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

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Project Title: The Migration and Entrapment of DNAPLs in Heterogeneous Systems: Impact of Waste and Porous Medium Composition

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RESEARCH OBJECTIVE

Previously funded EMSP research efforts have been directed towards the quantification of dense nonaqueous phase liquid (DNAPL) migration and entrapment behavior in physically and chemically heterogeneous systems. This important research has demonstrated that chemical heterogeneities can have a significant influence on DNAPL fate and persistence. Previous work, however, has been limited to pure DNAPLs and well defined aqueous and solid surface chemistries. Subsurface chemical heterogeneities at many DOE sites are generally more complex as a result of the disposal of mixtures of wastes into heterogeneous subsurface environments. The research planned 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 to be employed 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 are identified below.

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. Develop and validate a multiphase flow model to simulate the migration and entrapment of model DNAPL wastes in heterogeneous systems.
8. Investigate the upscaling 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 during the first 8 months of this 3-year project.

Experiments with a natural subsurface material (known as Ann Arbor II (AAII)) have been undertaken and completed in pursuit of objective 1. AAI consists of a solid quartz phase with an organic carbon (humic acid) coating that renders the surface more organic wetting. This soil was chosen since it is typical of many surface soils found throughout the US. Figure 1 is a capillary pressure-saturation curve for the AAI soil as well as for an AAI soil sample that has been stripped of its organic coating. These data reveal that natural organic coatings, such as those present on this soil, can affect both the shape and entry pressure of capillary pressure curves. This will, in turn, have an effect on the

flow and ultimate distribution of nonaqueous phase liquids in the subsurface. Many soils are heterogeneous and contain several types of particles with varying degrees of organic carbon coatings and ages.

Figure 1 - Capillary Pressure-Saturation Curves for AAI soil and stripped AAI soil. Note the differences in curve shape and entry pressure.

Further progress on objective (1) has also been achieved through characterization of a complex NAPL phase in the laboratory. The NAPL phase currently being considered is a spent (*i.e.*, used) chlorinated

solvent that was employed as a degreasing agent. It contains PCE as a primary solvent but may also contain

several co-solvents, special degreasing agents, surfactants, and debris including greases, organic acids and bases, and detergents. This particular waste has been selected for study for two reasons: a) to evaluate the potential impacts of impurities on interfacial properties, and b) to refine our analytical chemistry abilities for the analysis of different, potentially surface active, solutes in an organic waste. The PCE waste has been analyzed for interfacial tension and contact angle. Figure 2 shows the interfacial tension of this PCE waste with water over a range of pH values. Immediately, it can be seen that the spent solvent has a significantly lower interfacial tension value than that of pure PCE (46.1

Figure 2 - Variation of PCE/water interfacial tension with pH. Note dramatic reduction in IFT relative to pure PCE (46.1 dynes/cm). The variation in IFT with pH is indicative of the presence of a surface-active organic base.

Figure 3 - Schematic of sand tank used for infiltration experiments

viscosity reduction is due to the presence of surfactants, and the reduction in interfacial tension is due to the presence of surface-active organic bases.

PL, tetrachloroethylene (O'Carroll et al., 1998). Sands of various textures and grain sizes act as a very important factor in the distribution of the organic-wet lenses. Upon completion of the experiment, the organic-wet lenses were present in the sand. The results were used to account for the distribution of the DNAPL to simulate this sand box experiment. The results of the van Genuchten

(vanGenuchten 1980) and Brooks-Corey (Brooks and Corey 1966) capillary pressure/saturation relationships, fit to data from column experiments as well as wettability effects (O'Carroll et al., *in preparation*) on relative permeability relationships (Burdine 1953, Mualem 1976). Model predictions using alternative capillary pressure/relative permeability/saturation relationships are compared to experimental observations in Figure 4. When modeling DNAPL spill events it is commonly assumed that subsurface porous media is water-wet. A simulation, assuming a completely water-wet model domain, was conducted to assess the error associated with this assumption. The water-wet simulation, Figure 4f, fails to predict observed PCE pathways and retention behavior. These experimental observations illustrate the potential influence of subsurface wettability variations on DNAPL migration and entrapment and the limitations of traditional multiphase simulators for predictions in such systems.

To address objectives (4) and (5), transient outflow measurements, collected with an

Figure 4 - Comparison of observed and simulated infiltration experiments. PCE has been infiltrating for 60 minutes.

automated setup, are being used to estimate two phase aqueous/organic relative permeability relations in conjunction with inverse modeling 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 used to optimize the transient outflow experiment to ensure the maximum sensitivity to different relative permeability relationships. Laboratory outflow experiments are currently underway.

PLANNED ACTIVITIES

To maximize the impact of our research efforts, the exchange of information and coordination of research is on going with other EMSP projects that relate to NAPL transport and remediation. Professor Susan Powers of Clarkson University (grant 70035) is exploring the influence of surface-active chemicals and/or microorganisms on the interfacial phenomena governing the migration of NAPLs in the unsaturated soil zone. Surface-active materials are present in complex NAPL mixtures and are produced through microbial metabolic processes. We are currently developing a work plan to enhance collaboration efforts. Activities will include the use of common NAPLs and aqueous phase mixtures as well as the exchange of soil characterization data. Meetings between scientists in both groups have been held and additional meetings are planned throughout the summer. These inter-project discussions and sharing of techniques have already benefited research projects of both groups.

In collaboration with Dr. Powers personnel at the Savannah River site have collected field soil samples for our laboratory. Use of actual DOE site soils in a variety of experiments will be undertaken with the ultimate goal of determining the fate of NAPLs and their remediation potential at such DOE sites. We hope to collaboratively perform experiments on these samples in an effort to characterize the soil organic matter and, further, their surface chemistry characteristics.

Analytical methods are being developed to identify contaminants within the complex PCE waste so that further work can be conducted to determine what effect these have on the surface properties of the mixed waste (objective 1). Synthetic PCE wastes are also being made to investigate the influence of particular chemical constituents such as organic acids, bases, and alcohols on NAPL properties.

A series of experiments investigating the influence of a soil with geologically older organic content, Lachine Shale, is underway to determine the influence of organic carbon type on the two-phase hydraulic properties. Contact angle measurements and capillary pressure curves are currently being measured to determine if the presence of older, less hydrophilic, shale particles will alter the flow and entrapment of PCE in the subsurface.

Finally, work is continuing on the development of a compositional multiphase flow and transport simulator that can incorporate temporally varying aqueous and organic phase chemistry effects on k_r - S_w - P_c relationships.

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