Subsurface Transport of Metals and Radionuclides

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Biogeochemical Processes Controlling Microbial Reductive Precipitation of Radionuclides

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Sponsor: DOE Office of Science, Biological & Environmental Research

- Metal-reducing bacteria can precipitate Uranium, slowing the movement of this contaminant in groundwater.
- Environmental factors that promote or inhibit these reactions are poorly understood.
- Successful use of bacteria for remediation requires improved understanding of competing reactions that immobilize and mobilize uranium.

Ca causes significant decrease in rate and extent U(VI) reduction

Spectroscopic (synchrotron, luminescence, Raman) interrogation of samples reveals Ca-U(VI)-CO$_3$ complex

Link between chemical speciation and bacterial U reduction

Implications for biogeochemical immobilization of U(VI)?
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Laboratory research has shown that dissimilatory metal reducing bacteria (DMRB) can effectively reduce oxidized uranium (U(VI)) to the sparingly soluble U(IV) with the concomitant precipitation of UO₂ phases. Despite the promise of bioreduction as a remediation strategy, the factors that enhance or inhibit the rate and extent of biogeochemical U(VI) reduction under representative environmental conditions are not well defined. Before effective bioimmobilization can be realized, the factors governing contaminant reactivity in multicomponent systems must be better understood. Only recently has the quantification of a few key interactions been established. For example, we recently reported the inhibition of bacterial U(VI) reduction by DMRB in the presence of environmentally realistic concentrations of soluble calcium (Ca) (Brooks et al., 2003). This finding has significant implications for field applications of bioreduction because Ca²⁺ is a dominant soluble and cation-exchangeable species in soils and aquifers. Bioreductive immobilization of uranium (U) and technetium (Tc) offers considerable promise for in situ remediation of contaminated DOE sites. Before effective in situ bioimmobilization of these contaminants can be realized, complex biogeochemical interactions between contaminants, reactive mineral surfaces, and bacteria must be better understood. The goal of this research, building on previous results, is to investigate coupled microbiological-geochemical processes controlling: a) the microbial reduction of U and Tc in the presence of Mn oxides; and b) the role of advective transport on the rate and extent of the coupled reactions. Three hypotheses will evaluate: the reductive precipitation of U and Tc in relation to cell surface; the extent to which precipitation in the cell periplasm may protect the reduced contaminants against oxidation by Mn oxides; the extent to which Mn oxides, including those present in natural materials from the Oak Ridge FRC and Hanford, oxidize reduced U and Tc and impede reductive precipitation; the influence of reactive transport on net reductive precipitation; and the potential for transport of colloidal contaminant precipitates. Research results are expected to have significant implications for the in situ bioreduction and long-term immobilization of U and Tc.

Selected publications and abstracts
**In Situ Immobilization of Uranium in Structured Porous Media**

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- **Hypothesis:** U(VI) in low permeability micropores can be immobilized by stimulating *in situ* microbial U(VI) reduction in hydrologically accessible meso- and macropores.

- **Bacteria** (the agents of bioremediation) are too big to enter micropores where the majority of contaminants reside. Simply flushing the conductive macropores leaves a large source of contaminant that will enter mobile water when pumping stops.

- **Precipitation of low-solubility UO₂ within the mesopore domain will reduce or eliminate a long-term source of groundwater contamination that is otherwise extremely difficult to remediate.**

- **Results will contribute to the development of a general strategy for controlled bioremediation of metals and radionuclides in structured subsurface environments.**

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**Diagram:**
- **Macropore Domain:** Large fractures, Advevtive transport
- **Mesopore Domain:** Small fractures, Diffusive transport
- **Micropore Domain:** Pores within intact media, Diffusive transport
In Situ Immobilization of Uranium in Structured Porous Media

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Abstract: We propose a series of independent tasks culminating in an in situ field-scale biostimulation experiment at Area 2 of the NABIR Field Research Center (FRC) to evaluate the feasibility of stimulating microbial U(VI) reduction activity in targeted pore fractions of structured porous media. The research plan is designed to evaluate the hypothesis that U(VI) in low-permeability porous regions (micropores) of saprolite at the FRC can be immobilized and isolated from mobile groundwater by stimulating localized in situ microbial U(VI) reduction in hydrologically-accessible fractured zones (meso- and macropores). Such activity will cause precipitation of low-solubility UO$_2$ within the mesopore domain, thereby reducing or eliminating a long-term source of groundwater contamination that is otherwise extremely difficult to remediate. Planned research elements include field hydrologic and geophysical characterization, sediment wet chemical analysis and evaluation of microbial metal reduction potential, bench-scale reactive transport experiments using intact sediment blocks, and a field-scale biostimulation experiment. The proposed research will result in improved understanding of complex interactions between biogeochemical transformation and hydrologic flow and transport processes in structured media, and will lead to development of a general strategy for controlled bioremediation of metals and radionuclides in such subsurface environments. These results will also enhance our ability to upscale laboratory bioremediation experiments to the field scale.

Selected Publications and Abstracts


Intact Core experiments preserve the physical structure for controlled laboratory experimentation.
Humic substances -- naturally forming organic ligands in soil and groundwater -- are found to enhance the bioreduction of hexavalent U(VI), particularly in the presence of toxic metals such as Ni^{2+}.

This enhancement effect is attributed to the ability of humics to facilitate biological electron transfer reactions and to form complexes with toxic metals.

However, humics are also found to form soluble complexes with reduced U(IV), preventing it from precipitation and increasing its re-oxidation rate.

Humics, as well as other organic ligands, may thus present a potential challenge in maintaining the long-term stability of uranium solids, which is a proposed remedial strategy for contaminated soil and groundwater.
Humic Substances have surprising influence on Uranium Stability and Mobility  
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Humic substances, naturally forming organic ligands in soil and groundwater, have been shown to promote the biological electron transfer reactions and therefore the reductive immobilization of uranium (U) by precipitation of reduced U solids. Both laboratory and field studies suggest that the addition of humics enhances the rate of uranium bioreduction up to ten fold, particularly in the presence of toxic metals because humics form stable complexes with metal ions. However, further studies indicate that these same humics can also enhance the reverse reaction; that is making the reduced, precipitated uranium solids more soluble in groundwater. This new study found that humics form stable and soluble complexes with reduced uranium and, additionally, increase its oxidation rate once exposed to oxygen. These findings are significant because humics, as well as other complexing organic ligands, could present a potential challenge in maintaining the long-term stability of uranium solids – a proposed remedial strategy for contaminated soil and groundwater due to the lower solubility of reduced uranium in subsurface environments.