

Project #1024648

Title: Reaction-Based Transport Modeling of Iron Reduction and Uranium Immobilization at Area 2 of the NABIR Field Research Center

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Results To Date: This research project (started Fall 2004) was funded by a grant to The Pennsylvania State University, University of Central Florida, and The University of Alabama in the Integrative Studies Element of the NABIR Program (DE-FG04-ER63914/63915/63196). Dr. Eric Roden, formerly at The University of Alabama, is now at the University of Wisconsin - Madison. Our project focuses on the development of a mechanistic understanding and quantitative models of coupled Fe(III)/U(VI) reduction in FRC Area 2 sediments. This work builds on our previous studies of microbial Fe(III) and U(VI) reduction, and is directly aligned with the Scheibe et al. NABIR FRC Field Project at Area 2.

Long-term Area 2 Sediment Column Experiments

A series of columns (6 total) packed with sediments collected from Area 2 at the Field Research Center (FRC) have been in operation for nearly one year. No attempt was made to sterilize the sediment and experiments were designed to stimulate the native microbial community by ethanol addition (as conducted in field studies). An artificial groundwater designed to match the solution chemistry at Area 2 is continuously pumped through the columns at a single, constant flow rate equivalent to 0.05 pore volumes/day. This low flow rate was designed to simulate flow conditions expected in the micropore domain of the intact saprolite. The primary experimental variable is the ethanol concentration in the groundwater feed solution and is set at 0, 1.0 and 10 mM ethanol (each in duplicate). Nitrate, iron(III), uranium(VI), and sulfate all appear to be reduced within the column regardless of the supplied concentration of ethanol (i.e., all columns appear to have similar biologic activity). The invariance with respect to supplied ethanol could be due to sufficient background organic matter in the sediments and/or to the diffusion of H₂(g) from the anaerobic chamber atmosphere into the columns. The chamber atmosphere has since been changed from 95:5% N₂:H₂ to 100% N₂ to differentiate these possible effects. These column experiments will continue until at least the end of 2006. At the conclusion of these experiments, the columns will be deconstructed and the sediments subjected to a variety of detailed characterizations of both the microbial community, the mineralogy, and the long-term stability of the immobilized uranium.

Sorption and Bioreduction of Solid-Associated U(VI)

The sorption of U(VI) to a series of specimen minerals found in FRC sediments has been measured and modeled. Adsorption isotherm experiments were conducted with U(VI) and amorphous aluminum hydroxide, crystalline gibbsite, activated alumina and illite clay, in the presence and absence of humic substances. The molecular coordination environment of sorbed U(VI) was evaluated by extend X-ray absorption fine structure (EXAFS), in collaboration with Ken Kemner and Shelly Kelly (ANL), and by cryo laser-induced fluorescence spectroscopy (CLIFS), in collaboration with Zheming Wang and John

Zachara (PNNL). These spectroscopic evaluations revealed that solid-phase U(VI) was located in different molecular environments based on the mineral sorbent phase. A detailed comparison of the results from these two spectroscopic techniques will be the focus of an upcoming manuscript. We are currently running a series of experiments on the bioreducibility/bioavailability (using *Geobacter sulfurreducens*) of these U(VI)-loaded minerals. Those results will be the focus of another upcoming manuscript.

Iron Oxide Surface Chemistry

The reactions between sorbed ferrous iron(II) and a variety of oxidants have been studied to better understand the reaction mechanism(s) involved in these important modes of “indirect” contaminant reduction. We have studied the oxidation of sorbed Fe(II) by oxygen, nitrite and uranium(VI). The results obtained with trace amounts of oxygen have been published, and two separate manuscripts are in preparation for the nitrite and uranium(VI) results.

Kinetics of U(VI) Reduction and U(IV) Oxidation

A series of experiments were designed to vary the rate of U(VI) bioreduction to then characterize the reactivity of the different U(IV) solids produced (presumably biogenic uraninite). Experiments were conducted with variable concentrations of *Shewanella putrefaciens* CN32 in a 30 mM NaHCO₃ buffer with 1 mM U(VI) and 5 mM lactate. U(VI) was completely reduced at “slow”, “medium” and “fast” rates (varied over 1 order of magnitude). The reduced U(IV) solids were subjected to re-oxidation by oxygen, iron(III), nitrite, nitrite plus Fe(II), and *Thiobacillus denitrificans* (coupled to nitrate reduction). For all oxidants, U(IV) solids that were produced at a “fast” rate were most rapidly re-oxidized. The reduced U(IV) solids were examined by EXAFS, in collaboration with Ken Kemner and Shelly Kelly (ANL), and revealed that molecular structure and particle size of the solids were directly related to the bioreduction rate. These samples will be analyzed by transmission electron microscopy (TEM), in collaboration with Alice Dohnalkova and John Zachara (PNNL), to further characterize their physical associations with the bacteria. The field-scale implication of these findings is that electron donor addition that promotes the “slow” reduction of U(VI) may also produce U(IV) solids that are more stable with respect to re-oxidation. A manuscript summarizing these findings is in preparation and will be submitted for publication in the next few months.

Reactive Transport Modeling

We have focused on a systematic modeling approach in search of scale-independent rate formulations for biological reduction of hematite in iron-rich coastal sands. A reaction network of five reactions was proposed to describe these processes under laboratory-controlled batch and column experiments which were conducted using sediments taken from a field site. The key reaction in the experiments is the direct bioreduction of hematite. Four possible rate formulations were proposed to describe this key reaction. Two kinds of simulations were conducted to verify the rate formulations and reaction parameters: the first one is batch modeling and the second one is column modeling. Simulation results indicated that while all rate formulations can adequately model batch experiments, only the formulation based on dual Monod kinetics with inhibition of ferrous iron and the effect of DMRB is “universal?”. Furthermore, only this rate formulation can be upscaled to column experiments. Iterative modeling between batch and column experiments revealed that the equilibrium assumptions for surface hydration of hematite and adsorption of biogenic ferrous irons onto hematite may have to be revoked and substituted with kinetic rate formulations.

A reaction-based groundwater contaminant transport model in three dimensions was

developed. A system of M species transport equations were transformed into NE mass action equations, NKI kinetic-variable transport equations, and NC component transport equations (where $NE+NKI+NC = M$). A variety of numerical methods are investigated for solving the coupled transport and reaction equations. These numerical options and coupling strategies are necessary to deal with different types of problems for different application circumstances. Two validation examples involving simulations of uranium transport in soil columns were presented to evaluate the ability of the model to simulate reactive transport with reaction networks involving both kinetic and equilibrium reactions. A three-dimensional example was presented to demonstrate the model application to a field-scale problem involving reactive transport with a complex reaction network.

Future modeling efforts will continue to focus on the developments and numerical simulations of reaction networks and the formulation of reaction rates that can better and further elucidate the mechanisms of $Fe(III)$ oxide reduction, biosynthesis, abiotic geochemical processes, and coupled $Fe(III)$ oxide/ $U(VI)$ reduction in sediments at the NABIR field research center.

Deliverables: Listed below are only our most recent publications from the last year of effort divided into those In Press (or already published), In Review and In preparation.

In Press Jeon, B.H., B.A. Dempsey, W.D. Burgos, M.O. Barnett and E.E. Roden. 2005. Chemical reduction of $U(VI)$ at the solid-water interface using natural and synthetic iron(III) oxides. *Environmental Science & Technology*. 39:5642-5649.

Tuntoolavest, M., and W.D. Burgos. 2005. Anaerobic Phenol Oxidation by *Geobacter metallireducens* Using Various Electron Acceptors. *Environmental Engineering Science*. 22:421-426.

Fang, Y. L., S. B. Yabusaki, and G. T. Yeh, 2005. A general simulator for reaction-based biogeochemical processes. *Computers and Geosciences* 32:64-72.

Park, B., and B.A. Dempsey. 2005. Heterogeneous Oxidation of $Fe(II)$ on Ferric Oxide at Neutral pH and a Low Partial Pressure of O_2 . *Environmental Science & Technology*. 39:6494-6500.

Stone J.J., W.D. Burgos, R.A. Royer and B.A. Dempsey. 2006. Impact of Zinc on Biological $Fe(III)$ and NO_3^- Reduction by *Shewanella putrefaciens* CN32. *Environmental Engineering Science*.

Stone J.J., W.D. Burgos, R.A. Royer and B.A. Dempsey. 2006. Zinc and Manganese Inhibition of Biological Hematite Reduction. *Environmental Engineering Science*.

Burgos, W.D, J.M. Senko, B.A. Dempsey, E.E. Roden, J.J. Stone, K.M. Kemner and S.D. Kelly. 2006. Soil Humic Acid Decreases Biological Uranium(VI) Reduction by *Shewanella putrefaciens* CN32. *Environmental Engineering Science*.

Jang, J.H., B.A. Dempsey and W.D. Burgos. 2006. Solubility of Schoepite: Comparison and Selection of Complexation Constants for $U(VI)$. *Water Research*.

Suk, H. and G.T. Yeh, 2006. Three-dimensional three-phase flow simulations using the Lagrangian-Eulerian approach with adaptively zooming and peak/valley capturing scheme (LEZOOMPC). *ASCE Journal of Hydrologic Engineering*.

Chen, C.W., G.T. Yeh, W.D. Burgos and M.L. Minyard, 2006. A Systematic Approach to Uncovering Scale-Independent Rate Formulations for Bioreduction of Hematite in

Sediments at a Field Site. Proc. XVI International Conference on Computational Methods in Water Resources (Binning, P., Engesgaard, P., Dahle, H., Gray, W.G., and Pinder, G., eds). CD. Copenhagen, Denmark, June 19-22, 2006.

In Review Tan, H., O. Ezekoye, J. van der Schalie, M. Horn, A. Lakhtakia, J. Xu and W. Burgos. 2006. Biological Reduction of Nano-Engineered Iron(III) Oxide Sculptured Thin Films. Environmental Science & Technology. Re-submitted with minor revisions.

Zhang, F., G.T. Yeh, J.C. Parker, S.C. Brooks, M.N., Pace, Y.J. Kim, and P.M. Jardine, 2006. A reaction-based paradigm to model three-dimensional reactive chemical transport in groundwater. Journal of Contaminant Hydrology.

Suk, H., and G.T. Yeh. 2006. Multiphase flow modeling with general boundary conditions and phase configuration changes using fractional flow approaches. ASCE Journal of Hydrologic Engineering.

Suk, H., and G.T. Yeh. 2006. Particle tracking algorithm for the Lagrangian finite element method under transient conditions in multi-dimensions. International J. Numerical Methods in Engineering.

Roden, E. E. 2005. Geochemical and microbiological controls on dissimilatory iron reduction. Geoscience.

In Preparation Minyard, M.L., and W.D. Burgos. Hydrologic flow controls biologic iron(III) reduction in natural sediments. Environmental Science & Technology.

Burgos, W.D., M.L. Minyard, B.A. Dempsey and G.T. Yeh. Reaction-Based Reactive Transport Modeling of Biological Iron(III) Reduction. Geochimica Cosmochimica Acta

Stone, J.J., W.D. Burgos, R.A. Royer and B.A. Dempsey. Impact of Natural Organic Matter on Zinc Inhibition of Hematite Bioreduction. Environmental Engineering Science.

Senko, J.M., W.D. Burgos, B.A. Dempsey, S.D. Kelly, K.M. Kemner, A. Dohnalkova and J.M. Zachara. Kinetics of U(VI) reduction control kinetics of U(IV) re-oxidation. Environmental Science & Technology.

Dempsey, B.A., R. Kirkham, and W.D. Burgos. Complexation of Uranyl with Humic Acid as a Function of Pco₂ and pH. Water Research.

Jang, J-H., B.A. Dempsey, W.D. Burgos. Abiotic Reactions of U(VI) with Fe(II) in the Presence of Hydrous Ferric Oxide (HFO) and Hematite plus Natural Organic Matter (NOM): Sorption, Reduction, and Transformation. Water Research.

Jang, J-H., B.A. Dempsey, W.D. Burgos. Sorption and Solubility of U(VI) in the Presence of Hydrous Ferric Oxide and Hematite . Environmental Science & Technology.

Jang, J-H., B.A. Dempsey, W.D. Burgos. Similarity of Surface Reactivities of Hydrous Ferric Oxide and Hematite: Solubility, Sorption, Oxidation-Reduction Reactions. Environmental Science & Technology.