Retention and Permeability of Multi-Fluid Soil Systems

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Summary

Predicting the movement of a nonaqueous phase liquid (NAPL) in the vadose zone requires that the retentive and conductive properties of the soil be known for the aqueous, nonaqueous, and gaseous phases. Theories for the prediction and modeling of capillary pressure (Pc) - saturation (S) relationships for three-fluid porous media from two-fluid porous media are generally based on the limiting assumptions that the medium (solid) is strongly wetted by one fluid and that the intermediate wetting fluid forms a continuous layer between the wetting and nonwetting fluids. During the first year of this project, two- and three-fluid Pc-S relations were measured with an automated setup for samples of blasting sands containing: (i) air and water; (ii) air and oil; (iii) oil and water; and (iv) air, oil, and water. The blasting sands were treated with organosilane compounds to obtain various degrees of hydrophobicity. Mixed wettability media were made up from different fractions of untreated and treated sands. We found a substantial difference between measured and predicted (from scaling and Leverett's assumption) Pc-S curves for hydrophobic and mixed wettability media containing oil-water or air-oil-water. The model for predicting Pc-S curves of oil-water and hydrophilic air-oil-water media was improved successfully.

Key Words: hydraulic properties, capillary pressure, NAPL, wettability, Leverett's assumption, hysteresis.

Project Objectives Addressed in 1993-94

The general objective of this project is to measure and model the hydraulic functions of multi-fluid porous media containing NAPLs. The activities in this first year consisted of the measurement, modeling, and prediction of $P_r-S$ relations for two- and three-fluid soil systems with different wettabilities. In the second year these results will be analyzed further and the permeability of two- and three-fluid media will be investigated.

Research Plan and Procedures

Capillary Pressure

The capillary pressure is the pressure drop over the curved interface between the nonwetting and wetting fluids. In air-liquid systems the liquid (l), either oil or water, is the wetting fluid and air (a) is the nonwetting fluid. The air-liquid capillary pressure, $P_{ac}=P_a-P_c$, is always positive. In a two-fluid system with uniform wettability, either water (w) or oil (o) wets the solid; the other liquid is the nonwetting fluid. The capillary pressure is defined as $P_{ac}=P_a-P_w$ for a water-wet system and $P_{ac}=P_o-P_w$ for an oil-wet system. The definition is less clear for mixed wettability systems. Throughout this report we use $P_{ac}=P_{sw}$ and write $P_c$ as a function of the water saturation, $S_w^m$ (the subscript pertains to the volume of a particular fluid per unit pore volume and the superscript denotes all fluids present).

Measurement of Two- and Three-Fluid $P_r-S$ Relations

Two- and three-fluid $P_r-S$ relations were obtained with an automated setup by displacing a known quantity of fluid into or from a soil column (cf. Fig. 1). The column consisted of hydrophobic and hydrophilic ring tensiometers. For fluid systems involving air, the top of the column was allowed to remain open so air was at atmospheric pressure. A data logger controlled stepping motors and solenoid valves, and also registered pressure transducer readings (Fig. 2). The stepping motors adjusted vacuum-pressure regulators, connected to burets filled with water or oil through solenoid valves. The valves were open for establishing a new liquid saturation in the column or closed for achieving an equilibrium fluid distribution. Liquid pressures and saturations were measured with ring tensiometers and burets, respectively, connected to a pressure transducer.

Fluid and Media Properties

For all $P_r-S$ measurements, a column of known volume was filled with the initial wetting fluid and packed with a predetermined mass of a blasting sand mixture to obtain a dry bulk density ($\rho_d$) of 1.71 g/cm³. The porous medium was a mixture of blasting sands containing 12.6 % each of sizes #12 and #16, 25.2 % each of sizes #20 and #30, and 5.2 % each of sizes #60, #70, and #90. This distribution corresponds to 25% very coarse sand, 50% coarse/medium
sand, and 25% fine sand according to the USDA textural classification (Soil Survey Staff, 1975). The initial volume of the wetting fluid was considered to be equal to the product of the column volume and porosity; the latter was calculated assuming a specific density of 2.65 g/cm$^3$ (Danielson and Sutherland, 1986). Oil (Soltrol 220, $p_{w}=0.8$ g/cm$^3$) was the initial wetting fluid for air-oil systems, and water was used for all other systems. The fluid interfacial tensions, measured with a du Noüy ring (1919), were $\sigma_{\text{air}}=72$ N/m, $\sigma_{\text{oil}}=24$ N/m, and $\sigma_{\text{water}}=26$ N/m.

**Treating Media to Obtain Different Wettabilities**

To obtain media with different degrees of wettability, blasting sands were treated with organosilane compounds. The sands were added to a 5% solution of an organosilane (octadecyltrichlorosilane, OTS; vinyltriethoxysilane, VTS; or glycidoxypropyltrimethoxysilane, GPTS) in ethanol and mixed in a shaker for 5 hours; the sands were then air dried (Anderson et al., 1991). These organosilanes were selected based on reported values for the solid-air interfacial tensions, $\sigma_{\text{air}}$, of 22.5 N/m for OTS, 25 N/m for VTS, and 42.5 N/m for GPTS (Anderson et al., 1991; Wei et al., 1992) while the value for $\sigma_{\text{air}}$ of the untreated sand was assumed to be 78 N/m just as for fused silica (Hienemen, 1986). Note that a lower value for $\sigma_{\text{air}}$ reflects an increase in hydrophobicity. Mixed wettability media were obtained by combining untreated and OTS-treated blasting sands; mixtures of 0, 25, 50, 75, and 100% OTS sands were used. The untreated sands were strongly water-wet, while the OTS-treated sands were oil-wet in oil-water systems or water repellent in air-water systems.

**Results and Discussion**

**Quantifying Wettability**

The contact angle ($\theta$) is used to quantify the wettability of solids with uniform wettability. The advancing and receding contact angles ($\theta^A$ or $\theta^R$) of fluid system 2 can be obtained from $P_{c}$-$S$ data for fluid systems 1 and 2, with complete wetting for system 1, using a scaling relation based upon the Laplace-Young equation:

$$P_{c1}(S_{01}) = \frac{\sigma_1 \cos(\theta^R_1)}{\sigma_2 \cos(\theta^R_2)} P_{c2}(S_{02}) = \beta P_{c2}(S_{02})$$

(1)

where $\beta$ is a scaling factor to be determined from optimizing $P_{c}$-$S$ data; $\theta^A,R$ is an advancing or receding contact angle; and the effective saturation $S_0=|S-S_{r}|/(1-S_{r})$, with $S_{r}$ as the residual saturation. Note that $\theta^A,R$ can be determined
from $\sigma_1$, $\sigma_2$, and $\beta$ if $\phi_i^{A,R}=0$. Soltrol was found to completely wet air-oil media for various wettabilities (cf. Fig. 4). Table 1 shows the values of $\phi^{A}$ and $\phi^{R}$ obtained with the optimized scaling factor for air-water and oil-water media with uniform wettability (i.e., untreated, GPTS, VTS, and OTS sands).

The contact angle is position-dependent in oil-water media with mixed wettability; its value depends on surface roughness (Morrow, 1976), immobile adsorbed liquid layers (Adamson, 1967), and adsorptive properties of the solid (Anderson, 1986). An alternative method of quantifying the wettability is the United States Bureau of Mines (USBM) Method, which uses the principle that work necessary for displacement of the wetting by the nonwetting fluid is less than for the reverse process. The USBM wettability index is (Donaldson et al., 1969):

$$I_{USBM} = \log(A_w / A_o)$$  \hspace{1cm} (2)

where $A_o$ is the area under the $P_{aw}-S_{aw}^{ww}$ curve for a hydrophilic system ($P_{aw}<0$), and $A_w$ is the area above the $P_{aw}-S_{aw}^{ww}$ curve for a hydrophobic medium ($P_{aw}>0$). Figure 3 shows a plot of the calculated values of $I_{USBM}$ versus the fraction of OTS sand. The wettability index, $I_{USBM}$, was determined as: (i) $I_{USBM}$ from primary drainage and main imbibition $P_{aw}-S_{aw}^{ww}$ data and (ii) $I_{USBM}$ from main drainage and imbibition $P_{aw}-S_{aw}^{ww}$ data.

Wettability Effects on Air-Liquid Systems

Figures 4 and 5 show the $P_{aw}-S_{aw}^{ww}$ and $P_{aw}-S_{aw}^{ww}$ curves for drainage and imbibition in 0 and 100% OTS media filled with air-oil and air-water, respectively. All pressures are expressed in cm of water. The $P_{aw}-S_{aw}^{ww}$ curve is greatly affected by hydrophobicity (% OTS) in contrast with the $P_{aw}-S_{aw}^{ww}$ curve. This is primarily due to the difference in interfacial tension of each liquid with air (i.e., $\sigma_{aw}=24$ N/m and $\sigma_{aw}=72$ N/m). The low value for $\sigma_{aw}$ leads to a low $\phi^{A,R}$. Soltrol can therefore completely wet untreated (hydrophilic) and OTS (hydrophobic) media.

Wettability Effects on Oil-Water Systems

Figure 6 shows the $P_{aw}-S_{aw}^{ww}$ curves during primary drainage, main imbibition, and main drainage for the 50 and 100% OTS media. Note that during imbibition $P_{aw}$ at a particular $S_{aw}^{ww}$ decreases as the fraction of OTS sand increases, with $P_{aw}$ becoming negative at $S_{aw}^{ww}=0.69$ and 0.27 for the 50% and 100% OTS media, respectively. The negative $P_{aw}$ is a result of forced imbibition, i.e., water can only displace oil from the pore space when positive pressure is exerted on the oil phase relative to the water phase. The main drainage curve always has a lower $P_{aw}$ than the primary drainage curve for a given $S_{aw}^{ww}$. This feature has, of course, already been reported for air-water systems where it was attributed to air entrapment (e.g., Stonestrom and Rubin, 1989). An explanation for the increased difference for the 100% OTS media is that water (the saturating fluid) may initially prevent oil from wetting the sand.
during primary drainage. After oil replaces water as the wetting fluid (primary drainage), the solid is wetted more readily by oil during the subsequent (main) drainage of water. The observed difference between primary and main drainage curves illustrates the importance of the initial saturation conditions.

The $P_{ow}-S_w^{ow}$ relation is sometimes measured on an initially water saturated soil column with a hydrophilic capillary barrier at the bottom and an oil reservoir at the top. A change in oil pressure in the reservoir causes water to exit at the bottom ($S_w^{ow}$ decreases), similar to applying a pneumatic head for measuring the soil water retention curve. If water is not the wetting liquid ($P_{ow}>P_w$), changes in water content in the forced imbibition region can not be observed in this manner. A better way of measuring the $P_{ow}-S_w^{ow}$ relations has been to apply suction initially to the oil reservoir or, even better because of faster equilibration, to impose the liquid contents and to monitor the pressure subsequently (Figs. 1 and 2).

Empirical Model to Describe Oil-Water $P_{ow}-S_w$ Relations

Parametric models, such as those by Brooks and Corey (1964) and van Genuchten (1980), are commonly employed to describe $P_{ow}-S_w^{ow}$ data. These models are only suitable for positive capillary pressures. The $P_{ow}-S_w$ model of van Genuchten was therefore modified to account for negative capillary pressures as:

$$P_{ow} + \gamma = \frac{\alpha}{\alpha - \left(\frac{S_w^{ow}}{S_{w,0}^{ow}}\right)^{1/m} - 1}$$

where $S_w^{ow} = (S_{w,0}^{ow} - S_{w,0}^{ow})/(1 - S_{w,0}^{ow} - S_{w,0}^{ow})$ maps $S_w^{ow} = S_{w,0}^{ow}$ onto $S_w^{ow} = 0$, and $S_{w,0}^{ow} = 1 - S_{w,0}^{ow}$ onto $S_w^{ow} = 1$, and the subscript $r$ again denotes a residual value. The parameter $\gamma$ was set equal to the magnitude of the lowest value of $P_{ow}$ so that the value of $P_{ow} + \gamma$ is always greater than or equal to zero. The $P_{ow}-S_w$ model of van Genuchten was then used to describe this $(P_{ow}+\gamma)-S_w^{ow}$ relation. Table 2 shows the measured values of $S_{w,0}^{ow}$, $S_{w,0}^{ow}$, and $\gamma$ determined from the measured mixed wettability $P_{ow}-S_w^{ow}$ curves; $S_{w,0}^{ow}$ and $\gamma$ were set equal to zero during primary drainage. Table 2 also shows the fitted values of $\alpha_{PD}$, $\alpha_{MD}$, and $\gamma$ (denoting the values for $\alpha$ during primary drainage, main imbibition, and main drainage curves), and $n$ (note that $m=1-1/n$) for the $P_{ow}-S_w^{ow}$ curves. Parameter optimization was done according to Marquardt (1963). The coefficient of regression between measured and fitted values $(R)$ was always greater than 0.965.
Predicting Two-Fluid P-S Relations

Scaling $P_{c-S}$ data for a particular two-fluid medium is common for obtaining $P_{c-S}$ relations for other two-fluid systems involving the same porous medium. Figures 7a and 7b show the observed and predicted $P_{ae}$-$S_{ae}$ and $P_{cw}$-$S_{cw}$ curves for the OTS sand during drainage and imbibition. The predictions in Fig. 7a were obtained from scaling the $P_{ae}$-$S_{ae}$ curve using the ratios $\sigma_{ae}/\sigma_{aw}$ and $\sigma_{ae}/\sigma_{aw}$, respectively. The scaling in Fig. 7b was based on the ratio of interfacial tensions and contact angles (i.e., $\sigma_{aw}/\sigma_{aw} \cos(\phi_{aw})$ and $\sigma_{aw} \cos(\phi_{aw})/\sigma_{aw} \cos(\phi_{aw})$, respectively). The superscript * indicates the more realistic value for (oil) contaminated water. Note that the scaling in Fig. 7b, in contrast with Fig. 7a, results in a closer agreement between predicted and observed OTS $P_{c-S}$ data.

The conventional scaling is more appropriate for air-liquid systems, where the solid is wetted preferentially by the liquid, than for oil-water systems, where the solid may be wetted by both oil and water. Scaling according to Eq.(1) cannot account for both positive (spontaneous imbibition) and negative (forced imbibition) capillary pressures. An alternative approach is to shift the $P_{c-S}$ model as well:

$$P_{cw}(S_{cw}) = \frac{\sigma_{aw}}{\sigma_{ao}} P_{ao}(S_{ao}^{*}) - \gamma$$ (4)

where $S_{ao}^{*} = (S_{ao} - S_{ao}^{*})/(1 - S_{ao}^{*}) + S_{ao}^{*}$ while $\sigma_{cw}/\sigma_{ao}$ and $\gamma$ account for the differences between the systems in interfacial tensions and wetting properties, $r$ respectively. The $P_{ao}$-$S_{ao}^{*}$ relationship was used for scaling instead of $P_{aw}$-$S_{aw}$ because the relatively low $\sigma_{ao}$ compared to $\sigma_{aw}$ suggests that the solid is wetted better by oil than water. The relationship between $\gamma$ and the hydrophobicity/wettability (i.e., the % OTS) is shown in Fig. 8. Values for $\gamma$ were obtained by fitting the $(\sigma_{cw}/\sigma_{ao})P_{ao}$-$S_{ao}^{*}$ data to the $P_{cw}$-$S_{cw}$ curves during main drainage and imbibition. Figure 9 shows a comparison of the predicted and measured $P_{cw}$-$S_{cw}$ relations during main drainage and imbibition for the 25% and 75% OTS media. The regression formulas shown in Fig. 8 were used to predict $\gamma$ during drainage (D) and imbibition (I).

Three-Fluid P-S Relations

For three-fluid systems with a continuous intermediate fluid, a pressure drop occurs over the oil-water and air-intermediate fluid interfaces. Figure 10a shows the $P_{cw}$-$S_{cw}$ curves (left side) and $P_{cw}$-$S_{cw}$ (right side) curves for the untreated sand while Fig. 10b shows the $P_{aw}$-$S_{aw}$ curve. The total liquid saturation is defined as $S_{aw} = S_{aw} + S_{aw} + S_{aw}$. The oil-water and air-oil capillary pressures are unique functions of the wetting fluid and total liquid saturations, respectively.

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For a discontinuous intermediate fluid layer, a pressure drop occurs over the oil-water, air-water, and air-oil interfaces. Figure 11a shows the $P_{ow-S_{ow}^{aow}}$ (left side) and $P_{ow-S_{ow}^{bow}}$ (right side) curves for the (100%) OTS medium, while Fig. 11b and 11c show the $P_{ow-S_{ow}^{bow}}$ and $P_{ow-S_{ow}}^{aow}$ curves, respectively. The capillary pressures $P_{ow}$, $P_{os}$, and $P_{ow}$ depend on both $S_{ow}^{aow}$ and $S_{ow}^{bow}$. However, $P_{ow}$ and $P_{os}$ are mainly functions of $S_{ow}^{bow}$, while $P_{ow}$ is mainly a function of $S_{ow}^{aow}$. A change in $S_{ow}^{bow}$ (constant $S_{ow}^{aow}$) or $S_{ow}^{aow}$ (constant $S_{ow}^{bow}$) leads to changes in the air saturation; $P_{os}$ and $P_{ow}$ are therefore mainly functions of $S_{ow}^{bow}$ and $S_{ow}^{aow}$, respectively. Since water does not spread well on oil in hydrophobic media, in comparison to oil on water in hydrophilic media, air-oil interfaces exist. Changes in $S_{ow}^{bow}$ will obviously cause changes in $S_{ow}^{aow}$; this will affect the air-oil and oil-water interfaces, and $P_{ow}$ depends therefore on $S_{ow}^{bow}$.

A similar dependency of three-fluid capillary pressures on fluid saturations was found for the 25, 50, and 75% OTS media. The intermediate fluid for these cases is, obviously, also discontinuous since both water and oil act as the wetting fluid and the intermediate fluid in the same medium. As the fraction of oil-wet sand decreases in the medium, $P_{ow}$ and $P_{ow}$ are higher at a given $S_{ow}^{bow}$, while $P_{os-S_{os}^{bow}}$ is relatively unaffected. This may be attributed to the energy state of water which, in contrast to that of oil, differs depending on whether water acts as the wetting or intermediate fluid.

**Predicting Three-Fluid $P_C-S$ Relations**

Leverett (1941) predicted three-fluid $P_C-S$ curves for a particular medium from measured two-fluid $P_C-S$ curves for the same medium according to:

$$P_{ow}(S_{ow}^{aow}) = P_{ow}(S_{ow}^{bow})$$  \(\text{(5)}\)

$$P_{os}(S_{os}^{bow}) = P_{os}(S_{os}^{aow})$$  \(\text{(6)}\)

Three-fluid $P_C-S$ relations may also be predicted by scaling and invoking Leverett's assumption. Figure 12a shows the observed $P_{ow-S_{ow}^{b}}$ and $P_{os-S_{os}^{b}}$ curves for the untreated sand (left side) and GPTS sand (right side), while Fig. 12b shows the observed $P_{ow-S_{ow}^{b}}$ and $P_{os-S_{os}^{b}}$ curves for the untreated sand (left side) and GPTS sand (right side). Note that the three-fluid $P_C-S$ curves can be accurately predicted from the measured two-fluid $P_C-S$ curves for the hydrophilic media. Figure 13a displays the observed $P_{ow-S_{ow}^{b}}$ curve for the GPTS media and the predicted $P_{ow-S_{ow}^{b}}$ curves obtained by scaling the $P_{ow-S_{ow}^{b}}$ curve according to the previously discussed scaling approaches. Similarly, Fig. 13b shows the observed $P_{ow-S_{ow}^{b}}$ curve for the GPTS media and the predicted $P_{ow-S_{ow}^{b}}$ curves obtained by scaling the $P_{ow-S_{ow}^{b}}$ curve. Note that the scaling results improved by using the contaminated air-water interfacial tension and by including values for the contact angle.

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Methods for the prediction of the three-fluid $P_2$-S relations in hydrophobic and mixed wettability media based strictly on eqs. 5 and 6 are generally inadequate. Currently, we are working on improved predictions for such media.

Permeability

An automated steady flux method for the measurement of the unsaturated flow, air-water permeability ($k$)-$P_2$ has been developed at Riverside. Preliminary results suggest that this technique may also be applied for air-oil, oil-water, and air-oil-water systems. The measured $P_2$-S relations also allow the prediction of $k$-S relations. The work in Davis has focused on the numerical modeling of multiphase flow for use in inverse procedures to estimate two- and three-fluid $k$-$P_2$ relations.

References


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