Influence of Mass Transfer on U(VI) Microbial Reduction

Chongxuan Liu¹, Zheming Wang¹, John M. Zachara¹, James K. Fredrickson¹, Byong-Hun Jeon¹,², Paul D. Majors¹, James P. McKinley¹, and Steve M. Heald¹,³

¹Pacific Northwest National Laboratory
²Yonsei University, Korea
³Argonne National Laboratory

DOE Environmental Remediation Sciences Division 2006 Meeting
Uranium Physical Location in Contaminated Sediments

- At Hanford site, sorbed U exists as U(VI) with complex speciation, physical location, and mineral association.

Hanford 200 Area Sediments

- Sorbed U is commonly associated with intragrain regions.
Conceptual Model

Dissolution

Diffusive Mass Transfer

Porewater/Groundwater Microbial Activity

U(VI)

U(IV)
e\(^{-}\) donor
Characterization of Intragrain Diffusion

A $^1$H nuclear magnetic resonance, pulse-field gradient spin echo (NMR-PGSE) approach was developed to measure intragrain diffusion properties using H$_2$O as a tracer.

**Tortuosity factor (D$_p$/D$_{H2O}$):**
- 0.66    fast region
- 0.006   slow region

![NMR image of H$_2$O distribution](image)

**H$_2$O diffusivity in granitic lithic fragment**

![Graph showing apparent diffusivity vs. diffusion time interval](image)
Models of Ion Diffusion Coefficients

Geometrical model:  \( D_{p}^{i} = \tau D_{w}^{i} \)

- \( D_{p}^{i} \): pore diffusivity, \( \tau \): tortuosity; \( D_{w}^{i} \): diffusivity in water,

Schematic ion diffusion regions

- Restricted ions in double layers
- Non-restricted ion diffusion domain

Coupled electrodynamics-nonequilibrium thermodynamics (EDNT) model:  \( D_{p}^{i} = f(\tau, \rho_{c}, D_{p}^{j}, C_{j}) \)

- \( \rho_{c} \): surface charge density, \( D_{p}^{j} \) and \( C_{j} \): diffusivity and concentration of ion \( j \), respectively.
Microbial Reduction of Intragrain U(VI)

Coupling of Biogeochemical Processes: Synthetic System

Alginate beads with synthetic Na-boltwoodite

\[ R = 1 \text{ mm} \]

Dissolution/diffusion

Cell

Dissolved U(VI)

\[ \text{S. Oneidensis MR-1} \]

Cell spike (MR-1)

2x10^8 cells/mL

5x10^8 cells/mL

0 10 20 30 40

Dissolved U(VI) (mg/L)

0 200 400 600 800 1000

Time (day)
Intrabead U(VI) speciation and Distribution

- No change of intrabead U(VI) speciation;
- U(VI) dissolved/diffused starting from bead edge to center.
U(IV) Accumulation on Bacterial Surfaces and Periplasm

- Time = 2 days
- Time = 7 days
- Time = 100 days

- U(IV) accumulation on bacterial surfaces and periplasm
Modeling Coupled Biogeochemical Processes

Intragrain dissolution + Intrgrain diffusion + Extrgrain bioreduction
Microbial Reduction of Hanford Intragrain U(VI)

Effects of Calcite Dissolution

LIFS Spectra of Aqueous Solutions at liquid helium temperature

Cell spike

Simulation

Dissolved U(VI) (mg/L)

Time (day)

Wavelength (nm)

Relative Intensity

Control

$10^6$ cells/mL MR-1

$10^7$ cells/mL MR-1

Synthetic system

Sediment system

$\text{UO}_2(\text{CO}_3)_3^{4-}$ reference

$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ reference
Microbial Reduction of Hanford Intragain U(VI)

Coupling of Biogeochemical Processes

XRM analysis of Residual U

Dissolved U(VI) (µmol/L)

Time (day)

Cell spike

- Control
- MR-1 wild type = 1x10^8 cells/mL
- MR-1 Mtrc/OmcA = 1x10^8 cells/mL
Microbial Reduction of Hanford Intrgrain U(VI)

SEM analysis showed residual U silicate in occluded regions.
Microbial Reduction of Hanford Intragrain U(VI)

XANES analysis found mixed valence distribution of U(IV) and U(VI) inside grains.

Other Reduction Process?
Conclusions

- An NMR-PGSE technique indicated that a dual region diffusion model was required to simulate ion diffusion in the intragrain fractures of the granitic lithic fragment in Hanford sediment.

- Coupled electrodynamics and nonequilibrium thermodynamics (EDNT) model indicated that macroscopic ion diffusivity is a complex function of microscopic properties of mineral surface charges, ion exchange reactions, electrostatic double layers, and ion charge coupling.

- Macroscopic aqueous U(VI) concentration was determined by the microscopic coupling of biogeochemical processes of dissolution/desorption, diffusion and microbial activity.

- Microbial reduction of intragrain U(VI) in the contaminated Hanford sediment was complicated by the dissolution of calcite that released Ca to complex uranyl carbonates, which in turn slowed bioreduction rate and increased dissolution/diffusion rates. Some intragrain U(VI) in the contaminated Hanford 200 Area sediment was in occluded regions and might not be reactive due to mass transfer limitation.