

**ENVIRONMENTAL AND WASTE MANAGEMENT:  
ADVANCEMENTS THROUGH THE ENVIRONMENTAL  
MANAGEMENT SCIENCE PROGRAM**

**Organized by**

**T. Zachry**

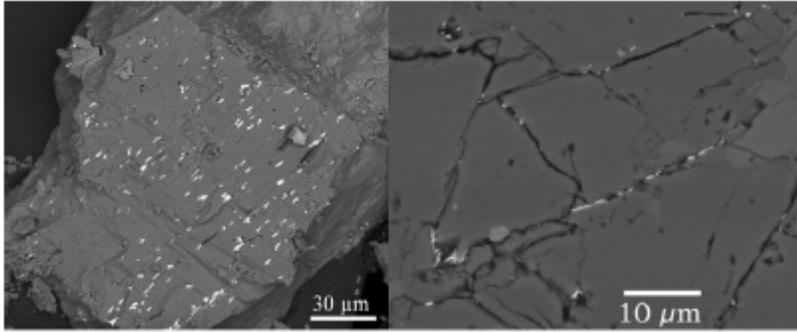
Symposia Papers Presented Before the Division of Environmental Chemistry  
American Chemical Society  
Anaheim, CA      March 28 – April 1, 2004

**INFLUENCE OF MICROSCOPIC DIFFUSIVE  
PROCESS ON URANYL PRECIPITATION AND DISSOLUTION  
IN SUBSURFACE SEDIMENTS AT HANFORD SITE, USA**

Chongxuan Liu, John M. Zachara, James P. McKinley,  
Zheming Wang and Paul D. Majors  
Pacific Northwest National Laboratory, P.O. Box 999, K8-96, Richland, WA  
[Chongxuan.liu@pnl.gov](mailto:Chongxuan.liu@pnl.gov), Fax: (509) 376-0129

**INTRODUCTION**

Nuclear waste, spilled onto sediments at the Hanford Site, USA, interacted selectively with granitic clasts (feldspar), forming precipitates of uranyl silicate that occurred almost exclusively in microfractures within the clasts (McKinley *et al.*, 2003). The waste was spilled in 1951 in a leak event from a storage-tank that totaled about 350 m<sup>3</sup>, dispersing over 7000 kg of uranium in an alkaline matrix of sodium carbonate, nitrate, phosphate and sulfate (Jones *et al.*, 2000). Most or all of the waste was entrained beneath the “tank farm” where it originated, in the vadose zone, and where the uranium precipitated as a uranyl silicate phase, perhaps sodium boltwoodite. The uranyl silicate precipitates were found to be discreetly distributed as minute, generally 1 to 3 μm across in either radiating or parallel arrays in intraparticle microfractures of a few microns width and variable connectivity to particle surfaces (Fig. 1) (Liu *et al.*, 2003). These microscopic observations suggested the potential importance of diffusive mass transport in uranium removal from waste plumes and concentration within particle grains and future dissolution and remobilization to the groundwater mobile regions in the sediments.



**Figure 1.** Back-scattered-electron SEM images showing intraparticle uranium distribution within a plagioclase feldspar grain. Electron dense U(VI) precipitates appear white in the images. Left image shows U(VI) crystallites that are aligned in parallel with cleavages on an intraparticle surface that was obtained by pressure-splitting the feldspar grain along a microfracture plane. Right image shows U(VI) precipitates within microfractures in a thin section that was perpendicular to the plane surface in the left image.

## EXPERIMENTAL PROCEDURES

The porosity, tortuosity, and diffusivity within sediment particles that were from both contaminated and uncontaminated core samples were determined using scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) techniques. The thermodynamic and kinetic behavior of the uranyl precipitates were studied using synthetic and natural sediments containing uranyl precipitates in electrolytes of Na, Na-Ca,  $\text{NH}_4$  in different pH and ambient  $\text{CO}_2$  pressure. X-ray diffraction (XRD), laser-induced fluorescence spectroscopy (LIFS), SEM, X-ray microprobe (XRM) and X-ray photon spectroscopy (XPS) were used to determine microscopic changes during thermodynamic and kinetic measurements of uranyl precipitates.

## MODEL DEVELOPMENT

A multicomponent reactive ion diffusion model was developed to describe species diffusion and reactions within microfractures of particle grains. The aqueous complex species were calculated using an equilibrium speciation code applicable at high ionic strength (Felmy, 1995). The model was numerically solved through iteration between reactive diffusion and speciation calculations.

## RESULTS AND DISCUSSION

The intraparticle porosity of the feldspar grains that were the host of uranyl precipitates was small (about 0.1%) determined from SEM images. The small intraparticle porosity posed a challenge to measure the intraparticle diffusivity and tortuosity using traditional tracer displacement approaches. Here we developed a NMR technique that magnetically labels  $\text{H}_2\text{O}$  as tracer molecules within intraparticle regions and measures their diffusion rates. The influence from surface-bound  $\text{H}_2\text{O}$  was suppressed by NMR filtering. The results showed that the  $\text{H}_2\text{O}$  diffusivity within intraparticle regions was a function of diffusion time and reached an asymptotic state after about 10 seconds. The asymptotic diffusivity was about one order of magnitude lower compared with that in

free water. The apparent tortuosity was calculated as a ratio of the asymptotic diffusivity to the diffusivity in free water. The apparent diffusivities for other species were estimated from their diffusivities in free H<sub>2</sub>O corrected by the tortuosity.

The solubility of the intraparticle uranyl precipitates was close to Na-boltwoodite, consistent with spectroscopic measurements. The dissolution rate and extent of the uranyl precipitates increased with increasing carbonate concentration. The rate was initially fast, but decreased with time as the solubility equilibrium was attained and diffusive mass transfer became rate-limiting. Spectroscopic changes of the uranyl precipitates during the dissolution experiments were negligible. A kinetic model that incorporates the influence of carbonate and solubility based on surface coordination chemistry was proposed for the dissolution of the intraparticle uranyl precipitates and were successfully tested against independent dissolution experiments using synthetic Na-boltwoodite.

Simulations using multicomponent ion diffusion model with transport parameters and tank waste compositions estimated independently indicated that the restricted diffusive mass transfer generated a thermodynamically favorable condition during waste sediment interactions for Na-boltwoodite precipitation and concentration in microfractures within feldspar particle grains. The calculations were consistent with the microscopic observations that uranyl precipitates were scarcely on the surface of sediment particles and more abundant inside particle grains. The multicomponent ion diffusion model also indicated that the dissolution rates of uranyl precipitates from the sediment grain microfractures was limited by the intraparticle ion diffusion. Model calculations indicated that 50-95% of the precipitated uranium was associated with microfractures that were in close contact with the aqueous phase. The remainder of the uranium was deeply imbedded in particle interiors and exhibited effective diffusivities that were over three orders of magnitude lower.

## **ACKNOWLEDGEMENTS**

This research was supported by the U.S. Department of Energy (DOE) through the Environmental Management Science Program (EMSP) and Natural and Accelerated Bioremediation Research Program (NABIR) and also supported by the Hanford Science and Technology Program managed by the River Protection Program.

## **REFERENCES**

- Felmy A. R. (1995) GMIN, A computerized chemical equilibrium program using a constrained minimization of the Gibbs free energy: Summary report. In *Chemical equilibrium and reaction models* (ed. R. H. Loeppert, Schwab, A.P. and Goldberg, S.), pp. 377-407. Soil Science Society of America.
- Jones, T. E., Watrous, R. A. and Maclean, G. T. (2000) Inventory Estimates for Single-Shell Tank Leaks in S and SX Tank Farms.
- Liu, C., Zachara, J. M., Qafoku, O., McKinley, J. P., Heald, S. C. and Wang, Z. (2003) Dissolution of Uranyl Microprecipitates from Subsurface Sediments at Hanford Site, USA. *Geochimica et Cosmochimica Acta* submitted.

McKinley, J. P., Zachara, J. M., Liu, C. and Heald, S. C. (2003) Precipitation of waste uranium as a uranyl silicate in microfractures. *Nature* Submitted.