Area 200 Vadose Zone: Contamination of vadose zone sediments under tank BX-102 at the Hanford site, WA, resulted from the accidental release of 7 to 8 metric tons of uranium dissolved in caustic aqueous sludge in 1951. We have applied synchrotron-based X-ray spectroscopic and diffraction techniques to characterize the speciation of uranium in samples of these contaminated sediments [Catalano *et al.*, *Environ. Sci. Technol.* 38, 2822, 2004]. U L_{III}-edge X-ray absorption fine structure (XAFS) spectroscopic studies demonstrate that uranium occurs predominantly as a U(VI)-silicate from the uranophane group of minerals. XAFS cannot distinguish between the members of this mineral group due to the near identical local coordination environments of uranium in these phases. However, these phases differ crystallographically, and can be distinguished using X-ray diffraction (XRD)

methods. As the concentration of uranium was too low for conventional XRD to detect these phases, X-ray microdiffraction (μ XRD) was used to collect diffraction patterns on ~ 20 μ m diameter areas of localized high uranium concentration found using micro-scanning x-ray fluorescence (μ SXRF). Only sodium-boltwoodite, $\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}$, was observed; no other uranophane group minerals were present. Sodium-boltwoodite formation has effectively sequestered uranium in these sediments under the current geochemical and hydrologic conditions. Attempts to remediate the uranium contamination will likely face significant difficulties because of the speciation and distribution of uranium in the sediments.

Speciation of Uranium in the Hanford Area 300 Vadose Zone: The disposal of basic sodium-aluminate and acidic U(VI)-Cu(II) wastes into the now-dry North and South 300 A Process Ponds at the Hanford site resulted in a U(VI) groundwater plume. To gain insight into the geochemical processes that occurred during waste disposal and that will affect the future fate and transport of this uranium plume, the solid-phase speciation of uranium in a depth sequence from the base of the North Process Pond through the vadose zone to the water table was investigated using electron microprobe measurements and XAFS spectroscopy [Catalano *et al.*, *Environ. Sci. Technol.* **40**, 2517, 2006]. Uranium in sediments from the base of the pond was predominantly co-precipitated with calcite. From ~ 2 m below the pond base to the water table uranium occurred dominantly in a sorbed form, likely on the surface aluminosilicate clay minerals. The presence of a U(VI)-phosphate phase was also observed in this region, but it only occurred as a major uranium species at one depth. The initial sequestration of U(VI) in these sediments likely occurred through co-precipitation with calcite as conditions did not favor adsorption. As the calcite-bearing pond sediments have been removed as part of a remediation effort, future uranium fate and transport will likely be controlled primarily by adsorption/desorption phenomena.

Model System Studies: In addition to a detailed XAFS study of uranyl environments in a wide variety of crystalline model compounds [Catalano and Brown, *Am. Mineral.* **89**, 1004, 2004], we have also conducted a series of model system studies in which the interaction of U(VI) with various mineral surfaces has been examined using synchrotron-based x-ray spectroscopy and x-scattering experiments. In bulk XAFS studies of the interaction of U(VI) with a Wyoming montmorillonite (SWy-2) under atmospheric conditions [Catalano and Brown, *Geochim. Cosmochim. Acta* **69**, 2995, 2005], we found that U(VI) forms dominantly outer-sphere complexes at pH 4 and an ionic strength of 10^{-3}M , consistent with binding in cation exchange sites. In contrast, at pH 7 and an ionic strength of 1M , we found that U(VI) binds dominantly in an inner-sphere fashion to edge sites, most likely as uranyl-carbonato complexes bound primarily to $\text{Fe}(\text{O},\text{OH})_6$ sites rather than $\text{Al}(\text{O},\text{OH})_6$ sites. In another study [Catalano *et al.*, *Geochim. Cosmochim. Acta* **69**, 3555, 2005] we carried out a combination of GI-XAFS and crystal truncation rod diffraction measurements on U(VI) complexes on hydrated $\alpha\text{-Al}_2\text{O}_3$ (1-102) and $\alpha\text{-Fe}_2\text{O}_3$ (1-102) surfaces, which have similar surface structures. On both surfaces we

found that uranyl-carbonato complexes form. However, the mode of binding is dominantly monodentate on the α -Al₂O₃ (1-102) surface and dominantly bidentate on the α -Fe₂O₃ (1-102) surface. Both XPS and CTR diffraction showed higher U(VI) surface coverages on α -Fe₂O₃ (1-102) than on the α -Al₂O₃ (1-102) surface. In addition, the surface complexes observed are different from the bidentate mononuclear complexes that are typically derived for U(VI) on powdered Al- and Fe-(oxyhydr)oxide surfaces. In a final model system study, we examined the structure and reactivity of biogenic UO₂ produced by *Shewanella putrificiens* CN-32 after reaction with aqueous uranyl ions [Singer *et al.*, *Am. Inst. Phys. Conf. Proc.*, 2007 (in press)]. UO₂ reactivity was studied by batch uptake of Zn(II) on nanoparticulate UO₂ produced by these bacteria and on macroparticles of abiogenic UO₂. We found that the nano-scale UO₂ is easier to oxidize and more reactive to aqueous metal ions than bulk UO₂ and that its structure is more disordered than that of bulk UO₂. We also found that the organic coating on the biogenic UO₂ interferes with the reaction of aqueous Zn(II) and prevents Ostwald ripening from occurring during heating of the biogenic UO₂ (@90°C for two weeks). These findings have implications for remediation of U-contaminated sites at Oak Ridge National Laboratory.

Selected results from these studies will be presented during the seminar.