

**Migration and Entrapment of DNAPLs in Heterogeneous Systems:
Impact of Waste and Porous Medium Composition**

The Offices of Energy Research and Environmental Management
U.S. Department of Energy
Grant # FG07-96ER14702

Annual Report
June 2003

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Research Objective

Previously funded EMSP research efforts were directed towards the quantification of dense non-aqueous phase liquid (DNAPL) migration and entrapment behavior in physically and chemically heterogeneous systems. This research demonstrated that chemical heterogeneities can have a significant influence on DNAPL fate and persistence. Previous work, however, was limited to examination of the behavior of pure DNAPLs in systems with simple and well-defined aqueous and solid surface chemistry. The subsurface chemical environments at many DOE sites, however, are generally more complex than these idealized systems, due to the release of complex mixtures of wastes and more complex physical and chemical heterogeneity. The research undertaken in this project seeks to build upon our previous research experience and expertise to explore the influence of waste and porous media composition on DNAPL migration and entrapment in the saturated zone. DNAPL mixtures and soils typical of those found across the DOE complex will be used in these studies. Many of the experimental procedures and protocols are based upon those developed under previous EMSP funding. This past work also provides the conceptual framework for characterizing and interpreting experimental results, mathematical model development, and inverse modeling protocols. Specific objectives of this research include:

- 1) Relate measured interfacial properties for representative wastes and soils to parameters such as mineralogy, organic carbon content, pH, ionic strength, and DNAPL acid and base numbers.
- 2) Assess predictive procedures to estimate interfacial properties for DOE wastes and soils.
- 3) Deduce mechanisms of interfacial property alteration.
- 4) Quantify the influence of waste and porous medium composition on hydraulic properties and residual saturation.
- 5) Develop and assess constitutive hydraulic property and residual saturation models.
- 6) Explore the migration and entrapment behavior of model DNAPL wastes in spatially and temporally heterogeneous systems.
- 7) Development and validation a multiphase flow model to simulate the migration and entrapment of model DNAPL wastes in heterogeneous systems.
- 8) Investigate the up-scaling of findings from batch and soil column experiments to larger systems.

Research Progress and Implications

This section summarizes research conducted towards the accomplishment of the above objectives in year 2 of this 3 year project.

As part of the research investigating the heterogeneity of wettability at waste sites, the wettability, surface composition and surface charge of six natural materials, clean silica, a geologically young agricultural soil containing humic acid (Ann Arbor II soil), two shales (Lachine and Garfield), a bituminous coal (Waynesburg), and graphite are being measured (objective 1, 2 and 3). Findings suggest that the presence of organic carbon on the surface of a material alone is not sufficient to cause it to be wetted by the representative DNAPL (tetrachloroethene), as demonstrated by measurements of wettability for the Ann Arbor II soil and the Lachine shale. These solids remain water-wet when equilibrated in water, in comparison to the Garfield shale and Waynesburg coal which are organic-wet. To explain the difference in the wettability behavior of these various natural organic materials, an examination of the material's surface functional groups is being conducted using Fourier Transform Infrared (FT-

IR) spectroscopy. The preliminary results suggest that decreased water wetness may be correlated with the number of carboxylic, aliphatic, and nitrogenous groups on the material's surface. Since the degree of water wetness may be related to the surface charge rather than to the exact chemical composition of the surface, the surface charge of the six materials immersed in water is being measured as a function of pH. It has been determined that two water-wet materials, silica and Lachine shale, have isoelectric points at pH 2 and 4, respectively. The isoelectric points of the organic-wet materials are currently being determined.

Work in a previous funding period examined the impact of an organic acid and an organic base individually on interfacial tension and wettability. In this funding period the behavior of a mixed waste consisting of a DNAPL containing both an organic acid and base was examined (objectives 1, 2 and 3). Results from this work suggest that the interfacial activity of waste mixtures cannot be predicted from the superposition of activities measured for individual waste components; in fact, the presence of a component that individually has no effect may enhance the impact of another component. The substantial increases in the contact angle and decreases in interfacial tension observed here will significantly alter DNAPL migration and entrapment in the subsurface as demonstrated in the numerical simulations produced as another part of this project (objectives 6, 7 and 8).

A series of capillary pressure/saturation experiments and multistep column outflow experiments were conducted to estimate capillary retention and relative permeability functions for DNAPL in media with various wetting properties (objectives 4 and 5). Capillary pressure/saturation data, generated in small pressure cell experiments, facilitate independent verification of the retention functions fit to the multistep outflow experiments. A modified form of Leverett scaling, using independently measured contact angles, to scale water-wet primary drainage curves to primary drainage and primary imbibition curves for soils of differing wettability has been developed. In addition, results from the outflow experiments indicate that traditional capillary-based predictive models fail to capture observed relative permeability behavior at endpoint saturations.

Numerical investigations were undertaken to examine the potential influence of coupled textural and chemical heterogeneity on predictions of DNAPL migration and entrapment at the field scale (objectives 6, 7 and 8). Simulations suggest that the coupled influence of textural and chemical heterogeneity can have an observable effect on the distribution of organic liquids at larger scales. Incorporation of just a small amount of organic-wet solids tends to increase maximum entrapped organic saturations and reduce depths of organic penetration and the degree of vertical spreading. Results also suggest that the presence of organic-wet may potentially mask the effects of textural heterogeneity variations.

Planned Activities

Due to the anticipated graduation of three research team Ph.D. candidates (Denis O'Carroll, Thomas Phelan and Hsin-Lan Hsu), within the next year, a one year no cost extension will be filed for this grant. Experimental research efforts will continue to focus on the effect of natural soil minerals and DNAPL waste constituents on interfacial properties (objective 1, 2 and 3). In addition capillary pressure/saturation and multistep column outflow experiments will be conducted for variously

wetted synthetic (uniform and fractional wettability) porous media (objectives 4 and 5). Results from the multistep outflow experiments will be used to determine relative permeability/saturation parameters in these systems. Hydraulic property relations, determined from the soil column experiments, will be utilized to further explore potential applications of wettability and interfacial property alterations on DNAPL control and recovery at larger scales (objectives 6, 7 and 8).

Information Access

Publications

- Abriola, L.M., A.H. Demond, D.M. O'Carroll, H. Hsu, T.J. Phelan, C.A. Polityka and J.L. Ryder, 2003. Compositional effects on interfacial properties in contaminated systems: Implications for organic liquid migration and recovery, American Chemical Society Monograph Series (submitted).
- Bradford, S.A., K.M. Rathfelder, J.R. Lang and L.M. Abriola, 2003. Entrapment and Dissolution of DNAPLs in Heterogeneous Porous Media. *Journal of Contaminant Hydrology* (in press).
- O'Carroll, D.M., S.A. Bradford, and L.M. Abriola, 2003. Infiltration of tetrachloroethylene in a system containing spatial wettability variations. *Journal of Contaminant Hydrology* (submitted).
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- Lord, D.L. 1999. Influence of organic acid and base solution chemistry on interfacial and transport properties of mixed wastes in the subsurface. Ph.D. Dissertation. Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI.

Presentations

- Abriola, L.M., D.M. O'Carroll and T.J. Phelan, 2003. Exploring the Influence of Medium Wettability on DNAPL Migration and Retention Behavior: Bench Scale Experiments and Field Scale Implications. SIAM Conference on Mathematical and Computational Issues in the Geosciences, Austin, TX. March 17-20, 2003.
- Abriola, L.M., A.H. Demond, D.M. O'Carroll, H. Hsu, T.J. Phelan, C.A. Polityka and J.L. Ryder, 2003. Compositional effects on interfacial properties in contaminated systems: Implications for organic liquid migration and recovery. 225th American Chemical Society National Meeting, New Orleans, LA. March 23-27, 2003.
- O'Carroll, D.M., C.A. Polityka, T.J. Phelan and L.M. Abriola, 2003. Influence of Wettability on Dense Nonaqueous Phase Liquid (DNAPL) Capillary Hysteresis Behavior and Relative Permeability in Saturated Porous Media. EGS-AGU-EUG Joint Assembly, Nice, France. April 6-11, 2003.
- Phelan, T. J. and L. M. Abriola, 2003, Simulation of mass recovery of entrapped tetrachloroethene in coupled physically and chemically heterogeneous porous media, in EGS-AGU-EUG Joint Assembly, Nice, France. April 6-11, 2003.
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Additional Information

Publications generated within this reporting period are available as appendices to the hard copy report.