

**Technical Progress Report – EMSP 73914 (Renewal of 55164)**

**Reporting Period: 14 November 2002 – 14 June 2004**

**Submission Data: July 8, 2004**

**Agreement Number: DE-FG07-96ER62321**

**Title: Reductive immobilization of U(VI) in Fe(III) oxide-reducing subsurface sediments: Analysis of coupled microbial-geochemical processes in experimental reactive transport systems**

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## 1. Research Objective

Although the fundamental microbiological and geochemical processes underlying the potential use of dissimilatory metal-reducing bacteria (DMRB) to create subsurface redox barriers for immobilization of uranium and other redox-sensitive metal/radionuclide contaminants are well-understood (Lovley et al., 1991; Gorby and Lovley, 1992; Lovley and Phillips, 1992; Lovley, 1995; Fredrickson et al., 2000; Wielinga et al., 2000; Wielinga et al., 2001), several fundamental scientific questions need to be addressed in order to understand and predict how such treatment procedures would function under *in situ* conditions in the subsurface. These questions revolve around the dynamic interactions between hydrologic flux and the coupled microbial-geochemical processes which are likely to occur within a redox barrier treatment zone. A brief summary of such questions includes the following:

- A. *What are the kinetic limitations to the efficiency of microbial U(VI) scavenging in subsurface sediments?*
- B. *Is U(VI) sorbed to Fe(III) oxide and other solid-phase surfaces subject to enzymatic reduction? If so, what are the relative kinetics of aqueous vs. sorbed U(VI) reduction?*
- C. *What are the relative kinetics of direct, enzymatic U(VI) reduction vs. abiotic reduction of U(VI) by surface-bound biogenic Fe(II)?*
- D. *Can coupled Fe(III) oxide/U(VI) reduction be sustained long-term in subsurface environments? What are the kinetic relationships between Fe(III) oxide reduction, DMRB growth, and U(VI) reduction in advectively open sedimentary systems?*

The overall objective of our research is to address the questions listed above through laboratory-based batch and reactive transport experiments with natural Fe(III) oxide-bearing subsurface materials and a representative pure culture DMRB. A unique feature of our research is that we are using levels of total uranium (ca.  $10^{-6}$  to  $10^{-4}$  mol per  $\text{dm}^3$  bulk volume) and aqueous/solid-phase ratios ( $\leq$  ca.  $10^{-3}$  mol U per kg sediment) which are much closer to those present in contaminated subsurface environments compared to levels employed in previous experimental studies of microbial U(VI) reduction. The goal is to develop a more realistic picture of the dynamics of U(VI) reduction and its interaction with Fe(III) oxide reduction in subsurface sedimentary environments. In doing so, our studies will provide benchmark information on process dynamics that will be useful for scaling up (e.g. through the use of field-scale reactive transport models) to *in situ* treatment scenarios. In addition, the experimental methodologies and modeling strategies developed for the project may be applicable to the evaluation of *in situ* remediation technologies for other redox-sensitive metal-radionuclide contaminants such as Cr(VI) and Tc(VII). Numerical simulations are being developed hand-in-hand with the experimental work to aid in the interpretation of the observed dynamics of U(VI) behavior, and to contribute to the development of a predictive framework for assessing *in situ* metal-radionuclide remediation strategies driven by the activity of DMRB.

## 2. Research Progress and Implications

This report summarizes ca. 3 years of work on a 3-year renewal of our original EMSP 96-10 project. Delays were encountered during recruitment and hiring of postdoctoral research associates at both UA and Auburn, such that these investigators did not begin work on the project until June 2002. Hence, we have requested and received a 1-year no cost extension to complete the project. However, we have made good progress on all three Phases of the project, and have begun producing manuscripts for publication of this work. A summary of our research accomplishments to date is provided below.

## Phase I – Microbiological and Geochemical Studies

### Overview of Research Methodology

**Aqueous phase.** The aqueous phase employed in our batch experiments is a Pipes-Buffered (10 mM, pH 6.8) Artificial Ground Water (PBAGW) containing ca. 10 mM dissolved inorganic carbon concentration (added as  $\text{NaHCO}_3$ ). The major ion composition of the PBAGW is similar to that formulated by DeFlaun et al. (1999) to model the groundwater at the DOE-NABIR bacterial transport research site in Oyster, VA, and to that employed in previous batch and column Fe(III) oxide reduction experiments in our laboratory (Roden et al., 2000). Sulfate was omitted from the AGW in order to prevent the activity of sulfate-reducing bacteria, whose spores could potentially survive autoclaving. Inorganic nutrient (10  $\mu\text{M}$   $\text{KH}_2\text{PO}_4$ , 100  $\mu\text{M}$   $\text{NH}_4\text{Cl}$ ) concentrations are ca. 1000-fold lower than those typically included in anaerobic growth medium for Fe(III)-reducing bacteria (Lovley and Phillips, 1988). Small quantities of acid (HCl) or base (NaOH) are added to suspensions of solids as needed to achieve a starting pH of 6.8. The standard concentration of U(VI) used in experiments on enzymatic U(VI) reduction was 100  $\mu\text{M}$  (added as uranyl-acetate). Lower concentrations (1  $\text{mg L}^{-1} = 4.2 \mu\text{M}$ , added as uranyl-nitrate) were typically employed in U(VI) sorption experiments (see below).

**Solid Phase.** The majority of experiments to date have been conducted with iron-rich subsurface sands from the Abbott's Pit collection site in Mappsville, VA. The Abbott's Pit Sand (APS) is a reference material for the DOE NABIR program, and is representative of Fe(III) oxide-rich subsurface materials on DOE lands. The mineralogy of APS is comparable to that of other subsurface materials in the vicinity of the Oyster research site on the Delmarva Peninsula (Zachara et al., 1989). The Fe(III) oxide pool is dominated by crystalline goethite and ferrihydrite (Zachara et al., 1989), with smaller quantities (ca. 10% of citrate dithionite-extractable Fe) of poorly crystalline Fe(III) oxides, as determined by short-term (1 hr) dilute (0.5M) HCl extraction. The APS material was wet-sieved through a 100  $\mu\text{m}$  sieve and freeze-dried prior to being used in bacterial Fe(III) oxide reduction experiments. The sieving procedure was required to remove large sand grains which otherwise prevented sampling of batch reactors with our standard syringe-and-needle procedure. The <100  $\mu\text{m}$  fraction of the subsurface material contained ca. 90% of the total citrate-dithionite extractable Fe. In most experiments, the sieved APS material was added to achieve a final Fe(III) oxide concentration of 50  $\text{mmol L}^{-1}$ , which corresponded to ca. 88 g of solids per  $\text{dm}^3$  of culture medium. This amount of solid in medium containing 100  $\mu\text{M}$  U(VI) yields a mass-normalized U(VI) concentration of ca. 1  $\mu\text{mol per g}$  of dry sediment, which is comparable to levels of total uranium in typical DOE-contaminated subsurface sediments (e.g. those at ORNL; (Watson, 2002)) Additional Fe(III)/U(VI) experiments were conducted with synthetic goethite, hematite, and ferrihydrite, prepared (or purchased) as described in previous research in our laboratory (Roden and Zachara, 1996; Roden et al., 2000), as well as other DOE-relevant subsurface materials.

**Microorganism.** The acetate-oxidizing, Fe(III)/U(VI)-reducing bacterium, *Geobacter sulfurreducens* (Caccavo et al., 1994) was employed in all of the Fe(III) and U(VI) reduction experiments described herein. This organism is the subject of several DOE (NABIR and GTL programs) research projects on the biochemistry and genetics of Fe(III), U(VI) and Tc(VII) reduction. Hence it is logical to compile information on the performance of this organism in experimental studies of the biogeochemistry of metal-radionuclide contaminant reduction. In addition, the fact that the majority of Fe(III)-reducing organisms which arise during stimulation of Fe(III) oxide (and U(VI)) reduction activity in subsurface sediments (Snoeyenbos-West et al., 2000; Holmes et al., 2002; Anderson et al., 2003) are closely related to *G. sulfurreducens* indicates that this is an appropriate model organism for experimental studies of subsurface metal reduction and associated biogeochemistry. *G. sulfurreducens* can be grown to a high cell density with malate (or fumarate) as an electron acceptor, and cells grown in this manner have a strong capacity

for solid-phase Fe(III) oxide and U(VI) reduction. Washed, malate-grown *G. sulfurreducens* cells therefore provided an ideal inoculum for our Fe(III) and U(VI) experiments.

### ***Kinetics of Fe(III) oxide reduction and DMRB growth***

We have conducted studies with a variety of synthetic Fe(III) oxide phases and pure cultures of *Shewanella putrefaciens* and *G. sulfurreducens* which indicate that surface area-normalized rates of electron transfer to Fe(III) oxides are comparable (in the presence of excess electron donor) across a wide range of oxide crystal structure and surface area (Roden, 2003a; Roden, 2003c). These results suggest a rate model in which enzymatic electron transfer is directly dependent on the abundance of reducible oxide surface sites (Roden, 2004). Studies of the influence of DMRB cell density on rates of oxide reduction demonstrate a hyperbolic relationship between total cell density and surface-area normalized reduction rate (Roden, 2003a; Roden and Sedo, 2003). The results of these studies, together with independent data on FeRB growth yield (with soluble ferric citrate), provided information required for simulation of oxide reduction kinetics in nonsteady-state systems in which DMRB cell density varies over time. A phospholipid fatty acid (PLFA)-based approach (Findlay et al., 1989) for quantifying changes in DMRB abundance in relatively low biomass (ca.  $10^5$  to  $10^8$  cells mL<sup>-1</sup>), mineral-rich reaction systems is underway. Finally, previous and ongoing studies of Fe(II) sorption to residual Fe(III) oxide and other mineral surfaces during enzymatic reduction have permitted development of a semi-empirical, reaction-based framework for depicting the influence of surface-bound Fe(II) accumulation on long-term oxide reduction kinetics (Roden, 2004). The developed framework accurately reproduces the results of batch and column studies of synthetic and natural Fe(III) oxide reduction (Roden and Sedo, 2003), and has been used to assess the impact of field-scale physical/chemical heterogeneity on spatial and temporal patterns of bacterial Fe(III) oxide reduction (Roden, 2003d).

### ***Kinetics of biotic and abiotic U(VI) reduction***

We have obtained kinetic parameters for reduction of soluble U(VI)-carbonate complexes by *G. sulfurreducens* (Roden and Scheibe, 2004). These parameters have been employed in numerical simulations of U(VI) bioreduction in bench-scale (Roden, 2003b) and field-scale (Roden and Scheibe, 2003) reaction systems. We have also conducted extensive studies of abiotic (by surface-associated Fe(II)) and enzymatic (by *Geobacter sulfurreducens*) reduction of U(VI) in the presence of synthetic Fe(III) oxides and natural Fe(III) oxide-containing solids (Jeon et al., 2004a; Jeon et al., 2004b). In these experiments, more than 95% of added U(VI) was sorbed to solids, so that U(VI) reduction was governed by reactions at the solid-water interface. Key findings of these studies are as follows: (i) the rate and extent of abiotic and enzymatic U(VI) reduction in the presence of synthetic Fe(III) oxides (hydrous ferric oxide, goethite, and hematite) was comparable to that observed during biological reduction of aqueous U(VI); (ii) both abiotic and enzymatic reduction of U(VI) sorbed to several different natural Fe(III) oxide-containing solids were slower and less extensive compared to synthetic Fe(III) oxide systems; (iii) long-term net U(VI) reduction was less than 30% in abiotic suspensions of six different natural solids containing an excess of surface-bound Fe(II), compared to 60-80% reduction in the presence of enzymatic activity; (iv) the addition of a catalytic amount of the electron shuttling agent anthraquinone-2,6-disulfonate (AQDS) to the natural Fe(III) oxide suspensions enhanced the rate and extent of U(VI) reduction. These findings suggest that AQDS facilitated electron transfer from *G. sulfurreducens* to U(VI) associated with surface sites at which both Fe(II)-catalyzed and enzymatic U(VI) reduction were limited. Our results demonstrate that association of U(VI) with diverse surface sites in natural soils and sediments has the potential to limit the rate and extent of both abiotic and enzymatic U(VI) reduction, and in turn modulate the effectiveness of in situ U(VI) bioremediation. They also indicate that addition of electron shuttling compounds, such as natural humic substances, could enhance the overall effectiveness of in situ U(VI) bioremediation. However, other project results indicate that humic complexation of U(VI) may inhibit enzymatic reduction of soluble U(VI) (Burgos et al., 2004), and additional studies are required to

evaluate the extent to which natural and synthetic electron shuttles may be able to facilitate U(VI) reduction in subsurface sediments.

### ***Batch U(VI) sorption on Fe(III) oxide-bearing materials***

The kinetics and equilibrium adsorption of U(VI) to a synthetic Fe(III) oxide-coated sand and unsieved APS were conducted in PBAGW containing 10 mM NaHCO<sub>3</sub> and in other background inorganic matrices. The results indicate that U(VI) adsorbs more strongly to the APS sediment than the Fe-coated sand under the conditions of equivalent mass loading, which is consistent with the higher Fe content of the APS material. These results also indicate that the rate of U(VI) uptake by these materials is relatively rapid: aqueous concentrations after one hour were not significantly ( $P < 0.05$ ) different than concentrations after 2 days. These findings indicate that U(VI) reaches equilibrium with these two materials over a relatively short time span (<2 hours), and that slow diffusion of U(VI) into interior particle porosity is not an important process. Additional experimentation showed that variations in dissolved inorganic carbon concentration from 2 to 10 mM did not strongly affect the rate of U(VI) sorption to these media.

Isotherms for U(VI) adsorption onto the two Fe(III) oxide-bearing materials indicate that U(VI) adsorption is linear up to a dry weight-normalized total U(VI) content ( $1\text{--}2 \mu\text{mol g}^{-1}$ ) comparable to that employed in the coupled Fe(III)/U(VI) reduction experiments described above. The combination of linear adsorption and the attainment of relatively rapid adsorption equilibrium indicate that relatively simple transport models (i.e. ones which assume linear local equilibrium) have the potential to accurately describe subsurface U(VI) transport. However, as previously reported for other synthetic (Hsi and Langmuir, 1985; Waite et al., 1994; Morrison et al., 1995; Kohler et al., 1996) and natural (Casas et al., 1994; Ticknor, 1994; Barnett et al., 2002) Fe(III) oxide minerals, U(VI) adsorption to these two media is strongly pH-dependent (Cheng et al., 2004b). The combination of rapid and linear, but pH-dependent, adsorption of U(VI) to these materials indicates that a simple non-electrostatic pH-dependent adsorption modeling approach has the potential to accurately describe U(VI) subsurface transport, and in particular the behavior of U(VI) in the experimental reactive transport experiments to be conducted in Phases II and III of this research project.

## **Phase II – Microbiological and Geochemical Studies**

### ***Semicontinuous Culture Reactor Experiments***

We have conducted a long-term semicontinuous culture experiment on coupled Fe(III) oxide/U(VI) reduction with natural subsurface sediment from the Oyster site in Virginia. The semicontinuous culture reactor (SCR) approach represents a middle ground between closed system batch cultures and column reactor systems involving continuous advective aqueous phase flux. In a SCR experiment, 10-30% of the aqueous phase of the reactor is carefully removed (so as to not disturb the layer of settled materials on the bottom of the reactor) every 3-4 days using a sterile syringe via an 18G needle fixed in the bottle closure (cf. (Roden and Urrutia, 1999)). An equal volume of fresh AGW medium is then added to the reactor, after which the sediment is resuspended by vigorous shaking prior to withdrawal of bulk sediment suspension samples (usually a few mL). The volume of aqueous phase replacement is decreased incrementally over time in order to maintain a constant solid:solution ratio in the reactor. This procedure can conveniently produce mean aqueous phase residence times of ca. 10 d, which is likely to approach reality for field-scale bioremediation systems. A significant advantage of the SCRs is that samples of solid-phase materials (containing residual and newly formed mineral phases and DMRB biomass) can be easily obtained on a periodic basis for chemical, microbiological, and mineralogical analysis – in contrast to column reactors, from which solid-phase samples can only be obtained through destructive sampling at the end of the experiment.

The results of the SCR experiment conclusively demonstrated the potential for sustained removal of U(VI) from solution via DMRB activity in excess of the U(VI) sorption capacity of the natural mineral assemblages as determined in abiotic controls (Fig. 1A,B). In addition, the abundance of sorbed U(VI) (a potential long-term source of U(VI) to the aqueous phase) was much lower in the biotic vs. abiotic systems. The latter results agree with other project findings which demonstrated the capacity for *G. sulfurreducens* to reduce sorbed U(VI) (Jeon et al., 2004b). Development of reaction-based numerical simulations of the experimental results are underway, and will include information on the Fe(II) and U(VI) sorption characteristics of the Oyster sediment materials (Jeon et al., 2004a).

### ***Reactive Transport of U(VI) in a Goethite-Coated Sand Column***

Column experiments were conducted to investigate U(VI) transport in porous media (Cheng et al., 2004a). Goethite-coated sand was used to mimic natural Fe coated media. At pH 4, and a total U(VI) concentration of ca.  $10^{-6}$  M, the presence of  $10^{-4}$  M phosphate caused significant retardation in U(VI) transport in column experiment. Retardation in U(VI) transport was also observed in a column experiment with phosphate pre-adsorbed to the goethite-coated sand. Batch kinetics experiments and U(VI) adsorption isotherm experiments were run to investigate the effects of solid solution ratio (SSR) and adsorption kinetics. It was found from batch kinetics experiments that: (i) in the absence of phosphate, the initial U(VI) adsorption rate was slow, but adsorption reached equilibrium in less than 48 hr; and (ii) the presence of  $10^{-4}$  M phosphate not only greatly increased the amount of U(VI) adsorbed at equilibrium but also greatly increased the rate of U(VI) adsorption. U(VI) adsorption reached equilibrium in less than 8 hr in the presence of phosphate. The results from U(VI) adsorption isotherm experiments indicated in the presence of phosphate, SSR had a significant effect on U(VI) adsorption isotherm, a lower SSR led to higher adsorption, while in the absence of phosphate, SSR did not have an effect on U(VI) adsorption isotherm. We conclude from these results that: (i) retardation in U(VI) transport in the presence of phosphate was caused by the formation of strong adsorbed ternary surface complex; (ii) due to the high flow rate used, adsorption equilibrium was not reached in the column experiments, so the adsorption in column experiments was controlled by kinetics. Adsorption data from batch experiments, which had a much longer reaction time and thus closer approach to equilibrium, cannot be directly applied to predict adsorption in column experiments; and (iii) in the presence of phosphate, SSR had a significant effect on U(VI) adsorption isotherm. Adsorption data obtained from batch experiments, which had a much lower SSR compared to that used in column experiments, cannot be applied to predict adsorption in porous media.

### **Phase III – Coupled Microbiological-Geochemical Reactive Transport in Column Reactors**

We have conducted a long-term column reactor experiment on coupled Fe(III) oxide/U(VI) reduction by *G. sulfurreducens*, once again using natural subsurface sediment (< 2 mm fraction) from the Oyster site in Virginia. The hydrological residence time of the reactors was ca. 2 d, significantly shorter than for the SCRs but not unrealistic with respect to field applications. As in the case of the SCR experiment, the results demonstrated the potential for sustained removal of U(VI) from solution via DMRB activity in excess of the U(VI) sorption capacity of the natural mineral assemblages (Fig. 1C,D). The column reactors are still in operation and will be maintained for a total time period of at least one year (i.e. at least until September 2004). Measurements of DMRB cell density in the column effluent are underway, and will be used to parameterize reaction-based numerical simulations of the experimental results which include DMRB growth and transport. Reaction-based simulations of previous experiments (Roden et al., 2000) have successfully reproduced the evolution of Fe(II) and DMRB export from experimental column reactors comparable to those employed in the coupled Fe(III)/U(VI) reduction experiment (Roden, 2003d).

### 3. Information Access

#### Referred Publications

Roden, E.E. 2004. Analysis of long-term bacterial vs. chemical Fe(III) oxide reduction kinetics. *Geochim. Cosmochim. Acta*. In press.\*

Roden, E.E. 2004. Analysis of Fe<sup>III</sup> oxide reactivity toward long-term bacterial vs. chemical reduction, pp. 1227-1230 In Wanty, R.B. and R.R. Seal II (Eds), Proceedings of the 11<sup>th</sup> International Symposium on Water-Rock Interaction. AA Balkema Publishers, New York.\*

Roden, E.E. Diversion of electron flow from methanogenesis to crystalline Fe(III) oxide reduction in carbon-limited cultures of wetland sediment microorganisms. *Appl. Environ. Microbiol.* 59:5702-5706.\*

Roden, E.E. 2003. Fe(III) oxide reactivity toward biological versus chemical reduction. *Environ. Sci. Technol.* 37:1319-1324.\*

Roden, E.E. and M.M. Urrutia. 2002. Influence of biogenic Fe(II) on bacterial crystalline Fe(III) oxide reduction. *Geomicrobiol. J.* 19:209-251.\*

Roden, E.E. and R.G. Wetzel. 2002. Kinetics of microbial Fe(III) oxide reduction in freshwater wetland sediments. *Limnol. Oceanogr.* 47:198-211.\*

Barnett, M.O., P.M. Jardine, S.C. Brooks. 2002. U(VI) adsorption to heterogeneous media: application of a surface complexation model. *Environ. Sci. Technol.* 36:937-942.†

Roden, E.E., M.R. Leonardo, and F.G. Ferris. 2002. Immobilization of strontium during iron biomineralization coupled to dissimilatory hydrous ferric oxide reduction. *Geochim. Cosmochim. Acta* 66:2823-2839.\*

\* PDFs available at:

<http://bama.ua.edu/~eroden/Publications/ListofPublications.htm>

† PDF available at:

<http://bama.ua.edu/~eroden/EMSPUVIFeIIIRedProject/EMSPUVIFeIIIRedProjectPublications.htm>

#### Submitted Manuscripts

Cheng, T., M.O. Barnett, E.E. Roden, and J. Zhuang. The effects of phosphate on uranium(VI) adsorption to goethite-coated sand. *Environ. Sci. Technol.*

Jeon, B.H., S.D. Kelly, K.M. Kemner, M.O. Barnett, W.D. Burgos, B.A. Dempsey, E.E. Roden. Microbial reduction of U(VI) at the solid-water interface. *Environ. Sci. Technol.*

Roden, E.E. and T.D. Scheibe. Conceptual and numerical model of uranium(VI) reductive immobilization in fractured subsurface sediments. *Chemosphere.*

## Manuscripts in Preparation

Jeon, B.H., S.D. Kelly, K.M. Kemner, M.O. Barnett, W.D. Burgos, B.A. Dempsey, E.E. Roden. Abiotic Fe(II)-catalyzed reduction of U(VI) at the solid-water interface. *Environ. Sci Technol.*

## Presentations at Scientific Conferences

Roden, E.E. 2003. Thermodynamic versus surface area control of microbial Fe(III) oxide reduction kinetics. American Geophysical Union Annual Fall Meeting.\*

Roden, E.E. and E. Sedo. 2003. Framework for numerical simulation of bacterial Fe(III) oxide reduction in circumneutral soil and sedimentary environments. American Geophysical Union Fall Meeting.\*

Roden, E.E. and M.O. Barnett. 2002. Reductive immobilization of U(VI) in Fe(III) oxide-reducing subsurface sediments. Poster at joint SCFA-DCFA meeting, March 2002.

Barnett, M.O., E.E. Roden, P.M. Jardine, S.C. Brooks. 2001. Biogeochemical interactions of U and Fe(III) oxides in subsurface environments: modeling and experimental results. American Chemical Society National Meeting, August 2001.\*

\*PowerPoint presentations or PDFs available at:

<http://bama.ua.edu/~eroden/EMSPUVIFeIIIRedProject/EMSPUVIFeIIIRedProjectIndex.htm>

## Workshop Presentations

Roden, E.E. 2004. Surface chemical and thermodynamic controls on bacterial metal reduction in subsurface environments. U.S. Federal Interagency Workshop on Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients, April 2004. †

Roden, E.E. 2003. Coupled microbial Fe(III) oxide reduction and uranium(VI) reduction in subsurface sediments. U.S. Department of Energy, Natural and Enhanced Bioremediation Field Research Center Workshop.\*

Roden, E.E. 2003. Microbial Fe(III) oxide reduction: an obvious choice for mesoscale experiments and numerical modeling. U.S. Department of Energy, Idaho National Engineering and Environmental Laboratory Workshop on Mesoscale Subsurface Science Research.\*

Roden, E.E. 2003. Reactive transport modeling of microbial-geochemical interactions in the subsurface: coupled Fe(III) oxide/uranium(VI) reduction. U.S. Department of Energy, Basic Energy Sciences Workshop on Integrating Numerical Models of Reactive Flow and Transport into Fundamental Geoscience Research.\*

† PowerPoint presentations or PDF available at:

<http://www.iscmem.org/Proceedings.htm>

\* PowerPoint presentations or PDFs available at:

<http://bama.ua.edu/~eroden/EMSPUVIFeIIIRedProject/EMSPUVIFeIIIRedProjectPublications.htm>



## **Graduate Theses**

McIndoe, M.J. 2003. Uranium(VI) adsorption to a heterogeneous iron containing subsurface soil: The effects of solid-solution ratio and carbonate. M.S. Thesis, Auburn University.

Phillippi, J.M. 2004. Characterizing uranium adsorption and transport in the presence of carbonate. M.S. Thesis, Auburn University.

Romero, M. 2004. The effects of phosphate on uranium adsorption onto goethite-coated sands: application of a surface complexation model. M.S. Thesis, Auburn University.

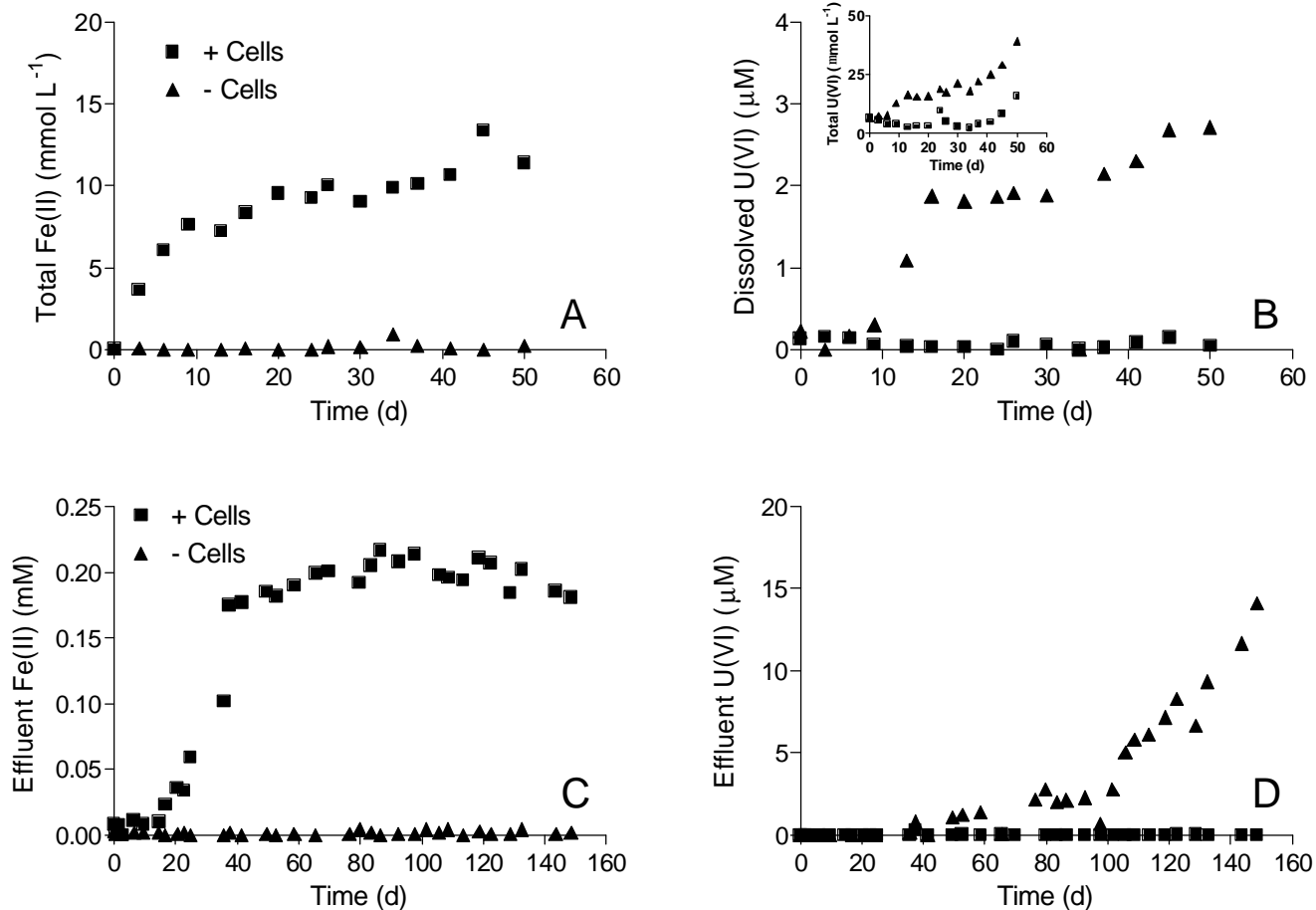


Figure 1. Coupled Fe(III) oxide/U(VI) reduction by *G. sulfurreducens* in semicontinuous culture (A, B) and column (C, D) reactors containing Atlantic Coastal Plain (Oyster, VA site) sediment (Roden, unpubl data). Inset in panel B shows total (aqueous + sorbed) U(VI) concentrations in the semicontinuous cultures. The electron donor was 10 mM acetate for all experiments. Mean hydrological residence times were 10 d and 1 d for the semicontinuous culture and column reactors, respectively. Data represent the mean of duplicate (semicontinuous culture) or triplicate (column) reactors.

## References

- Anderson, R. T., H. A. Vrionis, I. Ortiz-Bernad, C. T. Resch, P. E. Long, R. Dayvault et al. 2003. Stimulating in situ activity of *Geobacter* species to remove uranium from the groundwater of a uranium-contaminated aquifer. *Appl. Environ. Microbiol.* 69:5884-5891.
- Barnett, M. O., P. M. Jardine, and S. C. Brooks. 2002. U(VI) adsorption to heterogeneous subsurface media: application of a surface complexation model. *Environ. Sci. Technol.* 36:937-942.
- Burgos, W. D., J. J. Stone, Z. Shi, R. Kirkham, R. A. Royer, B. A. Dempsey et al. 2004. Humic materials inhibit biological uranium reduction by *Shewanella putrefaciens* CN32. *Environ. Sci. Technol.* Submitted for publication.
- Casas, I., D. Casabona, L. Duro, and J. Depablo. 1994. The influence of hematite on the sorption of uranium(VI) onto granite filling fractures. *Chem. Geol.* 113:319-326.
- Cheng, T., M. O. Barnett, and E. E. Roden. 2004a. Reactive transport of uranyl in a goethite-coated sand column: the effects of phosphate. *Environ. Sci. Technol.* Manuscript in preparation.
- Cheng, T., M. O. Barnett, E. E. Roden, and J. Zhuang. 2004b. The effects of phosphate on uranium(VI) adsorption to goethite-coated sand. *Environ. Sci. Technol.* Submitted for publication.
- DeFlaun, M. F., S. R. Oppenheimer, S. Streger, C. W. Condee, and M. Fletcher. 1999. Alterations in adhesion, transport, and membrane characteristics in an adhesion-deficient *Pseudomonas*. *Appl. Environ. Microbiol.* 65:759-765.
- Findlay, R. H., G. M. King, and L. Watling. 1989. Efficacy of phospholipid analysis in determining microbial biomass in sediments. *Appl. Environ. Microbiol.* 55:2888-2893.
- Fredrickson, J. K., J. M. Zachara, D. W. Kennedy, M. C. Duff, Y. A. Gorby, S. W. Li, and K. M. Krupka. 2000. Reduction of U(VI) in goethite ( $\alpha$ -FeOOH) suspensions by a dissimilatory metal-reducing bacterium. *Geochim. Cosmochim. Acta* 64:3085-3098.
- Gorby, Y. A., and D. R. Lovley. 1992. Enzymatic uranium precipitation. *Environ. Sci. Technol.* 26:205-207.
- Holmes, D. E., K. T. Finneran, R. A. O'Neil, and D. R. Lovley. 2002. Enrichment of members of the family *Geobacteraceae* associated with the stimulation of dissimilatory metal reduction in uranium-contaminated aquifer sediments. *Appl. Environ. Microbiol.* 68:2300-2306.
- Hsi, C.-K. D., and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* 49:1931-1941.
- Jeon, B. H., M. O. Barnett, W. D. Burgos, B. A. Dempsey, and E. E. Roden. 2004a. Abiotic Fe(II)-catalyzed reduction of U(VI) at the solid-water interface. *Environ. Sci. Technol.* In preparation.
- Jeon, B. H., S. D. Kelly, K. M. Kemner, M. O. Barnett, W. D. Burgos, B. A. Dempsey, and E. E. Roden. 2004b. Microbial reduction of U(VI) at the solid-water interface. *Environ. Sci. Technol.* Submitted for publication.
- Kohler, M., G. P. Curtis, D. B. Kent, and J. A. Davis. 1996. Experimental investigation and modeling of U(VI) transport under variable chemical conditions. *Wat. Resour. Res.* 32:3539-3551.
- Lovley, D. R. 1995. Bioremediation of organic and metal contaminants with dissimilatory metal reduction. *Journal of Industrial Microbiology* 14:85-93.
- Lovley, D. R., and E. J. P. Phillips. 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Appl. Environ. Microbiol.* 54:1472-1480.
- Lovley, D. R., and E. J. P. Phillips. 1992. Bioremediation of uranium contamination with enzymatic uranium reduction. *Environ. Sci. Technol.* 26:2228-2234.
- Lovley, D. R., E. J. P. Phillips, Y. A. Gorby, and E. R. Landa. 1991. Microbial reduction of uranium. *Nature* 350:413-416.
- Morrison, S. J., R. R. Spangler, and V. S. Tripathi. 1995. Adsorption of uranium(VI) on amorphous ferric oxyhydroxide at high concentrations of dissolved carbon (IV) and sulfur(VI). *J. Contam. Hydrol.* 17:333-346.

- Roden, E. E. 2003a. Fe(III) oxide reactivity toward biological versus chemical reduction. *Environ. Sci. Technol.* 37:1319-1324.
- Roden, E. E. 2003b. Modeling microbial-geochemical interactions in the subsurface: coupled Fe(III) oxide/uranium(VI) reduction. DOE-BES Workshop on Reactive Transport Modeling, Carmel Valley, CA June, 2003. Available at: [http://bama.ua.edu/~eroden/PSUNABIRProject/CarmelValleyWorkshopPresentation\\_Jun2003.ppt](http://bama.ua.edu/~eroden/PSUNABIRProject/CarmelValleyWorkshopPresentation_Jun2003.ppt).
- Roden, E. E. 2003c. Thermodynamic versus surface area control of microbial Fe(III) oxide reduction kinetics. *EOS Trans. AGU* 84(46), Fall Meet Suppl.:Abstract B42C-01.
- Roden, E. E. 2003d. Mesoscale experiments and numerical modeling of microbial Fe(III) oxide reduction in subsurface sediments. DOE-INEEL Workshop on Development of a Mesoscale Subsurface Geoscience Laboratory, Salt Lake City, Utah August, 2003. Available at: [http://bama.ua.edu/~eroden/EMSPUVIFeIIIRedProject/Roden\\_INEELSGLWorkshop\\_Aug2003.ppt](http://bama.ua.edu/~eroden/EMSPUVIFeIIIRedProject/Roden_INEELSGLWorkshop_Aug2003.ppt).
- Roden, E. E. 2004. Analysis of long-term bacterial versus chemical Fe(III) oxide reduction kinetics. *Geochim. Cosmochim. Acta* In press.
- Roden, E. E., and J. M. Zachara. 1996. Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth. *Environ. Sci. Technol.* 30:1618-1628.
- Roden, E. E., and M. M. Urrutia. 1999. Ferrous iron removal promotes microbial reduction of crystalline iron(III) oxides. *Environ. Sci. Technol.* 33:1847-1853.
- Roden, E. E., and T. D. Scheibe. 2003. Conceptual and numerical model of uranium(VI) reductive immobilization in fractured subsurface sediments. U.S. DOE, Natural and Accelerated Bioremediation (NABIR) Program, Field Research Center Web Site Library, Reports/Presentations by NABIR Investigators. [http://public.ornl.gov/nabirfrc/frcdoc\\_b.cfm](http://public.ornl.gov/nabirfrc/frcdoc_b.cfm).
- Roden, E. E., and E. Sedo. 2003. Framework for numerical simulation of bacterial Fe(III) oxide reduction in circumneutral soil and sedimentary environments. *EOS Trans. AGU* 84(46), Fall Meet Suppl.:Abstract B32A-0375.
- Roden, E. E., and T. D. Scheibe. 2004. Conceptual and numerical model of uranium(VI) reductive immobilization in fractured subsurface sediments. *Chemosphere* Submitted for publication.
- Roden, E. E., M. M. Urrutia, and C. J. Mann. 2000. Bacterial reductive dissolution of crystalline Fe(III) oxide in continuous-flow column reactors. *Appl. Environ. Microbiol.* 66:1062-1065.
- Snoeyenbos-West, O. L., K. P. Nevin, R. T. Anderson, and D. R. Lovley. 2000. Enrichment of *Geobacter* species in response to stimulation of Fe(III) reduction in sandy aquifer sediments. *Microb. Ecol.* 39:153-167.
- Ticknor, K. V. 1994. Uranium sorption on geological materials. *Radiochim. Acta* 64:229-236.
- Waite, T. D., J. A. Davis, T. E. Payne, G. A. Waychunas, and N. Xu. 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochim. Cosmochim. Acta* 58:5465-5478.
- Watson, D. B. 2002. U.S. DOE, Natural and Accelerated Bioremediation (NABIR) Program, Field Research Center Web Site. <http://www.esd.ornl.gov/nabirfrc/>.
- Wielinga, B., M. M. Mizuba, C. M. Hansel, and S. Fendorf. 2001. Iron promoted reduction of chromate by dissimilatory iron-reducing bacteria. *Environ. Sci. Technol.* 35:522-527.
- Wielinga, B., B. Bostick, C. M. Hansel, R. F. Rosenzweig, and S. Fendorf. 2000. Inhibition of bacterially promoted uranium reduction: ferric (hydr)oxides as competitive electron acceptors. *Environ. Sci. Technol.* 34:2190-2195.
- Zachara, J. M., C. C. Ainsworth, C. E. Cowan, and C. T. Resch. 1989. Adsorption of chromate by subsurface soil horizons. *Soil Sci. Soc. Am. J.* 53:418-428.