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(VI) under anoxic conditions yielding insoluble precipitate (UO2(OH)). Intraparticle U(VI) can only be reduced by DMRB if it dissolves and diffuses to the interparticle domain populated by microbes, or if the DMRB reduces, or dispose of electron to soluble compounds that can diffuse to, and react with intraparticle U(VI) precipitates.

Methods

The intraparticle porosity, diffusivity, and tortuosity of pristine and contaminated sediments will be characterized using 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).

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, microbiological reduction rate and location.
- Develop coupled kinetic models of the U(VI) dissolution, mass transfer processes, and microbially mediated U(VI) reduction.

Characterization of U-Contaminated Sediments

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Model study (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 sediments containing intraparticle uranyl microprecipitates will be studied in parallel to the model compound.

S. purpurea 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 Mass Transfer Process

Methods

The dissolution of intraparticle precipitates were measured under the constant conditions of mass transfer limitation on U(VI) reduction. The measured 1H2O diffusivity in mineral grains is used to calculate the mean square displacement of a single proton. The NMR approach is used to determine the average amplitude of spins and diffusion coefficients equaling to 1H2 diffusivity. The measured 1H2O diffusivity in mineral grains is used to calculate the mean square displacement of a single proton. The NMR approach is used to determine the average amplitude of spins and diffusion coefficients equaling to 1H2 diffusivity.

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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 in influence on the microbial reduction. NMR and CLIFS 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 shuttling compounds on microbial reduction of intraparticle U(VI). The measurements of intragran U(VI)/U(VI) locations by microscopic and spectroscopic methods will reflect on the presence and influence of ESC. Microscopic 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 onto intraparticle pores and microfractures, and whether the sorbed Fe(II) reduces, or dispose of electrons to soluble compounds that can migrate to, and react with intraparticle U(VI) precipitates.

The measured rate 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 reactions.