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

P.M. Jardine, S.C. Brooks, T.L. Mehlhorn, S.L. Carroll
Oak Ridge National Laboratory

S.E. Fendorf
Stanford University

J.E. Saiers
Yale University

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, $^{238/235}U$
  - Large inventories in existing waste sites (e.g. ORNL, SRL, and Hanford)
  - Relatively long half-life, high toxicity
  - High mobility from primary waste sources

- These contaminants are redox sensitive, with the reduced forms being significantly less mobile than the oxidized forms.

- Common soil minerals typically sustain the oxidation of these contaminants.

- Metal-reducing bacteria may effectively alter the redox state of these contaminants thereby immobilizing them in subsurface environments.

- Fundamental experimental research is needed to address the impacts of hydrological and geochemical processes on the effectiveness of microorganisms to transform and immobilize contaminants in subsurface environments.

Approach

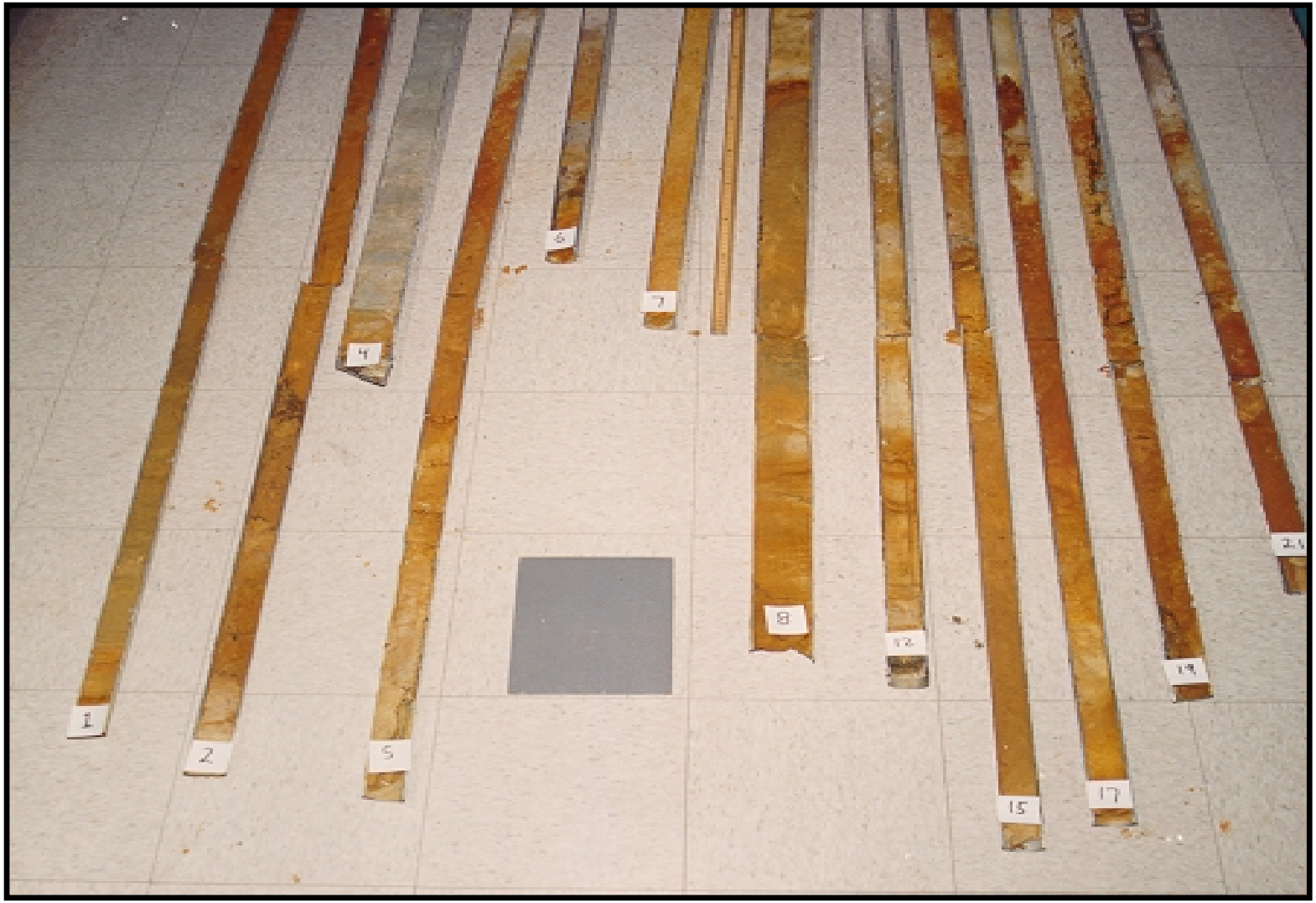
- Dynamic flow technique to quantify interfacial geochemical and microbiological redox processes for Cr, Co-EDTA, and U on Oak Ridge (ORNL), Hanford, and Savannah River (SRL) subsurface media.

- Use of novel spectroscopic techniques to monitor time-dependent redox transformations and solid phase sorption mechanisms.

- Numerical modeling that couples hydrologic-biogeochemical processes for simulating the experimental data.

Soils from Oak Ridge have been weathered from interbedded shale-limestone sequences, where the limestone has been weathered to massive clay lenses devoid of carbonate (red layers) and the more resistant shale has been weathered to an extensively fractured saprolite (brown layers). These acidic soils are predominately silts and illitic clays that are heavily coated with Fe- and Mn-oxides. These soils are the dominate subsurface media at Oak Ridge's Y-12 site.

Soils from Hanford were from the Upper Ringold formation which consists of laminated silts and clays that are interbedded with Fe- and Mn-oxide stringers. These alkaline soils are predominately quartz with lesser quantities of mica and hydroxy-interlayer vermiculite. They are a significant component of the subsurface media beneath the tank farms on the Hanford reservation.

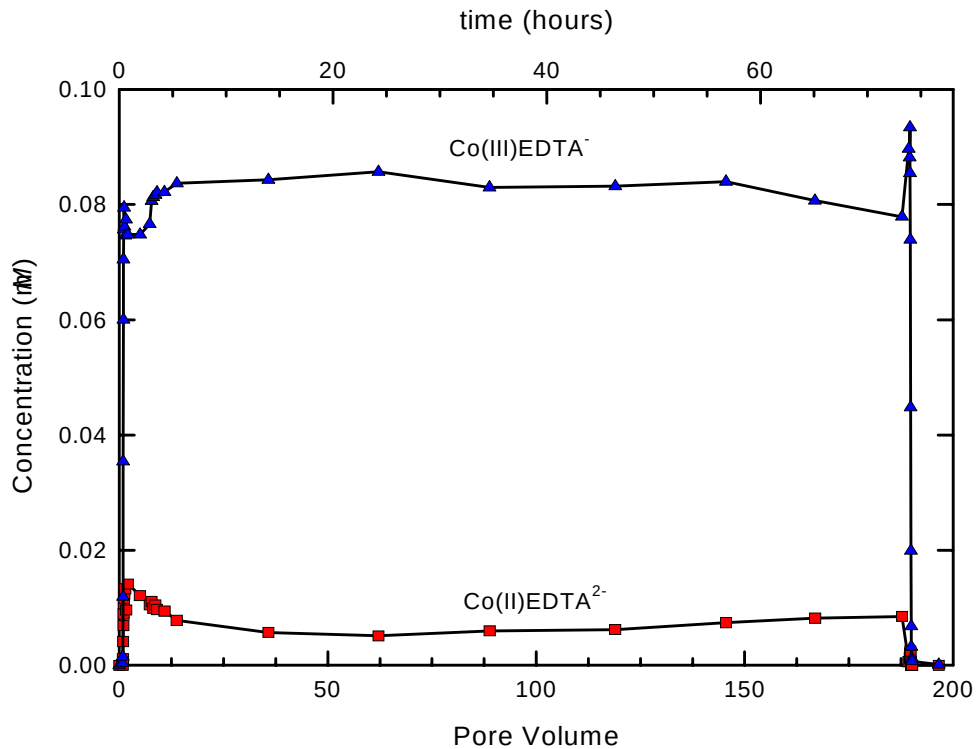


Soils from Savannah River are sandy coastal plain Ultisols whose mineralogy is dominated by smectite, illite, and kaolinite. A significant clay fraction exists (25%) which is heavily coated with Fe-oxides. These soils are the dominate subsurface media at Savannah River's Old Burial Ground site.

Column displacement experiments involving the microbially mediated reduction of toxic metals were performed in an anaerobic glove box. A multichannel HPLC pump was used to mix various combinations of electron donor, nutrients, and contaminants that were used in the transport studies. The experimental design coupled hydrological, geochemical, and microbial processes in a manner similar to conditions *in situ*.

Co-EDTA System

Oxidation of $Co(II)EDTA^{2-}$ by Pyrolusite (β-MnO_2)
under Anoxic Conditions During Dynamic Flow

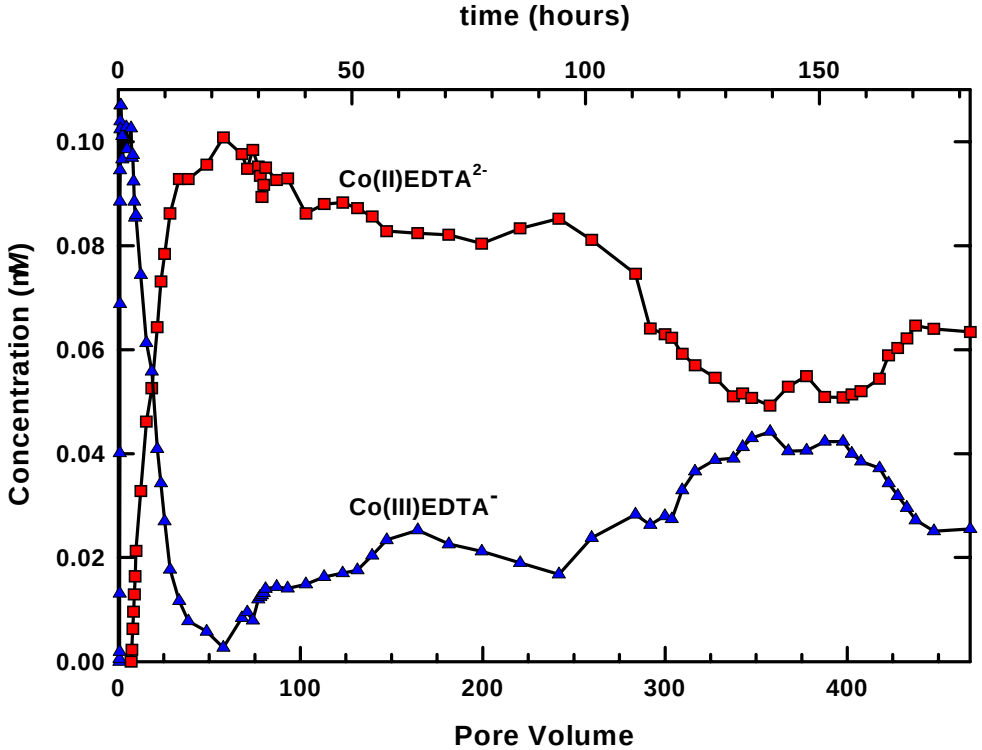


Transport of $Co(II)EDTA^{2-}$ through a packed bed of Mn-oxide coated silica.

$Co(II)EDTA^{2-}$ is effectively oxidized to $Co(III)EDTA^{-}$.

$Co(III)EDTA^{-}$ is significantly more stable then $Co(II)EDTA^{2-}$ 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 (β-MnO_2) During Dynamic Flow

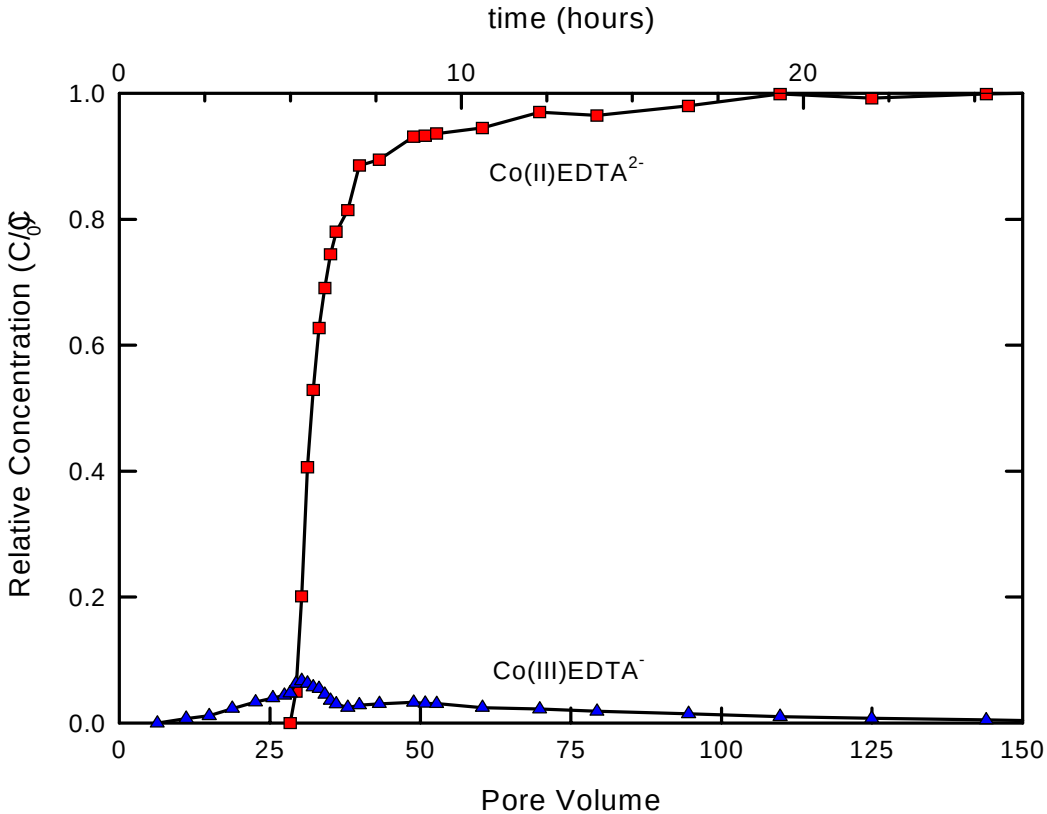


Transport of Co(III)EDTA$^-$ through a packed bed of Mn-oxide coated silica in the presence of *Shewanella alga* BrY.

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 ($Fe(OH)_{3,am}$) under Anoxic Conditions During Dynamic Flow

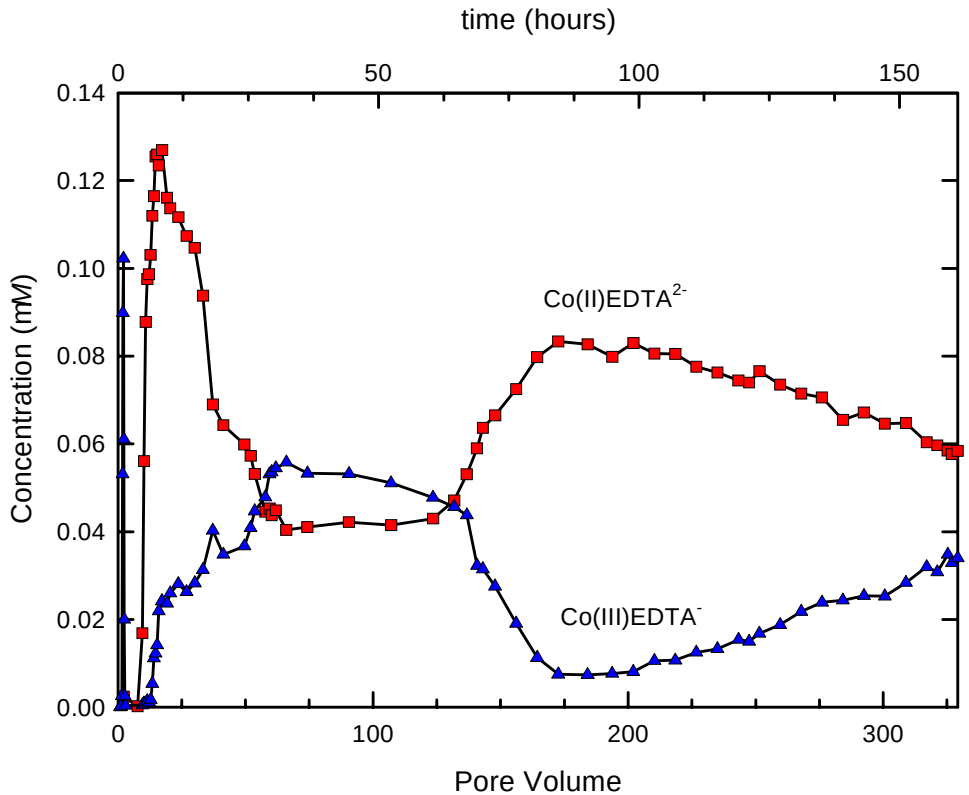


Transport of Co(II)EDTA^{2-} through a packed bed of Fe-oxide coated silica.

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 ($Fe(OH)_{3,am}$) During Dynamic Flow



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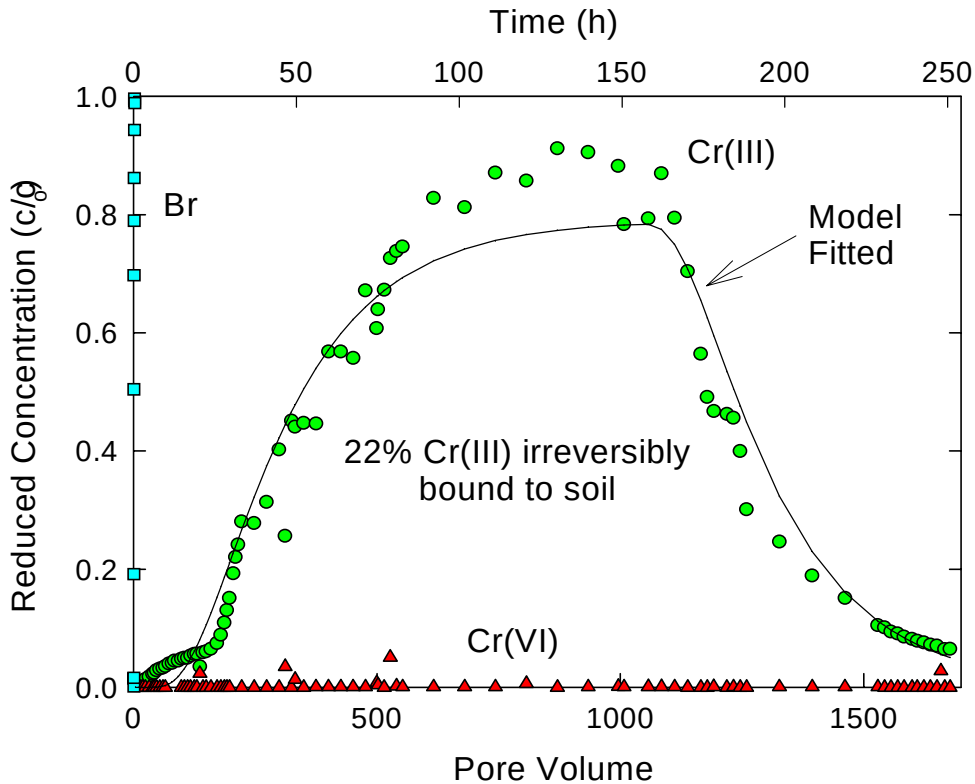
Cr System

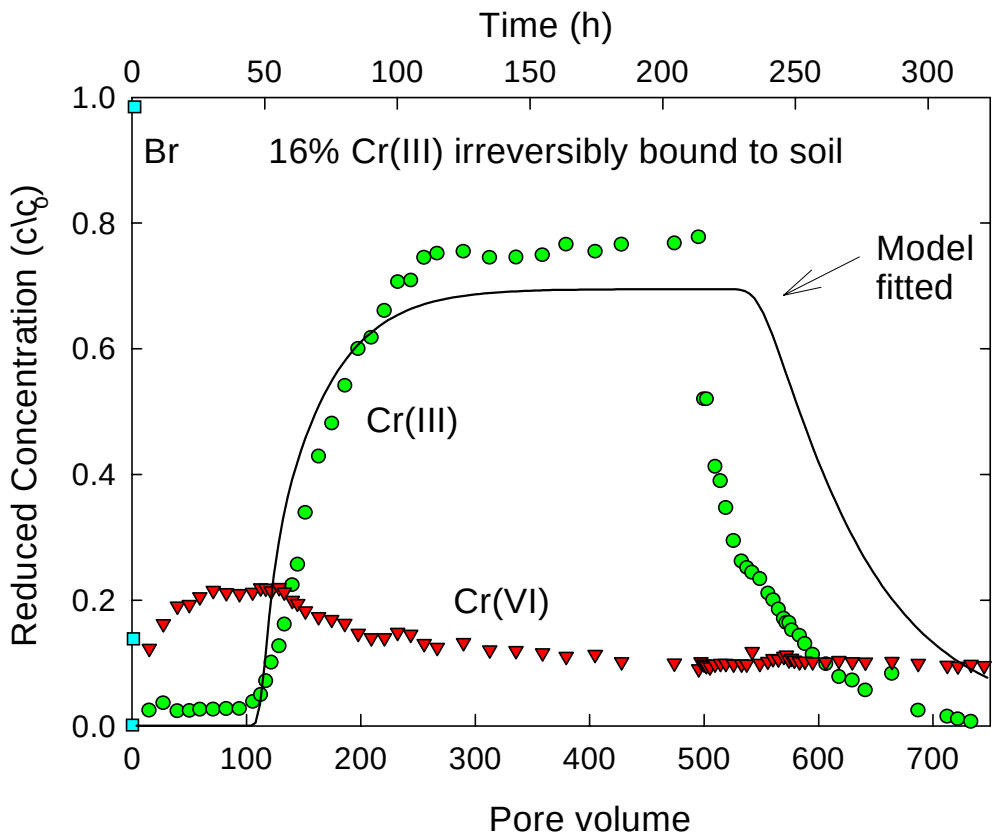
SRL soil, 0.2 mM Cr(III), pH=4.0
q=12.6 cm h^{-1}, residence time = 0.36h



- 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 cm h^{-1}, residence time=0.68h

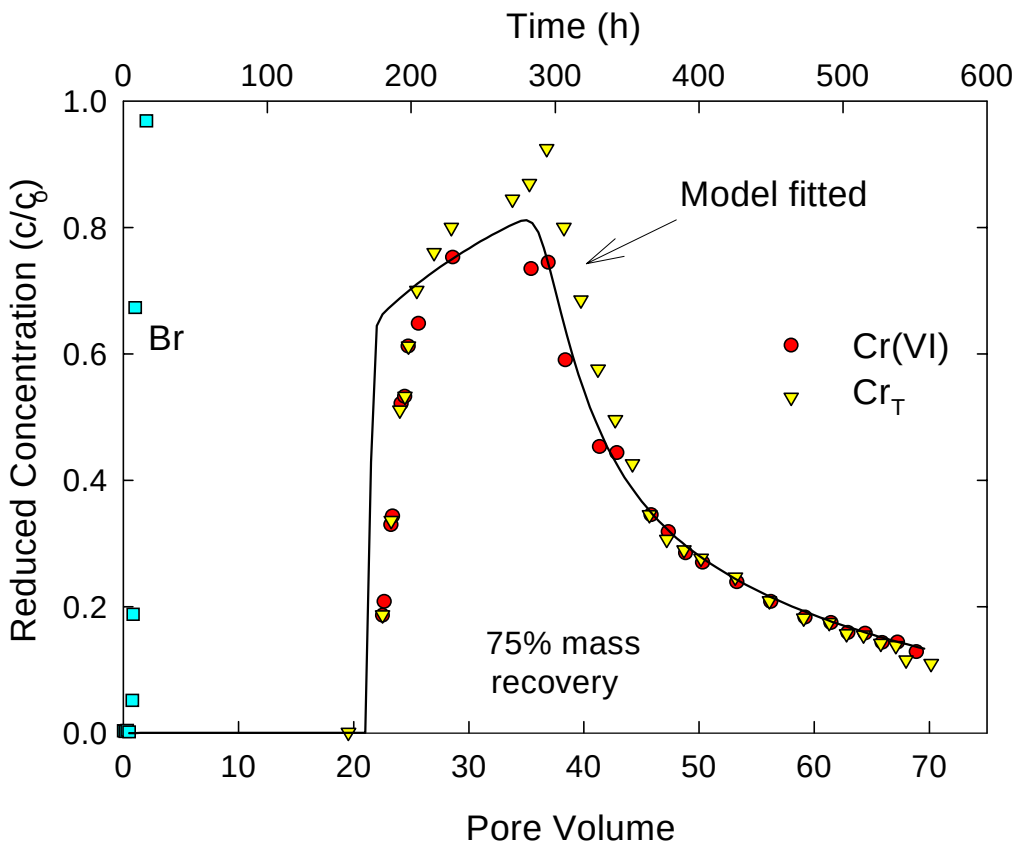


- Transport of Cr(III) through Hanford sediment with model fitted curve using a multireaction transport code.

- 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).

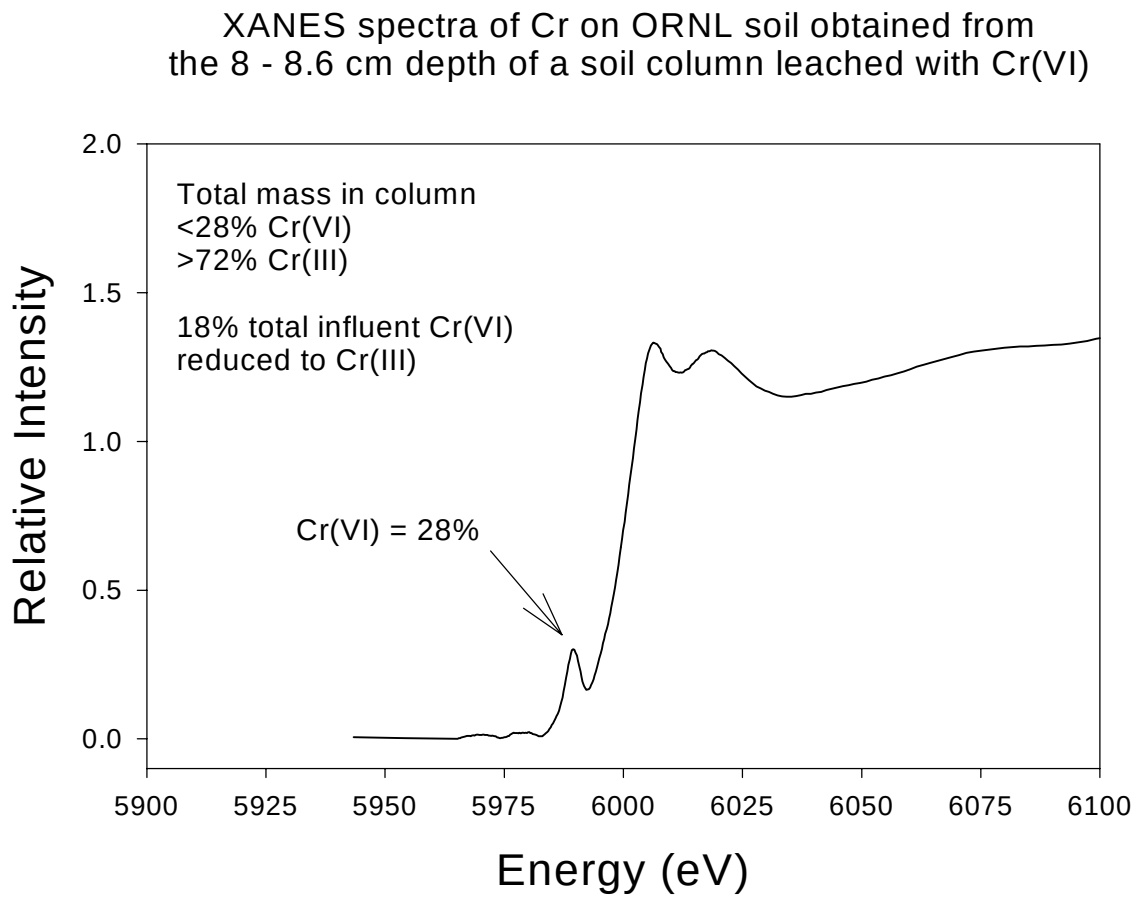
ORNL soil, 0.35 mM Cr(VI)
q=0.51 cm h^{-1}, residence time = 16.9 h



- 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).

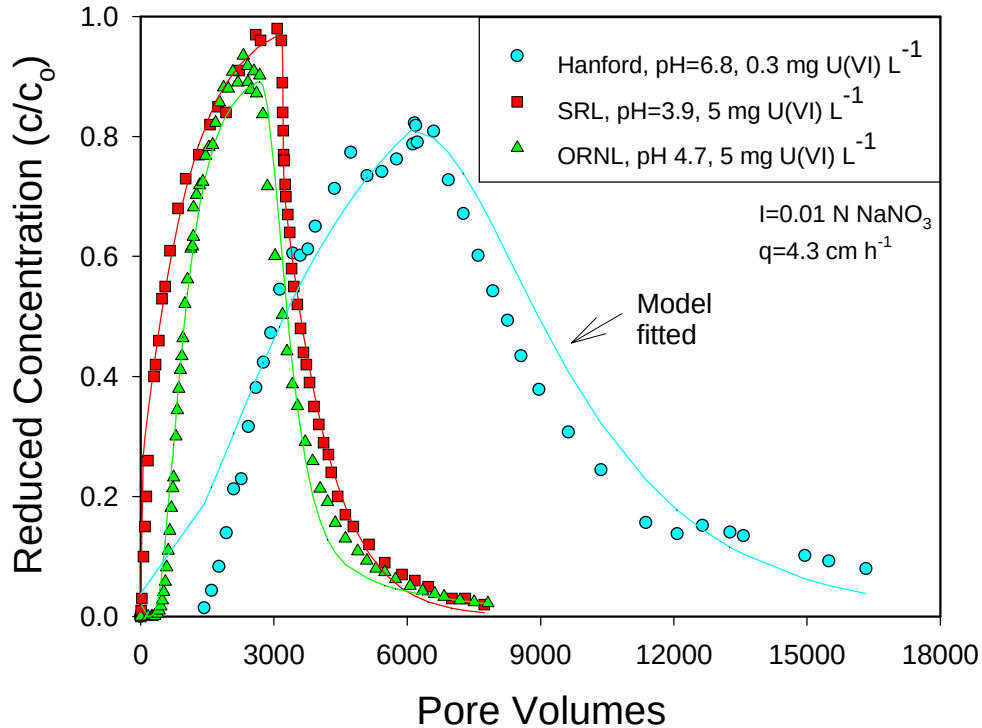


X-ray Absorption Near Edge Spectroscopy (XANES) spectra of Cr on ORNL soil obtained from the 8-8.6 cm depth of the soil column above which was leached with Cr(VI).

XANES was performed on eight 1 cm segments of the column.

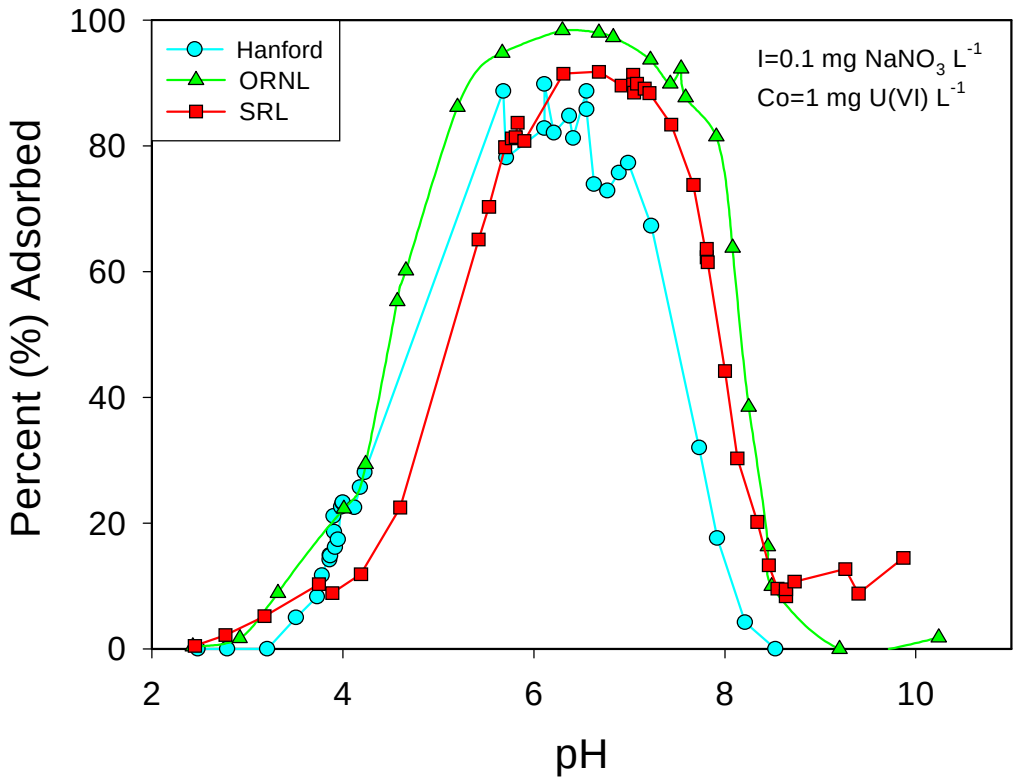
XANES confirmed that ORNL soils can reduce a significant portion of Cr(VI) to Cr(III) thereby enhancing Cr stabilization by nearly 25 fold. Cr mass loss in the system could be attributed solely to the formation of Cr(III).

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 cm^3 g^{-1}.
- XAS analysis has been performed on the solid phase U in order to determine the mechanism of surface sorption. The improved conceptual understanding of the microscopic processes will assist in the modeling of the macroscopic transport experiments.

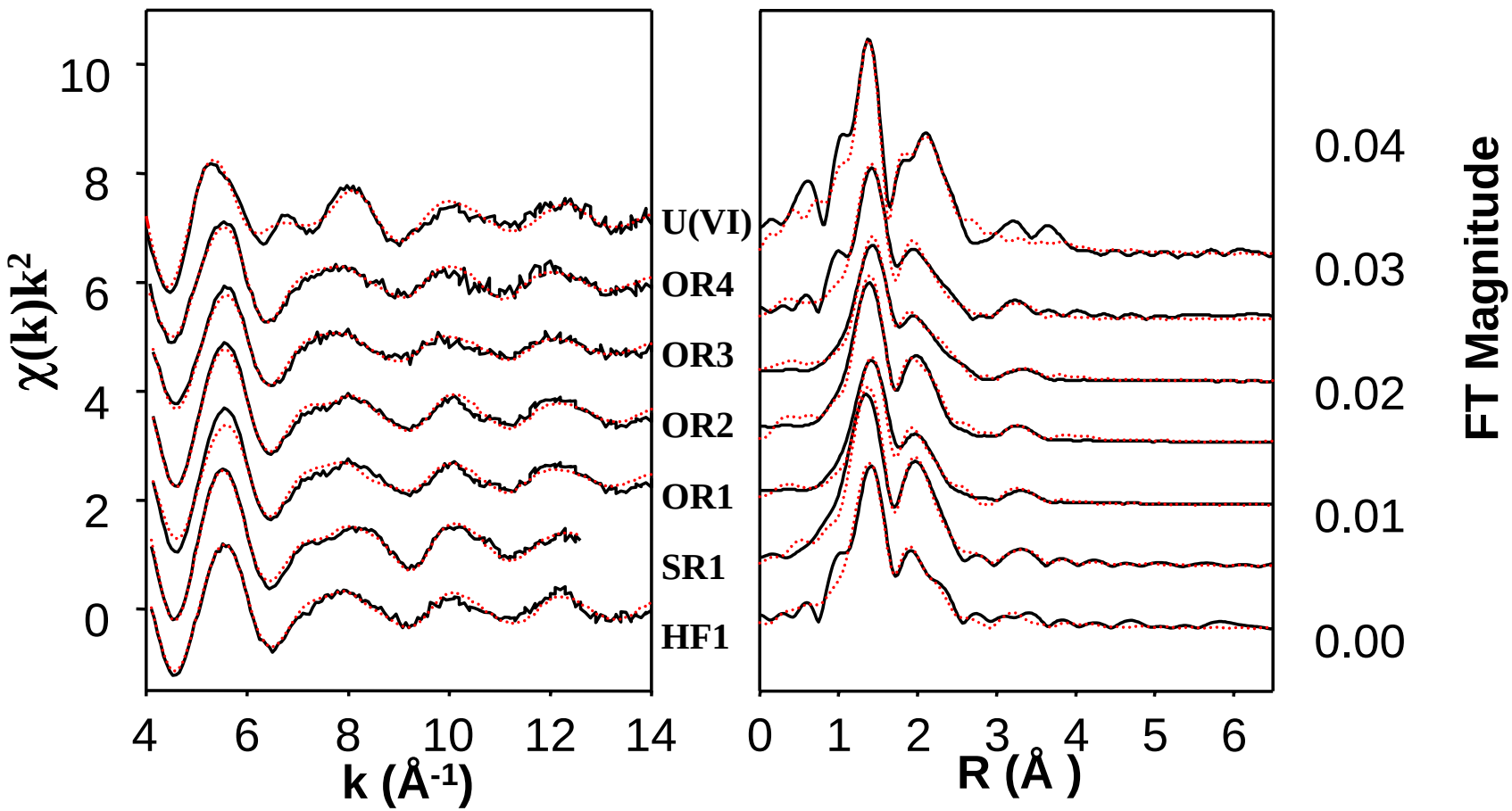
U(VI) pH adsorption envelopes



- 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-CO_3 species dominate the equilibrium solutions and U(VI) sorption rapidly decreases with small increases in pH.

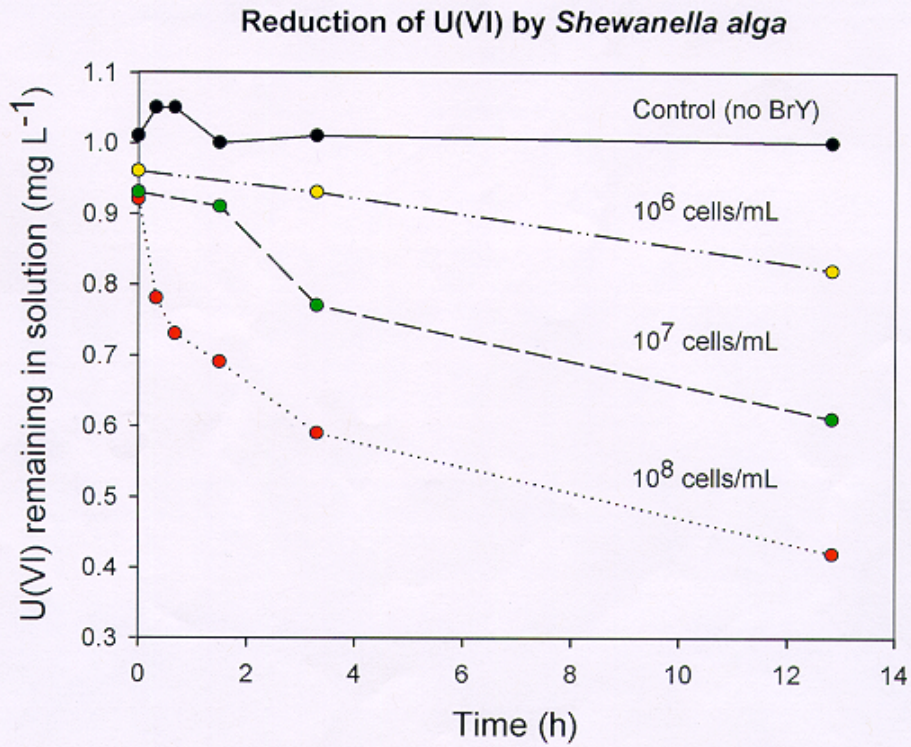
- The sharp edge for U(VI) sorption will strongly influence the transport of U in subsurface environments and thus the need for remedial action.



- X-ray Absorption Fine Structure (EXAFS) is used to decipher the sorption mechanisms of U on Oak Ridge, Savannah River, and Hanford sediments.

- Ternary complexes of uranyl carbonate and phosphate were the dominant surface complexes.

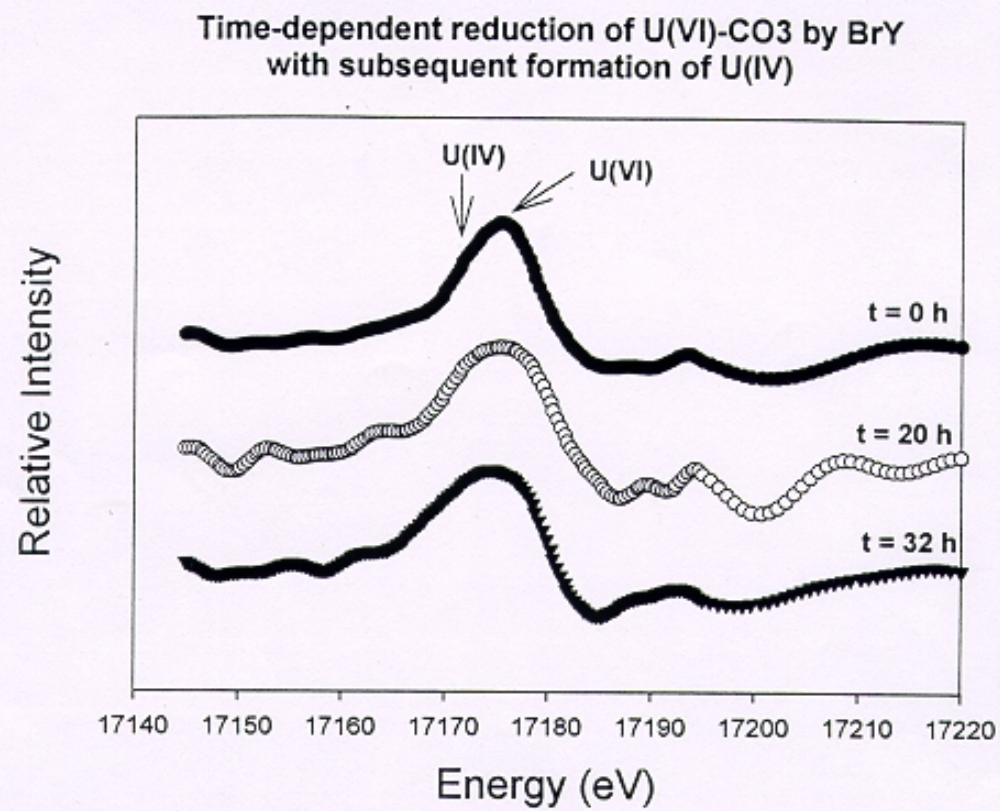
- Much of the U was present as disordered inner-sphere and outer-sphere surface complexes suggesting that the bound U is labile and that sorption is reversible. These findings are consistent with the macroscopic U transport experiments and they have important implications on future remedial strategies at these contaminated sites.



- 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 O_2 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.



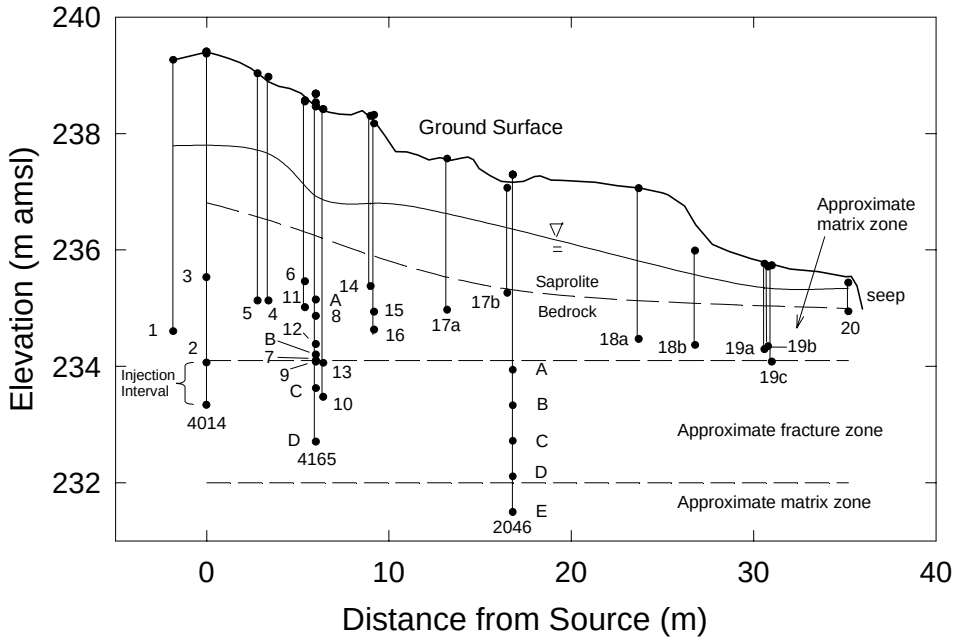
- Time-resolved XANES spectra of U(VI) solutions in the presence of BrY.
- The spectra show an increase intensity at lower energy (noted by the broadening) which corresponds to the formation of U(IV). Thus, BrY is reducing U(VI) to U(IV) as a function of time.

Opportunities for Scale-up and Demonstration
(laboratory scale)

Undisturbed cores from various DOE facilities are available to investigate the influence of nutrient amendments and delivery rates on the bioreduction of Cr(VI), U(VI), and Co(III)EDTA$^-$ in heterogeneous media influenced by coupled hydrological and geochemical processes.

These mesoscale investigations provide knowledge and information for enhancing the opportunity for successfully implementing biostimulation strategies in the field.

Opportunities for Scale-up and Demonstration
(field scale)



A well-characterized, intensively instrumented field facility is available at ORNL to assess biostimulation remedial strategies involving Cr(VI), U(VI), and Co(III)EDTA$^-$.

The spatial and temporal variability of hydrological, geochemical, and microbial processes have been intensively characterized at the site. Solute transport processes were quantified with two long-term (each 2 y duration), natural gradient injections of multiple nonreactive and reactive tracers. Metal reducing bacteria have been isolated and their kinetics of toxic metal reduction quantified.

Flow and transport processes have been rigorously modeled using high performance multicomponent, multiprocess numerical models that simulate coupled hydro-biogeochemical processes

Research Products

- Improved knowledge regarding the optimum conditions necessary for bacteria to effectively immobilize contaminants in the presence of competing geochemical reactions and complex hydrodynamic flow.

- New insights regarding remedial strategies involving *in situ* geochemical and microbial treatment barriers for immobilizing Cr, U, and Co in the subsurface.

- Rapid dissemination of results to the scientific and user community through peer-reviewed publications (15 total) and public presentations (13 total).

- Opportunity for scale-up and field demonstration of the bioreduction remedial strategy.