

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

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TABLE OF CONTENTS

TABLE OF CONTENTS.....	2
EXECUTIVE SUMMARY	3
RESEARCH OBJECTIVES	4
METHODS AND RESULTS	4
RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER	18
PROJECT PRODUCTIVITY	19
PERSONNEL SUPPORTED.....	19
PUBLICATIONS.....	20
INTERACTIONS	21
PATENTS.....	22
LITERATURE CITED	22

EXECUTIVE SUMMARY

Dense nonaqueous phase liquids (DNAPLs) pose a significant threat to soil and groundwater at Department of Energy (DOE) sites. Evidence suggests that subsurface wettability variations are present at many of these sites as a result of spatial and temporal variations in aqueous phase chemistry, contaminant aging, mineralogy and organic matter. The presence of such heterogeneity may significantly influence DNAPL migration and entrapment in the saturated zone. Despite its potential importance, the physics of DNAPL flow in non-water-wetting systems has not been adequately investigated. If the assumption that subsurface soils are completely water-wet does not hold, large errors may be introduced into estimates of DNAPL migration and remediation. This report highlights research, funded by the DOE Environmental Management Science Program (EMSP), undertaken to improve our understanding of the impact of waste and porous medium composition on DNAPL flow and entrapment. The prediction of interfacial properties was shown to be quite complex for natural soil systems and in multicomponent waste mixtures. A new model was developed to predict capillary retention function data in fractional wettability systems and the analysis of experimental multistep outflow data suggested that dynamic effects in capillary pressure should be considered when simulating multiphase flow. A two-dimensional DNAPL infiltration experiment also demonstrated that subsurface wettability significantly influences DNAPL migration due to differences in entrapment behavior and capillary barrier effects at interfaces of capillary contrast. Two numerical simulators, incorporating laboratory-measured information, were used to predict the field-scale migration, entrapment and subsequent remediation of a DNAPL in subsurface systems with textural and wettability heterogeneities over a wide range of heterogeneity scenarios. Experimental and numerical studies indicate that the spatial distribution of subsurface waste and wettability characteristics should be quantified to improve the prediction of DNAPL fate and persistence, and that the importance of this information may equal to that of hydraulic conductivity variations in some systems. A more complete understanding of the influence of waste and porous medium composition on DNAPL migration and entrapment may lead to improved methods for DNAPL recovery and containment during aquifer remediation operations.

RESEARCH OBJECTIVES

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 built upon our previous research experience and explored the influence of waste and porous media composition on DNAPL migration and entrapment in the saturated zone. Specific objectives of this research included:

- 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.

METHODS AND RESULTS

- (i) *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.*

Methods:

Several types of measurements were undertaken to determine the effects of waste and soil parameters on the interfacial transport properties that govern the migration and entrapment of waste liquids representative of those found at DOE waste sites. Representative systems of five components, including a nonaqueous fluid, water, two surface-active co-contaminants, and solid phase were selected. Tetrachloroethene (also known as perchloroethylene or PCE) was chosen as a typical DNAPL because of its widespread use and resulting contribution to numerous contamination sites.

The relationship between organic carbon content and contact angle was investigated for 6 naturally occurring soil materials differing in both organic carbon form and maturity. These soils included clean quartz sand (S), Ann Arbor II soil, Lachine Shale (LS), Garfield Shale (GS), Waynesburg Coal (WC), and Plumbago Mineral Carbon (graphite - MC). The materials were selected to include

mineral surfaces (quartz and graphite), humic based soil organic matter that is geologically young and unprocessed (Ann Arbor II), and kerogen organic matter that has been hardened by temperature and pressure over geologic time (Lachine Shale, Garfield Shale, Waynesburg Coal). All of these materials are representative of the types of particles present in heterogeneous soil systems. For these systems both receding and advancing contact angles were measured, since measurements are complicated by the fact that the wettability of pores will depend on the first fluid to reach the pore. Contact angle measurements were conducted for the following four cases:

- 1) Air receding, water advancing
- 2) Water receding, air advancing
- 3) PCE receding, water advancing
- 4) Water receding, PCE advancing

Interfacial tensions and contact angles were measured as a function of pH in PCE/water/quartz systems containing an organic acid or/and an organic base, whose concentrations indicate acid and base numbers, respectively (Hsu and Demond, 2004). The selected representative organic acid was octanoic acid (OA) and the organic base was dodecylamine (DDA), both of which have been identified in petroleum products and at hazardous waste sites (Riley and Zachara, 1992; Borgund and Barth, 1994).

Results:

A plot of receding water contact angles as a function of the oxygen/carbon ratio for four naturally occurring soil materials is presented in Figure 1. Guy et. al. (1996) suggested that the contact angle in oil-water systems on coal is a function of oxygen/carbon ratio. The results presented in Figure 1, however, indicate that this ratio is not strongly correlated to contact angles.

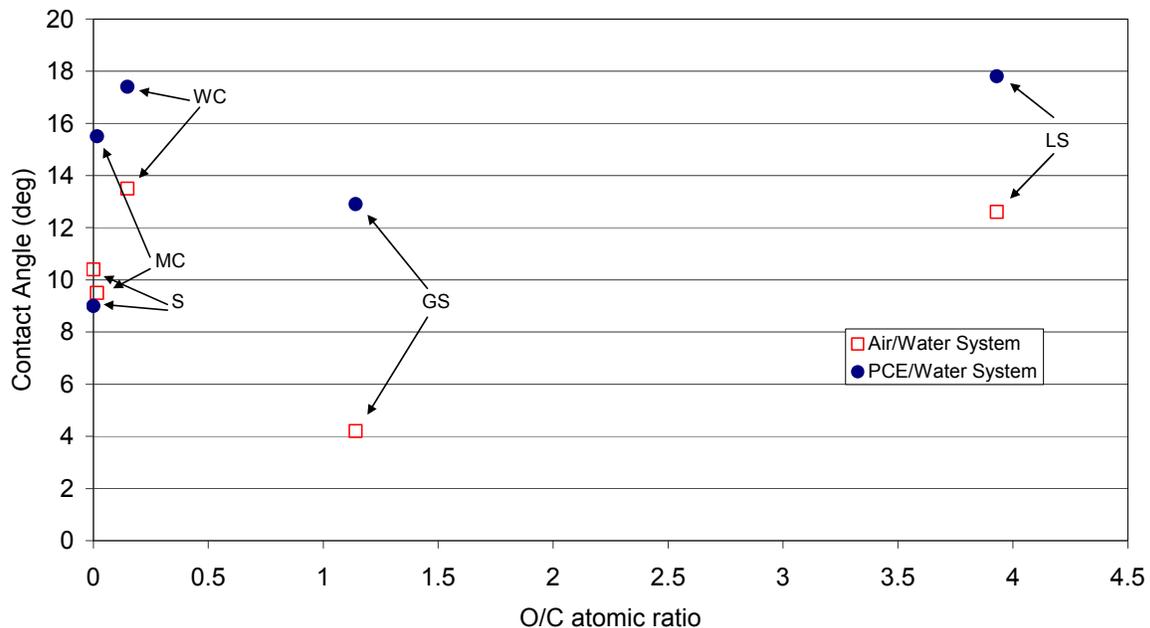


Figure 1: Receding water contact angle as a function of the elemental composition of selected soil materials (contact angles are measured through the water phase)

To further examine the influence of elemental composition on wettability, FT-IR analyses were conducted to identify the presence or absence of specific functional groups on selected soil materials. In oil reservoir studies, the sorption of nitrogenous compounds has been associated with wettability alterations (Denekas et al., 1959). None of the materials analyzed in this study, however, show a significant presence of nitrogen containing functional groups although a range of wetting conditions were present for these materials (Table 1). Functional groups present in each soil material are presented in Table 2 (note absent functional groups are not presented). All the materials examined contain oxygen in the form of aliphatic alcohol groups. These groups may provide the polar forces that cause the surfaces to be water wet when initially contacted with a polar liquid like water.

Table 1: Wettability results for selected soils (* Did not measure contact angle on Ann Arbor II coated slide. OW=oil wet. WW=water wet. Contact angles are measured through the aqueous phase.)

Solid	Air-Water Cont. Angle (deg. - case 1)	Water-Air Cont. Angle (deg. - case 2)	PCE-Water Cont. Angle (deg. - case 3)	Water-PCE Cont. Angle (deg. - case 4)	PCE-Water Bottle Test (case 3)	Water-PCE Bottle Test (case 4)	ME D	% Carbon
Silica	-	10.5	45.4	9.0	WW	WW	0	0
Ann Arbor II*	-	-	-	-	WW	WW	0	
Lachine Shale	44.6	12.6	130.9	17.8	OW	WW	0	9.08
Garfield Shale	53.4	4.2	147.6	12.9	OW	WW	4.5	25.06
Waynesburg Coal	81.6	13.5	127.1	17.4	OW	WW	6	68.31
Graphite	62.2	9.5	153.1	15.5	OW	WW	0.5	96.03

Table 2: Surface functional group composition of selected soil materials

Material/Group	OH Monomeric	Quartz, Mineral oxides	Fe-O-Si	Al-O-Si	CH aromatic out of plane	Aromatic C=C	Aromatic Ether	Aliphatic Alcohols	CH2 asymmetric	Unsaturated Alkanes	Sp2 C-H	Sp3 C-H	Methyl groups	4+ methylenes
Silica	x	x	x	-	x	x	-	x	-	-	-	-	-	-
Ann Arbor II	x	x	x	-	x	x	x	x	-	-	-	-	-	-
Lachine Shale	x	x	x	-	x	x	-	x	x	x	-	x	-	-
Garfield Shale	x	x	x	-	-	x	-	x	x	x	-	x	x	x
Waynesburg Coal	x	x	-	-	-	x	-	x	x	x	x	x	-	-
Graphite	-	-	-	x	-	-	-	-	-	-	-	-	-	x

Interfacial tensions and contact angles were quantified for a variety of representative DOE waste

compositions. No pH dependent interfacial tension behavior was observed for OA systems at low concentrations (Figure 2a). DDA, on the other hand, significantly lowered the interfacial tension at low pH due to the relatively large cationic concentrations present in the aqueous phase below the pKa. Mixtures of both OA and DDA also showed pH dependent interfacial tension behavior with a dip around neutral pH. Similar enhanced interfacial activity was also found for contact angle measurements in the mixed OA/DDA systems (Figure 2b). Individually, OA, in its neutral or anionic form, did not sorb onto negatively charged quartz surfaces and alter its wettability (Lord, 1999). In its cationic form, DDA sorbed onto the quartz surfaces rendering the solid surface less water-wet. The increasing oil-wetness, with increasing pH, was a result of the increasing negative charge on the quartz surface with increasing pH (Lord et al., 2000). Contact angle trends with pH for the mixed OA/DDA system were similar to that of the DDA system except around neutral pH. In this range the quartz surface became oil-wet for the mixed OA/DDA system (i.e., contact angle $> 90^\circ$). These results show that interfacial properties of a system containing both an organic acid and an organic base are pH dependent. Furthermore these results suggest a synergism around neutral pH (Hsu and Demond, 2004).

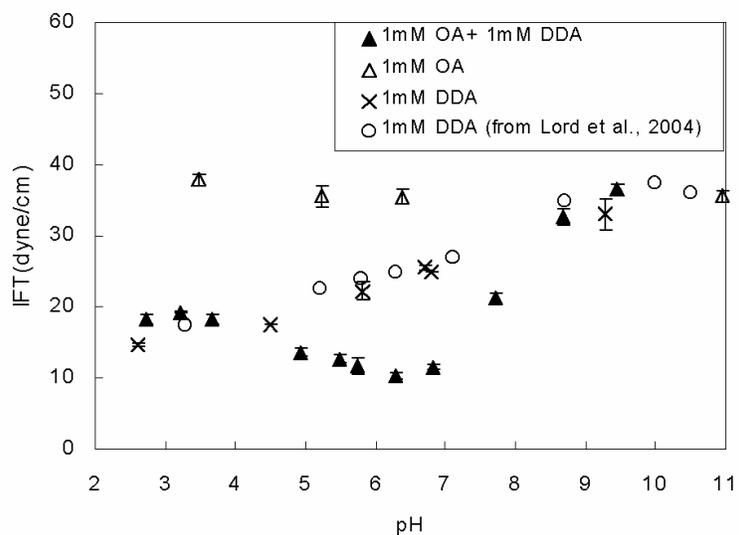


Figure 2a: Interfacial tension between PCE and aqueous solution initially containing $[OA]_T = 1\text{mM}$, $[DDA]_T = 1\text{mM}$ or both. The error bars represent 95% confidence intervals (Hsu and Demond, 2004).

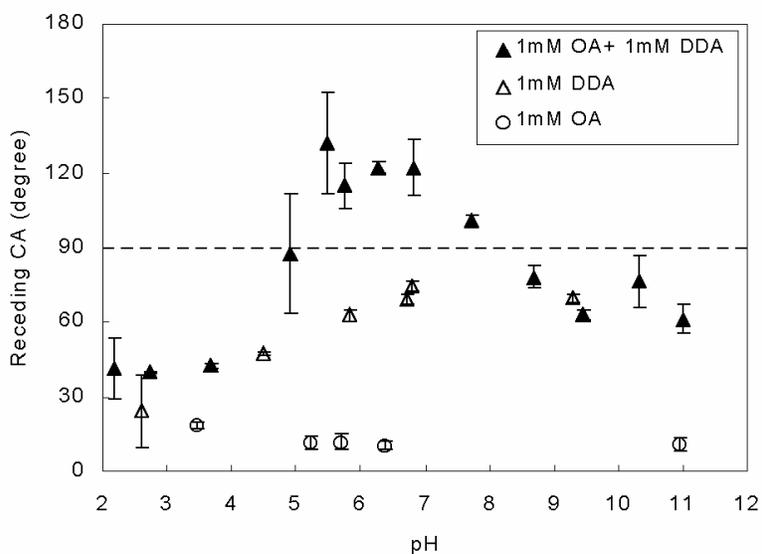


Figure 2b: Receding contact angle (measured through aqueous phase) of PCE on quartz in aqueous solution containing $[OA]_T = 1\text{mM}$, $[DDA]_T = 1\text{mM}$ or both. The dash line indicates a contact angle of 90° , above which the system is oil-wet. Error bars represent 95% confidence intervals (Hsu and Demond, ; 2004).

ii) *Assess predictive procedures to estimate interfacial properties for DOE wastes and soils.*

Methods:

Experimental determination of the contact angle is relatively time consuming and difficult. Alternative methods to quickly and accurately predict contact angles would facilitate the analysis of soil samples at DOE hazardous waste sites. Two wettability tests were compared to sessile drop contact angle measurements to assess their ability to quickly and accurately predict the interfacial properties of soils. The two tests selected were the bottle test (Dubey and Doe, 1993) and the molarity of an ethanol droplet (MED) test (King, 1981).

The prediction of waste mixture interfacial tension is also difficult. In this study waste mixture interfacial tensions were compared to those of the single solute systems to see if the interfacial behavior of the mixtures could be predicted by summing the contributions of the added constituents.

Results:

Bottle tests have proven useful for the estimation of contact angle when conditional wettability was not expected (Dubey and Doe, 1993). In this study bottle test results were consistent with contact angle measurements (Table 1), however, no information about the degree of wetting can be obtained from this method. The MED test was not a good predictor of contact angle. This is most likely due to the fact that particle size and shape, and hence pore sizes, are uncontrolled in the traditional field MED test whereas in this study a narrow grain size distribution was used. While it may be suitable for field purposes, where the objective of the MED test is to determine the wetting behavior of a soil in-situ, the MED value seems to be a poor indicator of the actual contact angle behavior.

These results also suggest that dependence of the contact angle on carbon content can not be assessed in the absence of the history of advancing and receding phases. All surfaces initially in contact with water remain water-wet after the addition of a second phase (cases 1 and 4). However, PCE is not displaced from the organic carbon containing surfaces if water is introduced as the advancing phase (case 3).

As discussed above, individually OA does not alter the interfacial tension or wettability of a quartz surface whereas the presence of DDA serves to decrease interfacial tension and reduce the water-wetness of the quartz surface. If there were no interactions between OA and DDA, a mixture of containing both constituents should behave similar to that of a system containing only DDA. The results presented in Figures 2a and 2b, however, show that the interfacial properties of the mixture exhibited enhanced interfacial activity, particularly in the neutral pH range. These results suggest the interfacial properties of the mixtures can not be predicted based on the constituents added. Interaction among the constituents must be taken into account in order to capture the synergistic effect in the mixed solute systems (Hsu and Demond, 2004).

iii) Deduce mechanisms of interfacial property alteration.

Methods:

Experimental results from the previous two sections were used to help deduce the mechanisms of interfacial property alteration. In addition, to further investigate the observed interfacial property synergism in the mixed OA and DDA systems titrations of aqueous phase OA and DDA were performed and distribution coefficients between PCE and water were measured.

Results:

As described above, even in the absence of surface active agents, the interfacial behavior of a surface may differ depending on the history of advancing and receding phase contact with the surface. Figures 3 and 4 further illustrate the magnitude of this hysteresis. It appears that a water film formed over the surface that cannot be displaced by the air bubble or PCE drop when water was the receding phase (case 2, Figure 3 and case 4, Figure 4). This may occur because the surface groups could dissociate and developed a charge when equilibrated in water. The slides were equilibrated at the isoelectric pH to minimize the electrostatic contribution to surface forces however the water film was persistent.

The expected behavior, increased non-aqueous wettability as carbon content increased and mineral content decreased, is clearly evident when the non-aqueous phase was the receding phase, as in cases 1 and 3. The natural soil materials were all wet by the non-aqueous phase when they contacted the solid first. One possible explanation for this behavior is that the PCE or air, which are a non-polar phases, prevented the development of surface charge and dissociated surface groups on the solid. A second possibility is that the PCE was physically sorbing into the microporous surface during equilibration so that the 'surface' presented to the water drop was actually a layer of PCE. Hydrophobic sorption would not be expected on the silica surface and silica remains water wet under all conditions.

For the enhanced interfacial activity of the mixed OA/DDA systems two postulated mechanisms were considered. These were the formation of a neutral surface active complex and the nonideal attractive interaction between the adsorbed cations and anions (also known as surface excess) at the interfaces. These mechanisms were examined by conducting speciation and surface excess simulations (Hsu and Demond, 2004). The speciation and distribution data suggest the formation of a neutral surface active complex in the mixed OA and DDA system. The speciation simulation showed that this neutral complex predominantly forms around neutral pH coinciding with the pH at which maximum interfacial tensions reductions and contact angles alterations were observed. The surface excess simulation showed the maximum nonideal attractive interaction, where the adsorbed cations equal anions at the water/PCE interfaces, is at pH 8.4. Since this pH is not in the range of the maximum enhanced interfacial activity it was concluded that the mechanism of the interfacial synergism in the mixed solute system is mainly attributed to the formation of the neutral complex formation (Hsu and Demond, 2004).

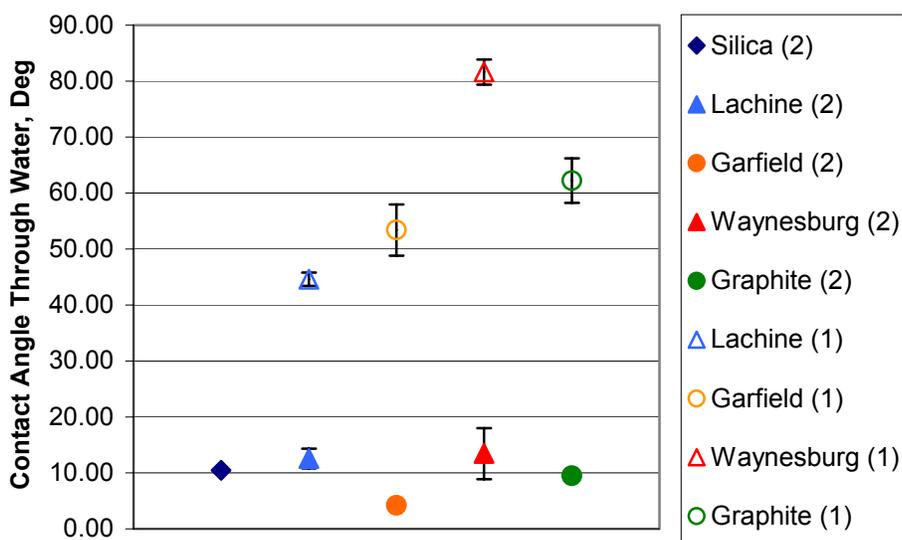


Figure 3: Air-Water contact angles at material isoelectric points

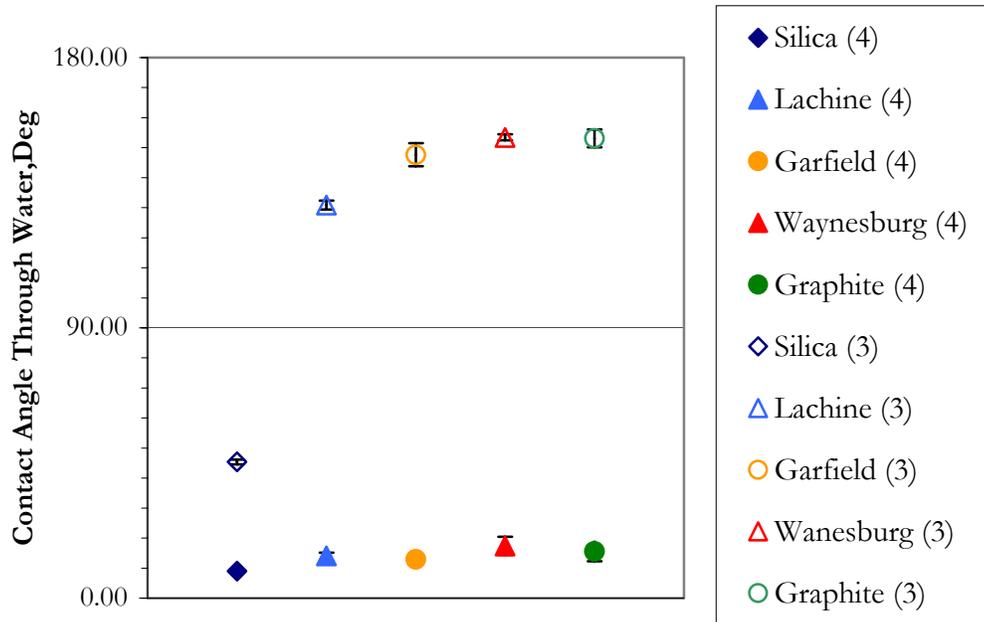


Figure 4: PCE-Water contact angles at material isoelectric points

iv) *Quantify the influence of waste and porous medium composition on hydraulic properties and residual saturation*

Methods:

Equilibrium capillary pressure/saturation and multistep outflow experiments were conducted to determine the effects of waste and porous medium properties on the interfacial and subsurface transport properties. The equilibrium capillary pressure/saturation experiments were undertaken in uniform wettability systems (either water, intermediate or organic-wet sands) and fractional wettability systems (mixtures of water and intermediate-wet sands or water and organic-wet sands) (O'Carroll et al., 2004b). Similarly the multistep outflow experiments were conducted with sands of varying wettability to produce data for the estimation of multiphase flow constitutive relationships using a multiphase flow parameter optimization routine (O'Carroll et al., 2004c). In these experiments the selected fluids were water and tetrachloroethene.

Results:

The results of drainage and imbibition PCE/water equilibrium capillary pressure/saturation experiments conducted for F35/F50/F70/F110 mixtures of water-wet and intermediate-wet sands are presented in Figures 5 and 6, respectively (O'Carroll et al., 2004b). Here the symbols represent measured data. Figure 5 reveals that, as the fraction of intermediate-wet sand increased, the drainage entry pressure decreased. The drainage capillary pressures were positive for all mixtures. The imbibition capillary pressures, however, had ranges of negative values for all but the water-wet sand (Figure 6). Thus, water spontaneously imbibes into the completely water-wet system but forced imbibition was required to completely displace the PCE in the fractional and intermediate-wet systems. Similar behavior was observed for equilibrium capillary pressure/saturation experiments conducted in the fractional water/organic-wet systems.

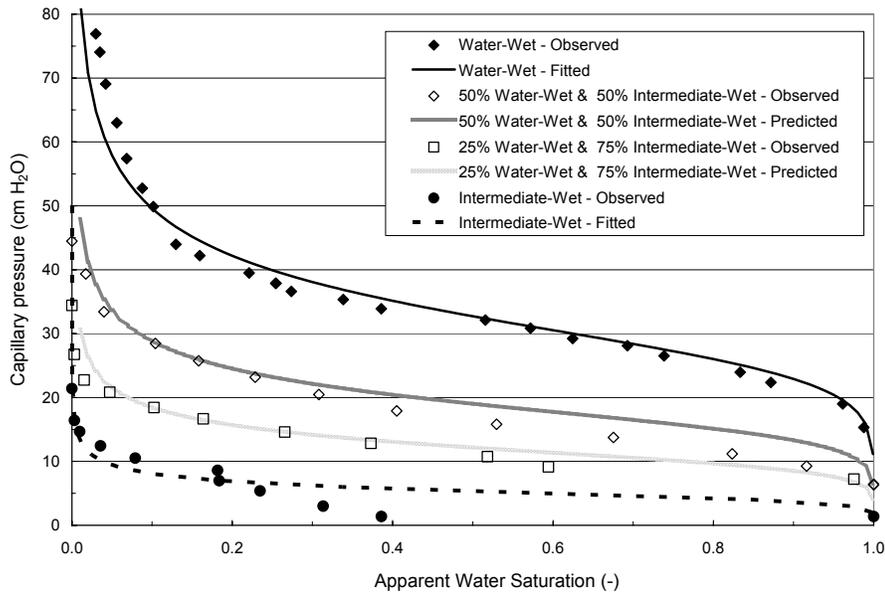


Figure 5: Observed, Fitted and Predicted Primary Water Drainage PCE/Water Capillary Pressure/Saturation Relations for Fractional Water and Intermediate-Wet F35/F50/F70/F110 Sand. Predicted curves were found using the Leverett-Cassie Equation (O'Carroll et al., 2004b).

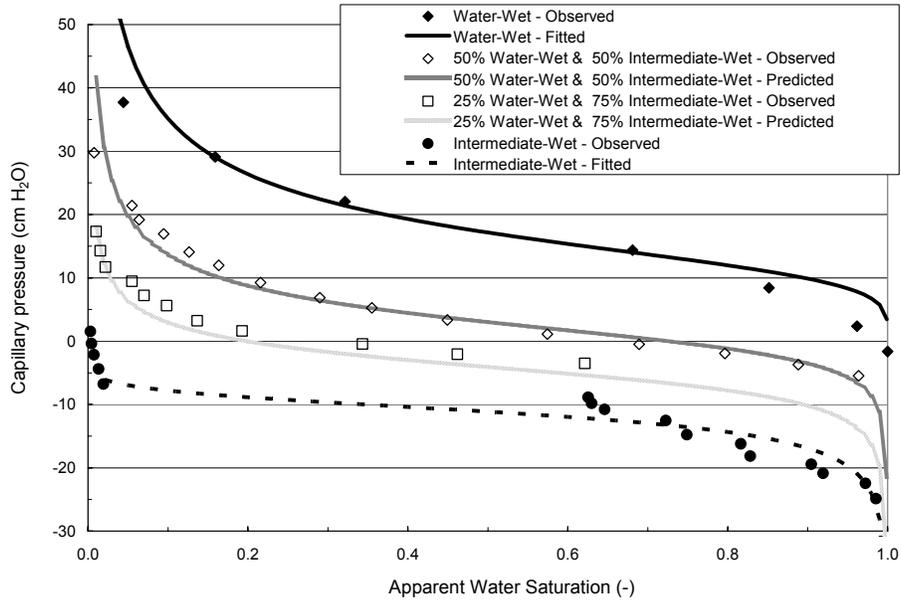


Figure 6: Observed, Fitted and Predicted Primary Water Imbibition PCE/Water Capillary Pressure/Saturation Relations for Fractional Water and Intermediate-Wet F35/F50/F70/F110 Sand. Predicted curves were found using the Leverett-Cassie Equation (O'Carroll et al., 2004b).

Results of a F35/F50/F70/F110 water-wet sand multistep outflow experiment are presented in Figure 7 (O'Carroll et al., 2004c). The observed water outflow (solid black line) rapidly increased following an increase in PCE phase boundary pressure and then gradually decreased. As water outflow decreased, the PCE phase boundary pressure was again increased. Observed water outflow did not decrease to zero prior to an increase in PCE phase boundary pressure.

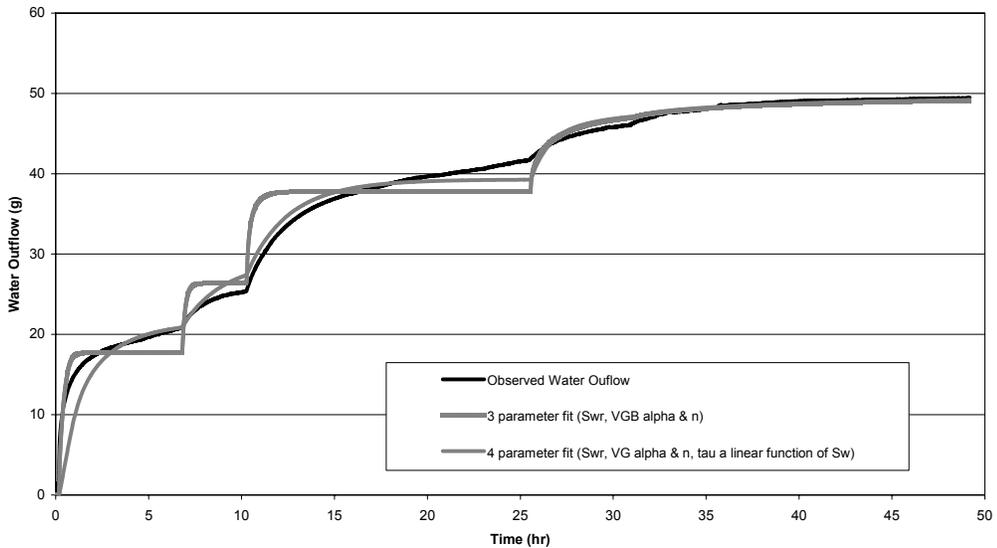


Figure 7: Comparison of Observed and Fitted Cumulative Water Outflow for F35/F50/F70/F110 Water-Wet Sand (O'Carroll et al., 2004c).

In this study systematic trends in residual water and organic saturations were not observed.

v) *Develop and assess constitutive hydraulic property and residual saturation models.*

Methods:

Experimental data from the equilibrium capillary pressure/saturation and multistep outflow experiments, presented in the previous section, were used to assess the ability of existing constitutive hydraulic property models to predict observed behavior.

Results:

Analyses of the equilibrium capillary pressure/saturation data found that existing models were unable to predict capillary pressure/saturation curves for the broad range of wettability conditions likely in the contaminated subsurface. As a result a new capillary pressure/saturation model, based upon the Leverett and Cassie equations (Leverett, 1941; Cassie, 1948), was developed to predict drainage and imbibition capillary pressure/saturation functions over this range (O'Carroll et al., 2004b). The Leverett-Cassie equation was partially validated by predicting the 50% water-wet / 50% intermediate-wet and the 25% water-wet / 75% intermediate-wet drainage and imbibition curves (Figures 5 and 6). The shape and general magnitude of the predicted curves are consistent with the water/intermediate fractional wettability experimental data (Figures 5 and 6). This Leverett-Cassie equation was also validated with data from a number of water/organic fractional wettability DNAPL/water experiments conducted in this research, as well as with data from two published studies (Bradford and Leij, 1995a; Ustohal et al., 1998). The Leverett-Cassie equation provided good representations of observed primary drainage and imbibition capillary pressure/saturation behavior. This model is easy to implement, with relatively few input parameters, and is applicable to a broad range of wetting conditions.

The van Genuchten/Burdine (VGB) constitutive model was used to fit observed cumulative outflow data, presented in the previous section, to explore the ability of a traditional parametric model to capture observed multistep outflow behavior. Examination of the fit generated using the VGB model (3 parameter fit – Figure 7) suggests that there are significant discrepancies between observed and simulated outflow data (O'Carroll et al., 2004c). In general the model fit tended to approach equilibrium at a rate faster than the experimental observations, reaching zero outflow more rapidly, with a different cumulative outflow plateau. Examination of published work suggests that discrepancies of this nature are common (Chen et al., 1999; Schultz et al., 1999; Hwang and Powers, 2003).

vi) *Explore the migration and entrapment behavior of model DNAPL wastes in spatially and temporally heterogeneous systems.*

Methods:

A PCE infiltration experiment was conducted in a "two-dimensional" sandbox to investigate and quantify the effect of spatial wettability variations on DNAPL migration and entrapment in saturated sands (O'Carroll et al., 2004a). The sandbox was packed with predominantly water-wet sand, in which two water-wet lenses, one organic-wet lens and one organic-wet layer were emplaced (Figure 8).

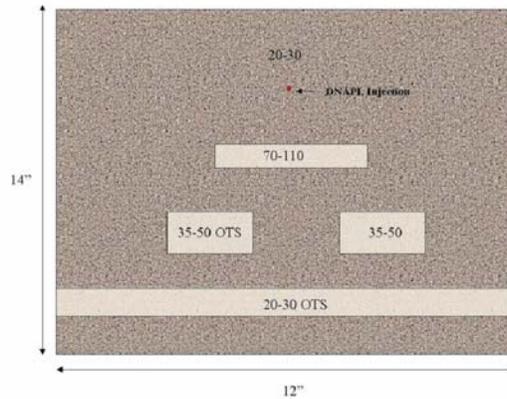


Figure 8: Schematic of sand tank used for flow and entrapment experiments (O'Carroll et al., 2004a).

Results:

Experimental observations of the PCE infiltration showed that organic-wet sand lenses acted as very effective capillary barriers, retaining PCE and inhibiting its downward migration (O'Carroll et al., 2004a). A multiphase numerical simulator was used to model this sand box experiment. The simulator incorporates wettability-modified van Genuchten and Brooks-Corey capillary pressure/saturation relationships as well as Burdine and Mualem relative permeability relationships. PCE mass distributions, estimated by image analysis of digital photographs taken during the infiltration event, were compared to simulation results. Comparison of estimated and simulated PCE saturations at elapsed time = 30 minutes are presented in Figure 9 (O'Carroll et al., 2004a). At 30 minutes, both Mualem simulations predicted PCE migration that was faster than the experimental observations. On the other hand, the van Genuchten/Burdine and Brooks-Corey/Burdine simulation results compare reasonably well with the experimental observations. Similar agreement between estimated and simulated PCE saturations was observed throughout this experiment. Although both relative permeability models were qualitatively able to predict the PCE retention in the organic-wet layers, simulations with the Mualem model generally failed to capture the observed rate of PCE migration. In addition a traditional multiphase simulator, incorporating water-wet capillary retention relations, failed to predict both PCE pathways and retention behavior. This study illustrates the potential influence of subsurface wettability variations on DNAPL migration and entrapment and supports the use of modified capillary relations in conjunction with the Burdine model in multiphase flow simulators (O'Carroll et al., 2004a).

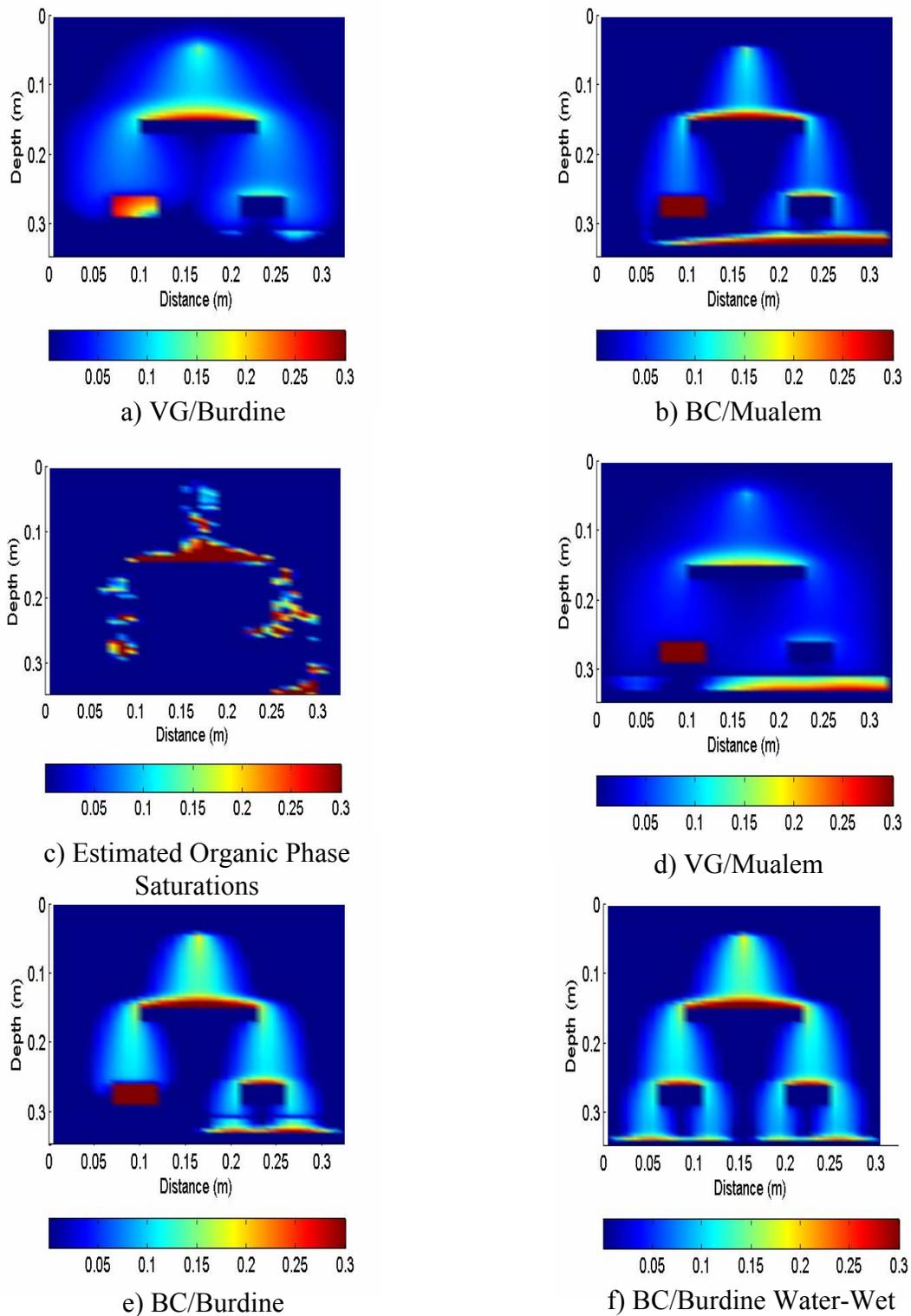


Figure 9: Two-Dimensional Infiltration Simulations and Estimated Organic Phase Saturations at elapsed time = 30 minutes (O’Carroll et al., 2004a)

- vii) *Development and validation a multiphase flow model to simulate the migration and entrapment of model DNAPL wastes in heterogeneous systems.*

Methods:

Experimental data from the multistep outflow experiments (presented above) were used in the development of a new multiphase flow model. As discussed above, multiphase flow models, incorporating traditional constitutive relationships, were unable to capture observed multistep outflow behavior. Differences in observed and fit cumulative outflow, such as those observed in this study, may be attributed to dynamic effects in capillary pressure that are not accounted for in traditional multiphase flow simulators (Schultz et al., 1999; Hassanizadeh et al., 2002). To explore if the inclusion of a dynamic capillary pressure term in the multiphase flow governing equations would improve the outflow fit, a new multiphase flow model was developed (O'Carroll et al., 2004c).

Additionally, a compositional flow and transport simulator was developed that is capable of predicting temporal and spatial evolution of aqueous phase and NAPL composition in the subsurface. This simulator incorporates the effect of spatial and temporal changes in waste composition and porous media composition on multiphase flow constitutive relationships (e.g., capillary pressure-saturation, relative permeability, and entrapment) as well as the kinetics of interphase mass transfer. This simulator was used extensively in the execution of objective 8.

Results:

Comparison of observed and fit cumulative water outflow for a F35/F50/F70/F110 water-wet sand is presented in [Figure 7](#) (O'Carroll et al., 2004c). The inclusion of dynamic effects in capillary pressure in the numerical simulator (4 parameter fit) resulted in significant improvements in the fit to observed cumulative water outflow when compared to the fit using a traditional constitutive relationship (3 parameter fit). Here the dynamic capillary pressure term was assumed to vary linearly with saturation. A number of other researchers have also speculated that the dynamic term may be a function of saturation (Kalaydjian, 1992; Hassanizadeh et al., 2002; Celia et al., 2004; Gielen et al., 2004; Manthey et al., 2004). Inclusion of the water saturation dependent dynamic term resulted in a 30% reduction in the RMSE when compared to the traditional three parameter fit (O'Carroll et al., 2004c). This study suggests that the inclusion of dynamic effects in capillary pressure in multiphase flow simulators will improve the predictive capabilities of these simulators.

- viii) *Investigate the up-scaling of findings from batch and soil column experiments to larger systems.*

Methods:

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. Additional numerical simulations were then performed to investigate the efficiency of pump-and-treat mass recovery from contaminated aquifers possessing these coupled spatial variations in textural and chemical properties. Previous authors (e.g. (Bradford et al., 1998; Bradford et al., 2000)) have suggested that variations in porous medium chemical properties could have an observable impact on entrapment and mass recovery behavior, although a comprehensive examination of the coupled effect of physical and textural heterogeneity had not been performed.

Results:

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 tended to increase maximum entrapped organic saturations and reduced depths of organic penetration and the degree of vertical spreading. Results also suggest that the presence of organic-wet solids may potentially mask the effects of textural heterogeneity variations. Simulations indicated that mass removal behavior (*i.e.*, the temporal evolution in aqueous phase contaminant concentration and flux) can be directly linked to DNAPL saturation architecture. Solid phase wettability was found to affect removal behavior by controlling the accessibility of the aqueous phase to the entrapped DNAPL; the impact of wettability on the kinetics of DNAPL dissolution was determined to be a secondary effect. Further, this suite of numerical simulations indicated that mass recovery behavior is highly realization specific. In contrast to flow and entrapment behavior, it is not possible to correlate mass recovery metrics to the global geostatistical parameters (Phelan et al., 2004).

RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER

Natural mineral surfaces display varying wettability characteristics. For example, shale and coal may be preferentially wetted by organics, whereas other aquifer materials, such as quartz and some carbonates, are water-wet. This work suggests that the origin of these wettability variations is quite complex and not simply related to one component of the elemental composition. Measurements of surface functional groups and the oxygen/carbon ratio have not yielded an observable relationship to the measured contact angle. It was also shown that the wetting order plays an important role in solid surface wettability.

Interfacial property experiments using waste mixtures representative of those found at DOE hazardous waste sites suggest enhanced interfacial activity due to the interaction of solutes present in the waste mixture. The observed interfacial activity was greater than that expected based on the contribution of the individual solute constituents. It was hypothesized that the interfacial synergism was due to the formation of a neutral complex.

Retention function data are often difficult and time consuming to measure, particularly for non-water-wetting soils. A simple predictive retention function model was, therefore, developed for the broad range of wettabilities that may be encountered in the contaminated subsurface. This model, based upon the Leverett and Cassie equations, was developed to predict drainage and imbibition retention functions in fractional water, intermediate and organic-wet systems. The Leverett-Cassie equation was validated with data from number of water/intermediate and water/organic fractional wettability DNAPL/water systems measured in this research, as well as data from two published studies.

Traditional steady-state experiments to measure constitutive relations governing two-phase (organic-aqueous) flow in the subsurface often extend over periods of weeks or months. Alternatively multistep outflow experiments can be combined with application of a multiphase flow simulator and an optimization algorithm to achieve a more rapid technique for parameter estimation. A sensitivity analysis for the multistep outflow experiments conducted in this research found that outflow predictions were very sensitive to the retention function, but fairly

insensitive to the selected relative permeability model. In addition simulation results, based upon traditional multiphase flow equations, failed to adequately fit observed outflow rates. To improve the outflow fit, the multiphase flow governing equations were modified to incorporate dynamic effects in capillary pressure. Inclusion of a saturation-dependent dynamic capillary pressure term significantly improved water outflow and outflow rate fits.

Larger scale experimental and simulation infiltration components of this research suggest that the organic-wet sands can act as very effective capillary barriers, retaining the DNAPL and inhibiting its downward migration. Simulations results also suggest that the source zone architecture is highly dependent on wettability and significantly affects mass removal rates.

PROJECT PRODUCTIVITY

A majority of the goals proposed for this project were accomplished with success. Significant inroads were made into developing a greater understanding of the effect of soil and aqueous phase chemistry on interfacial properties and, by extension, flow and transport parameters. The work detailed in the publication by *Hsu and Demond (2004)* explored the enhanced interfacial activity of an organic acid and base in organic-water systems. A new retention function model was developed for uniform and fractional wettability systems (O'Carroll et al., 2004b). Results from a series of multistep outflow experiments and subsequent simulations suggest that dynamic effects in capillary pressure should be considered when predicting multiphase flow (O'Carroll et al., 2004c). Sand tank experiments and multiphase flow simulator M-VALOR simulations demonstrated the remarkable effect of spatial wettability on the distribution of organic chemicals in the porous media (O'Carroll et al., 2004a). Finally larger scale simulations suggest that wettability has a significant impact on the migration, entrapment and subsequent remediation of organic liquids in the subsurface (Phelan et al., 2004).

To date, this research has resulted in the publication or submission of eight referred papers and sixteen conference presentations. It has supported the dissertation work of four PhD students and the training of three undergraduate assistants.

PERSONNEL SUPPORTED

Linda M. Abriola, Project Director
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PUBLICATIONS

- Abriola, L.M., A.H. Demond, D.M. O'Carroll, H. Hsu, T.J. Phelan, C.A. Polityka and J.L. Ryder, 2004. Compositional effects on interfacial properties in contaminated systems: Implications for organic liquid migration and recovery, American Chemical Society Monograph Series (in press).
- Hsu, H.L. and A.H. Demond, 2004. Influence of Organic Acid and Organic Base Interaction on Interfacial Tension and Wettability in Tetrachloroethylene-Water Systems. *Environ. Sci. Technol.* (submitted).
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INTERACTIONS

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- O'Carroll, D.M., L.M. Abriola, C.A. Polityka, S.A. Bradford and A.H. Demond, 2004. Prediction of two-phase capillary pressure-saturation relationships in fractional wettability systems, CGU-AGU-SEG-EEGS Joint Assembly, May 17-21, Montreal, QC.
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PATENTS

The project has not generated new inventions; in addition there are no patents pending.

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