Influence of Reactive Transport on the Reduction of U(VI) in the Presence of Fe(III) and Nitrate: Implications for U(VI) Immobilization by Bioremidation/Biobarriers

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Project Overview

- Purpose:
  - To determine how flow and transport influence
    - The distribution of U(VI) under field-relevant conditions
    - The transfer of reductive equivalents to the aqueous and solid phases by DMRB
  - To examine the solid-phase stability of bioreduced uranium phases
    - Effects of mass transfer on reoxidation of U(IV) by O_2 and other oxidants (e.g., NO_3^-, denitrification products)

Research Challenges

- Organism cultivation and growth…

Challenges (Cont.)

- Has been grown in pure culture for over 20 months
- Complex media
  - 90% toroidal oat-based substrate (Cheerios™)
  - 10% Uncharacterized substrates
- Has **not** been show to reduce Uranium
  - Will eat Nickels opportunistically
  - **Does reduce**: ability to think straight and / or hold a coherent conversation

Overview of Progress to Date

- We have been productive during our first two years of the project
  - **5** Published papers for the project (Wood)

    1. **Wood**, B.D., Whitaker, S., and Quintard, M. 2004. Estimation of adsorption coefficients on the basis of the Smoluchowski Equation, Chemical Engineering Science, doi:10.01016/j.ces.2003.12.021.
    2. **Wood**, B.D., F. Cherblanc, M. Quintard, and S. Whitaker, 2003. Volume averaging for determining the effective dispersion tensor: Closure using periodic unit cells and comparison with ensemble averaging, Water Resour. Res., 39(8), 1210, doi:10.1029/2002WR001723,
    3. **Wood**, B.D., Quintard, M., Golfier, F. and Whitaker, S., 2002, Biofilms in Porous Media: Development of Macroscopic Transport Equations via Volume Averaging with Closure, in Computational Methods in Water Resources, vol. 2, 1195-1202, edited by S.M. Hassanizadeh, R.J. Schotting, W.G. Gray and G.F. Pinder, Elsevier, Amsterdam.
    4. Ginn, T.R., B.D. **Wood**, K.E. Nelson, T.D. Scheibe, E.M. Murphy, and T.P. Clement, 2002. "Processes in Microbial Transport in the Natural Subsurface," Advances in Water Resources. 25:1017-1042.
    5. Scheibe, T.D., and B.D. **Wood**, A particle-based model of size or anion exclusion with application to microbial transport in porous media, Water Resour. Res., 39(4), 1080, doi:10.1029/2001WR001223, 2003.

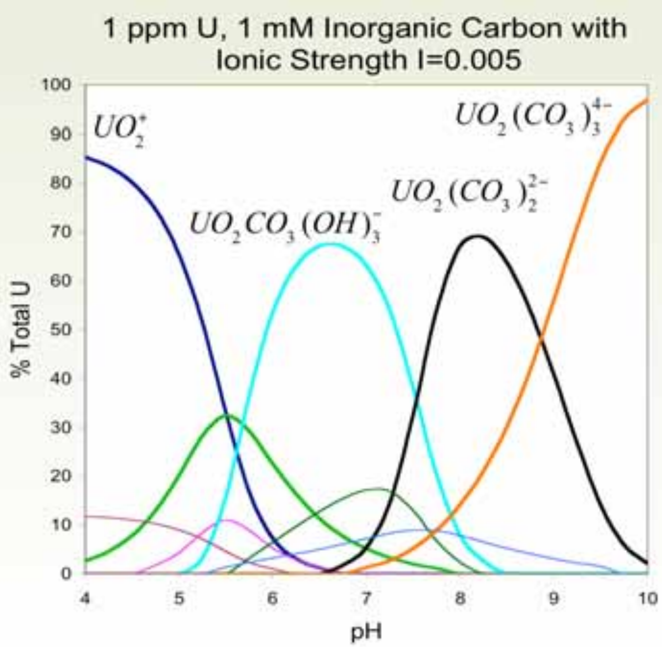
  - **1** Paper accepted (Szecsody)
  - **6** Papers submitted / in preparation (Liu / Wood / Zachara)

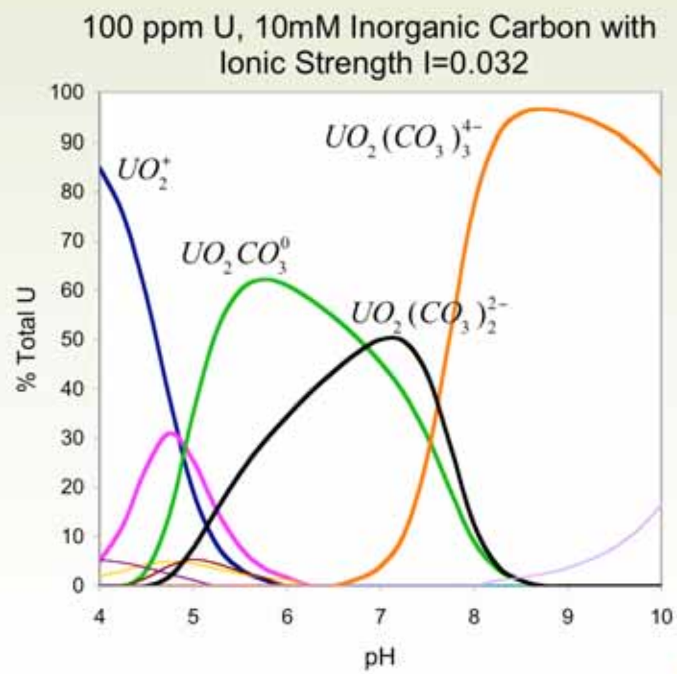
Summary of Research…
(Or, what are all of those papers in progress about?)

- Our most current work has focused on four areas of research
  1. Transport of U(VI) in natural sediments
     (Wood / Harrington / Liu / Zachara)
  2. Oxidation/remobilization of bioreduced U(VI)
     (Liu / Zachara / Zhong / Wood)
  3. Biofilms of DMRB in porous media
     (Wood)
  4. U(VI) interaction wtih microbially/abiotically-reduced sediments
     (Liu / Zachara / Zhong)

Background

- **Background**. U(VI) has a complicated geochemistry
  - Depends strongly on pH
  - Complexes with OH, carbonates, sulfate





Background (Cont.)

- Fe Oxyhydroxides are probably the most important mineral phase for adsorption
  - Phyllosilicates may play a role in some cases
- *Equilibrium* sorption of U has been described by a two-site (strong / weak) model (e.g., Barnett, Jardine, Brooks, 2002; Liu et al., 2004)

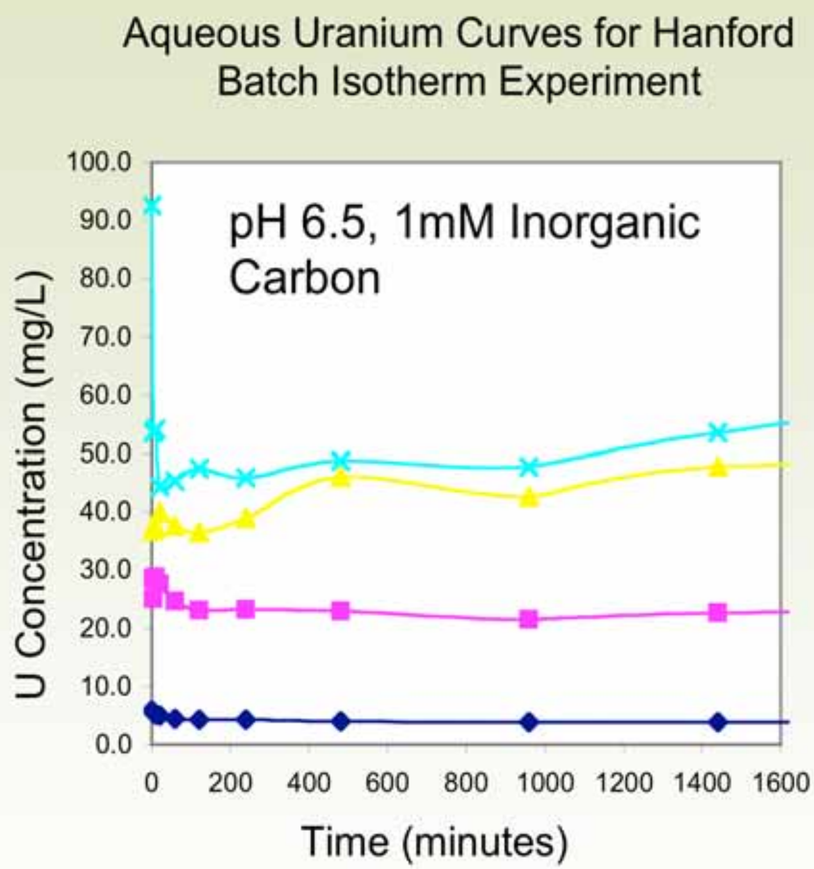
$$S_{(s)}(OH)_2 + UO_2^{2+} \Leftrightarrow (S_{(s)}O_2)\,UO_2^0 + 2H^+$$
$$S_{(w)}(OH)_2 + UO_2^{2+} \Leftrightarrow (S_{(w)}O_2)\,UO_2^0 + 2H^+$$
$$S_{(s)}(OH)_2 + UO_2^{2+} + H_2CO_3 \Leftrightarrow (S_{(s)}O_2)\,UO_2CO_3^{2-} + 4H^+$$
$$S_{(w)}(OH)_2 + UO_2^{2+} + H_2CO_3 \Leftrightarrow (S_{(w)}O_2)\,UO_2CO_3^{2-} + 4H^+$$

1. Transport of U(VI) in Natural Sediments (cont.)

- **Hypothesis**: U sorption under remediation conditions can show substantial kinetic (non-equilibrium) behavior
  - Interaction between the rate of kinetic sorption compared with the rate of transport
- **Experimental Protocol**:
  - Hanford sediments (~6-7.5% Fe by wt; ~0.1-0.2% amorphous Fe(III))
  - Packed in 5 cm diameter, 50 cm long prep-scale columns
  - Closed system, inorganic carbon = 1, 10 mM, pH = 6.5, 9

1. Preliminary Batch Experiments

- Conducted at *very high* sediment:water ratio (1g sediment: 1.2 g water)
- Batch data yielded fairly linear equilibrium sorption behavior between 0< U < 100 ppm



1. Transport of U(VI) in Natural Sediments (cont.)

- Experimental system set up

Gilson 223 Fraction Collector

Flow Through pH meters

Closed System Groundwater Reservoir With Scale output

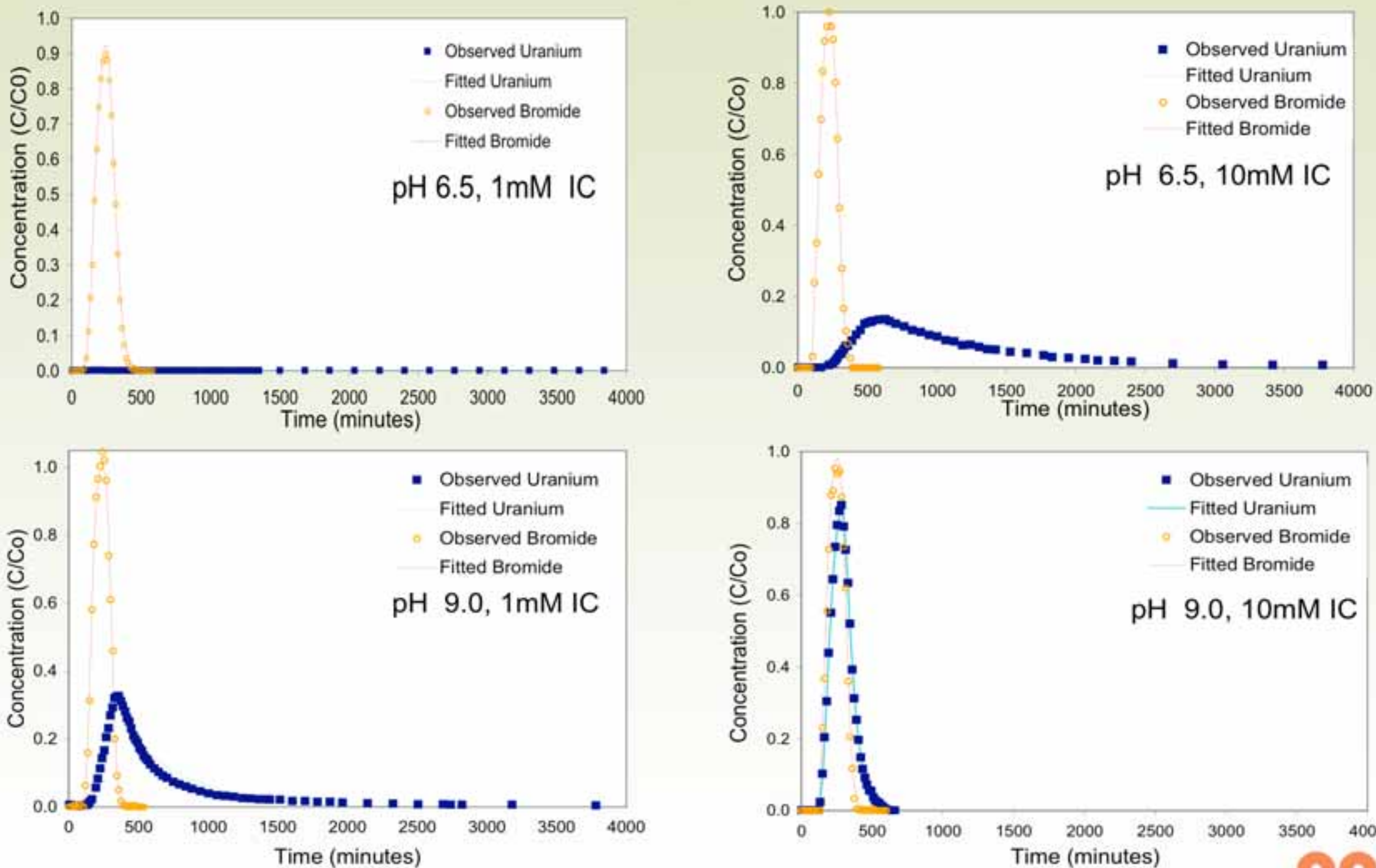
Column Packed With Hanford Sediment

Groundwater Injection Pump

Tracer Injection Pump

1. Results – Effluent BTC

v=20 cm/hr U Pulse length = 1 PV = 150 minutes



1. Results - Interpretation

- A two-site model was also required to fit the kinetic data
  - In this case there were
    - fast sites (equilibrium)
    - slow sites (non-equilibrium)
- Mathematical model

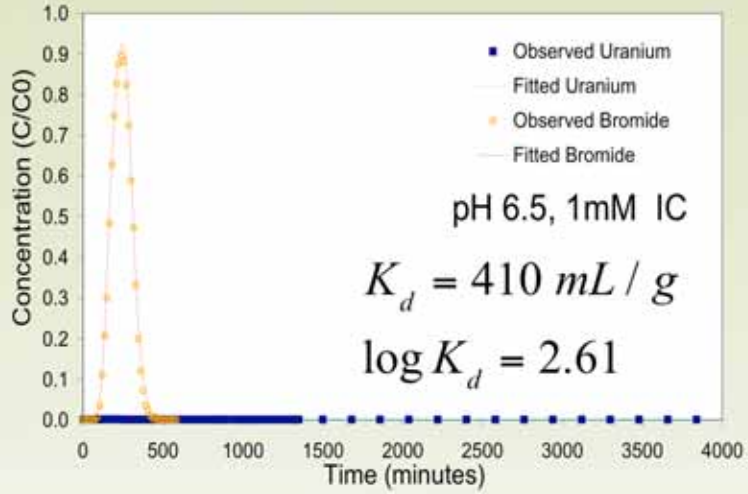
$$\underbrace{R\frac{\partial c}{\partial t}}_{Accumulation} = \underbrace{D\frac{\partial^2 c}{\partial x^2}}_{Dispersion} - \underbrace{v\frac{\partial c}{\partial x}}_{Convection} - \underbrace{\frac{\rho_b}{\theta}\left[k_1 c - k_{-1} s_k\right]}_{Mass\ Transfer}$$

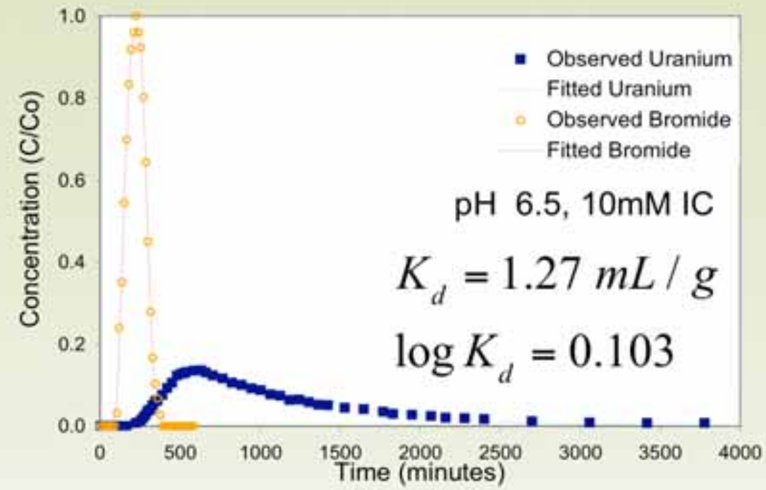
$$\underbrace{\frac{\partial s_k}{\partial t}}_{\substack{Accumulation \\ (Solid\ Phase)}} = \underbrace{\left[k_1 c - k_{-1} s_k\right]}_{Mass\ Transfer}$$

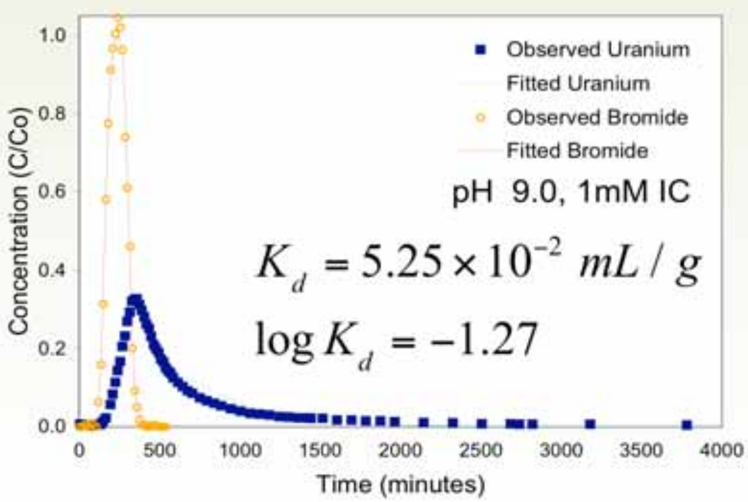
$$K_d = \frac{1}{(1-f)}\frac{k_1}{k_{-1}}$$

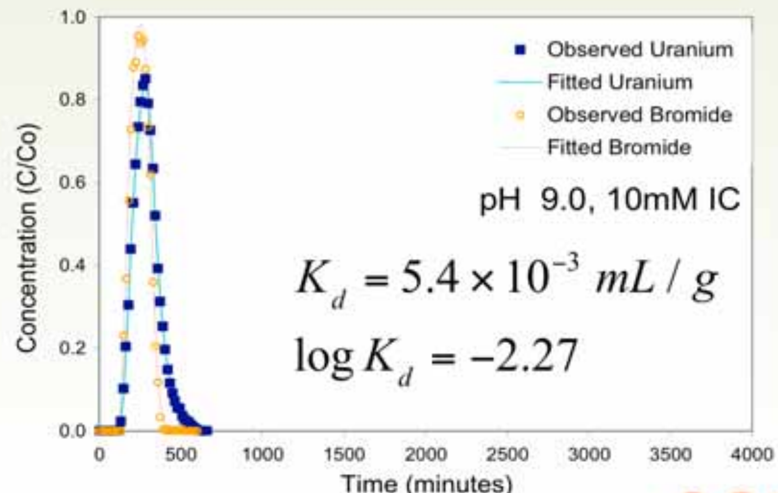
f = fraction of 'equilibrium' sites

1. Results – K_d Values









1. Interpretation

- A two-site model appears to be consistent with the observed results
- The K_d values that were measured for closed systems are consistent with those observed in batch equilibrium experiments
- Uranium adsorption during transport is a decidedly *non-equilibrium* process at field-relevant groundwater velocities
  - Question: can the fraction of equilibrium vs. non-equilibrium sites be related to fractions of 'strong' and 'weak' sites used in equilibrium studies?

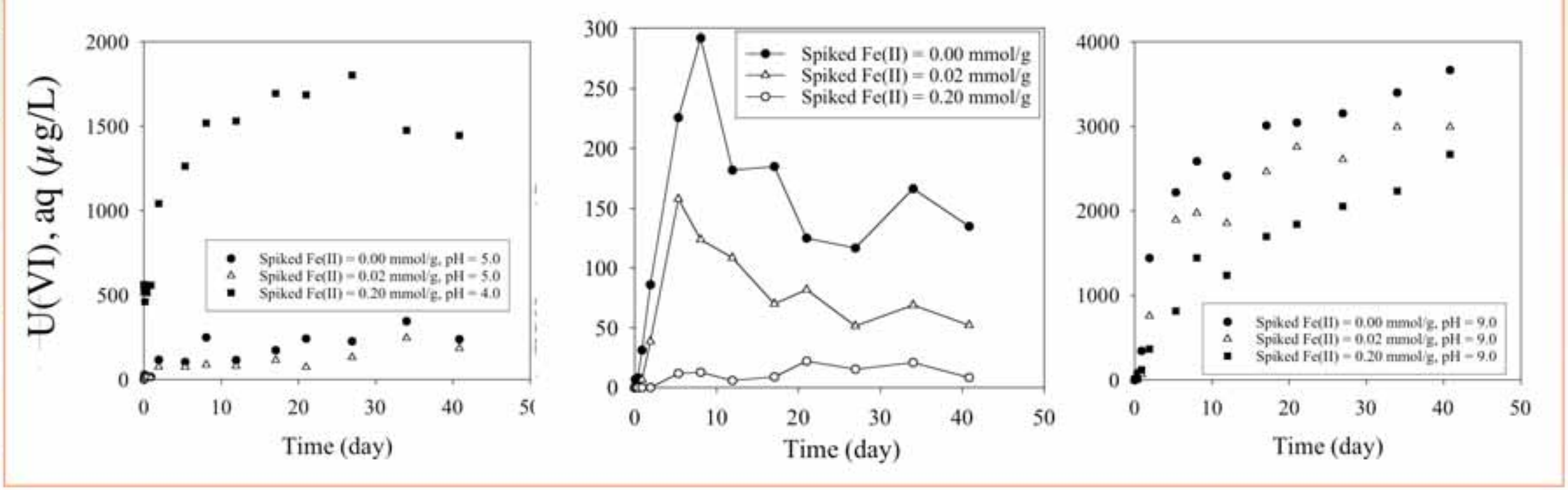
2. Oxidation and Remobilization of Bioreduced U(VI)

- **Hypothesis**: Upon reoxidation, the presence of Fe(II) in bioreduced sediements will help to decrease the *rate* and *extent* of U(IV) reoxidation by forming protective precipitates
- **Experimental Protocol**: Bioreduced U in sediments was treated as follows
  - Fe(II) added at 0-0.2 mmol/g sediment
  - pH adjusted to between 4 and 9
  - Reoxidize sediments, look for U(VI) release

2. Results

- Remobilization of U(IV) depends upon
  - Fe(II) added
  - pH
  - Time

a. pH 4 and 5 b. pH 7 c. pH 9



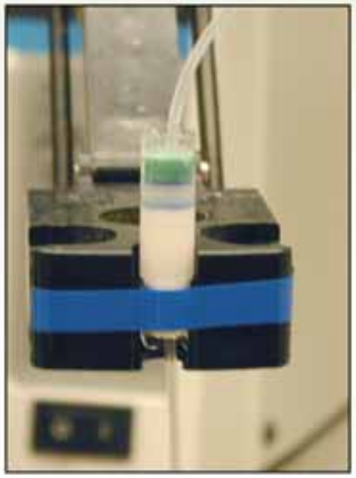
2. Results (Cont.)

- Decrease in U(IV) remobilization hypothesized to be caused by
  - Precipitation of 'protective' oxide coatings
    - Reduce mass transfer of oxidants to U(IV)
  - Adsorption onto newly-formed iron oxides (at pH 5-8)
  - Aging. The mechanisms and role of aging of the sediments is currently being explored…

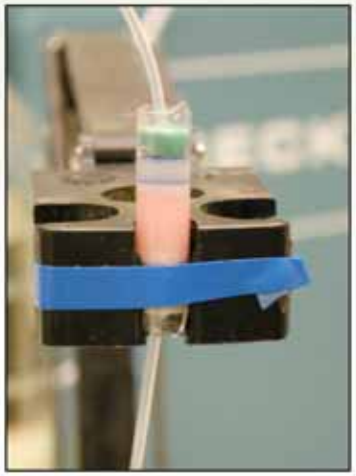
3. NMR Microscopy of DMRB Biofilms

- **Hypothesis**: Under high-substrate (excess carbon) loadings, *S. onidensis* will form biofilms in porous media
- **Experimental Protocol**:
  - *S. onidensis* grown *in situ* in 4 mm column, on TSB
  - Support matrix was 250 μm biosilon™ beads

t = 0 hours



t = 48 hours



3. Experimental Protocol (Cont.)

- NMR Images were collected at EMSL at 30 μm isotropic resolution

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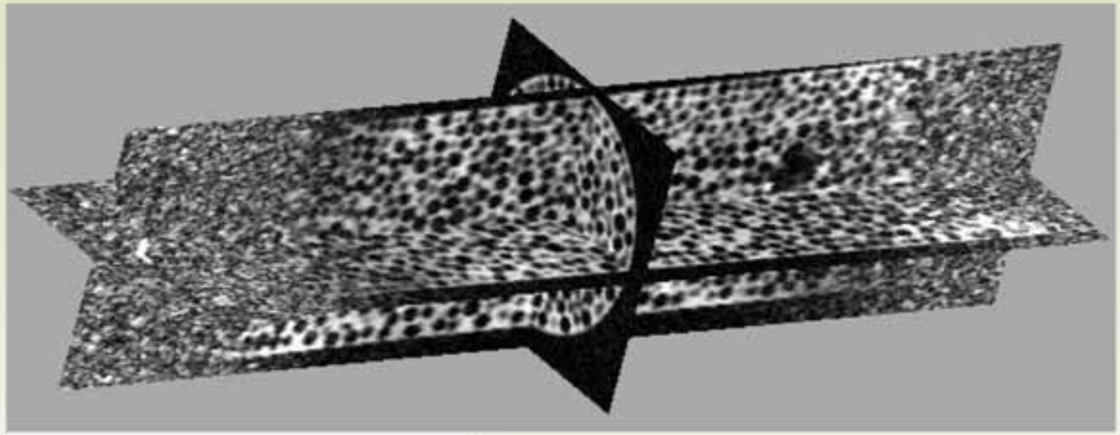
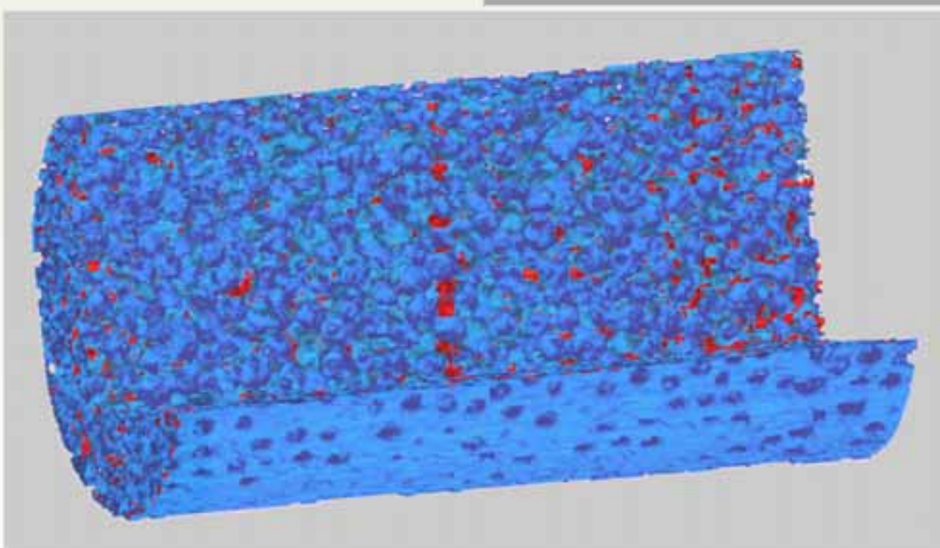
3. NMR Data to Biofilm Data…

- Raw NMR Data





- Diffusion-Filtered Data set (Isosurface)
  - Biofilms in Red
  - Fluid in Blue

3. Results & Implications

- DMBR can form biofilms in porous media under carbon-excess conditions
- The 3-D structure of these biofilms can be measured using NMR microscopy (30 μm resolution)
- These 3-D structures can be used to predict more about the processes of mass transfer and reactions in biofilms during biostimulation

Continuing Work…

- We are continuing to explore the interactions between transport and reactions in our current and proposed work
- New questions:
  - Is it possible to control fluxes of electron donor and other chemicals to maximize e- transfer to the subsurface while minimizing or controlling growth?
  - How do physical / chemical / microbial heterogeneities affect U immobilization by biostimulation?
    - Metal reducing microsites?
  - Can we promote the formation of protective mineral precipitates to limit the mass transfer of oxidants to immobilized U(IV)?

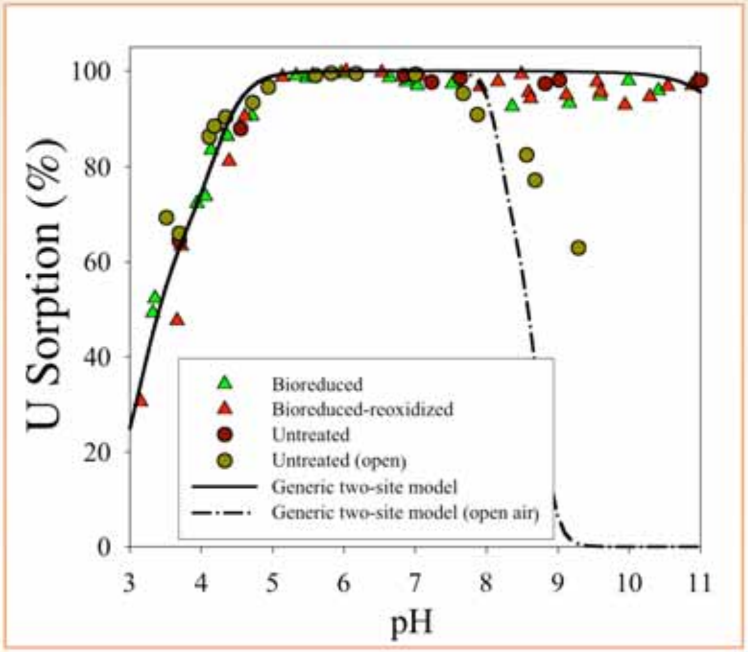
Questions?

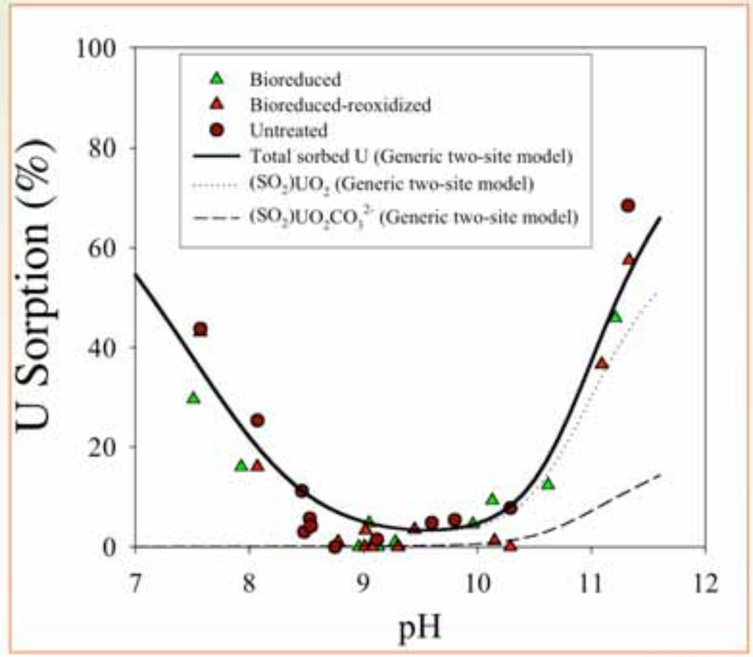
2. U(VI) Interaction with Bioreduced Sediments

- **Hypothesis**: Microbially-reduced sediments may contain altered mineral phases that adsorb U(VI) differently than untreated sediments.
  - Question: Can U(VI) reduction by sorbed Fe(II) be observed in systems with carbonate?
- **Experimental Protocol**:
  - FRC sediments reduced by *S. onidensis*
  - U(VI) adsorption edges were measured for fixed carbonate concentrations, and fixed P_{CO2}

2. Results

- U(VI) sorption did not depend strongly upon method of reduction
- U(VI) was not observed to be reduced by adsorbed Fe(II)





2. Results (Cont')

- U(VI) adsorption was modeled best by a generic, 2-site (strong/weak) model
- Comparing to previous work (Barnett, Jardine, Brooks), the model yielded
  - log *K* values that were **similar** to those reported earlier for Fe(III) oxy-hydroxides for UO_2^+
  - log *K* values that were **more negative** than those reported earlier for Fe(III) oxyhydroxides for $UO_2CO_3^-$
- Implications:
  - Adsorption models from untreated sediments may be OK for application to the field
  - Possibly multiple mineral phases involved