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

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Research Objective

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.

Research Progress and Implications

This report summarizes work after 1.5 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, and (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 $^{60}\text{Co(III)EDTA}$ to $^{60}\text{Co(II)EDTA}$ under dynamic flow conditions. The net reduction of the $^{60}\text{Co(III)EDTA}$ 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 $^{60}\text{Co(III)EDTA}$ is extremely stable, 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 $^{60}\text{Co(II)EDTA}$ in a flowing subsurface system. This is advantageous from a remedial perspective since $^{60}\text{Co(II)EDTA}$ is a weaker complex than $^{60}\text{Co(III)EDTA}$, and therefore easier to decouple and remediate.

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).

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.

Planned Activities

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

Pursue indirect immobilization strategies for Cr(VI) in DOE soils and sediments. Experiments will focus 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 mid 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.

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.

Propose 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/>).

Other Access To Information

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