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Title: Reaction-Based Reactive Transport Modeling of Iron Reduction and Uranium Immobilization at Area 2 of the NABIR Field Research Center – Subproject to Co-PI George Yeh, UCF

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Executive Summary

A. Overview

The research described in this report was conducted in conjunction with a project entitled “Reaction-Based Reactive Transport Modeling of Iron Reduction and Uranium Immobilization at Area 2 of the NABIR Field Research Center”, which was funded through the Integrative Studies Element of the former NABIR Program (now the Environmental Remediation Sciences Program) within the Office of Biological and Environmental Research. Dr. Will Burgos (The Pennsylvania State University) was the overall PI/PD for the project, which included Brian Dempsey (Penn State); Eric Roden (formerly at The University of Alabama, now at the University of Wisconsin); and Gour-Tsyh (George) Yeh (Central Florida University) as separately-funded co-PIs. The project focused on development of a mechanistic understanding and quantitative models of coupled Fe(III)/U(VI) reduction in FRC Area 2 sediments. The work builds on our previous studies of microbial Fe(III) and U(VI) reduction.

Area 2 is a shallow pathway for migration of contaminated groundwater to seeps in the upper reach of Bear Creek at ORNL, mainly through a ca. 1 m thick layer of gravel located 4-5 m below the ground surface. The gravel layer is sandwiched between an overlying layer of disturbed fill material, and 2-3 m of undisturbed shale saprolite derived from the underlying Nolichucky Shale bedrock. The fill was put in place when contaminated soils were excavated and replaced by native saprolite from an uncontaminated area within Bear Creek Valley, and the gravel layer was presumably installed prior to addition of the fill in order to provide a stable surface for the operation of heavy machinery. The undisturbed saprolite is highly weathered bedrock that has unconsolidated character but retains much of the bedding and fracture structure of the parent rock (shale with interbedded limestone). Hydrological tracer studies that have been conducted indicate that the gravel layer receives input of uranium from both upstream sources and from diffusive mass transfer out of highly contaminated fill and saprolite materials above and below the gravel layer. This research sought to examine biogeochemical processes likely to take place in the less conductive materials above and below the gravel during the in situ ethanol biostimulation experiment conducted at Area 2 during 2005-2006. The in situ experiment in turn examined the hypothesis that injection of electron donor into this layer would induce formation of a redox barrier in the less conductive materials, resulting in decreased mass transfer of uranium out these materials and attendant declines in groundwater U(VI) concentration. 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 report summarizes research activities conducted at The University of Central Florida (2004-2007), the development of biogeochemical and reactive transport models and the conduction of numerical simulations at laboratory, column, and field scales.

B. Development of Biogeochemical and Reactive Transport Models

We have revised, validated, and documented a series of diagonalized reaction-based biogeochemistry codes (Fang, et al., 2006; Yeh et al., 2007a, b) and reactive transport computer models (Yeh et al., 2007c, d). We have also modified a subsurface reactive transport model to make it more robust and efficient (Zhang et al, 2007a). As a bonus, we have demonstrated that this diagonalization approach is applicable to modeling water quality in surface water such as

river/stream network as well (Zhang et al., 2007b). Although this is not the focus of this project, it would make the application of the model to the FRC site for future simulations of coupled groundwater and surface water reactive transport feasible.

A new concept of defining reaction rates of fast reactions was proposed, which make the modeling of mixed fast/equilibrium and slow/kinetic reactions consistent. The argument of what is the rate for an equilibrium reaction is very controversial. It has been argued that the rate of an equilibrium reaction “can be mathematically abstracted as infinity” for the convenience of decoupling equilibrium reactions from kinetic reactions (Fang et al., 2003). It has also been argued that the rate of an equilibrium reaction is indefinite (Lichtner, 1996). This controversy should not have been aroused at all since, by definition, an equilibrium reaction should not have been associated with a rate per se. We can associate a rate to an equilibrium reaction only if we treat it as a fast kinetic reaction. When we treat an equilibrium reaction as a fast kinetic reaction, then “the rate of an equilibrium reaction is that rate which is ‘necessary’ to assure that the corresponding thermodynamic equation remains fulfilled.” With this definition of equilibrium reactions, we can make posteriori calculation of the rates of equilibrium reactions after all species concentrations are solved (Yeh et al., 2008). Furthermore, with this definition, all equilibrium reactions must be linearly independent so the system of governing equations are exactly determined.

C. Modeling of Biogeochemistry and Reactive Transport at Laboratory and Field Scales

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 (Chen 2005; Chen et al., 2007). 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.

We have also conducted simulations of column experiments using materials from the FRC site with the revised HYDROGEOCHEM 5.0 (Yeh et al., 2007b). Two validation examples involving simulations of uranium transport in soil columns were performed to evaluate the ability of the model to simulate reactive transport with reaction networks involving both kinetically and equilibrium-controlled reactions (Zhang et al., 2007a). A hypothetical three-dimensional example was presented to demonstrate the model application to a field-scale problem involving reactive transport with a complex reaction network.

D. References

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Yeh, G. T., Y. Li, P. M. Jardine, W. D. Burger, Y. L. Fang, M. H. Li, and M. D. Siegel, 2007c. HYDROGEOCHEM 4.5: A Coupled Model of Fluid Flow, Thermal Transport, and HYDROGEOCHEMical Transport through Saturated Unsaturated Media Version 4.1. Dept. of Civil and Environ. Engineering., University of Central Florida, 4000 Central Florid Blvd, Orlando, FL 32816

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Zhang, F., G. T. Yeh, J. C. Parker, S. C. Brooks, M. N., Pace, Y. J. Kim, and P. M. Jardine, 2007a. A reaction-based paradigm to model three-dimensional reactive chemical transport in groundwater. *J. Contaminant Hydrology*. Volume 93, 10-32.

Zhang F., G. T. Yeh, J. C. Parker, and P. M. Jardine, 2007b. A reaction-based river/stream water quality model: Model development and numerical schemes. *Journal of Hydrology* (in press)

Research Products

A. Referred publications

Fang, Y. L., S. B. Yabusaki, and G. T. Yeh, 2006. A general simulator for reaction-based biogeochemical processes. *Computers and Geosciences* 32:64-72.

Suk, H. and G. T. Yeh, 2007. 3D, three-phase flow simulations using the Lagrangian-Eulerian approach with adaptively zooming and peak/valley capturing scheme (LEZOOMPC). *Hydrologic Engineering*, ASCE, 12(1): 14-32.

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Zhang, F., L. Jiang, and G. T. Yeh. 2008. An adaptive local grid refinement and peak/valley capture algorithm to solve transport problems with moving sharp-fronts *J Transport in Porous Media*. 72:53–69, DOI 10.1007/s11242-007-9135-2.

B. Publications in press

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C. Publications submitted and in preparation (Yeh group only)

Yeh, G. T., Y. L. Fang, F. Zhang, J. T. Sun, Y. Li, M. H. Li, and M. D. Siegel, 2008. Numerical Modeling of Coupled Fluid Flow and Thermal and Reactive Biogeochemical Transport in Porous and Fractured Media. (Submitted to Computers and Geosciences)

Chen, C. W., G. T. Yeh, and W. D. Burgos, 2008. A Scale-independent Rate Formulation for Bioreduction of Hematite in Sediments at a Field Site. Environmental Sciences and Technology.

Suk, H. and G. T. Yeh, 2008. Particle tracking algorithm for the Lagrangian finite element method under transient conditions in multi-dimensions. Computer and Geosciences.

D. Proceeding Papers (Yeh group only)

Chen, C. W., G. T. Yeh, W. D. Burgos, and M. L. Minard, 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.

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Yeh, G. T., M. H. Li, and Y. Li, 2007. Numerical Modeling of Reactive Chemical Transport under Non-isothermal Conditions in Porous and Fractured Media. World Environment and Water Resources Congress 2007, ASCE. Tampa, Florida, May 15-19, 2007.

F. Workshop presentations (Yeh group only)

Yeh, G. T., J. T. Sun, P. M. Jardine, W. D. Burgos, Y. L. Fang, M. H. Li, and M. D. Sigel. HYDROGEOCHEM 5.0 A Three-Dimensional Model of Coupled Fluid Flows, Thermal Transport, and HYDROGEOCHEMical Transport under Variably Saturated Conditions: Version 5.0. FRC Workshop, Oak Ridge, TN., October 18-20 (Oral Presentation).

Yeh, G. T., Y. L. Fang, J. T. Sun, F. Zhang, and C. W. Chen, 2008. Numerical Modeling of Coupled Fluid Flow and Thermal and Reactive Biogeochemical Transport in Porous and Fractured Media. International Workshop "Modeling Reactive Transport in Porous Media," Strasbourg, France, January 21-24, 2008.