FINAL PROJECT SUMMARY REPORT

Project title: Development of Modeling Methods and Tools for Predicting Coupled Reactive Transport Processes in Porous Media at Multiple Scales
Project ID 0011966
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Investigators: T. Prabhakar Clement and Mark O. Barnett (PD/PI and co-PI, Auburn University), Chunmiao Zheng (co-PI, University of Alabama), and Norman L. Jones (co-PI, Brigham Young University). Unfunded Collaborators: Christian D. Johnson (Collaborator, Pacific Northwest National Laboratory), and Eric E. Roden (Collaborator, University of Wisconsin)

Research Objectives

As outlined in numerous national studies, one of the most vexing problems facing the Department of Energy (DOE) and its stakeholders is the inability to predict the transport of reactive contaminants in the subsurface to accurately assess risks and guide remedial activities at contaminated sites. The goal of this investigation is to develop scalable-modeling approaches that will help predict the transport of DOE-relevant contaminants in subsurface systems. We studied the reactive transport of two major classes of DOE-relevant contaminants, a radioactive cation [U(VI)] and a metal(loid) oxyanions [As(III/V)] to investigate the scaling issues inherent in the interactions of these contaminants with two major classes of subsurface materials, iron and manganese oxyhydroxides. We conducted several laboratory experiments to study the interaction of these two contaminants with subsurface materials. The data was then used to develop and test various types of model formulations.

The Project Team

Overall, the project has supported 25 researchers. At AU, the project, in part, supported the work of 2 faculty members, 1 technician, 1 post-doctoral associate, 6 PhD students, 6 Masters students, and 3 undergraduate-student helpers). At BYU the project, in part, supported 1 faculty and 2 MS students, and at UA it partly supported a faculty and 2 MS students. The project, so far, has resulted in 15 journal articles (more are expected), 3 book chapters, and 1 Pacific Northwest National Laboratory Technical Report, 6 PhD dissertations and 6 MS theses.

Summary of Research Outcomes

The section below provides a brief summary of various accomplished made in this project. For more technical details please refer to the cited journal publications related to the work.

We first completed batch experiments to study the interactions of arsenic with a commonly observed MnO_2(s) mineral, pyrolusite. We completed both batch and column experiments and then modeled the results using a scalable geochemical transport model. The results of this study were published in Radu et al. (2007). We developed a scalable surface-complexation modeling framework for predicting arsenate adsorption on synthetic goethite-coated sands (Jeppu et al. 2009; Jeppu et al. 2010). We also compared various approaches for analyzing arsenic adsorption data and determined the best method for reporting and interpreting the results of adsorption experiments that aid in extrapolating laboratory data to the field. The results were published in Hartzog et al. (2009).

Our past studies have indicated that U(VI) adsorption in near surface environments is strongly controlled by interactions with Fe oxyhydroxides. We quantified the sorption and reactive transport of U(VI) in the presence of a common subsurface Fe oxide, goethite (Romero-Gonzalez et al. 2007; Cheng et al. 2007; and Phillipi et al. 2007). We developed a novel protocol for synthesizing and characterizing goethite-coated sands (GCS). We synthesized three types of sands with different levels of iron coating. Batch experiments were completed to understand the geochemical interaction of uranium with these sands, and the data was modeled using a scalable surface complexation model. The results of this study were published in Loganathan et al. (2009). We produced hydroxyapatite from channel catfish bones and characterized it using XRD and SEM techniques. The natural apatite material was subjected to thermal treatment at 100°C and 300°C. The fish-bone derived hydroxyapatite (CFHA) prepared at the lowest temperature was found to be the most effective reactant and hence was selected for further studies. Multiple pH edge experiments were performed to understand the variations in uranium removal capacities. We also completed several column experiments. The study results are summarized in Chattanathan (2009).

The numerical reactive transport model development efforts focused on developing a new version of the DOE code RT3D, which uses the latest transport and flow simulation module available in MODFLOW and MT3DMS codes. The new version supports shared memory parallel computing framework available with the INTEL-Fortran compiler. As a test case, the new RT3D model was used in research study to simulate natural attenuation processes at a landfill site (Rolle et al. 2008), and also we helped researchers at the Idaho National Engineering Laboratory to simulate co-metabolic bioremediation processes occurring at one of their demo sites (TAN site). We also transferred the latest update to researchers at the Pacific Northwest National Laboratory and worked with them to develop a new user guidance document (Johnson and Clement, 2009). Furthermore, we have derived a set of new analytical solutions for modeling the transport of sequentially degrading radio-nuclide in groundwater aquifer (Srinvasan and Clement 2008 a, b). This analytical solution is good screening tool for simulating reactive transport at radio-active metal contaminated sites, and it is also a benchmark for testing numerical codes. The research team at the University of Alabama have investigated the scalability of the solute transport processes in heterogeneous domain where the flow is influenced by reactive preferential flow paths present the decimeter scale. The simulations results have shown that it is possible to upscale the reactive heterogeneities (Cao et al., 2010). Finally, we developed laboratory methods for visualizing density-coupled reactive plume transport scenarios that can be used to generate benchmark datasets for testing numerical models and also used to study the fate and transport of injected density-modified amendments in saturated groundwater systems (Goswami et al. 2008; Kanel et al. 2008).

Post-doctoral Fellow
Dr. Sushil Kanel, Fall 2005- Summer 2008. He is currently with USEPA-Cincinnati lab.

PhD Dissertations Partly Funded by this Project

1) Dr. Massimo Rolle, 2004-2006. Visiting Graduate Student from Turin Polytechnic University, Italy. Massimo studied at Auburn University for year and worked on RT3D development efforts. Dissertation topic: Modeling redox controlled reactive transport processes in groundwater aquifers. Current position: Research fellow, University of Tubingen, Germany.
2) Dr. Tanja Radu, 2002-2007, Dissertation title: Factors affection arsenic transport in experimental subsurface systems, Current position: Research Asst., Belfast University.
3) Dr. Rohit Goswami, 2002-2008. Dissertation topic: Experimental and numerical analysis of variable-density flow and transport scenarios. Current position: Consulting Engineer, Geosyntech, Florida.
4) Gautham Jeppu, 2005-2010, PhD student, Dissertation topic: Comprehensive investigation of the scalability of arsenic sorption and transport using batch and sequential-batch experiments. Expected to graduate in Fall 2010.
5) Vijay Loganathan, 2005-2010PhD student, Dissertation topic: An Assessment of U(VI) Adsorption at Multiple Scales, expected to graduate Fall 2010.
6) Jagdish Torlapati, 2004-2010, PhD student, Dissertation topic: Development and testing of parallel reactive transport codes. Expected to graduate in Fall 2011.

MS Theses Partly Funded by this Project

1) Mr. Venkat Srinivasan, MS, 2007. Thesis title: Analytical solution for sequentially coupled multi-species reactive transport problems. This thesis received a national award for best MS thesis 2nd place. Awarded by the Association of Environmental Engineering and Science Professors sponsored Montgomery-Watson-Harza Cash Prize.
2) Mr. Jared McLaughlin, MS, 2008. Brigham Young University. MS Thesis topic: Use of parallel computing techniques for solving reactive transport problems.
3) Mr. Anjani Kumar, MS 2006. Thesis topic: Coupling transport codes with reactive transport models.
4) Mr. Kent Hartzog, MS 2008. Thesis topic: Methods for scaling and comparing arsenic absorption data sets.
5) Mr. Shayamsunder Ayalur, MS, 2009, Thesis topic: Use of hydroxyapatite derived from catfish bones for remediating uranium contaminated groundwater.
6) Mr. Scott McLaughlin, Expected Fall 2010. Thesis topic: Quantitative Analysis of the Effects of Phosphate on Uranium Adsorption to Iron Coated Sands.

Submitted/draft journal manuscripts

1) Jeppu, G., T.P. Clement, M.O. Barnett, Understanding the scaling behavior of metal transport using sequential and sequencing batch reactor experiments, to be submitted to Applied Geochemistry Journal, 2010.
2) Cao, G., T.P. Clement, C Zheng, 2010, Effect of decimeter-scale preferential flow paths on reactive transport in porous media, Ground Water, Draft under preparation.

Manuscripts in press or published in 2009

1) Jeppu, G., T.P. Clement, M.O. Barnett, K-K Lee, A scalable surface complexation modeling framework for predicting arsenate adsorption on goethite-coated sands: model development and testing, *Environmental Engineering Science Journal*, 27(2): 147-158. doi:10.1089/ees.2009.0045, 2010.
2) Zheng, C., M Bianchi, S.M. Gorelick, 2010, Lessons learned from 25 years of research at the MADE site, Ground Water, in press.
3) Loganathan, V., M.O. Barnett, T.P. Clement, S.R. Kanel, Scaling of adsorption reactions: U(VI) experiments and modeling, Applied Geochemistry Journal, In press, 2009.
4) Goswami R.R., B. Ambale and T.P. Clement, Estimating errors in concentration measurements obtained from image analysis, Vadose Zone Journal, vol.8(1), p.108-118, 2009.
5) Hartzog, O.K., V.A. Loganathan, S.R. Kanel, G.P. Jeppu, M.O. Barnett, Normalization, comparison, and scaling of adsorption data: Arsenate and goethite, Journal of Colloid and Interface Science, 333, 6–13, 2009.

Published Journal Articles in 2008

1) Radu, T., Kumar, A., T.P. Clement, G. Jeppu, M.O. Barnett, Development of a scalable model for predicting arsenic transport coupled with oxidation and adsorption reactions, In press, Journal of Contaminant Hydrology, v.95, pages 30–41, 2008.
2) Rolle, M., T.P. Clement, R. Sethi, A.D. Molfetta, A Kinetic Approach for Simulating Redox-controlled Fringe and Core Biodegradation Processes in Groundwater: Model Development and Application to a Landfill Site in Piedmont, Italy, Hydrological Processes Journal, Vol 22 (25), P 4905 – 492, 2008.
3) Kanel, S.R., R. R. Goswami, T. P. Clement, M. O. Barnett, and D. Zhao, Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media, Environmental Science & Technology, v.42, p.896-900, 2008.
4) Srinivasan, V. and T.P. Clement, Analytical solutions for sequentially coupled one-dimensional reactive transport problems – Part I: Mathematical Derivations, Advances in Water Resources, v. 31(2), P. 203-218, 2008.
5) Srinivasan, V. and T.P. Clement, Analytical solutions for sequentially coupled one-dimensional reactive transport problems – Part II: Special Cases, Implementation and Testing, Advances in Water Resources, v. 31(2), P. 219-232, 2008.

Published Journal Articles that appeared in 2007

1) Romero-Gonzalez MR, Cheng T , Barnett MO, Roden EE, Surface complexation modeling of the effects of phosphate on uranium(VI) adsorption, Radiochimica ACTA, 95 (5): 251-259 2007.
2) Cheng T, Barnett MO, Roden EE, Zhunag JL, Reactive transport of uranium(VI) and phosphate in a goethite-coated sand column: An experimental study, Chemosphere, 68 (7): 1218-1223, 2007.
3) Phillippi, J.M., V. A. Loganathan, M. J. McIndoe, M. O. Barnett, T.P. Clement and E. E. Roden, Theoretical analysis of solid-to-solution ratio effects on the adsorption and transport of strongly interacting solutes-- uranium (VI) and carbonate system, Soil Science Society of America Journal, 7(2), 329-335, 2007.
4) Srinivasan, V., T.P. Clement, and K.K. Lee, Domenico model – Is it valid? Ground Water, v45(2), p. 136-146, 2007.

Published Technical Reports

1) Johnson, C.D., and T.P. Clement, Description of the RT3D code with application case study examples, p. 65, Pacific Northwest National Laboratory Technical Report.

Peer Reviewed Book Chapters

1) Clement, T.P., and C.D. Johnson, Chapter 4. RT3D – Modeling of reactive transport in 3-dimensions, accepted for publications, Advances in Reactive Transport Modeling Book, 2009.
2) Srinivasan V. and T.P. Clement, Analytical methods of modeling contaminant fate and transport, in press, Ground Water Manual, edited by Aral and Taylor, Chapter-6, American Society of Civil Engineers (ASCE), 2009.
3) T.P. Clement, Bioremediation of contaminated groundwater systems, in press, Ground Water Manual, edited by Aral and Taylor, Chapter-12, American Society of Civil Engineers (ASCE), 2009.