COMPOSITIONAL EFFECTS ON INTERFACIAL PROPERTIES IN CONTAMINATED SYSTEMS: IMPLICATIONS FOR ORGANIC LIQUID MIGRATION AND RECOVERY

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Introduction

An understanding of the transport behavior of dense non-aqueous phase organic liquids (DNAPLs) is a prerequisite for the accurate assessment of chemical exposure and the design of effective subsurface remediation strategies. Evidence suggests that subsurface chemical heterogeneity, attributed to spatial and/or temporal variations in aqueous phase chemistry, mineralogy, and organic matter, as well as contaminant aging, is common at many sites. 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 chemically heterogeneous systems has not been adequately investigated, and multiphase flow simulators typically assume that subsurface soils are completely water wet and chemically homogeneous. This paper highlights efforts of an ongoing research project designed to explore the influence of solid and organic phase composition on DNAPL migration, entrapment, and recovery from contaminated aquifers. The integrated research program includes small-scale laboratory investigations, to examine the dependence of organic contaminant constitutive relationships on interfacial properties, larger "bench scale" experiments to validate proposed constitutive models, and numerical simulations to assess the impact of these phenomena at the field scale.

Small-scale laboratory investigations

Interfacial properties of DNAPL/water systems containing surface-active acids and bases

One component of this research is designed to investigate the influence of organic acids and bases on the interfacial behavior of organic wastes. Figure 1 compares equilibrium interfacial tension and contact angle measurements for various chlorinated solvent (tetrachloroethene (PCE))/aqueous systems containing dodecylamine (DDA) and octanoic acid (OA). Here interfacial tension was measured via a spinning drop tensiometer and contact angles were obtained using axisymmetric drop shape analysis on quartz slides. Notice that the presence of OA (10^{-3} M) alone does not alter the wettability or interfacial tension of the system. Conversely, in the presence of DDA (10^{-3} M) both the interfacial tension and contact angle are observed to decrease with decreasing pH. This behavior is attributed to the larger extent of DDA partitioning into the aqueous phase. As pH increases, the surface charge of the quartz becomes increasingly negative and can, consequently, adsorb more positively charged ammonium ions, increasing the contact angle. When both OA and DDA are present, enhanced interfacial activity is observed. This synergistic effect is pH dependent; at both ends of the pH spectrum, contact angle and interfacial tension behave as if only DDA was present. The synergistic effect can be attributed to the formation of a neutral surface-active complex, composed of carboxylate $RCOO^-$ and ammonium RNH_3^+, at neutral pH.

These results suggest that the surface activity of mixed organic wastes may not be predictable from the superposition of activity observed in the presence of individual waste components. Since both organic acids and organic bases often co-exist in waste mixtures, the mechanisms explored here can help us understand and predict the interfacial behavior of such wastes.

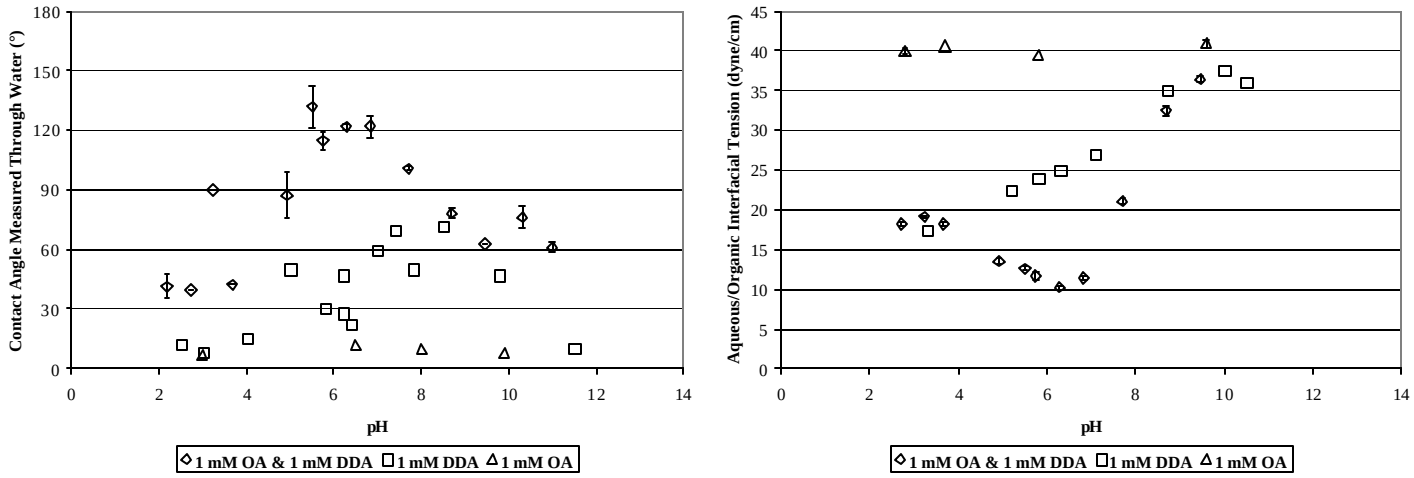

Figure 1 – Interfacial tension and contact angle as a function of pH for several organic acid & base combinations.

The effect of aquifer material wettability on interfacial properties

A range of laboratory experiments has been undertaken to examine the effect of aquifer material wettability on capillary relations. Bottle tests were performed and capillary pressure-saturation curves [1] were obtained for a range of natural and synthetic aquifer materials to provide qualitative and quantitative measures of solid phase wettability. Synthetic aquifer materials included Ottawa sands coated with octadecyltrichlorosilane (OTS), Rhodorsil Siliconate 51T (a potassium methylsiliconate solution), and a commercially prepared humic material similar to those found in natural soils. The OTS sands were strongly organic-wetting; with contact angles approaching 165° while the siliconate-coated sands were more intermediate-wetting with contact angles around 76.8°. Natural aquifer materials included a young humic coated sand, denoted Ann Arbor II, and an Upper Devonian kerogen containing shale known as Lachine shale.

Figure 2 shows representative scaled capillary pressure-saturation curves for the natural and synthetic intermediate-wet systems. These data suggest that Leverett scaling is an effective tool for predicting these relationships. More important, however, is the conclusion that these coatings do not appear to be able to produce non-water-wetting conditions (which would be evidenced here by negative capillary pressures). This result is consistent with bottle point tests conducted when water is the first wetting phase the solid surface contacts. Bottle point tests suggest that when the organic phase is the initial wetting phase, a wetting reversal may be possible in the capillary pressure-saturation relationship. In a natural setting, this particular wetting history can be envisioned in both the unsaturated zone or in a system where significant contaminant aging has occurred. Further investigations are ongoing to increase understanding of this behavior.

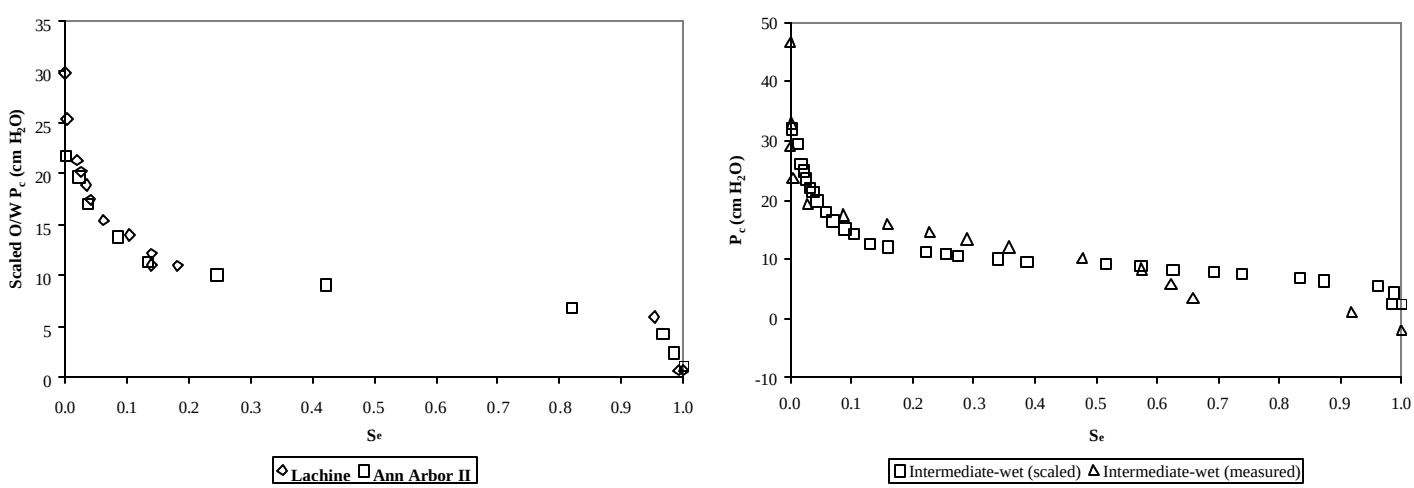

Figure 2 – Capillary pressure-saturation curves for various natural and synthetic intermediate-wet aquifer materials.

Bench-scale investigations exploring the effect of solid phase wettability on organic liquid migration and entrapment

Recent investigations have explored the infiltration and entrapment behavior of DNAPLs in larger, "bench-scale" systems which incorporate both textural and chemical heterogeneity (*i.e.*, wettability). PCE infiltration experiments were conducted in a "two-dimensional" sandbox, 1.7 cm thick [2]. The box was constructed with aluminum back and sidewalls as well as a tempered glass front, facilitating visual observation of PCE migration, and incorporated three sand layers of different textures and wetting properties (Figure 3). A known volume of PCE (47.33 ml) was injected with a syringe pump (Harvard Apparatus, South Natick, MA, 01760) for a 66.6-minute period at a constant rate (0.71ml/min). The injection location was at the midpoint between the glass and the aluminum backing, 28.7 cm above the aluminum base.

The digital photograph of the distribution of PCE at the conclusion of the injection period is shown in Figure 4. Of note in this photograph is the spontaneous imbibition behavior observed in the strongly organic-wet lenses and layers. These layers adsorb and retain the DNAPL, acting as a capillary barrier to effectively inhibit further migration.

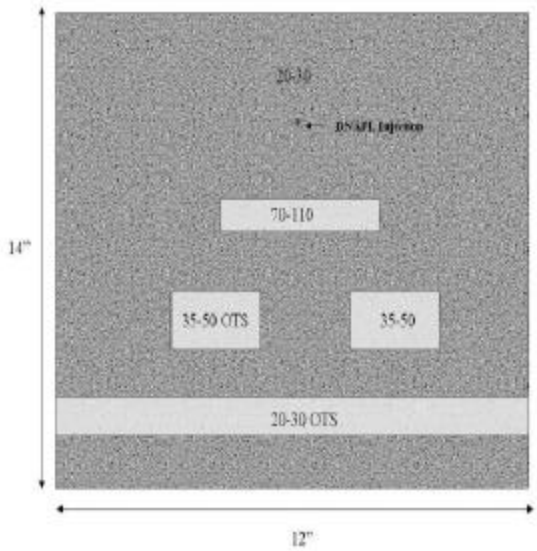

Figure 3 – Schematic for sandbox infiltration experiments

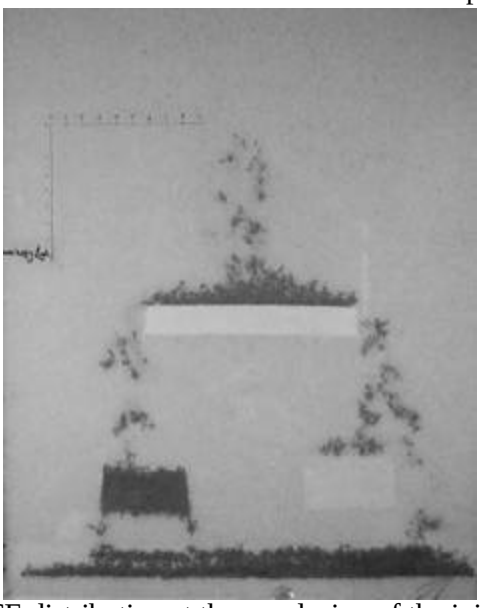

Figure 4 – PCE distribution at the conclusion of the injection period.

Field-scale simulation of the coupled effect of spatial textural and chemical heterogeneity on DNAPL migration and entrapment

Numerical investigations are being undertaken to examine the potential influence of coupled textural and chemical heterogeneity on predictions of DNAPL migration and entrapment at the field scale. The effect of textural (*i.e.*, permeability) heterogeneity on field scale migration and entrapment is well understood, but the potential effect of chemical heterogeneity (*i.e.*, solid phase wettability) on these predictions is not.

The predictive constitutive capillary model of Bradford et al. [3] was incorporated into a multiphase flow simulator which solves the full multiphase mass balance equations for mobile aqueous and organic phases. A suite of simulations was then conducted to examine the influence of different permeability/wettability correlations and different levels of textural heterogeneity on organic phase entrapment and dissolution. Here, PCE was injected into a 10 m × 5 m domain and allowed to redistribute. Selected metrics used to quantify the effect of these coupled phenomena include 1) depth of organic penetration and 2) degree of lateral spreading. Results for representative simulations are presented in Figure 5.

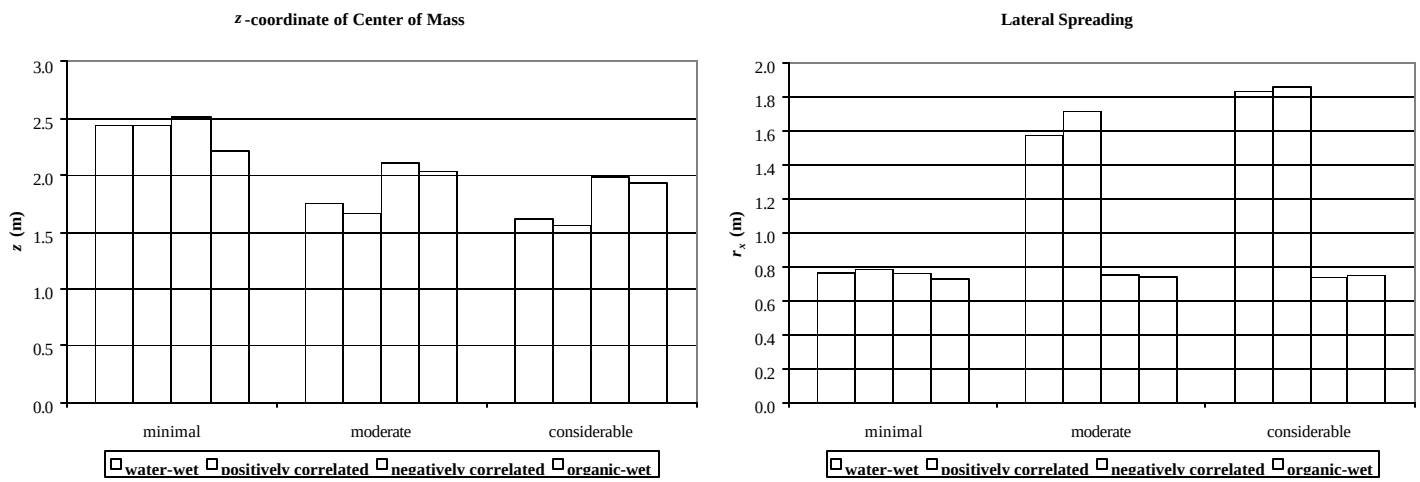

Figure 5 – Depth and penetration and lateral spreading (radius of gyration) metrics for various textural and chemical heterogeneity correlations.

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. Interestingly, when considering the depth of penetration and lateral spreading metrics, it appears that systems that have their organic-wet mass fraction associated with the high permeability zones (positive correlation) behave similarly to those that are completely water-wet. Conversely, systems that have the organic-wet mass fraction associated with the low permeability zones (negative correlation) behave similarly to completely organic-wet systems [4]. Further studies are ongoing to investigate these observations more thoroughly.

Acknowledgements

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