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Time-Dependent Interfacial Properties and DNAPL Mobility

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Abstract

Interfacial properties play a major role in governing where and how dense nonaqueous phase liquids (DNAPLs) move in the subsurface. Interfacial tension and contact angle measurements were obtained for a simple, single component DNAPL (tetrachloroethene, PCE), complex laboratory DNAPLs (PCE + Sudan IV dye), and a field DNAPL from the Savannah River Site (SRS) M-Area DNAPL (PCE, trichloroethene [TCE], and machining oils). Interfacial properties for complex DNAPLs were time-dependent, a phenomenon not observed for PCE alone. Drainage capillary pressure-saturation curves are strongly influenced by interfacial properties. Therefore time-dependence will alter the nature of DNAPL migration and penetration. Results indicate that the time-dependence of PCE with relatively high Sudan IV dye concentrations is comparable to that of the field DNAPL. Previous DNAPL mobility experiments in which the DNAPL was dyed should be reviewed to determine whether time-dependent properties influenced the results. Dyes appear to make DNAPL more complex, and therefore a more realistic analog for field DNAPLs than single component DNAPLs.

Introduction

Subsurface dense non-aqueous phase liquids (DNAPLs) pose a major environmental problem for the Savannah River Site (SRS) and other government and industrial sites. Understanding DNAPL behavior in porous media is important for designing DNAPL detection and remediation strategies. Interfacial properties play a major governing role in subsurface DNAPL movement. These properties are generally treated as static, either explicitly in pore-scale models or implicitly in continuum models. This is sufficient for single component DNAPLs. The complex chemical mixtures of real field DNAPLs, on the other hand, are likely to have time-dependent interfacial properties. My objectives are to illustrate time-dependent interfacial properties for a dye commonly used to stain DNAPLs in lab and field experiments and provide an example of how that time-dependence may be important in multiphase flow.

Theory

Most lab and field experiments are conducted using a single major DNAPL component with hydrophobic dye to make it visible. The most commonly used dyes, oil-red-O and Sudan IV, are chemically similar (Tuck and Rulison, *Azo Dyes and their surface chemistry: Implications for Multiphase flow experiments*, submitted to *Ground Water*, 1999). Dyes can be surface active, since they frequently have polar functional groups. Field DNAPLs are generally complex chemical mixtures, often having more than one major component and numerous minor components, some of which are likely to be surface active.

Pore Entry Pressure

Stability limits of a DNAPL lens trapped in a coarse, permeable unit at the contact with a fine-grained capillary barrier can be quantified using Hobson's equation [*Hobson and Tiratsoo*, 1975]

$$L_{\max} = \frac{2\gamma_{nw} \cos\theta}{\Delta\rho g r_{\text{eff}}} \quad (1)$$

where L_{\max} is maximum stable DNAPL lens height before a critical pore entry pressure is exceeded (cm), γ_{nw} is DNAPL-water interfacial tension (mN/m), θ is the fluid-fluid interface-solid surface contact angle (degrees), r_{eff} is an "effective" pore throat radius (cm), $\Delta\rho$ is the fluid density difference (g/cm^3), and g is acceleration of gravity (980 cm/sec^2). An analogous equation gives the entry pressure for a crack or fracture in a capillary barrier or rock, with effective pore throat radius replaced by the fracture aperture [*Kueper and McWhorter*, 1991]. Thus pore (or fracture) entry pressure depends on two interfacial properties, interfacial tension and contact angle.

Multicomponent solutions often exhibit time-dependent interfacial properties [*Ward and Tordai*, 1944]. Substituting time-dependent relationships for γ_{nw} and θ yields the following equation for the gravitationally stable vertical DNAPL height before a critical capillary pore entry pressure is exceeded.

$$L_{\max} = \frac{2\gamma_{nw}(t) \cos[\theta(t)]}{\Delta\rho g r_{\text{eff}}} \quad (2)$$

where $\gamma_{nw}(t)$ and $\theta(t)$ are the time-dependent IFT and contact angle functions, respectively.

Capillary Pressure-Saturation

The capillary pressure-saturation relationship is a fundamental constitutive property required for continuum DNAPL modeling in porous media. This relationship is, at least in part, a pore-throat size distribution measurement since pore throats control whether or not DNAPL at a given capillary pressure can enter a pore. Rearranging equation 1, placing effective pore radius on the left side shows that a given capillary pressure determines which pore throats the DNAPL can penetrate. Thus time-dependent IFT and/or contact angle implies a time-dependent capillary pressure-saturation relationship.

A characteristic average pore-throat interface age during primary drainage can be estimated if we make several assumptions. First, DNAPL-front penetration rates are controlled by pore-throat capillary forces as well as the applied capillary pressure or gravitational head. Second, the DNAPL front moves by a series of "Haines jumps", that is the time required for DNAPL-water interfaces to move through pore bodies is negligible compared to the time interfaces are held in pore throats. Third, there is an average geometrical arrangement of grains, and therefore pores. And fourth, there exists a reasonable average grain size and therefore pore size. For the sake of simplicity, we assume cubic packing of uniform grains, which means average pore size is equal to median grain size and pore-to-pore flow paths are all either vertical or horizontal. The following equation may now be derived for the average pore-throat interface age along a drainage front.

$$t_c = \frac{d_{50}}{V_{front}} \quad (3)$$

where τ_c is the characteristic average pore-throat interface age at the penetrating front, d_{50} is the median grain size, and V_{front} is the average vertical DNAPL-front penetration rate.

Materials and Methods

Solutions and Interfacial Properties.

Sudan IV was used as received from Sigma. All PCE solutions were prepared using "Tetrachloroethylene 99%" as received from Mallinckrodt Inc. Dyed PCE solutions were prepared by dissolving 0.508 g of dye in 100 mL of PCE and making dilutions from this stock. A Savannah River Site (SRS) M-Area DNAPL sample and associated aqueous colloidal emulsion was obtained from well MSB-3D in June 1994. The M-Area DNAPL composition is approximately 95% PCE and 5% TCE (trichloroethylene) [Looney, *et al.*, 1992]. M-Area DNAPL was transferred to 40 mL vials. Deionized water (DIW) was added to some vials, and ground water (GW) collected with the DNAPL was added to the others.

Dynamic DNAPL-water interfacial tension (IFT) was measured with a Krüss Drop Volume Tensiometer (model DVT10) as a function of DNAPL flow rate from a precision syringe pump

into the water phase through an alumina tip. Drop volumes were determined by pump rate and length of time between successive drops. IFT was computed with the drop volume equation [Tate, 1864]. Contact angles were measured using a Krüss Goniometer (model G10). A drop of each DNAPL was placed on a glass slide submerged in pre-equilibrated water. Contact angle was measured through the DNAPL, with the supplement giving the angle required for equations (1) and (2).

Drainage Front Velocity

Average drainage front velocities for dyed-trichloroethylene (TCE) were estimated from three large-diameter column experiments presented by [Schwille, 1988]. Oil-red-O dye concentration was given as 1 to 2 g/L. Each experiment was run with a different sand-size porous media. Average grain diameters were taken to be the median size obtained from grain-size distributions. TCE break-through times were given for two columns, and TCE penetration depth and time were given for the third. Average front velocities were calculated as the distance covered divided by the time.

Time-Dependence of Capillary Pore Entry Pressure

Experiments were conducted using two different Sudan IV-dyed PCE solutions, 0.5 and 0.005 g/L. The latter solution has much lower interfacial property effects. The porous medium for each experiment consisted of very fine sand sized glass beads. Pore entry pressure for this medium, at a dye concentration of 0.5 g/L over a relatively short time (less than 5 hours), was determined to be approximately 15 cm of PCE [Tuck, et al., 1996]. A 12 cm PCE depth was set on each water saturated medium. The experiments ran for approximately 30 days.

Results

Time-Dependence of Interfacial Properties

Contact angle and interfacial tension (IFT) time-dependence is illustrated in Figure 1. In all cases, the contact angle changes represent decreasing water-wet conditions with time. The rate of change for undyed PCE is very small. The rate of change generally increases with increasing DNAPL complexity, both as a function of dye concentration and the number of components (compare results for SRS DNAPL with dyed PCE). Rates are approximately log linear with time. In all cases the IFT decreases with interface age, also in an approximately log-linear fashion. The rate and magnitude of contact angle change also depend on DNAPL complexity. Log-linear regression equations for contact angle and PCE-water interfacial tension for the 0.508 g/L Sudan IV-dyed PCE are

$$\theta = 17.335 + 7.3150 \cdot \log[\text{time}(\text{sec})] \quad r^2 = 0.987 \quad (4)$$

$$\gamma_{\text{nw}} = 48.610 - 3.6390 \cdot \log[\text{time}(\text{sec})] \quad r^2 = 0.991 \quad (5)$$

Similar equations were generated for the other DNAPLs. Equations 4 and 5 were substituted in equation (2) along with a r_{eff} value of 0.002 cm (medium silt). Resulting time-dependence curves for capillary barrier pore entry pressure as an equivalent PCE height, are shown in Figure 2.

Comparison of dyed PCE interfacial property results with results obtained for the SRS DNAPL indicate that typical Sudan IV dye concentrations (1 to 2 g/L) would be expected to make dyed-PCE behavior similar to SRS DNAPL behavior (see Figure 1).

Time-Dependent Pore Entry Pressure

Effect of time-dependent interfacial properties on DNAPL penetration of a capillary barrier was demonstrated with glass bead experiments. The 0.005 g/L dyed PCE contact remained razor sharp throughout the experiment which lasted more than 30 days. The 0.5 g/L solution, however, penetrated 3 to 4 mm into the capillary barrier after a period of approximately six days. PCE saturation in this region appeared to increase slowly during the remainder of the experiment.

Characteristic Average Interface Age

The best estimator for average TCE front velocity as a function of hydraulic conductivity for the model sands used by [Schwille, 1988] was found to be

$$V_{\text{front}} = 0.321 * K - 0.270 * K^2 \quad r^2 = 0.995 \quad (6)$$

where K is the medium's hydraulic conductivity. A beach deposit model for estimating hydraulic conductivity from median grain diameter [Shepherd, 1989] gave the best hydraulic conductivity predictions for Schwille's model sands. Front velocity values were all too high when calculated using equation 6 with Shepherd's beach deposit model for K. Corrections were made using the following equation to predict the actual-front-velocity:estimated-front-velocity ratio (V_{ratio}).

$$\log(V_{\text{ratio}}) = 2.523 + 2.174 * \log(d_{50}) \quad (7)$$

A $V_{\text{front}} * V_{\text{ratio}}$ product should yield reasonable drainage front velocity estimates for media grain sizes somewhat smaller than those of Schwille. Characteristic average interface ages of draining dyed-TCE fronts were estimated from the extrapolated data of Schwille using equation 3. Assuming PCE would behave in a comparable fashion, average interface age can be used to calculate appropriate IFT values governing primary drainage as a function of median grain size. Figure 3 contains the average pore throat ages and corresponding IFT for 0.5 g/L dyed-PCE.

It is important to note this analysis is only a crude first approximation. Average front velocity will be a complex function of excess capillary pressure above average pore entry pressure for the medium, resulting DNAPL penetration rate, and the time-dependent interfacial properties. Capillary pressure in Schwille's experiments was not controlled nor evaluated in any way. The analysis here is only presented to demonstrate that time-dependent interfacial properties are likely to be important for accurate prediction of DNAPL behavior during primary drainage.

Conclusions

Time dependence of interfacial properties is an important variable in complex DNAPLs. Changing IFT and contact angles can lead to significantly different behavior with respect to penetration of capillary barriers. In general, a capillary barrier becomes less "competent" as a barrier with time. Time-dependence of interfacial properties is also likely to effect the capillary pressure-saturation relationship for a given unit. It will cause the relationship to be a complex

function of excess capillary pressure above the average pore entry pressure for the unit, the resulting penetration rate of the DNAPL front, and the time-dependence of the interfacial tension and contact angle. The stable depth to which DNAPL can accumulate in a lense shape in a coarser unit overlying a capillary barrier will also decrease with time. This effect might cancel the decreased entry pressure into a capillary barrier under some conditions, since the DNAPL is likely to thin more quickly than the rate of capillary barrier entry pressure decreases. This will be true of horizontal or sloped capillary barrier surfaces, but not for a "bowl" shaped surface. Sudan IV dye concentrations commonly used in experimental work (1 to 2 g/L) appear to make PCE mimic SRS DNAPL reasonably well. The dye is thus a reasonable analog for the complex chemistry of real DNAPLs. The properties and behavior introduced by this complexity, however, have not, to date, been accounted for by multiphase flow models or when interpreting experimental results. I currently believe that as a DNAPL interface advances into a "new" pore that the time clock for IFT and contact angle must be restarted, and it is this restarting which controls how DNAPLs migrate, particularly at relatively low hydrostatic capillary pressures.

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References

- Hobson, G. D. and E. N. Tiratsoo, *Introduction to Petroleum Geology*, Scientific Press, Ltd., Beaconsfield, England, 1975.
- Kueper, B. H. and D. B. McWhorter, The behavior of dense, nonaqueous phase liquids in fractured clay and rock, *Ground Water*, 29(5), 716-728, 1991.
- Looney, B. B., J. Rossabi, D. M. Tuck, J. E. Jordan, C. L. Bergren, R. Van Pelt, W. E. Jones, A. E. Stevenson and B. S. Kristiansen, *Assessing DNAPL Contamination, A/M-Area, Savannah River Site: Phase I Results*, WSRC-RP-92-1302, Westinghouse Savannah River Company, Aiken, SC, December 1992.
- Schwille, F., *Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments*, 146 pp., Lewis Publishers, Inc., Chelsea, MI, 1988.
- Shepherd, R. G., Correlations of permeability and grain size, *Ground Water*, 27(5), 633-638, 1989.
- Tate, T., On the magnitude of a drop of liquid formed under different circumstances, *Philosophical Magazine*, 27, 176-180, 1864.
- Tuck, D. M., G. M. Iversen and W. A. Pirkle, Complex Organic Co-contaminant Effects on DNAPL Mobility in Saturated Porous Media, *Eos*, 77(46), F257, 1996.
- Ward, A. F. H. and L. Tordai, Existence of time-dependence for interfacial tension of solutions, *Nature*, 154, 146-147, 1944.

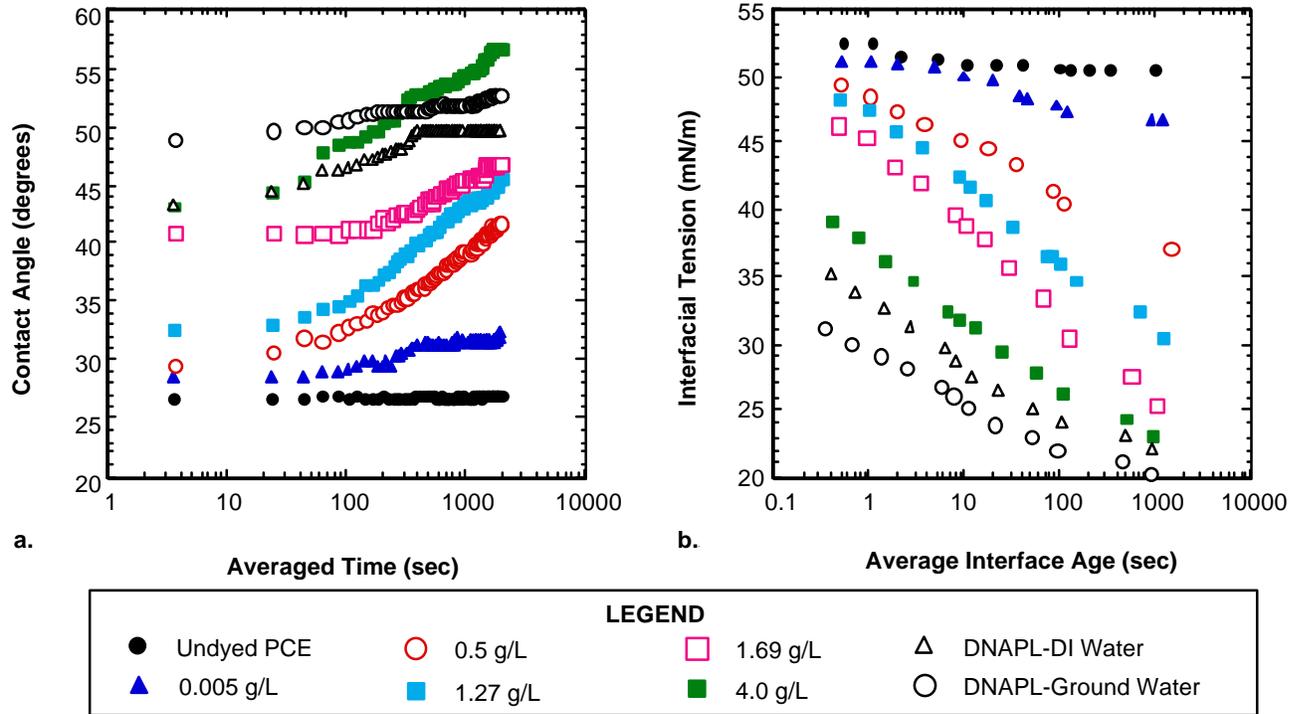


Figure 1. Time-dependent interfacial properties. a. Contact angles between PCE (or DNAPL), water, and glass. b. Interfacial tension between PCE (or DNAPL) and water.

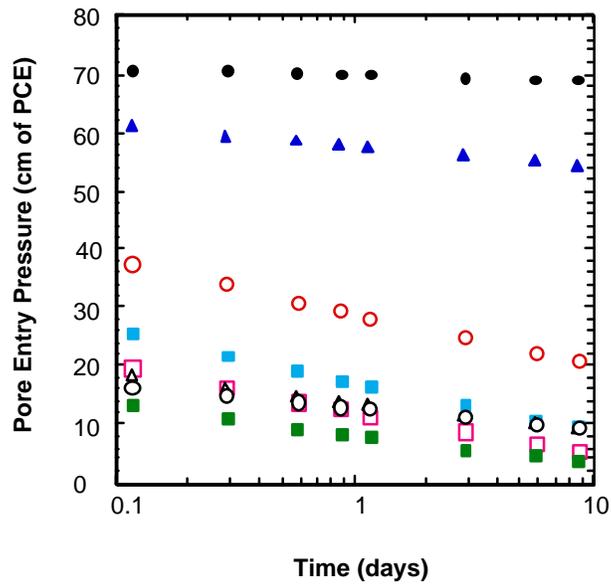


Figure 2. Time-dependence of pore entry pressure into a homogeneous medium silt capillary barrier. ($r_{eff} = 0.002$ cm, See Figure 1 for legend)

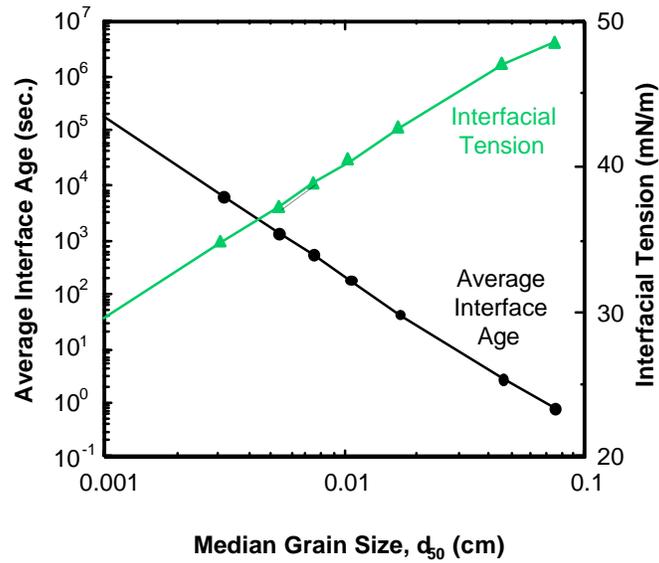


Figure 3. Characteristic average interfacial age and corresponding interfacial tension extrapolated from data in Schuille (1988) as a function of grain size.