Project ID: **55267**

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

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## Research Objectives

The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods. Our objectives are to (1) develop an improved understanding of the rates and mechanisms of competing geochemical oxidation and microbiological reduction reactions that govern the fate and transport of redox-sensitive metals and radionuclides in the subsurface, and (2) quantify the conditions that optimize the microbial reduction of toxic metals and radionuclides, for the purpose of contaminant containment and remediation in heterogeneous systems that have competing geochemical oxidation, sorption, and organic ligands. The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs in situ contaminant immobilization. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater.

This report summarizes work after 2.5 y of a 3 y project.

## Progress and Relevance to EM Needs

In an effort to control the off-site migration of redox sensitive metals (Cr) and radionuclides (Co, U, and Tc), research within this project is using metal-reducing bacteria to stabilize contaminant plumes in the subsurface. Our challenge is to optimize microbial reduction processes in the presence of competing geochemical oxidation and sorption reactions, and to sustain microbial reduction processes in -situ for long periods of time. Our approach involves the use of (a) a sophisticated dynamic flow technique to quantify geochemical oxidation/sorption and microbial reduction rates and mechanisms controlling the mobility of U, Cr, and Co-EDTA in heterogeneous soils/sediments, (b) novel spectrophotometric techniques to monitor the time-dependent redox transformations and immobilization of U, Cr, and Co-EDTA by subsurface media, (c) an advanced numerical model that couples hydrologic-biogeochemical transport processes for simulation of the experimental data.

To date, we are the first research group to demonstrate the sustained microbial reduction of $^{60}$Co(III)EDTA to $^{60}$Co(II)EDTA under dynamic flow conditions. The net reduction of the $^{60}$Co(III)EDTA dominates the fate and transport of this contaminant, even in the presence of strong mineral oxidants commonly found in the subsurface (e.g. Mn- and Fe-oxides). The environmental implications of these findings are pronounced since $^{60}$Co(III)EDTA is extremely stable and soluble, and this enhances its persistence and transport in subsurface environments. By discovering a way to keep the bacteria healthy and growing, we were able to effectively stabilize $^{60}$Co(II)EDTA in a flowing subsurface system. This is advantageous from a remedial perspective since $^{60}$Co(II)EDTA is a weaker complex than $^{60}$Co(III)EDTA, and therefore easier to decouple and remediate. These findings are currently being published in the journal Environmental Science and Technology. Within this subtask we have also used synchrotron based radiation (X-ray

Absorption Near Edge Structure - XANES) to identify the mechanisms and reaction pathways involved in the mineral catalyzed oxidation of $^{60}$Co(II)EDTA to $^{60}$Co(III)EDTA. By quantifying the kinetics and mechanisms of the redox reaction, an accurate numerical formulation of the processes can be performed and thus the system can be rigorously modeled. These results are published in a special American Chemical Society book series and in the journal Geochimica et Cosmochimica Acta.

The fate and transport of U(VI) and U(IV) in ORNL, Savannah River, and Hanford sediments have been quantified for a variety of environmental conditions. Investigations are emphasizing the effects of geochemical oxidation and interfacial sorption reactions, and the effects of biological reduction processes on the time-dependent mobility of U in the subsurface media. The reduction is generally quite rapid, with time scales on the order of minutes to hour. The reduction of U(VI) is advantageous from an environmental perspective since reduced U(IV) is significantly less soluble and less mobile in subsurface environments relative to the oxidized species. A unique aspect of this research is our use of time-resolved X-ray Absorption Spectroscopy (XAS) located at the Stanford Synchrotron Radiation Laboratory, in Stanford CA. Since this technique is sensitive to metal redox shifts and interfacial surface reactions, we used XAS to quantify the time-dependent bacterial reduction of U(VI) to U(IV). Often times geochemical sorption reactions dominate U(VI) dynamics. We have found that U(VI) sorption on ORNL, Hanford, and Savannah River sediments is highly dependent on pH and $pCO_2$. Classic U(VI) adsorption envelopes are observed with adsorption edges increasing sharply from pH 4 to 6 and then decreasing sharply from pH 7 to 8. Sorption $k_d$ values range from ~50 $cm^3/g$ at pH 4 and 8 to nearly 2000 $cm^3/g$ at pH 6-7. Above pH 7, $U\text{-}CO_3$ species dominate the equilibrium solution and they are less retarded than U(VI) and its hydrolysis products. The surface bound U species appear resistent to microbial reduction. These research findings are currently being published in Soil Science Society of America Journal and other publications are being prepared.

The fate and transport of Cr(III) and Cr(VI) in ORNL, Savannah river, and Hanford sediments have been quantified for a variety of environmental conditions. The reduction of Cr(VI) to Cr(III) is desirable from an environmental perspective since Cr(VI) is a potent carcinogen and highly mobile in the environment, whereas Cr(III) is significantly less soluble and less toxic. Bacterial reduction of Cr(VI) to the less toxic and less mobile Cr(III) species seems improbable due to toxicity considerations. Fortunately we have discovered two alternative routes to reduce Cr(VI). The first route is abiotic, where natural organic carbon (NOM) is used to effectively reduce Cr(VI) to Cr(III) thereby slowing its subsurface mobility many orders of magnitude. This technique shows real promise for use in geochemical barriers since NOM sorbs extremely well to soils and sediments and serves as an efficient, cost effective means of immobilizing Cr. The second route uses metal reducing bacteria to reduce Fe-oxides to Fe(II), where the latter quickly reduces Cr(VI) to Cr(III). The process is catalytic where the only reactant being lost is Cr(VI). The technique shows promise for use in active biowall technologies for the in-situ containment of Cr. The efficiency of both techniques for immobilizing Cr has been quantified using time-resolved XAS since this instrument probes for contaminants on the surface of sediments and bacteria, thereby permitting the determination of the contaminant chemical and structural state. These results are being published in the journal Environmental Science and Technology and several other publications are being prepared.

## Planned Activities

Continue investigations of strategies to optimize U(VI) immobilization using metal reducing bacteria. Experiments are using realistic dynamic flow conditions to quantify microbial induced U(VI) reduction in the presence of competing geochemical sorption reactions. Completed by the end of FY99.

Finalize research that is investigating indirect immobilization strategies for Cr(VI) in DOE soils and sediments. Experiments are focusing on abiotic reduction strategies using natural organic carbon and microbial reduction strategies using reduced products of Fe-oxides to convert Cr(VI) to the highly immobile Cr(III) species. Completed by the end of FY99.

Continue to use X-ray Absorption Spectroscopy at the Stanford Synchrotron Light Source to define the mechanisms of Cr(VI) and U(VI) reduction by bacteria and subsequent immobilization by soils and sediments. Completed by end of FY99.

Continue to simulate our experimental data with the newly developed biohydrogeochemical model and use the calibrated code to assist with various DOE site needs. Completed by end of FY99.

## Possible Demonstration Phase Activities (pending EM50 support)

Pilot scale bioreduction experiments using undisturbed cores and large scale blocks instrumented with active biowalls.

Propose field scale bioreduction demo at a well characterized field tracer facility on the Oak Ridge Reservation (see http://www.esd.ornl.gov/facilities/hydrology/WAG5/). This would involve coupling our EMSP findings with our field scale hydrogeochemical experiments funded by DOE's OBER in an effort to biostimulate indigenous subsurface metal-reducing bacteria for the purpose of immobilizing toxic metals and radionuclides through bioreduction (see http://www.esd.ornl.gov/programs/ETPI/).

## Information Access

### Peer-reviewed manuscripts and book chapters

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Press Releases

Intiated by Waste Policy Institute of Blacksburg, VA. Contact: Dale Norton. Scheduled release Summer 1999.

Initated by Department of Energy, one of 5 out of 200 EMSP projects to be featured in a press release package. Contact: Robert Evans and Debra Hill (INEL).