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Progress Report III
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**The Migration and Entrapment of DNAPLs in
Physically and Chemically Heterogeneous Porous Media**

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Project Title: The Migration and Entrapment of DNAPLS in Physically and Chemically Heterogeneous Porous Media

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RESEARCH OBJECTIVE

Dense nonaqueous phase liquids (DNAPLs) are common subsurface contaminants at many Department of Energy (DOE) hazardous waste sites. The migration and entrapment of DNAPLs at these sites is greatly influenced by subsurface heterogeneity, both physical and chemical. Unfortunately, the physics of DNAPL flow in chemically heterogeneous systems is poorly understood and, hence, multiphase flow simulators typically assume that subsurface soils are completely water-wet (chemically homogeneous). The primary objective of this research is to improve our understanding of and ability to simulate the influence of subsurface chemical heterogeneities on DNAPL flow and entrapment in the saturated zone. Laboratory and numerical investigations are being conducted for a matrix of organic contaminants and porous media encompassing a range of wettability characteristics. Specific project objectives include: (1) quantification of system wettability and interfacial tensions; (2) determination of hydraulic property relations; (3) investigation of DNAPL infiltration behavior in two-dimensional systems; (4) modification of a continuum based multiphase flow simulator to account for coupled physical and chemical heterogeneity; and (5) exploration of the migration of DNAPLs and the development of innovative remediation schemes under heterogeneous conditions using this model.

RESEARCH PROGRESS AND IMPLICATIONS

This section summarizes research conducted towards the accomplishment of the above objectives during the first 2.5 years of this 3 year project.

The work on objectives (1) and (2) relating the solution chemistry of organic acids and bases to the capillary pressure relationship is now completed. In this period, the impact of octanoic acid and dodecylamine on the capillary pressure relationship for a tetrachloroethylene (PCE)-water-quartz system was examined [Lord, 1999] and compared to previous [Lord *et al.*, 1997ab] results obtained for the same solutes in an *o*-xylene-water-quartz system to determine the impact of solvent properties. Despite the differences between PCE and *o*-xylene in polarity, aromaticity, density, and pure solvent interfacial tensions, the speciation, sorption and partitioning of the solutes were similar and impacted the capillary pressure relationship similarly. For example, the pKa of octanoic acid remained at 4.8, regardless of the nature of the nonaqueous phase. Furthermore, as Figure 1 shows, the distribution coefficient of octanoic acid, or the ratio of the concentration of octanoic acid in the organic liquid phase to that in the aqueous phase, had the same dependence on pH independent of whether the organic liquid was PCE or *o*-xylene. Because both the speciation and distribution coefficient were similar, the variation in interfacial tension was also similar, as Figure 2 illustrates. Since octanoic acid is preferentially in an anionic form above the pKa, it remains in the aqueous phase (Figure 1) where it influences the interfacial tension to a greater extent (Figure 2). This behavior is reflected in the primary drainage capillary pressure relationship by the fact that the capillary pressure at a particular aqueous phase saturation is lower at pH values above the pKa (Figure 3). Again, this result is independent of the nature of the organic liquid phase. The results shown here are for octanoic acid-NAPL-water-quartz systems; a similar lack of dependence on the nature of the organic liquid phase was observed in the dodecylamine-NAPL-water-quartz systems.

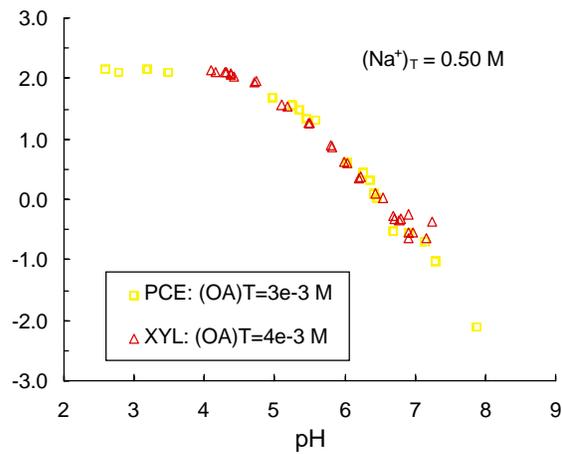


Figure 1. Distribution coefficient of octanoic acid between NAPL and water as a function of pH.

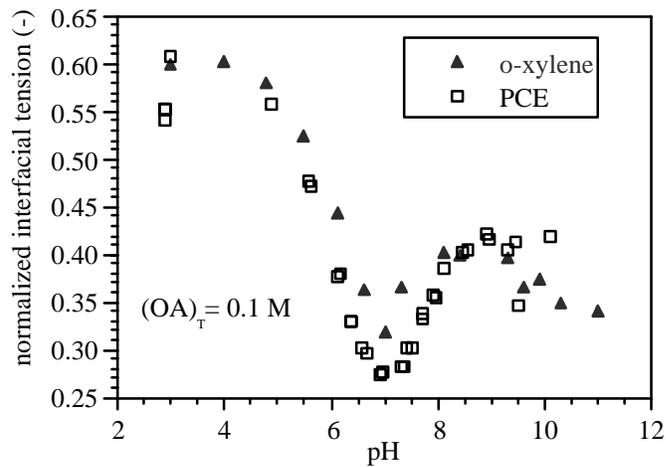


Figure 2. Interfacial tension between NAPL and water containing octanoic acid, normalized by the value in the absence of octanoic acid, as a function of pH.

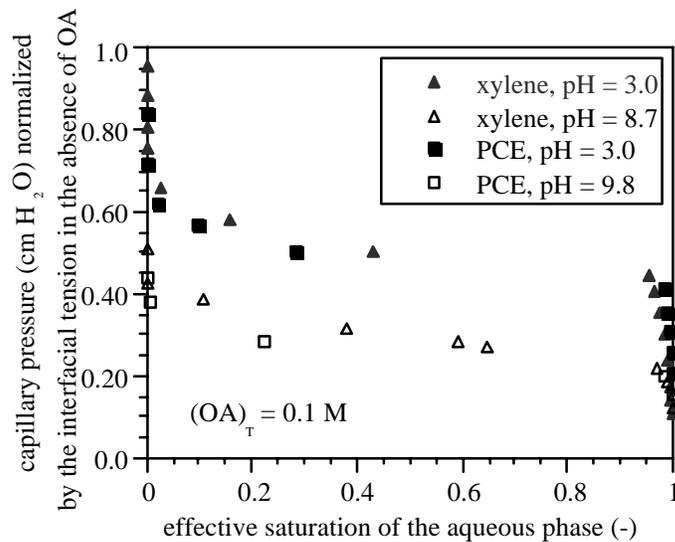


Figure 3. Primary drainage capillary pressure-saturation relationships for NAPL-water-quartz systems, normalized by the respective interfacial tension in the absence of octanoic acid.

Additional research efforts directed towards the accomplishment of objective (2) have focused on the determination and quantification of hydraulic property relations for PCE, water, and fractional wettability porous medium systems. Capillary pressure relations are being measured using manual and automated setups that are based upon the pressure cell approach; i.e., saturations change in response to imposed boundary conditions until equilibrium conditions are achieved. Favorable comparison of experimental results from these setups for selected soils has provided a quality control check on the measured data. Results indicate that the magnitude and shape of the capillary pressure curves are strongly dependent on the porous medium wettability [Bradford *et al.*, 1999; Demond *et al.*, 1999; Lord *et al.*, 1999]. As the DNAPL-wet fraction of a soil increases, for a given saturation and saturation history, the DNAPL-water capillary pressure decreases, becoming negative during water imbibition. Residual water and DNAPL saturations were also found to systematically vary by 52 to 80% as a function of fractional wettability [Bradford and Abriola, 1998]. Transient outflow measurements collected with the automated setup (Figure 4) are being used to determine the relative permeability relations according to history matching procedures. Due to the inability of previously developed multiphase models at the University of Michigan to handle the measured time dependent water and DNAPL pressure boundary conditions, a new one-dimensional multiphase flow simulator has been developed. This simulator has been successfully coupled with a nonlinear least-squares fitting routine and is currently being used to analyze the collected outflow data and determine the relative permeability relations.

F35-F50 100% OTS

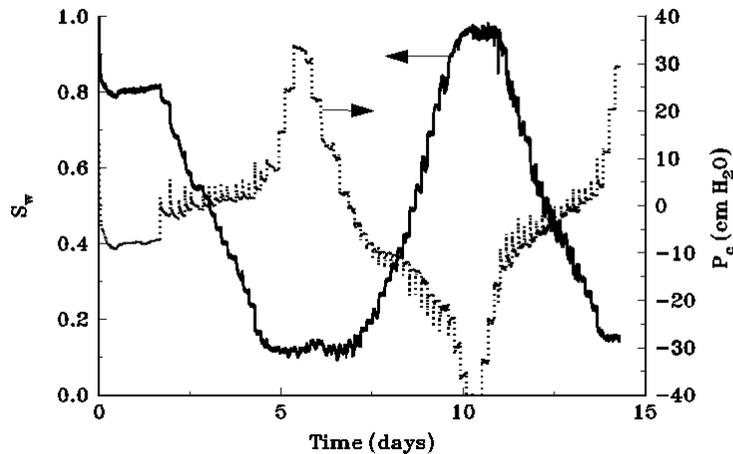


Figure 4. Transient column-averaged water saturation and capillary pressure for an organic-wet F35-F50 sand (mean grain size equals 0.36 mm).

To address (3), a two-dimensional sand tank has been built and instrumented for experimental studies. The back of the 33" (vertical) x 15" (horizontal) x (1" or 5/8") chamber is equipped with a network of sampling ports and tensiometers (water and DNAPL) to monitor the aqueous phase composition and the liquid pressures, respectively, during infiltration and remediation experiments. An estimate of the fluid saturation at a particular point is obtained from the pressure readings and measured capillary pressure-saturation data (cf. objective 2). The chamber has a glass front panel to facilitate the qualitative tracking of dyed (Oil-Red O) PCE distribution over time with a high resolution digital camera. The chamber is also equipped with injection and extraction wells. These wells are used to establish constant water pressure boundary conditions and steady-state water flow during tracer and remediation studies. Experimental protocols have been established for chamber packing, tracer studies, DNAPL introduction, and visualization of DNAPL infiltration front evolution. Experimental results from these two-dimensional experiments will be used to investigate scale-up issues in multiphase systems, validate and refine the constitutive and numerical models, and explore innovative remediation schemes.

To address (4) and (5), a two-dimensional multiphase flow simulator has been adapted to account for coupled physical and chemical aquifer heterogeneity [Bradford *et al.*, 1998ab]. Saturation independent and saturation dependent wettability effects on the hysteretic hydraulic property relations are currently included, but the simulator does not yet account for concentration dependent wettability and interfacial tension. Simulations suggest that spatial variations in wettability can have a dramatic influence on DNAPL distributions. In physically homogeneous coarse textured systems, increasing the contact angle or organic-wet fraction of a soil produced a prolonged slow migration of the DNAPL, creating larger contaminated aquifer regions with lower organic saturations. In coupled physically and chemically heterogeneous systems, interfaces of capillary property contrast (soil texture or soil wettabilities) led to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration (Figure 5).

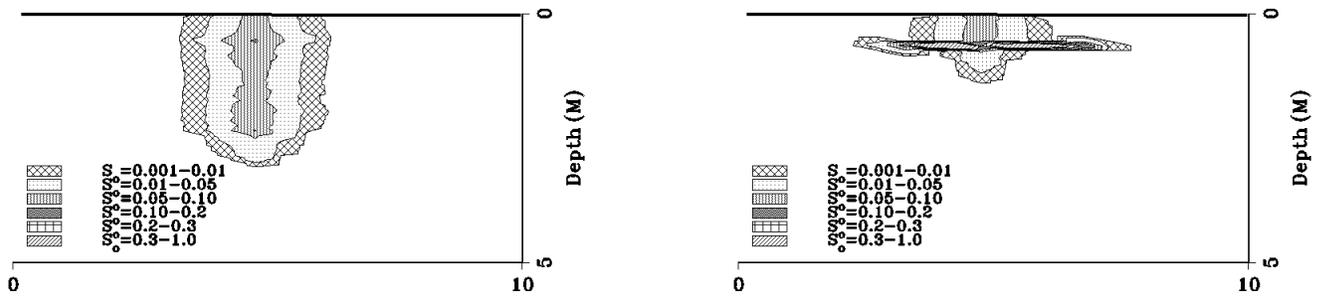


Figure 5. Spatial distribution of PCE saturation after 10 days when a physically heterogeneous aquifer (left and right) is completely water-wet (left) and when the contact angle is inversely correlated with the intrinsic permeability and the geometric mean contact angle is 66° (right).

PLANNED ACTIVITIES

Due to a late project initiation and the unanticipated departure of a key member of the research team (Mark Wilkins, a Ph.D. candidate), an one year no cost extension has been filed for this grant. Experimental research efforts will continue to focus on DNAPL hydraulic property measurements (objective 2) and two-dimensional infiltration experiments (objective 3) for variously wetted synthetic (surface coatings of various natural organic matter constituents, iron oxide, aluminum oxide, and organosilane) and natural porous media. Hydraulic property relations determined from the soil column experiments will be utilized to evaluate predictive procedures and characterize soils employed in the two-dimensional experiments. Numerical modeling efforts (objectives 4 and 5) will continue to be directed towards the simulation of transient outflow experiments (to determine the relative permeability relations) and two-dimensional infiltration experiments (to validate and refine the constitutive and numerical model). Additional numerical studies will be initiated to further explore potential applications of wettability alteration in DNAPL control and recovery.

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