Office of Biological and Environmental Research,
Natural and Accelerated Bioremediation Research Program

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

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Background

In contaminated subsurface sediments, U(VI) resides in both interparticle (where active water flow occurs) and intraparticle domains (where static water resides). Dissimilatory metal reducing bacteria (DMRB) can reduce aqueous (interparticle) U(VI) to U(IV) under anoxic conditions yielding an insoluble precipitate [U(IV)O_2]. Intraparticle U(VI) can only be reduced by DMRB if it dissolves and diffuses to the interparticle domain populated by microbiota, or if the DMRB release, or dispose of electron to soluble compounds that can diffuse to, and react with intraparticle U(VI) precipitates.

At DOE Hanford site, recent characterization of U(VI) speciation and physical location in 30-year contaminated sediments demonstrated that U(VI) resides as a U(VI)-silicate microprecipitates in small fractures and cleavages within sediment particle grains exhibiting pore sizes of a few microns or less. The U(VI) microprecipitates dissolved slowly into undersaturated pore water, but the dissolution kinetics and diffusive rate of U(VI) transport from intraparticle regions was slow when compared to the reduction rate of aqueous U(VI) by DMRB. These results indicated that: 1) a majority of the sorbed U(VI) pool was not physically accessible to DMRB due to size restrictions of the grain porosity, and 2) the bioavailability and overall rates of microbial U(VI) reduction in the sediments could be limited by the mass transfer rates of U(VI) from intraparticle regions.

This research is focused on the bioavailability and kinetic rates of microbial reduction of U(VI) associated with intraparticle regions. The understanding of the influence of mass transfer on microbial reduction of U(VI) is needed not only at the Hanford site, but also at Oak Ridge FRC, where a critical issue is the long term diffusion of U(VI) from fine-grained saprolite matrix that is physically inaccessible to DMRB.

Objectives

- Develop approaches to characterize microscopic properties of mass transfer processes.
- Identify and characterize biogeochemical strategies for accessing intraparticle U(VI) by representative dissimilatory metal reducing bacteria.
- Evaluate the influence of mass transfer on U(VI) bioavailability, microbiologic reduction rate and location.
- Develop coupled kinetic models of the U(VI) dissolution, mass transfer processes, and microbially mediated U(VI) reduction.

Methods

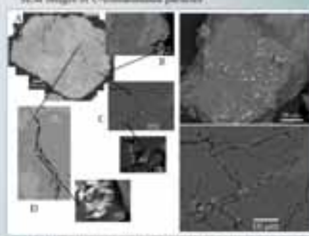
The intraparticle porosity, diffusivity, and tortuosity of pristine and contaminated sediments will be characterized using the approaches under development by this project including nuclear magnetic resonance (NMR) and confocal laser induced fluorescence spectroscopy (CLIFS). The mineralogical and chemical properties of the sediments and uranium will be determined by various methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), CLIFS, and X-ray microscopy (XRM).

Model uranyl compound (Na-boltwoodite) that was observed in the contaminated Hanford sediments has been synthesized using hydrothermal method. The model compound will be embedded into silicate supports or biological materials to rigorously study the mass transfer process and its influence on microbial reduction. Contaminated Hanford sediments containing intraparticle uranyl microprecipitates will be studied in parallel to the model compound.

S. putrefaciens and *Geobacter* will be used as model bacteria to study the bioavailability and rates of microbial reduction of intraparticle uranyl. Electron shuttling compounds, such as AQDS, will be used to examine its enhancement of microbial reduction.

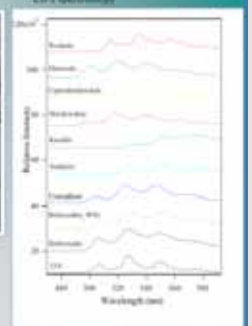
Characterization of U-Contaminated Sediments

SEM images of U-contaminated particles



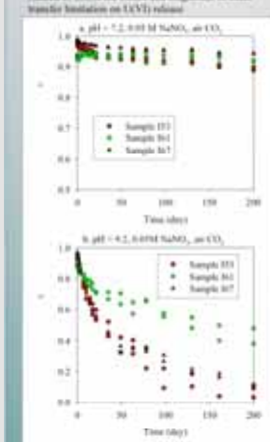
- U(VI) precipitates (white) distributed within plagioclase microfractures and cleavages.

LIFS spectroscopy



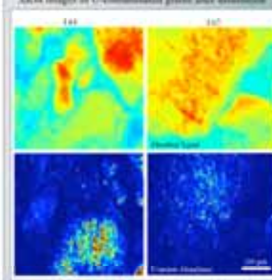
- Reference uranyl phases.
- U(VI) microprecipitates in the contaminated sediments were most consistent with boltwoodite or uranophane.

Dissolution kinetics of intraparticle precipitates were studied to assess the extent and magnitude of mass transfer limitation on U(VI) release



- The dissolution rates of intraparticle U(VI) precipitates were slow. Rates were lower at pH 7.2 than 9.2.

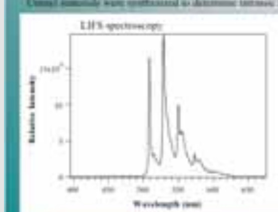
XRM images of U-contaminated grains after dissolution



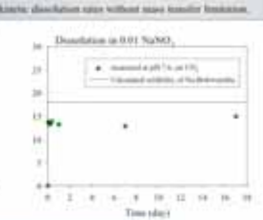
- Uranium was abundant within particle grains after 200 days of dissolution (pH 9.2). Sample I61 retained more U than I67.

Synthetic U(VI)-silicate

Uranyl silicates were synthesized to determine intrinsic kinetic dissolution rates without mass transfer limitation.



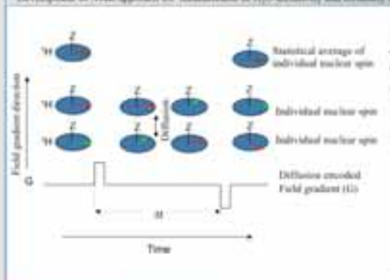
- LIFS measurements showed that the synthetic materials were Na-boltwoodite.

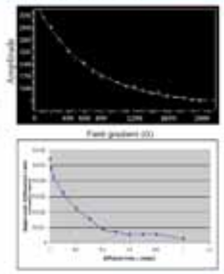


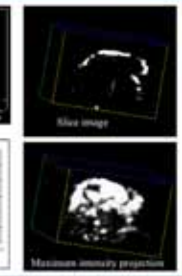
- Dissolution of the synthetic Na-boltwoodite was fast.

Characterization of Mass Transfer Process

Development of NMR approach for measurement of H_2O diffusivity and tortuosity in porous or fractured mineral grains







- Individual protons are labeled with pulse-field gradient magnetization. Diffusion of protons along pulse-field gradient direction decreased the statistical average of amplitudes of individual proton nuclear spins. The NMR approach is to correlate the amplitude decrease with the diffusivity of protons. Because only ^1H_2O is involved as a diffusion tracer, the mass transfer properties of porous or fractured materials can be measured without displacement experiments.
- The measured ^1H_2O diffusivity in mineral grains is used to calculate diffusion tortuosity, which is required to calculate mass transfer rates of other species (e.g., U(VI)).
- Top plot: given a constant diffusion time (Δt), the average amplitude of ^1H spins decayed in first order to pulse-field gradient with a first order coefficient equaling to $^1H_2$ diffusivity.
- Bottom plot: the measured ^1H_2O diffusivity for a feldspar particle from the Hanford 200 area decreased with increasing diffusion time until reaching an asymptotic value. The asymptotic value is used for diffusion tortuosity calculation.
- 3D NMR images showed water as ^1H (white) on the surface of and within the feldspar grain immersed in a fluorinated oil. The results indicated that the apparent diffusivity measured (left plots) was contributed from both water movements on the surface and within the particle grains.

Development of confocal LIFS approach for measurement of uranium diffusion in mineral grains

- A confocal laser-induced fluorescence (CLIFS) approach is being developed to characterize uranyl diffusion and mass transfer properties within sediment particle grains.

Planned Work

This is a new project. Besides the development of the approaches (NMR and CLIFS) for characterizing intraparticle mass transfer properties, following three tasks will be performed by this project:

- Task 1: Direct enzymatic reduction of intraparticle U(VI): to determine the rate of U(VI) mass flux out of intraparticle regions and its influence on the microbial reduction. NMR and CLIFS measurements will provide insights of mass transfer processes, and macroscopic measurements will define the overall rates and extents of U(VI) bioreduction. Numerical models of linking mass transfer with microbial reduction will be developed for result interpretation
- Task 2: Intraparticle U(VI) reduction by electron shuttling compounds: to evaluate the influence of biogenic or exogenous electron shutting compounds (ESC) on microbial reduction of intraparticle U(VI). The measurements of intragrain U(VI)/U(IV) locations by microscopic and spectroscopic methods will provide insights on the presence and influence of ESC. Macroscopic measurements will determine the enhancement of ESC on the rates and extents of microbial reduction of uranyl microprecipitates.
- Task 3: Reduction of intraparticle U(VI) by sorbed biogenic Fe(II): to examine whether biogenic Fe(II) can migrate into and sorb to intraparticle pores and microfractures, and whether the sorbed Fe(II) can reduce U(VI). The spatial distribution of U(VI)/U(IV) and Fe(II)/Fe(III) within particle grains will be determined by microscopic and spectroscopic methods. The measured rates of U(VI) reduction and Fe(II) oxidation will be used to define a model of linking the mass transport of U(VI) and biogenic Fe(II) with U(VI)/Fe(II) redox reaction.

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