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Influence of Mass Transfer on Bioavailability and Kinetic Rate of Uranium(VI) Biotransformation

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Research Objective

This research is investigating the influence of mass transfer process on the rate and extent of microbial reduction of U(VI) associated with intragrain domains in the Hanford subsurface sediments. The project will develop instrumental techniques to characterize microscopic mass transfer process at the sediment grain scale and to develop kinetic data and process models that describe microbial reduction of intragrain U(VI). Scientific knowledge and process models developed from this research will enhance our understanding on the future behavior of in-ground U(VI) at Hanford and other DOE sites where sediments contain U(VI) in intragrain domains or fracture-matrix systems.

Research Progress and Implications

This project started on Oct. 1, 2003. The report summarizes results from its inception to 9/31/2006. The project has been focused on: 1) developing techniques and models to characterize and simulate intragrain diffusive mass transfer process in granitic lithic fragment of the Hanford 200A sediment, which contains intragrain U(VI) precipitates; and 2) investigating microbial reduction of intragrain U(VI) using synthetic grains and Hanford 200A contaminated sediments.

We have developed a nuclear magnetic resonance (NMR) pulse-field gradient spin echo (PGSE) technique to identify and characterize intragrain diffusion process at the grain scale. The approach nondestructively measures the self-diffusion of H₂O molecules as a tracer in intragrain fractures by measuring the magnetic moment of H₂O (actually ¹H associated with H₂O) molecules in conjunction with position-encoding magnetic field gradients (*G*) to determine the statistical displacement of ¹H₂O molecules during a known diffusion time interval Δ . The technique can avoid chemical retardation or exclusion effects that may associate with traditional tracers such as bromide. Using the developed technique, two diffusive mass transfer domains with distinctive diffusivity values were defined in the granitic lithic fragment of the Hanford 200A sediments. The fast diffusion domain was associated with large and well-connected fractures that had an averaged tortuosity of 1.5. The slow diffusion domain was associated with small and poorly connected fractures that had an average tortuosity of 161. The results implied that the rates of U(VI) release from intragrain regions will be time-variable with initial rates dominated by coupled U(VI) desorption/dissolution and mass transfer in the fast diffusion domain, followed by slow ones from the slow diffusion domain. The microscopic characterization provided insights and diffusion parameters for constructing

numerical models for modeling intragrain mass transfer, and interpreting the time-variable U(VI) release from Hanford 200-area sediment observed in both batch and column experiments.

The tortuosity determined from NMR measurements can be used to scale ion (e.g., UO_2^{2+}) diffusivity from bulk water to intragrain domain. The ion diffusivity in bulk water is relatively easy to measure and many ion diffusivity values in bulk water have been reported in literature. However, the diffusion of ions in porous media is coupled by electrostatic potentials, and affected by mineral surface charge and electrostatic double layers. We have developed a theory that can explicitly incorporate such microscopic mineral surface properties into an effective diffusivity model. The model is based on coupled ion electrodynamics and nonequilibrium thermodynamics (EDNT) that allows to explicitly include the effect of dynamic interactions of ions between mineral surfaces and pore spaces. The model has been validated against experimental measurements of ion diffusivity as a function of ion strength, which affects the electrostatic interactions between ions and mineral surfaces. The important implication of this work is that ion diffusive mass transfer rates in porous media can now be theoretically scaled from ion diffusive rates in bulk water. This work not only advances theoretical knowledge of ion diffusive mass transfer in porous media, but also significantly simplifies the characterization of intragrain diffusion measurements, which are often challenging and difficult for most environmentally relevant species such as those containing U(VI).

We initially evaluated microbial reduction of intragrain U(VI) using a synthetic uranyl silicate phase, Na-boltwoodite, which has the same spectroscopic properties as the uranyl precipitates in the contaminated sediments from the Hanford 200A. The synthetic phase was characterized in solutions that are representative of Hanford groundwater to determine its solubility and kinetic properties. The bioreduction was studied with Na-boltwoodite in suspension or entrapped within alginate beads to evaluate the coupling of U(VI) dissolution, diffusion, and microbial activity using a representative dissimilatory metal-reducing bacterium (DMRB), *Shewanella oneidensis* strain MR-1. Microscopic and spectroscopic analyses with transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and laser-induced fluorescence spectroscopy (LIFS) collectively revealed that solid phase U(VI) was first dissolved and diffused out of grain interiors before it was reduced on bacterial surfaces and/or within bacterial periplasm. The overall rates of microbial reduction of intragrain U(VI) could be well described by a model coupling dissolution of intragrain U(VI) promoted by aqueous U(VI) complexation, diffusion of U(VI) aqueous species out of intragrain region, and microbial reduction of dissolved U(VI) (Figure 1). The important implication of this result is that the observed aqueous U(VI) concentration in subsurface sediments will be a complex function of geochemical dissolution/desorption reaction, microscopic mass transfer kinetics, and microbial activity.

Similarly as observed in the synthetic systems, the aqueous U(VI) concentration during microbial incubation of contaminated Hanford sediments was also controlled by the coupling of dissolution/diffusion of intragrain U and microbial reduction of dissolved U(VI). The behavior of intragrain U(VI) in the sediment was, however, more complicated

than that observed in synthetic systems. Figure 2A showed a grain containing residual U that was heterogeneously distributed, but generally more abundant toward the grain center despite that sediment had been biologically reduced for 60 days and strong U(VI) concentration gradient between intra- and inter- grain regions was maintained by microbial activity in bulk solutions. The results were consistent with the NMR-PGSE measurements, which implied that U(VI) release would be rate-limited by slow intragrain diffusion after U(VI) was removed from the domains near grain surfaces and large fractures. Valence analysis using X-ray absorption near edge structure (XANES) revealed the mixed valence of U(IV)/U(VI) (Figure 2B) that coexisted with mixed valence of Fe(II)/Fe(III) (Figure 2C) in the intragrain regions after 60 days of microbial incubation. There was no intragrain U(IV)/Fe(II) in the initial sediments and no intragrain U(IV) was observed in the microbially incubated synthetic grain systems, implying that Fe(II) that was solubilized from the sediments have migrated into the intragrain regions and interacted with U(VI). The results also implied that U stability in subsurface sediments may be enhanced by microbial reduction that produces biogenic Fe(II) to reduce intragrain U(VI) with contaminant precipitation of Fe(III) and U(IV), which subsequently decreases intragrain U solubility and mass transfer rates.

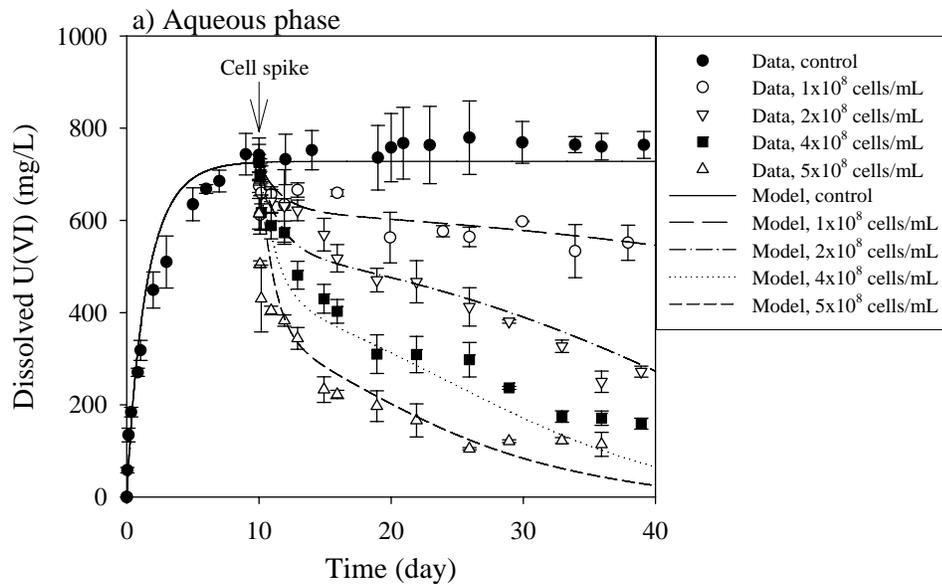


Figure 1. Experimental and modeling results of U(VI) release from intragrain Na-boltwoodite through dissolution and diffusion within the first 10 days, and coupled dissolution and diffusion with microbial reduction of dissolved U(VI) after 10 days when MR-1 cells with variable concentrations were provided.

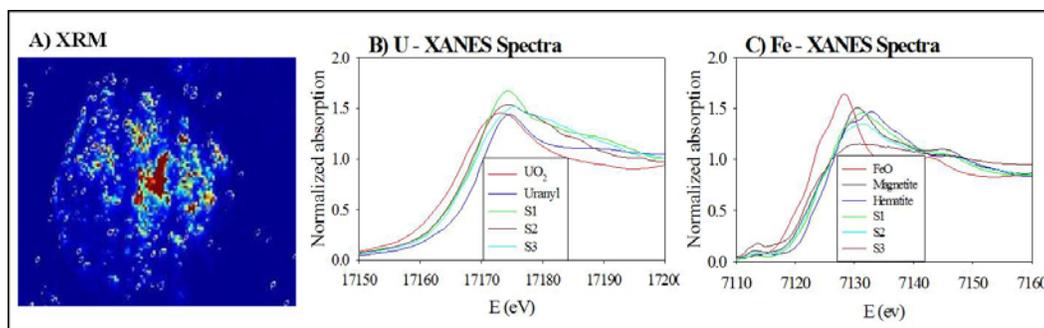


Figure 2. A) X-ray microprobe (XRM) showed the increasing abundance (redness) of residual U within the sediment grains toward the grain center after microbial reduction for 60 days. XANES analysis indicated a mixed valence distribution of U(VI) and U(IV) (plot B) and mixed valence distribution of Fe(II) and Fe(III) (plot C) inside the grain.

Planned Activities

The project is near completion in September, 2006. The post-doc research associate working on the project, Dr. Byong-Hun Jeon, has moved to become a university faculty in Yonsee University, South Korean, which has slowed the progress. The carryover funds will be used to analyze experimental results and summarize the results for journal publications in FY07.

Information Access

Journal Publications

Liu, C., B. -H. Jeon, J. M. Zachara, Z. Wang, A. Dohnalkova, and J. K. Fredrickson. 2006. Kinetics of microbial reduction of solid phase U(VI). *Environ. Sci. Technol.*, **40**, 6290-6296.

Ilton, E. S., C. Liu, W. Yantasee, Z. Wang, D. Moore, and J. M. Zachara. 2006. The effect of carbonate on the dissolution of synthetic Na-boltwoodite. *Geochim. Cosmochim. Acta*, **70**, 4836-4849.

Liu, C., J. M. Zachara, L. Zhong, R. K. Kukkadapu, J. E. Szecsody, and D. W. Kennedy. 2005. Influence of sediment bioreduction and reoxidation on uranium sorption. *Environ. Sci. Technol.* **39**: 4125-4133.

Liu, C., J. M. Zachara, A. R. Felmy, and Y. A. Gorby. 2004. An electrostatics-based model for ion diffusion in microbial polysaccharides. *Colloids and Surfaces B*, **38**:55-65.

Conference or seminar presentation

Liu C, JM Zachara, B Jeon, Z Wang, JP McKinley, and JK Fredrickson. 2006. Microscopic mass transfer process and its influence on microbial reduction of sorbed uranium(VI) in subsurface sediments. Contributed talk in American Geophysical Western Conference, July 2006, Beijing, China.

Liu C., Microscopic mass transfer process and theory, Invited speaker at International Groundwater Workshop, Beijing, China on July 22, 2006.

Liu C, Z Wang, JM Zachara, JK Fredrickson, B-H Jeon, L Zhong, JP McKinley, and Heald SM 2006. Microscopic mass transfer process and its influence on microbial reduction of U(VI). Invited talk at DOE ERSP PI Meeting, Warrenton, VA. 2006.

Liu C, PD Majors, JM Zachara, and JP McKinley. 2005. Microscopic reactive diffusion of U(VI) in subsurface sediments: characterization and modeling." Invited talk at 15th Goldschmidt Conference: A Voyage of Discovery, Moscow, ID on May 23, 2005

Liu C, Z Wang, JM Zachara, JK Fredrickson, B Jeon, PD Majors, W Yantasee, and Y Fang. 2005. Influence of mass transfer on bioavailability and kinetic rate of uranium(VI) biotransformation." Invited poster presentation Annual NABIR PI Workshop, Warrenton, VA on April 18, 2005.

Felmy AR, C Liu, and T Straatsma. 2005. The importance of diffusion at the microbe-mineral interface: electrical double layer effects and the impact on precipitation/dissolution." Contributed talk at Annual Goldschmidt Conference: A Voyage of Discovery, Moscow, ID on May 23, 2005.

Liu C, JM Zachara, JP McKinley, Z Wang, and PD Majors. 2004. Influence of microscopic diffusive process on uranyl precipitation and dissolution in subsurface sediments at Hanford Site, U.S.A. Contributed talk at American Chemical Society National Meeting, Anaheim, CA on March 30, 2004.

Liu C., 2004, Microscopic diffusion of contaminants in the Hanford sediments. Invited seminar at Johns Hopkins University, Baltimore, MD, May, 2004.

Zhong L, C Liu, JE Szecsody, and JM Zachara. 2004. Influence of biogeochemical conditions on the stability and remobilization of biogenic U(IV). Contributed talk to THE 2004 JOINT ASSEMBLY, a partnership between CGU, AGU, SEG and EEGS, Montreal, PQ, Canada on May 20, 2004.