2006 ERSD Annual Report
DOE-BER Environmental Remediation Sciences Project # 1020166

In Situ Immobilization of Uranium in Structured Porous Media via Biomineralization at the Fracture/Matrix Interface

PI: Timothy D. Scheibe
Co-PIs: Scott C. Brooks and Eric E. Roden
Pacific Northwest National Laboratory
Oak Ridge National Laboratory
University of Wisconsin

Research Objective: Although the biogeochemical processes underlying key bioremediation technologies are increasingly well understood, field-scale heterogeneity (both physical and biogeochemical) remains a major obstacle to successful field-scale implementation. In particular, slow release of contamination from low-permeability regions (primarily by diffusive/dispersive mass transfer) can hinder the effectiveness of remediation. This research aims to evaluate strategies that target bioremediation efforts at interfaces between high- and low-permeability regions of an aquifer in order to minimize the rate of contaminant transfer into high-permeability (high-flux) zones, and thereby reduce ultimate contaminant delivery to environmental receptors.

Research Progress and Implications: Fiscal Year (FY) 2006 was the fourth and final full year of this project. Interim funding has been provided for continuation of project activities in FY 2007 until a final decision is made regarding our current ERSP LAB06-12 proposal for continued research at the field site. This project involves several elements, but the focal point is a field-scale biostimulation experiment conducted at the ERSD Field Research Center (FRC) at Oak Ridge, TN. Beginning in September 2005 and ending in August 2006 (total of eleven months), an in situ uranium bioreduction experiment was conducted at Area 2 of the FRC. During this time period, a solution of bromide (tracer) and ethanol (electron donor) was injected into the contaminated surficial aquifer using a pulsed (one hour daily) injection strategy. The ethanol stimulated activity of native nitrate-, sulfate- and metal-reducing bacteria in the subsurface and resulted in significant decreases in contaminant levels (in particular uranium and nitrate) in site groundwater. At several monitoring locations, dissolved uranium concentrations decreased below drinking water limits. As a result, contaminant fluxes to Bear Creek, downgradient of the research site, were also decreased. Sediment cores were collected upon termination of electron donor delivery and are currently being analyzed to identify changes in uranium concentration and valence state with particular focus on the interfaces between high- and low- permeability layers of the aquifer.

In the following sections, we briefly summarize key activities and findings for each past year of the project. We then provide additional results from the past year, with emphasis on the field biostimulation experiment. Additional details of all activities conducted at the site are available in a series of ten Field Work Plans developed by this project, submitted to the FRC Manager, and reviewed by the Field Research Review Panel

(FRRP). These Field Work Plans are available by request from the PI (e-mail tim.scheibe@pnl.gov).

Background Information: Geologic materials that comprise the unconfined aquifer at Area 2 of the FRC can be broadly lumped into three general classes:

1. Underlying bedrock of the Nolichucky Shale (shale with interbedded limestone)
2. Undisturbed shale saprolite (highly weathered bedrock that has unconsolidated character but retains much of the bedding and fracture structure of the parent rock)
3. Disturbed fill within a zone from which contaminated soils were historically excavated and replaced by unspecified materials (probably primarily native saprolite excavated from an uncontaminated area within Bear Creek Valley).

Examination of borehole cores from Area 2 and results of hydraulic tests (pumping and tracer tests) indicates that there exists a highly conductive gravelly layer at the bottom of the disturbed fill zone. Cores taken from existing wells and boreholes at Area 2, as well as surface seismic surveys conducted by the project team, indicate that the interface between disturbed fill materials and undisturbed saprolite is approximately 19 feet below ground surface. The highest uranium concentrations are found in the fill and saprolite immediately above and below the gravel.

FY2003 Activities and Key Findings: *Initial coring, site characterization, and well installation (Field Work Plan #1).* Two wells were installed and core was collected. Analysis of the sediment core identified gravel/saprolite interfaces and determined sediment concentrations and redox speciation of iron and uranium. A total of 10 cores were characterized spanning a depth interval of 10-20 ft. *Installation of deep (saprolite) wells and core collection (Field Work Plan #2).* Nine wells were installed, screened from 23-26 feet below ground surface in the intact saprolite. Water level monitors were installed and groundwater chemistry monitoring initiated. *Large intact column experiments.* Three large intact saprolite cores were collected in the FRC background area (uncontaminated) and set up in the laboratory. The cores were loaded with dissolved uranium under partial vacuum (to force uranium into small pores), then subjected to three alternative experimental treatments. *Biogeochemical slurry experiments.* Sediment from FRC cores was used to establish batch slurry experiments with and without ethanol amendment. The results of this experiment were used to assemble and parameterize a batch reaction model of terminal electron-accepting processes (TEAP) and other geochemical processes in ethanol-stimulated sediments.

FY2004 Activities and Key Findings: *Conducted pumping tests in deep saprolite zone (Field Work Plan #3).* Although hydraulic connection exists between the saprolite wells, hydraulic conductivity (and therefore expected groundwater flow velocity) was found to be extremely low. Based on this finding, it was determined that it would not be feasible to conduct the biostimulation experiment in the intact saprolite and focus was subsequently shifted to characterization of the gravel and disturbed saprolite (fill) zones. *Exploratory well installation in disturbed saprolite zone (Field Work Plan #4).* Six wells were installed, screened in the fill zone. Sediment core was collected and sent to the laboratory for analysis. Two cores were analyzed for Fe and U concentration, with a focus on fine-scale (2-5 cm intervals) gradients at the gravel/saprolite interfaces. One of these cores was analyzed for pH and size-fractionated Fe and U concentration and speciation Three of these wells were placed to create the injection well gallery. *Hydraulic characterization of fill zone (Field Work Plan #5).* Pumping episodes at GW-835 were monitored by in-well transducers and the results used to estimate hydraulic properties of the fill. The gravel zone was determined to be highly conductive and suitable for ethanol injection. *Tracer test (Field Work Plan #6).* A week-long field-scale tracer test was conducted using bromide tracer injected at well FW215. *Small intact and repacked column experiments.* To supplement results from the large intact column experiments, smaller intact and repacked saprolite column studies were undertaken to quantify uranium transport in site sediments.

<u>FY2005 Activities and Key Findings:</u> *Tracer test interpretation.* Multiple numerical models of the field site were developed and used to simulate the tracer experimental results. Based on the tracer data, the hydraulic properties of the models were refined and rates of mass transfer between the gravel and saprolite were estimated. *Design of the field-scale biostimulation experiment.* The numerical models were used to evaluate several alternative ethanol delivery strategies, and a one-hour daily pulsed injection was selected based on the results. The multiple TEAP model developed based on results of laboratory slurry experiments was implemented in the field-scale model to simulate reactive transport. Predictions of system response were made for the selected ethanol delivery strategy for the first week of biostimulation, with the expectation that the strategy could then be modified if necessary based on preliminary field observations. The proposed experimental plan was reviewed by the FRRP and revised in response to panel suggestions. *Installation of multi-level samplers (MLS) and geophysical wells (Field Work Plan #7).* Five MLS wells were installed to provide vertical resolution of transport observations. Five geophysical wells were installed around the perimeter of the site for use in cross-well tomographic studies.

<u>FY 2006 Activities and Key Findings:</u> *Biostimulation experiment:* The field-scale biostimulation experiment was initiated at the end of FY 2005 (late September) and continued through most of FY 2006. Details of the experimental plan are provided in Field Work Plan #8. Selected results of the field experiment are presented below. *Preliminary coring in the biostimulated zone (Field Work Plan #9).* A single core was collected several months into the biostimulation experiment for sediment analyses. A multi-level sampling well was installed in the borehole. *Post-stimulation coring (Field Work Plan #10).* Three additional cores were collected upon termination of ethanol delivery and shipped to the laboratory for analysis. Two multi-level sampling wells and a two-level well were installed in the boreholes.

<u>Biostimulation Results:</u> Ethanol was injected into three wells and moved under natural gradient flow toward Bear Creek to the south. Groundwater samples (duplicate filtered, acidified and non-acidified) were collected regularly from several monitoring locations including the five MLS wells. Laboratory analyses (primarily IC, ICP, and GC) were performed on groundwater samples to determine concentrations of key groundwater constituents including ethanol, acetate, bromide, nitrate, sulfate, iron, manganese, and uranium. At selected times and locations, larger volumes of groundwater were collected

and filtered to obtain microbial biomass samples. Filters were bagged and frozen for preservation prior to microbial analysis. Uranium concentrations in the groundwater were significantly lowered following ethanol injection. At some locations, concentrations decreased by two orders of magnitude or more, to below the drinking water standard. Large-scale flow patterns, influenced both by physical heterogeneity and transient water levels (changes in natural gradient direction), caused a high degree of spatial variability in system response. Comparisions of field observations with premodel predictions for the first week of the experiment were favorable. However, the system remained in a reducing state under the pulsed injection strategy for nearly the entire 11-month period, contrasting with model predictions that indicated loss of sulfate and uranium reduction after the first two weeks. During a period of high rainfall and recharge in November 2005, oxygenated recharge water led to increases in sulfate and uranium levels, in some cases higher than background (indicating possible re-oxidation of sulfide minerals), but reducing conditions were restored subsequently without modification of the injection strategy.

Planned Activities: In FY 2007, we are monitoring site conditions as the system rebounds from biostimulation and returns to the background state. Sediment cores collected during and after the biostimulation are being analyzed to determine the amount and location of uranium minerals precipitated and other changes in sediment-associated metals. Additional numerical modeling studies are being undertaken to provide quantitative interpretations of the experimental observations and determine the causes of discrepancies between the premodel and field data. We have submitted a proposal to the LAB06-12 call that, if funded, will extend this research to evaluate the long-term stability of immobilized uranium minerals (both bioreduced and inorganic phosphate mineral compounds).

Information Access: (Project Publications and Presentations listed by Fiscal Year)

2003:

Roden, E. E. and T. D. Scheibe, "Multiple Pore Region Model of Uranium(VI) Reductive Immobilization in Structured Subsurface Media," *EOS Trans. AGU*, 83(47), Fall Meeting Suppl., Abstract B12C-12, 2002.

2004:

Scheibe, T. D., Y. Fang, E. E. Roden, S. C. Brooks, Y. Chien, and C. J. Murray, "Microbial Reduction of Fe(III) and U(VI) in Aquifers: Simulations Exploring Coupled Effects of Heterogeneity and Fe(II) Sorption", *EOS Trans. AGU*, 85(17), Jt. Assem. Suppl., Abstract H24A-05, 2004.

Kim, Y., W. Kamolpornwijit, S. C. Brooks, T. D. Scheibe, and E. E. Roden, "Rate and extent of uranium(VI) sorption onto weathered saprolite", *EOS Trans. AGU*, 85(17), Jt. Assem. Suppl., Abstract H41E-03, 2004

2005:

Roden, E. E. and T. D. Scheibe, “Conceptual and numerical model of uranium(VI) reductive immobilization in fractured subsurface sediments,” *Chemosphere* 59(5): 617-628, 2005.

Scheibe, T. D., Y. Fang, E. Roden, S. C. Brooks, S. S. Hubbard, J. Chen, Y.-J. Chien, C. J. Murray, and Y. Xie, "Transport and biogeochemical reaction of metals in a physically and chemically heterogeneous aquifer," Geological Society of America Abstracts with Programs, 36(5):325, Nov. 2004.

Scheibe, T. D., S. C. Brooks and E. E. Roden, "Numerical Simulation of Field-Scale Transport and Biogeochemical Reactions Using a Particle-Based Method," *EOS Trans. AGU*, 85(47), Fall Meet. Suppl., Abstract H21E-1068, Dec. 2004.

Spane, F. A., T. D. Scheibe, S. C. Brooks, and W. Kamolpornwijit, "Analysis of a Micro-Pumping Test Conducted Within a Saprolitic Aquifer," EOS Trans. AGU, 85(47), Fall Meet. Suppl., Abstract H21E-1066, Dec. 2004.

Scheibe, T. D.,S. C. Brooks, W. Kamopornwijit, Y. Fang, and E. E. Roden, "Identification of Physical and Chemical Mass Transfer Processes by a Tracer Flush Experiment", *EOS Trans. AGU*, 86(18), Jt. Assem. Suppl., Abstract H51A-02, May 2005.

Kamopornwijit, W., Y. Kim, S. C. Brooks, T. D. Scheibe, and M. A. Mayes, "Estimation of groundwater flow distribution in structured media from non-reactive tracer results under unsaturated condition", *EOS Trans. AGU*, 86(18), Jt. Assem. Suppl., Abstract H51A-05, May 2005.

Kim, Y., S. C. Brooks, W. Kamopornwijit, T. D. Scheibe, and E. E. Roden, "Immobilization of uranium (VI) in structured saprolite with microbial U(VI) reduction", *EOS Trans. AGU*, 86(18), Jt. Assem. Suppl., Abstract H51A-06, May 2005.

Scheibe T. D., Y. Fang, E. E. Roden, S. C. Brooks, and A. M. Tartakovsky. 2005. "Simulation of metal biogeochemistry in multiple-porosity groundwater flow systems." Presented by Timothy D. Scheibe (Invited Speaker) at Joint International Symposia for Subsurface Microbiology (ISSM 2005) and Environmental Biogeochemistry (ISEB XVII), Jackson, WY on August 15, 2005.

2006:

Scheibe, T. D., Y. Fang, C. J. Murray, E. E. Roden, J. Chen, Y.-J. Chien, S. C. Brooks, and S. S. Hubbard. "Transport and biogeochemical reaction of metals in a physically and chemically heterogeneous aquifer," *Geosphere* 2(4): 220-235, 2006.

Fang, Y., T. Scheibe, E. Roden, W. Kamolpornwijit, and S. Brooks,"3D field-scale reactive transport modeling of in situ immobilization of uranium in structured porous media via biostimulation," in *Proceedings of the XVI International Conference on Computational Methods in Water Resources*, edited by Philip J. Binning, Peter K. Engesgaard, Helge K. Dahle, George F. Pinder and William G. Gray. Copenhagen, Denmark, June, 2006.

Hubbard, S., J. Chen, Y. Fang, K. Williams, S. Mukhopadhyay, E. Sonnenthal, K. McFarlane, N. Linde, and T. Scheibe, "Improved parameterization of hydrological models and reduction of geophysical monitoring data ambiguity through joint use of geophysical and numerical modeling methods," in *Proceedings of the XVI International Conference on Computational Methods in Water Resources*, edited by Philip J. Binning, Peter K. Engesgaard, Helge K. Dahle, George F. Pinder and William G. Gray. Copenhagen, Denmark, June, 2006.

Kamolpornwijit, W., S. C. Brooks, Y.-J. Kim, and T. D. Scheibe, "A Novel Approach to Estimate the Distribution of Reducible Iron Oxides Within Different Pore Domains of

Structured Media," submitted to *Applied Geochemistry*, July 2006, accepted conditional to revision.

Roden, E. E., "TEAPREV: A numerical tool for assessing rates of terminal electron-accepting processes in a representative elementary volume of subsurface sediment," Geological Society of America *Abstracts with Programs*, 37(7): 535, Oct. 2005.

Fang, Y., T. D. Scheibe, E. E. Roden, and S. C. Brooks, "Field-scasle reactive transport simulations of multiple terminal electron accepting processes," Geological Society of America *Abstracts with Programs*, 37(7): 535, Oct. 2005.

Kamolpornwijit, W., S. C. Brooks, Y. Kim, and T. D. Scheibe, "A Novel Approach to Estimate the Distribution of Reducible Iron Within Different Pore Fractions of Structured Media," EOS Trans. AGU, 86(52), Fall Meet. Suppl., Abstract B24B-07, Dec. 2005.

Scheibe, T. D., S. C. Brooks, E. E. Roden, Y. Fang, and W. Kamopornwijit, "In Situ Bioremediation of Uranium in a Heterogeneous Aquifer: Field-Scale Monitoring and Numerical Simulation", EOS Trans. AGU, 87(36), Jt. Assem. Suppl., Abstract H42B-03, Dec. 2005.

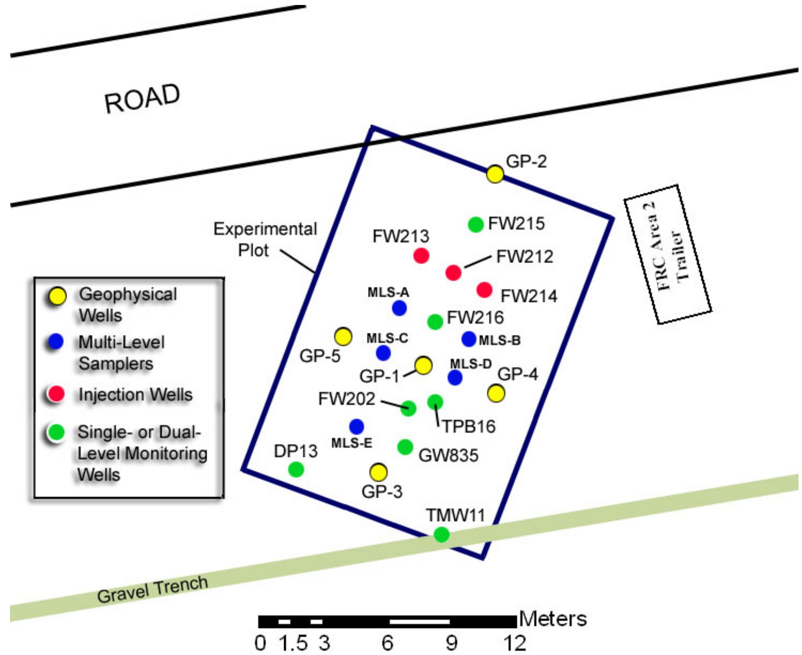

Figure 1. Plan view map of the experimental field site.

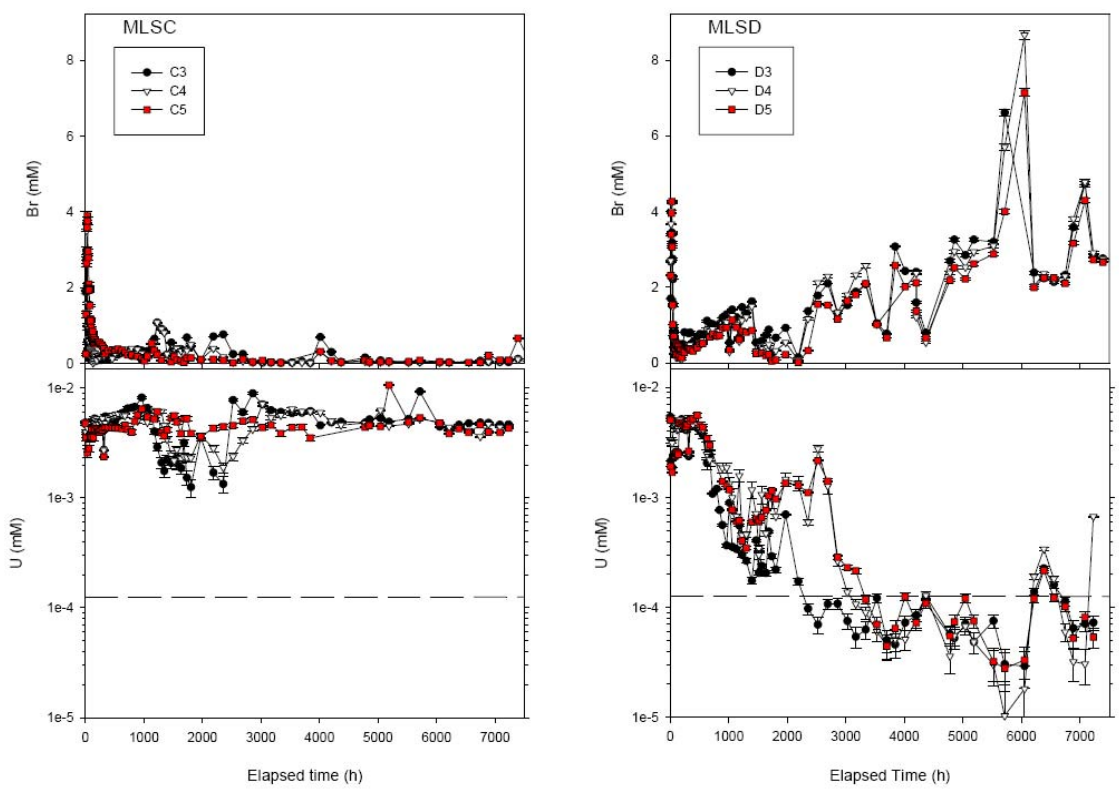

Figure 2 Bromide (upper panel) and uranium (lower panel) concentrations at multi-level samplers MLSC (left) and MLSD (right) over the entire biostimulation period (eleven months). The dashed line indicates the drinking water standard for dissolved uranium.

Figure 3. Photograph of the field site, looking toward the west. Well stickups in the center foreground (white PVC with yellow cables) are two of the three ethanol injection wells; the third is hidden behind the table. Groundwater flow is from right to left. Blue tubing connects multi-level samplers and other wells to a central groundwater sampling station under the tent. The white tank under the tent is used for mixing the daily injectate solution; the larger green tank to the right of the tent is for general water storage. A system of peristaltic pumps, timers, a mixer, and flowmeters (on and under the table in the foreground) was used to automate the process of daily injection of a one-hour pulse of ethanol and bromide solution. Yellow cables are attached to in-well pressure transducers with dataloggers and are used to upload high-frequency water level data.