

**Containment of Toxic Metals and Radionuclides in Porous and
Fractured Media: Optimizing Biogeochemical Reduction
versus Geochemical Oxidation**

M.O. Barnett, S.C. Brooks, and P.M. Jardine
Oak Ridge National Laboratory

S.E. Fendorf
University of Idaho

J.E. Saiers
Florida International University

Environmental Management Science Program

Objectives

- Develop an improved understanding of the rates and mechanisms of competing geochemical and microbiological oxidation/reduction reactions that govern the fate and transport of chromium, cobalt-EDTA, and uranium.
- Quantify the conditions that optimize the microbial reduction of toxic metals for the purpose of contaminant containment and remediation in heterogeneous systems.

Rationale

- Cr, ^{60}Co , $^{238,235}\text{U}$
 - large inventories in existing waste sites
 - relatively long half-life, high toxicity
 - high mobility from primary waste sources
- These elements are redox sensitive
 - reduced forms are significantly less mobile than the oxidized forms.
- Geochemical oxidation versus biogeochemical reduction.

Relevance to EM Needs

Provide basic knowledge to define the optimum conditions for the microbial reduction and concomitant immobilization of redox sensitive toxic metals (Cr) and radionuclides (Co and U) in the subsurface.

Challenges:

Competing geochemical oxidation and sorption reactions

Nutritional requirements and sustained bacterial metabolism

Hydrodynamics

Toxicity

Site Needs:

Uranium - Paducah, Hanford, ORNL

Technetium - Hanford, Paducah, ORNL, Portsmouth

Chromium - SRL, Hanford

Cobalt - ORNL

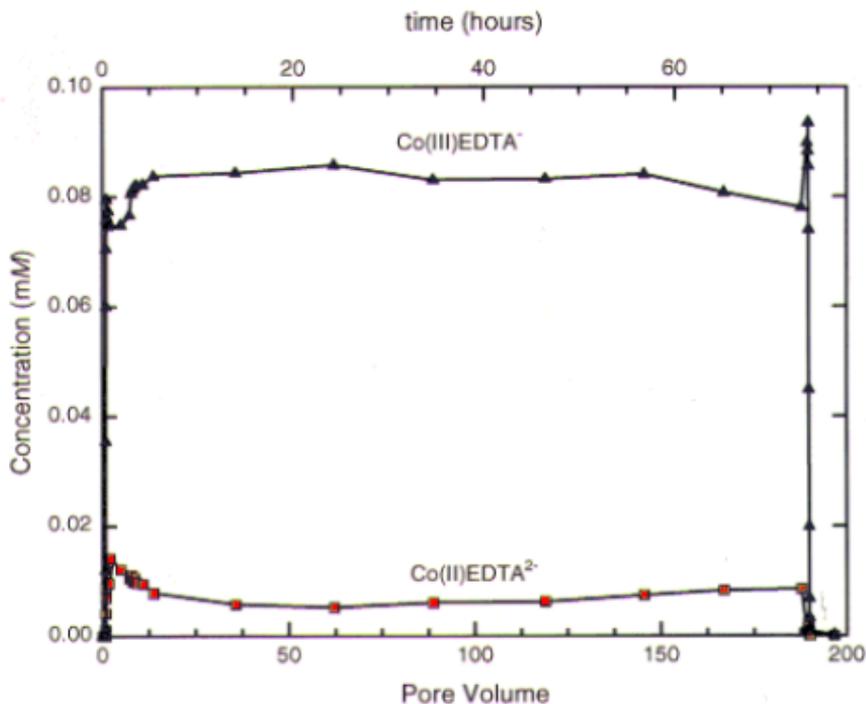
Approach

Hypothesis-driven tasks that focus on

- **dynamic flow techniques to quantify interfacial geochemical and microbiological redox processes for Cr, Co-EDTA, and U on Hanford, ORNL and SRL subsurface material.**
- **use of novel spectroscopic techniques to monitor time-dependent redox transformations and solid phase sorption mechanisms.**
- **supercomputer modeling that couples hydrologic-biogeochemical processes for simulating the experimental data.**

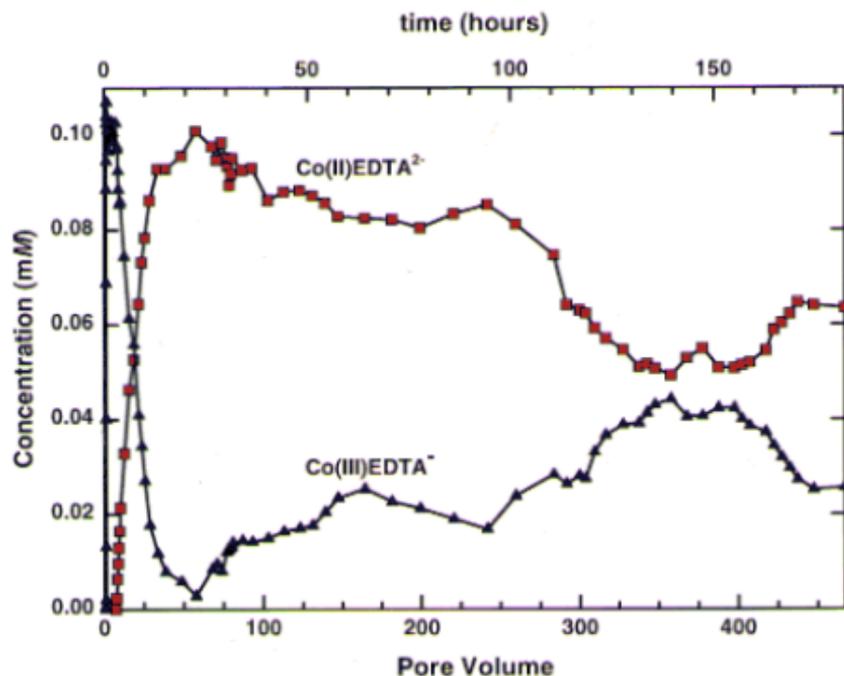
Co-EDTA System

Oxidation of Co(II)EDTA^{2-} by Pyrolusite ($\beta\text{-MnO}_2$)
under Anoxic Conditions During Dynamic Flow



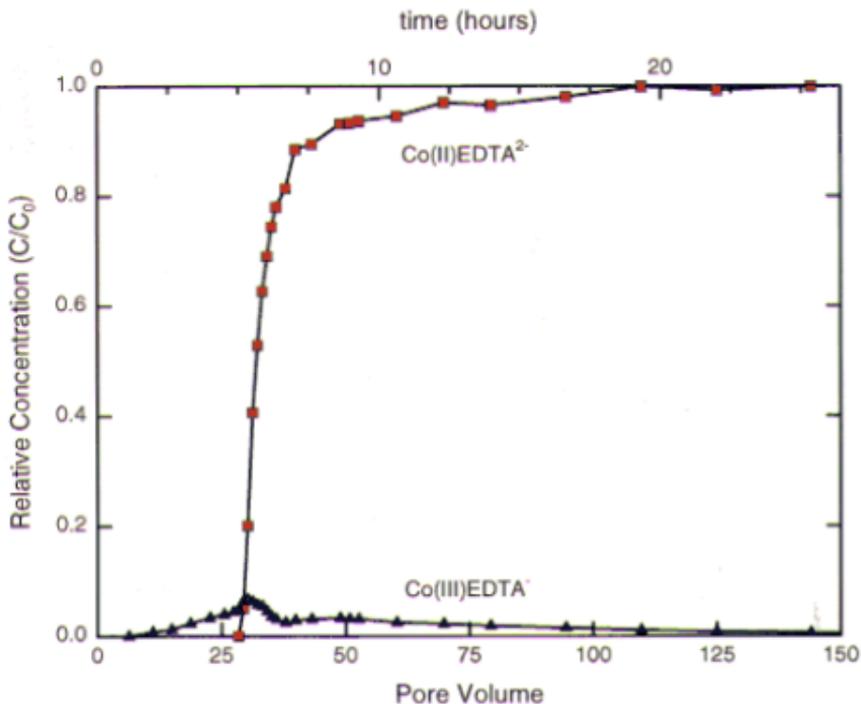
- Transport of Co(II)EDTA^{2-} through a packed bed of Mn-oxide coated silica.
- Co(II)EDTA^{2-} is effectively oxidized to Co(III)EDTA^- .
- Co(III)EDTA^- is significantly more stable than Co(II)EDTA^{2-} which enhances the persistence and mobility of ^{60}Co in subsurface environments.

Reduction of Co(III)EDTA^- by *Shewanella alga* BrY in the Presence of Pyrolusite ($\beta\text{-MnO}_2$) During Dynamic Flow



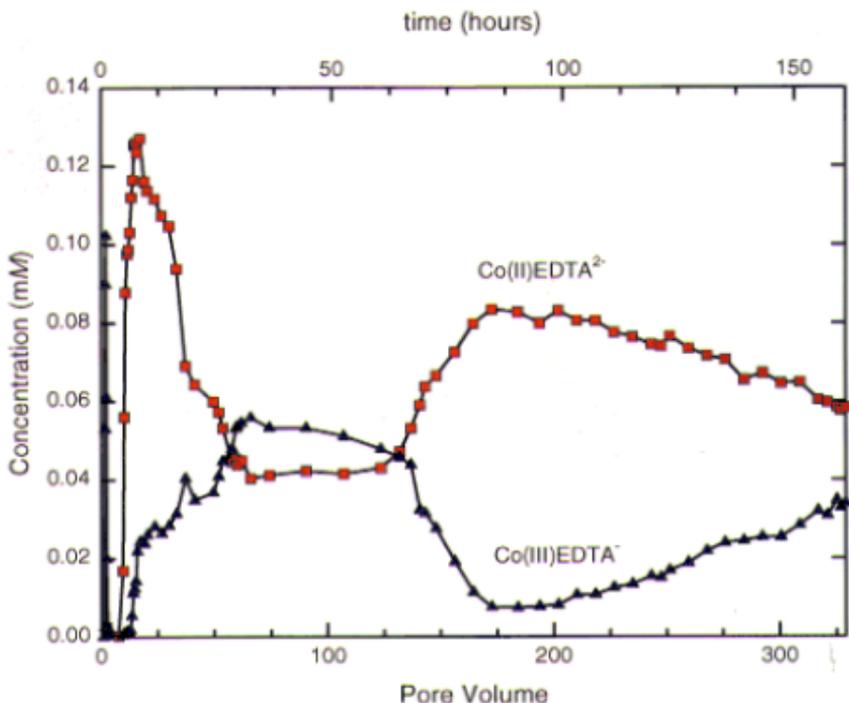
- Transport of Co(III)EDTA^- through a packed bed of Mn-oxide coated silica in the presence of *Shewanella alga* BrY.
- BrY effectively reduced Co(III)EDTA^- to the less stable Co(II)EDTA^{2-} species in the presence of competing geochemical reactions.
- Sustained reduction of Co(III)EDTA^- by BrY is encouraging from an environmental perspective since the reduced product, Co(II)EDTA^{2-} , can be more easily decoupled by geochemical processes.

Oxidation of Co(II)EDTA^{2-} by Ferrihydrite ($\text{Fe(OH)}_{3,\text{am}}$)
under Anoxic Conditions During Dynamic Flow



- Transport of Co(II)EDTA^{2-} through a packed bed of Fe-oxide coated silica.
- Limited oxidation of Co(II)EDTA^{2-} to Co(III)EDTA^- ; however, both species are significantly retarded by the solid phase. The oxidation of Co(II)EDTA^{2-} by Fe-oxides significantly increases as the pH and flow rate decrease (not shown).

Reduction of Co(III)EDTA^- by *Shewanella alga* BrY in the Presence of Ferrihydrite ($\text{Fe(OH)}_{3,\text{am}}$) During Dynamic Flow

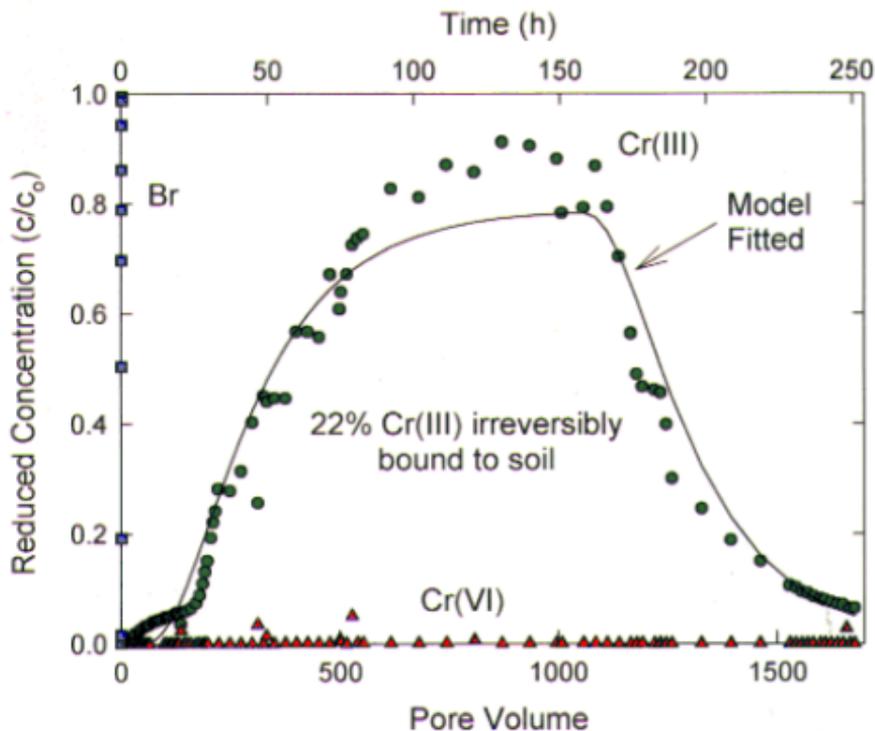


- Transport of Co(III)EDTA^- through a packed bed of Fe-oxide coated silica in the presence of *Shewanella alga* BrY.
- BrY effectively reduced Co(III)EDTA^- to the less stable Co(II)EDTA^{2-} species in the presence of competing geochemical oxidation reactions.
- Sustained reduction of Co(III)EDTA^- by BrY is encouraging from an environmental perspective.

Cr System

SRL soil, 0.2 mM Cr(III), pH=4.0

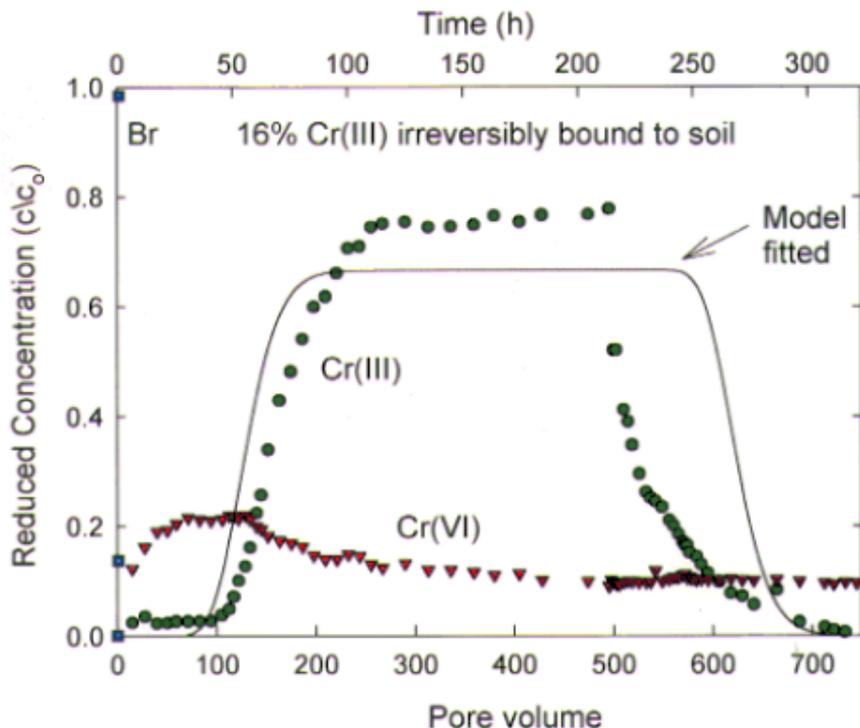
$q=12.6 \text{ cm h}^{-1}$, residence time = 0.36h



- Transport of Cr(III) through Savannah River sediment with model fitted curve using a multireaction transport code.
- Multispecies, time-dependent sorption with limited oxidation to Cr(VI). The latter is advantageous from an environmental perspective.
- X-ray Absorption Spectroscopy (XAS) revealed that the unrecovered Cr(III) was bound to the soil surface via inner-sphere complexes coupled with a Cr(III)-hydroxide phase.

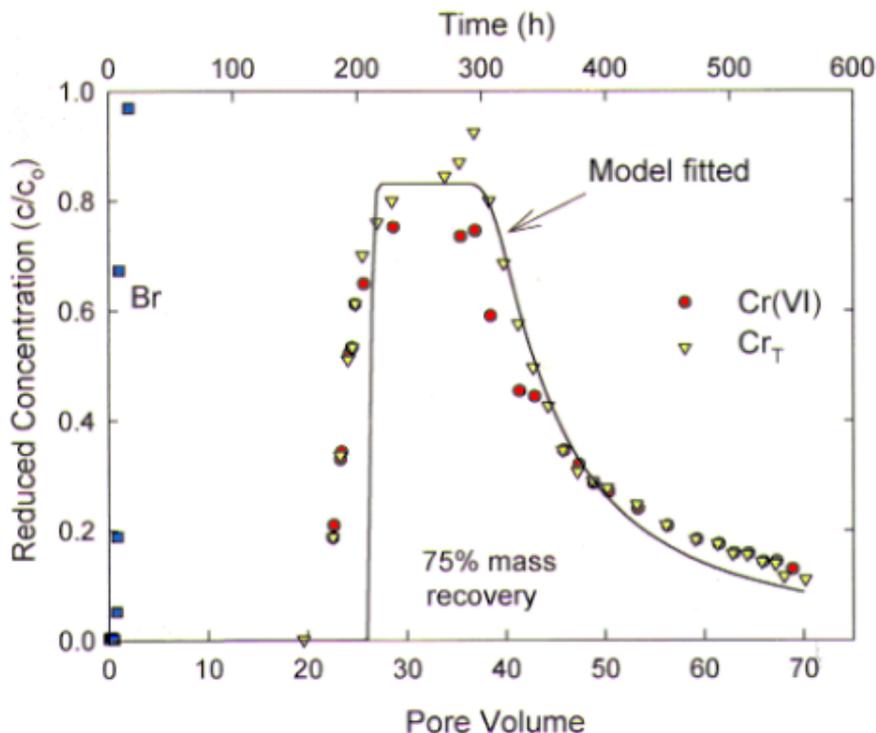
Hanford soil, 0.2 mM Cr(III), pH=4.3

$q=2.0 \text{ cm h}^{-1}$, residence time=0.68h



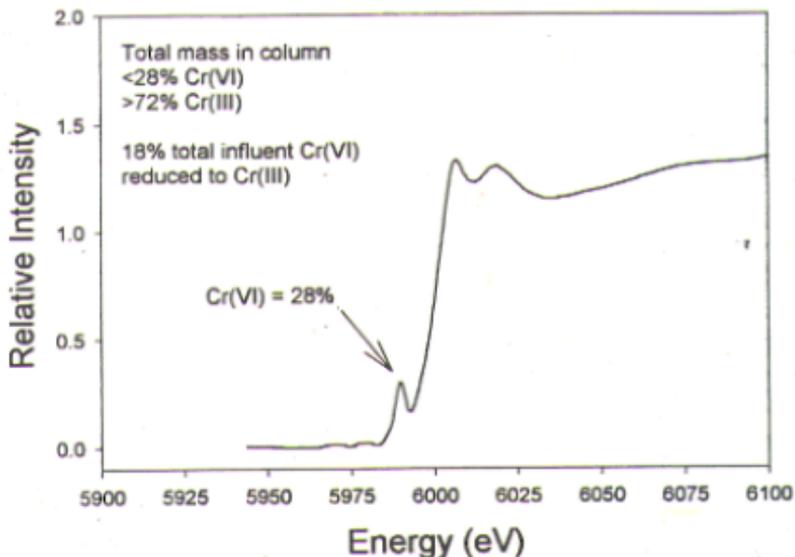
- Transport of Cr(III) through Hanford sediment with model fitted curve using a multireaction transport code.
- Significant oxidation of Cr(III) to Cr(VI) even in the presence of competing Cr(III) precipitation reactions. Mn-oxides most likely catalyzed the oxidation reaction.
- Cr(VI) is significantly more mobile in the subsurface relative to Cr(III).

ORNL soil, 0.35 mM Cr(VI)
 $q=0.51 \text{ cm h}^{-1}$, residence time = 16.9 h



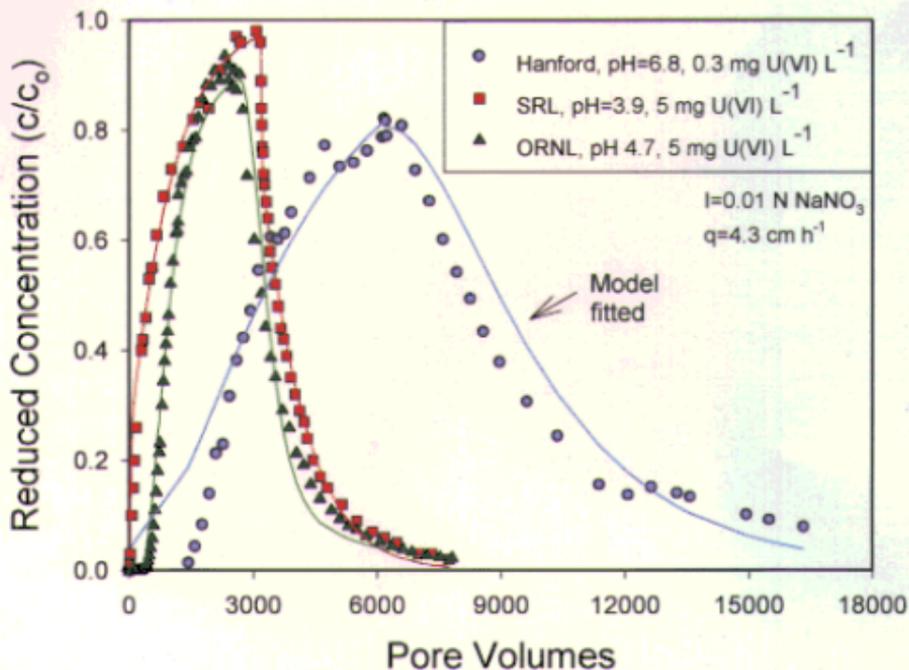
- Transport of Cr(VI) through Oak Ridge soil with model fitted curve using a multireactive transport code.
- Effluent analysis shows no Cr(III); however, significant Cr mass loss results.
- Column displacement was prematurely terminated since the set-up was taken to the Stanford Synchrotron Radiation Laboratory to perform XAS analysis on the solid phase (see below).

XANES spectra of Cr on ORNL soil obtained from the 8 - 8.6 cm depth of a soil column leached with Cr(VI)



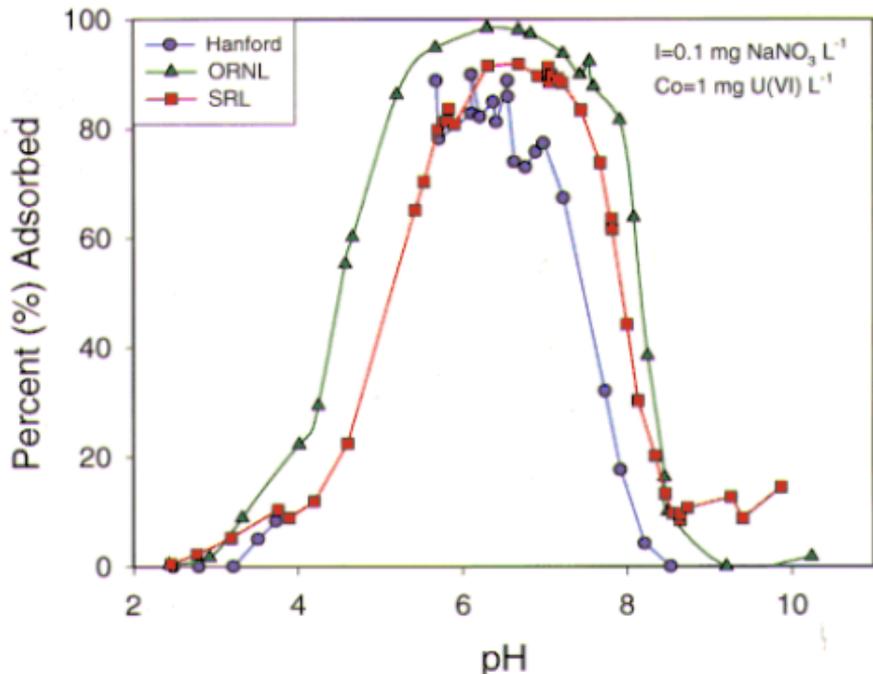
- XANES (X-ray Absorption Near Edge Spectroscopy) spectra of Cr on ORNL soil obtained from the 8-8.6 cm depth of the soil column above which was leached with Cr(VI).
- XANES was performed on eight 1 cm segments of the column.
- XAS confirmed that ORNL soils can reduce a significant portion of Cr(VI) to Cr(III) thereby enhancing Cr stabilization by nearly 25 fold. Cr mass loss in the system could be attributed solely to the formation of Cr(III).

U System



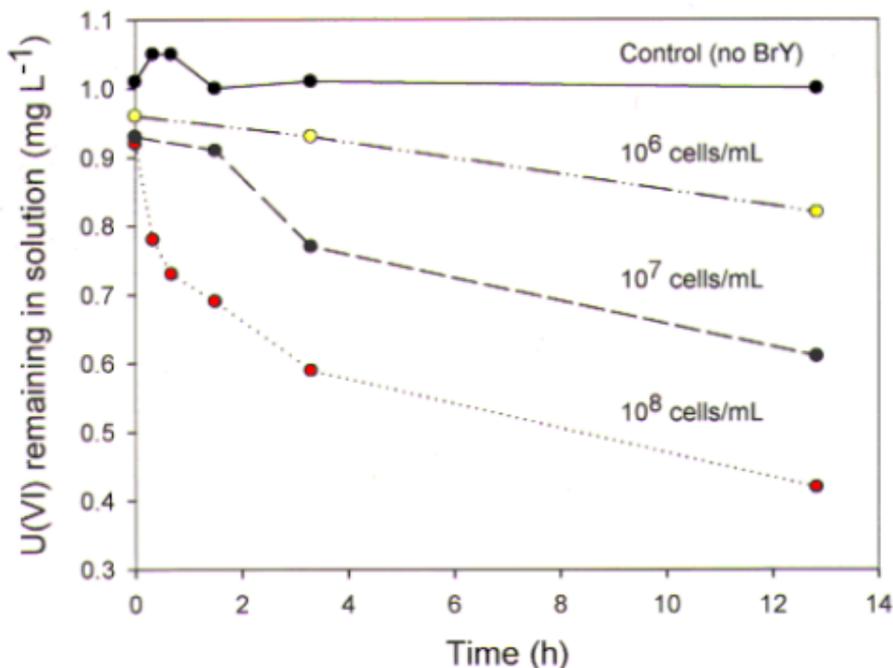
- Transport of U(VI) through Oak Ridge, Savannah River and Hanford soils and sediments with model fitted curves (lines) using a nonequilibrium multisite transport code.
- The subsurface media have a large retention capacity for U(VI) with k_d values near $1000\text{ cm}^3\text{ g}^{-1}$.
- XAS analysis has been performed on the solid phase U in order to determine the mechanism of surface sorption. The interpretation of results is pending. The improved conceptual understanding of the microscopic processes will assist in the modeling of the macroscopic transport experiments.

U(VI) pH adsorption envelopes



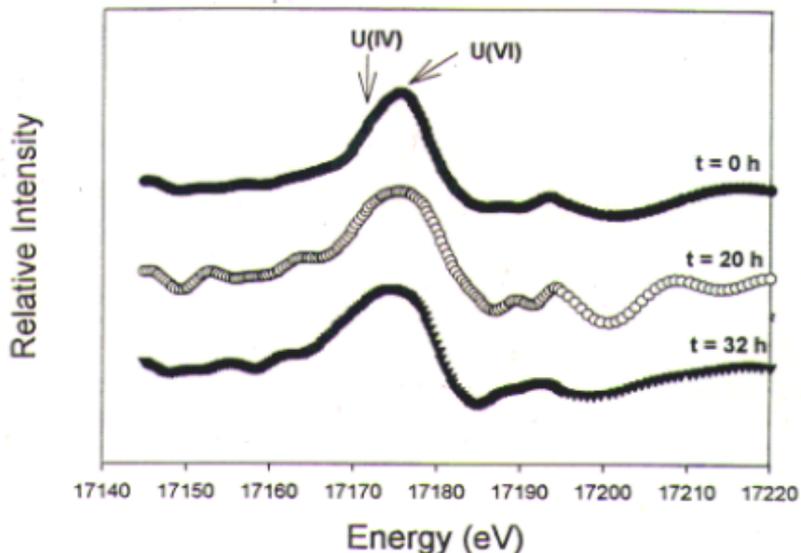
- Batch U(VI) sorption experiments on Hanford, Savannah River, and ORNL soils and sediments as a function of pH.
- U(VI) sorption is strongly pH dependent with the maximum loss from solution occurring at pH 5-7. Above pH 7, U-CO₃ species dominate the equilibrium solutions and U(VI) sorption rapidly decreases with small increases in pH.
- The sharp edge for U(VI) sorption will strongly influence the transport of U in subsurface environments and thus the need for remedial action.

Reduction of U(VI) by *Shewanella alga*



- Batch U(VI) bacterial reduction experiments using *Shewanella alga* BrY.
- The rate of U(VI) reduction by BrY is strongly influenced by cell number. The reduction rate has also been quantified for a variety of environmental conditions such as pH, ionic strength, temperature, and dissolved O₂ concentration.
- The rapid reduction of U(VI) is advantageous from an environmental perspective since reduced U species (e.g. U(IV)) are significantly less soluble and less mobile than the oxidized U(VI) species.

Time-dependent reduction of U(VI)-CO₃ by BrY
with subsequent formation of U(IV)



- Time-resolved XANES spectra of U(VI) solutions in the presence of BrY.
- The spectra show an increase intensity at lower energy (noted by the broadening) which corresponds to the formation of U(IV). Thus, BrY is reducing U(VI) to U(IV) as a function of time.

Opportunities for Deployment

EMSP (Basic Sci.) FY97-99

- ↓ Basic principles refined
- Defined areas for positive focus

Science and Technology (Applied Sci.) FY99-01

- ↓ Pilot scale: Undisturbed cores from various DOE sites, large scale blocks with active biowalls
- Demo: WAG 5 Source Area A Field Tracer Facility

Deployment (commercial Appl.) FY02-

- State permission to inject non-indigenous bacteria strain into groundwater
- Survival issues
- Transport issues

Possible Sites: ORNL, Paducah, Hanford, Savannah River

Summary

Active biowall technologies to contain priority EM contaminant plumes can only succeed if a basic scientific understanding of the interacting microbial, geochemical, and hydrological processes are understood.

This project provides basic knowledge regarding the optimum conditions necessary for bacteria to effectively immobilize contaminants in the presence of competing geochemical reactions and complex hydrodynamic flow.

By placing treatment barriers where contaminants are located, remediation time and costs are decreased relative to ex situ strategies (e.g. groundwater pumping, soil excavation, and disposal costs are avoided).