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Prediction of two-phase capillary pressure–saturation relationships in fractional wettability systems

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Abstract

Capillary pressure/saturation data are often difficult and time consuming to measure, particularly for non-water-wetting porous media. Few capillary pressure/saturation predictive models, however, have been developed or verified for the range of wettability conditions that may be encountered in the natural subsurface. This work presents a new two-phase capillary pressure/saturation model for application to the prediction of primary drainage and imbibition relations in fractional wettability media. This new model is based upon an extension of Leverett scaling theory. Analysis of a series of DNAPL/water experiments, conducted for a number of water/intermediate and water/organic fractional wettability systems, reveals that previous models fail to predict observed behavior. The new Leverett–Cassie model, however, is demonstrated to provide good representations of these data,

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as well as those from two earlier fractional wettability studies. The Leverett–Cassie model holds promise for field application, based upon its foundation in fundamental scaling principles, its requirement for relatively few and physically based input parameters, and its applicability to a broad range of wetting conditions.

Keywords: Multiphase flow; NAPL; Wettability; Retention; Capillary pressure; Saturation; Tetrachlorethene; Leverett; Cassie; Scaling

1. Introduction

Multiphase flow simulators, developed to model migration of nonaqueous phase liquids (NAPLs), typically require the specification of fluid and porous medium specific constitutive relationships, including capillary pressure/saturation relationships. The capillary pressure/saturation relationships, in turn, depend on wettability, the "tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid" (Craig, 1971). The contact angle, a measure of wettability, is the angle the fluid–fluid interface makes with the solid support (Hiemenz and Rajagopalan, 1997). As the contact angle, measured through the water phase in a NAPL/water/solid system, approaches 0°, the surface is said to be strongly water-wetting. Conversely, as the contact angle approaches 180°, the surface is said to be strongly NAPL-wetting. A surface is termed intermediate-wet if the contact angle ranges from approximately 70° to 120° (Treiber et al., 1972; Morrow, 1976). Two terms are frequently used in the literature to describe media with solids that have differing surface wetting properties. 'Mixed wettability' is commonly used to describe the condition where wettability is a function of pore size (Salathiel, 1973). Although 'fractional wettability' is a more general term used to describe media composed of surfaces of varying wettability (Anderson, 1987), in this study, 'fractional wettability' is used to describe a medium that contains specific proportions of grains of differing wettability (across all grain sizes). This definition of fractional wettability is consistent with that used by previous investigators (Bradford and Leij, 1995a; Bradford and Leij, 1996).

Water-, intermediate- and organic-wettting conditions can exist in the subsurface through the interaction of the released NAPLs and the porous medium or due to natural variations in porous medium composition. For example, at many sites, NAPLs were not disposed of as pure liquids, but as mixtures containing surface-active compounds (Sloat, 1967; Riley and Zachara, 1992; Jackson and Dwarakanath, 1999). Contact with NAPL mixtures containing surfactants can render a porous medium intermediate- to organic-wet (Demond et al., 1994; Powers and Tamblin, 1995; Powers et al., 1996; Barranco and Dawson, 1999; Lord, 1999). Furthermore, natural subsurface constituents, such as iron oxides, carbonates, and silica, have a variety of wetting characteristics (Anderson, 1986). Previous studies suggest that variations in wettability may be common in the contaminated subsurface. Thus, constitutive relationships measured with pure fluids in water-wet sand may not be readily applicable to subsurface contamination problems.

A variety of models have been proposed to fit or predict capillary pressure/saturation relationships in systems that are not water-wetting (Leverett, 1941; Bradford and Leij, 1996; Lenhard and Oostrom, 1998; Ustohal et al., 1998; Skjaeveland et al., 2000). For example, the Leverett scaling function has been used in conjunction with the empirical capillary pressure/saturation relationships proposed by Brooks and Corey (1964) and van Genuchten (1980) to model capillary pressure/saturation data in systems with decreased interfacial tension and weakly water-wet conditions (Demond and Roberts, 1991; Demond et al., 1994). Leverett scaling, however, cannot replicate both the spontaneous and forced imbibition behavior observed in some fractionally wet systems (Fatt and Klikoff, 1959; Bradford and Leij, 1995a). As an alternative method to capture both positive and negative capillary pressures, Bradford and Leij (1996) proposed the following modified capillary pressure/saturation equation:

$$P_c^{fw}(S_w) = P_{NAPL} - P_w = P_c^{ww}(S_w) - \eta \tag{1}$$

where P_c^{fw} is the capillary pressure in the fractional wettability system, P_c^{ww} is the capillary pressure in the water-wet system, P_{NAPL} is the NAPL phase pressure, P_w is the aqueous phase pressure, S_w is the water saturation and η is a shifting parameter, used to facilitate incorporation of negative capillary pressures. Capillary pressure is typically defined as the difference between the nonwetting phase pressure and the wetting phase pressure. To avoid possible confusion in applications to mixed or fractional wettability systems, in this work the capillary pressure will be defined as the difference between the NAPL and water phase pressures. Bradford and Leij (1996) found that the shifting parameter, η, is a function of the fraction of hydrophobic surfaces present in the system. This functional form was developed from capillary data for a medium with a single grain size distribution. A similar model has been suggested by other researchers (Lenhard and Oostrom, 1998). These models have been applied to fractional wettability systems containing both water- and NAPL-wet materials but, as formulated, are not applicable to capillary pressure/saturation relationships in systems containing intermediate wettability surfaces.

Other researchers have suggested a statistical approach for estimating capillary pressure/saturation in fractional water-, intermediate- or organic-wet systems (Ustohal et al., 1998). Although the model of Ustohal et al. (1998) is applicable to a variety of wetting conditions, it has limited predictive capability in natural settings due to the large number of input parameters required for this model and because it does not incorporate differences in interfacial tension. Still other researchers, such as Skjaeveland et al. (2000), have suggested treating the positive and negative portions of the capillary pressure/saturation curves as separate functions. In its present form, however, their model is not predictive, since the parameters are found by fitting the model to capillary pressure/saturation data.

A review of the literature suggests that existing capillary pressure/saturation models are unable to predict retention functions for the broad range of wettability conditions likely to be encountered in the contaminated subsurface. Furthermore although a few experimental studies have quantified capillary pressure/saturation data for fractional water- and organic-wet systems few data exist to test the applicability of proposed predictive models in fractional water- and intermediate-wet systems. The goal of this work was to develop a simple predictive capillary pressure/saturation model that is applicable to fractional, intermediate- and organic-wet conditions and that can be scaled based on interfacial tension. This new model is based upon an extension of Leverett scaling theory and is derived from first principles with relatively few input parameters, all of which are physically meaningful. Field scale wettability is a complex phenomenon, dependent on a solid, aqueous, and NAPL chemistry. In this study a series of relatively simple, well-defined fractional wettability porous media systems have been used as a first-step to understand the more complex real-world systems. The system of capillary pressure/saturation measurements undertaken to explore the utility of the proposed model included fractional water- and organic-wet experiments, as well as fractional water- and intermediate-wet experiments. In addition, capillary pressure/saturation experimental data from other studies were also used to evaluate the model (Bradford and Leij, 1995a; Bradford and Leij, 1996; Ustohal et al., 1998). The predictive capability of the model was also compared to that of the model of Bradford and Leij (1996) for fractional water- and organic-wet experiments.

2. Two-fluid fractional wettability capillary pressure/saturation model

Consider a solid surface that is comprised of surface materials 1 and 2, each with a different wettability. The apparent contact angle (θ_c) for this surface can be estimated using the Cassie equation (Cassie, 1948):

$$\cos(\theta_c) = f_1\cos(\theta_1) + f_2\cos(\theta_2) \tag{2}$$

where f_i is the surface area fraction for the i material and θ_i is the contact angle on the i material.

To derive constitutive relationships for porous media, the pore structure is often idealized as a collection of capillary tubes. Incorporating the Cassie Eq. (2) into the Laplace–Young equation yields an estimate for the capillary rise, h_c, of the fluid α in a capillary tube with surfaces of different wettability (Ustohal et al., 1998):

$$h_c = \frac{4\gamma^{\alpha\beta}}{\Delta\rho g d}\left(f_1\cos(\theta_{\alpha,1}) + f_2\cos(\theta_{\alpha,2})\right) \tag{3}$$

where $\gamma^{\alpha\beta}$ is the fluid/fluid interfacial tension, $\Delta\rho$ is the difference in density between the fluids, g is the gravitational constant, $\theta_{\alpha,i}$ is the contact angle of fluid α on solid surface i in the presence of fluid β and d is the diameter of the capillary tube.

In order to develop a capillary pressure/saturation relationship for fractionally-wet porous media it can be assumed that the processes governing capillary rise in a capillary tube with heterogeneous wettability are analogous to those governing capillary pressure in fractionally-wet porous media. Based upon Eq. (3) an expression for the α–β capillary pressure/saturation relationship, $P_c^{\alpha\beta}(S_\alpha^{app})$, for a fractionally-wet porous medium, composed of n different constituents, can be developed by scaling the relationship for a uniformly wetted system with the same pore structure:

$$P_c^{\alpha\beta}\left(S_\alpha^{app}\right) = \frac{\gamma^{\alpha\beta}}{\gamma^{AB}}\left[\sum_{i=1}^{n} f_i\cos(\theta_{\alpha,i})P_{c,i}^{AB}\left(S_{wet,i}^{app}\right)\right] \tag{4}$$

This equation, referred to herein as the Leverett–Cassie equation, sums contributions from n surfaces with different wettability properties in the porous medium. Here f_i is the surface area fraction of material i in the porous medium and $\theta_{\alpha,i}$, the operative contact angle of fluid α on the solid surface i in the presence of fluid β, is the contact angle governing the displacement of the fluids in the porous medium. Here $P_{c,i}^{AB}(S_{\mathrm{wet},i}^{\mathrm{app}})$ is the 'reference' capillary pressure/saturation relationship for two fluids A and B in a structurally identical porous medium in which fluid A completely wets the solid in the presence of fluid B. $S_{\mathrm{wet},i}^{\mathrm{app}}$ is the apparent wetting fluid saturation and $\gamma^{\alpha\beta}$ and γ^{AB} are the interfacial tensions for the fluid pairs α, β and A, B, respectively.

In Eq. (4), apparent saturation is defined as (Bradford et al., 1998):

$$S_\alpha^{\mathrm{app}} = S_\alpha^{\mathrm{eff}} + S_{\beta\mathrm{t}}^{\mathrm{eff}} - S_{\alpha\mathrm{t}}^{\mathrm{eff}} \qquad \text{where} \quad S_\alpha^{\mathrm{eff}} = \frac{S_\alpha - S_{\alpha\mathrm{im}}}{1 - S_{\alpha\mathrm{im}} - S_{\beta\mathrm{im}}}$$
$$\text{and} \quad S_{\alpha\mathrm{t}}^{\mathrm{eff}} = \frac{S_{\alpha\mathrm{t}}}{1 - S_{\alpha\mathrm{im}} - S_{\beta\mathrm{im}}} \tag{5}$$

Here S_α is the total α-phase saturation, $S_{\alpha\mathrm{im}}$ is the immobile α-phase saturation and $S_{\alpha\mathrm{t}}$ is the saturation of the entrapped α-phase. At the immobile saturation the fluid is present as thin films coating the solid surface (Bradford et al., 1998). The entrapped saturation, on the other hand, is present in the center of the pores as a discontinuous fluid (Bradford et al., 1998). S_α^{eff} and $S_{\alpha\mathrm{t}}^{\mathrm{eff}}$ are the effective α-phase and effective entrapped α-phase saturations, respectively.

The operative contact angle appearing in Eq. (4) is the contact angle governing the displacement of fluid α from the porous medium. Thus, it is taken as the receding contact angle when α drains from the porous medium and the advancing contact angle for the imbibition of α. The 'reference' capillary pressure/saturation relationship, $\mathrm{P}_{c,i}^{AB}(S_{\mathrm{wet},i}^{\mathrm{app}})$, is either the capillary pressure/saturation relationship governing the drainage of fluid A from or the imbibition of fluid A into the porous medium, depending on the magnitude of the operative contact angle, $\theta_{\alpha,i}$. Rules for the determination of the appropriate 'reference' capillary pressure/saturation relationship are summarized in Table 1. If $\theta_{\alpha,i}$<90°, fluid α wets the surface and $S_{\mathrm{wet},i}^{\mathrm{app}} = S_{\alpha,i}^{\mathrm{app}}$. Similarly, if $\theta_{\alpha,i}$> 90° then $S_{\mathrm{wet},i}^{\mathrm{app}} = S_{\beta,i}^{\mathrm{app}}$.

Note that, in the derivation of the Leverett–Cassie equation, it has been implicitly assumed that surface roughness effects (Morrow, 1975; Morrow, 1976) and differences between the pore geometry of the selected medium and capillary tube networks (Melrose, 1965) are accounted for in the cos($\theta_{\alpha,i}$) term. As a result, similar to experience with the application of Leverett scaling to permeable media systems (Morrow, 1976; Lord, 1999), a contact angle measured on a smooth surface may not necessarily be a good estimate of the operative contact angle necessary for Eq. (4) to yield a good prediction of the capillary pressure/saturation relationship for the experimental system.

Table 1
Selection of the appropriate 'reference' capillary pressure/saturation relationship

	α drains from medium	α imbibes into medium
$\theta_{\alpha,i}$>90°	P_c/S governing the imbibition of A	P_c/S governing the drainage of A
$\theta_{\alpha,i}$<90°	P_c/S governing the drainage of A	P_c/S governing the imbibition of A

3. Materials and methods

In this study a series of uniform and fractional-wet capillary pressure/saturation experiments was undertaken to validate the Leverett–Cassie equation. Uniform wettability capillary pressure/saturation experiments were conducted for water-, intermediate- and organic-wet sands. Fractional wettability experiments were conducted for water/intermediate-wet and water/organic-wet sand mixtures. Finally, contact angles were quantified on smooth slides for comparison with operative contact angles derived by fitting Eq. (4) to the measured capillary pressure/saturation data.

3.1. Materials

Laboratory grade (99%) tetrachloroethene (PCE) (Aldrich Chemical, Milwaukee, Wisconsin) was used as the representative NAPL. The aqueous phase in all systems was Milli-Q water pre-equilibrated with the organic and solid phases to ensure that no temporal changes in interfacial tension occurred during the experiments. Experiments were conducted in the absence of surface active agents in order to decouple the effects of varying wettability and interfacial tension.

The porous media consisted of two different mixtures of Ottawa sand size fractions, F35/F50 and F35/F50/F70/F110 (US Silica, Ottawa, Illinois). The mean grain size and uniformity index for each mixture are provided in Table 2. Organic-wet sands were created by treating quartz sands with a 5% (by volume) octadecyltrichlorosilane (OTS) in ethanol solution (Anderson et al., 1991). Intermediate-wet sands were created by immersing the sand mixture in a 5% (by volume) solution of Rhodorsil Siliconate 51T (Rhodia Silicones, Rock Hill, South Carolina) in Milli-Q water and lowering the pH below 8 (Fleury et al., 1999). The desired fraction (on a weight basis) of water-wet sands (from each particle size range) were mixed with the desired fraction (on a weight basis) of intermediate- or organic-wet sands (from each particle size range) to generate the fractional wettability sand mixtures.

3.2. Contact angle measurements

The axisymmetric drop shape analysis (ADSA) technique was used to measure the solid/water/PCE contact angle (Cheng et al., 1990; Lord et al., 1997b). Advancing and receding contact angles were measured on smooth slides preequilibrated with PCE and the aqueous phase. Smooth quartz slides (Fisher Scientific, Pittsburgh, Pennsylvania) were treated to intermediate- (Fleury et al., 1999) and organic-wet (Anderson et al., 1991) conditions employing the same method used to treat the sand mixtures. Quartz slides were

Table 2
Physical properties of sand mixtures

	F35/F50	F35/F50/F70/F110
Median grain size, d_{50}, cm	0.036[a]	0.026
Uniformity index, U_i	1.88[a]	2.79

[a] Bradford et al. (1999).

cleaned using the following procedure: rinsing them with Milli-Q water, rinsing with methanol (Fisher Scientific, Pittsburgh, Pennsylvania), rinsing with 0.01 M HCl, rinsing with Milli-Q water, rinsing with 0.01 M NaOH and finally rinsing with Milli-Q water. The treated slides were not scrubbed due to the possibility of removing the coating but were cleaned by rinsing them with ethanol. Slides were stored in PCE-equilibrated Milli-Q water for at least 24 h prior to contact angle measurements. For the purposes of this study, the reported contact angles are those measured through the aqueous phase. For the PCE/aqueous phase system, a PCE drop was placed on top of a slide immersed in water. Measurement of the receding contact angle was made by increasing the size of the drop; the advancing contact angle was measured by decreasing the size of the drop (Lord, 1999). A minimum of five replicate measurements was made for each wettability condition (Table 3).

3.3. Capillary pressure/saturation experiments

Two-phase (water–PCE) primary drainage and primary imbibition capillary pressure/saturation data were measured using two different approaches. Data for the F35/F50/F70/F110 sand were generated using a pressure cell system (total volume=6.37 cm^3), based upon the design of Salehzadeh and Demond (1999). The F35/F50 capillary pressure/saturation data were measured using a rapid automated pressure cell system (total volume=94.25 cm^3) (Bradford and Leij, 1995b; O'Carroll et al., 2004). In both systems, the sand mixtures were dry packed, flushed with carbon dioxide and then saturated with 200 pore volumes of Milli-Q water. This packing technique yielded reproducible column porosities averaging 31.4±1.0%. The temperature in the room in which the capillary pressure/saturation experiments were conducted was 23±2 °C (Lord et al., 1997a). The base of a pressure cell was connected to a PCE reservoir and the top was connected to a water reservoir.

In two-phase air–water systems some researchers have observed that the water saturation is not only a function of capillary pressure but also depends on the rate of water saturation change in the system (Topp et al., 1967; Smiles et al., 1971; Vachaud et al.,

Table 3
Measured and operative PCE/water/solid contact angles—reported through the aqueous phase (standard deviation in parentheses)

		Smooth slide			Operative contact angle (P_c/S scaling)
		Average measured contact angle	Number of slides	Total number of replicate measurements	
Water-wet	Receding	34.4° (8.8°)	2	6	34.4°[a]
	Advancing	47.0° (7.5°)	2	6	47.0°[a]
Intermediate-wet	Receding	66.4° (4.4°)	3	12	82.3°[b] (1.4°)
	Advancing	106.4° (4.3°)	3	12	107.6°[b] (1.4°)
Organic-wet	Receding	137.6° (18.0°)	3	6	87.4°[b] (1.2°)
	Advancing	156.1° (4.7°)	3	5	128.0°[b] (1.2°)

[a] Assumed based on the contact angle measured on a smooth slide.
[b] Determined by fitting the Leverett–Cassie equation (Eq.(4)) to P_c/S data.

1972). They have observed larger water saturations when one large pressure step is imposed in comparison to saturations measured for a series of smaller imposed pressure steps. In the literature this phenomena, where saturation is a function of capillary pressure and the rate of saturation change, has been labeled as a dynamic or nonequilibrium effect in capillary pressure (Barenblatt and Gil'man, 1987; Hassanizadeh and Gray, 1990; Kalaydjian, 1992). Capillary pressure in the pressure cells in this study was adjusted by incrementally increasing or decreasing the boundary fluid phase pressure. Following each incremental increase or decrease in fluid pressure, the fluids in the column were equilibrated for 2 h and then the presence of equilibrium was assessed. Equilibrium was assumed achieved when the difference in column saturation was less than 0.8% over a 2 h period. Once the system had reached equilibrium the fluid pressure was again incrementally increased. Very small pressure increments were used such that the rate of water saturation change was gradual, minimizing dynamic effects in capillary pressure and ensuring reproducible measurements. All capillary pressure/saturation experiments started at 100% water saturation. Interfacial tension measurements for the fluids were conducted before and after the capillary pressure/saturation experiments to confirm that no interfacial tension reductions had occurred during the experiment.

To ensure the accuracy and consistency of the capillary pressure/saturation measurement systems, F35/F50/F70/F110 and F35/F50 water-wet water drainage experiments were conducted using both the traditional and automated pressure cell experimental setups. These results were compared quantitatively by fitting the van Genuchten (1980) capillary pressure/saturation model parameters (α and n) to each dataset using a nonlinear least squares minimization procedure (SAS 8.01-nlin, Cary, NC). In this fitting procedure, the square difference between the observed apparent water saturation and fit apparent water saturation, at a given capillary pressure, was minimized. Residual water saturations were estimated as the water saturation at which increases in capillary pressure resulted in minimal or no decrease in water saturation. In instances where the aqueous phase broke through the organic-wet membrane, the residual organic saturation was estimated or fit. Note that, in the fitting procedure, the square difference in saturation was minimized, rather than the difference in capillary pressure, to reduce the importance of data at high and low apparent water saturations and increase the importance of data in the intermediate apparent water saturation range.

In this study, the 'reference' capillary pressure/saturation relationships were taken as water drainage and imbibition capillary pressure/saturation curves in quartz sand in a water/nonwetting fluid (NAPL or air) system. The van Genuchten model parameters (α and n) for these reference curves were obtained by fitting the van Genuchten model to the P_c/S data. Operative advancing and receding contact angles were then obtained by using these 'reference' van Genuchten model parameters and fitting the Leverett model to capillary pressure/saturation data for the sands of uniform wettability. Based upon Eq. (4), nine input parameters are required to predict drainage and imbibition capillary pressure/saturation curves in a fractional wettability system comprised of two sands of different surface composition. These nine parameters include the surface area fraction of each sand, reference capillary pressure/saturation curve parameters, α and n, for drainage and imbibition, and the advancing and receding contact angles for each distinct sand component surface of uniform wettability.

4. Results and discussion

4.1. Contact angle measurements

Average measured contact angles and standard deviations are presented in Table 3. The larger variance obtained for the organic-wet receding contact angle measurements is attributed to measurement difficulties. As the PCE drop increased in size, it did not slowly advance across the surface but jumped. The contact angle was, therefore, quantified at local minima. Six measured receding contact angles, on three treated organic-wet slides, ranged from 115.5° to 158.4°. Contact angles at the lower end of this range are likely most representative of the receding contact angle.

The average receding and advancing contact angles for the water-, intermediate-and organic-wet slides presented in Table 3 are within the range typically used to define water, intermediate and organic wettability (Treiber et al., 1972; Morrow, 1976). For the water-wet slides, little hysteresis was observed between the advancing and receding contact angles. On the other hand, considerable contact angle hysteresis was observed for the intermediate-wet slide. Finally, the organic-wet slide exhibited less contact angle hysteresis than the intermediate-wet slide but more than the water-wet slide. This phenomenon, where contact angle hysteresis decreases when a fluid strongly wets the solid surface, has been reported by others (Morrow, 1975).

4.2. Comparison of capillary pressure/saturation measurement systems

Measured data for a particular medium using each experimental system were similar, as illustrated in Fig. 1. The automated pressure cell system data, however, exhibited more scatter particularly for the F35/F50/F70/F110 sand. The van Genuchten capillary pressure/saturation model parameters (1980) (Table 4) fit to the measured data for each measurement system are within the standard error range of the parameters generated by fitting the model to the data from the other measurement system, demonstrating that both measurement systems yielded comparable parameters for the capillary pressure/saturation curves.

4.3. Quantification of goodness of fit

The fitted curves presented in Fig. 1 illustrate the quality of the goodness of fit of capillary pressure/saturation functions to observed data. In this work, the root mean squared error (RMSE) was used as a basis for the classification of the quality of fit. Curves with RMSE$<1.0\times10^{-1}$ were classified as a 'good' fit and curves with a RMSE$>2\times10^{-1}$ were classified as a 'poor' fit. In Fig. 1, the van Genuchten (1980) capillary pressure/saturation model fits to the F35/F50 sand data from both experimental setups are, thus, considered 'good' given the relatively small root mean square error (RMSE) values (Table 4). Similarly, the curve fit to the F35/F50/F70/F110 sand data, generated using the traditional pressure cell system, was also considered good. On the other hand, the fit to the F35/F50/F70/F110 sand data, generated using the automated pressure cell system, yielded a poorer but acceptable

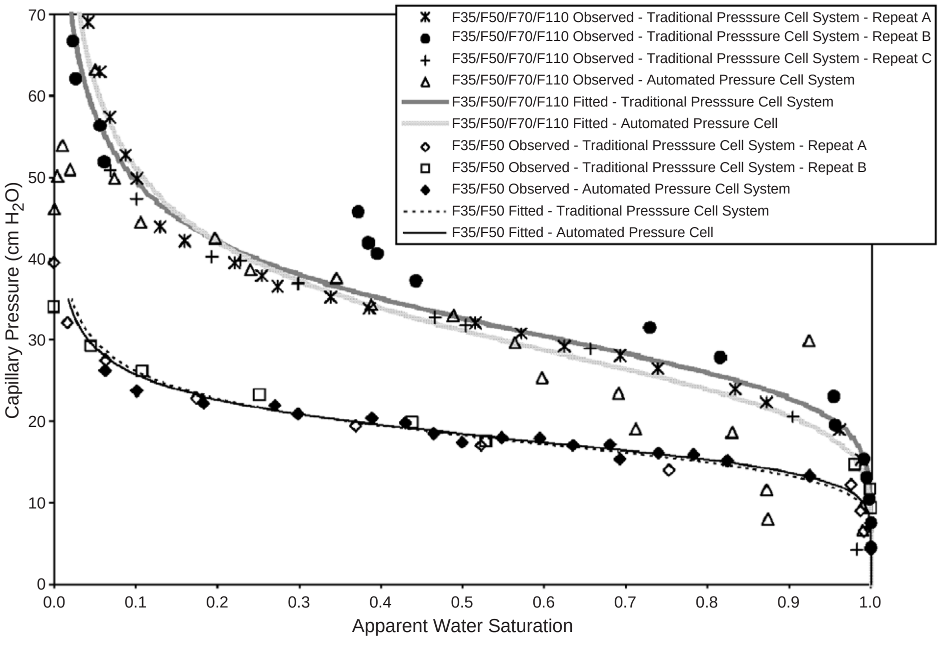

Fig. 1. Observed (measured using both the traditional and automated pressure cell systems) and fitted primary water drainage PCE/water capillary pressure/saturation relations for water—wet F35/F50 and F35/F50/F70/F110 Ottawa sand.

RMSE value (2.0×10^{-1}>RMSE>1.0×10^{-1}) due to scatter in the measured data (Table 4).

Here RMSE is defined as:

$$RMSE = \sqrt{\frac{(estimate - observation)^2}{N}} \tag{6}$$

where estimate is the modeled apparent saturation (fit or predicted) at a given capillary pressure, observation is the measured apparent saturation at the same capillary pressure and N is the number of observations.

4.4. Water/intermediate-wet fractional wettability systems

The results of drainage and imbibition PCE/water capillary pressure/saturation experiments conducted for F35/F50/F70/F110 mixtures of water- and intermediate-wet sands are presented in (Figs. 2 and 3), respectively. Here the symbols represent measured data. Fig. 2 reveals that, as the fraction of intermediate-wet sand increases, the drainage entry pressure decreases. The drainage capillary pressures are positive for all mixtures. The imbibition capillary pressures, however, have ranges of negative values for all but the water-wet sand (Fig. 3). Thus, water spontaneously imbibes into the completely water-wet system but forced imbibition is required to completely displace the PCE in the fractional

Table 4
Fitted PCE/water P_c/S model parameters and RMSE values (standard error in parentheses)

		F35/F50	F35/F50/F70/F110
Traditional pressure cell apparatus	α—Water drainage-VG (cm H_2O)$^{-1}$	5.82×10^{-2} (1.16×10^{-3})	3.32×10^{-2} (8.3×10^{-4})
	n—Water drainage-VG	7.38 (0.29)	6.58 (0.38)
	α—Water imbibition-VG (cm H_2O)$^{-1}$	N/A	7.15×10^{-2} (4.71×10^{-3})
	n—Water imbibition-VG	N/A	4.49 (0.38)
Automated pressure cell apparatus	α—Water drainage-VG (cm H_2O)$^{-1}$	5.72×10^{-2} (6.06×10^{-4})	3.58×10^{-2} (2.2×10^{-3})
	n—Water drainage-VG	7.85 (0.48)	5.78 (0.82)
	α-Water imbibition-VG (cm H_2O)$^{-1}$	1.85×10^{-1} (1.09×10^{-2})	N/A
	n—Water imbibition-VG	3.61 (0.16)	N/A
RMSE[a]	Traditional pressure cell apparatus (observed data and fitted curve)	5.49×10^{-2}	5.73×10^{-2}
	Automated pressure cell apparatus (observed data and fitted curve)	4.73×10^{-2}	1.21×10^{-1}

Note: VG model is described by: $P_c = \left(S_w^{\mathrm{app}^{-1/m}} - 1\right)^{1/n}/\alpha$ where $m = 1 - 2/n$ (van Genuchten, 1980).
[a] Using Eq. (6).

and intermediate-wet systems. Capillary pressures for the 50% water/50% intermediate-wet and 25% water/75% intermediate-wet sand mixtures become negative at apparent saturations of 70% and 33%, respectively. Water imbibition capillary pressures are negative over the entire saturation range for the 100% intermediate-wet sand. To explore the utility of the Leverett–Cassie equation in the prediction of the behavior of fractional wettability media, the van Genuchten (1980) capillary pressure function was fit to the water-wet drainage and imbibition data (Figs. 2 and 3) to yield values of α and n shown in Table 4. Residual water and organic saturations are presented in Table 5. Imbibition curves have been reported to appear more 'graded' than drainage curves (Steffy et al., 1997). Different capillary pressure/saturation model parameters (α and n) were therefore fit for water drainage and imbibition branches. This difference may be attributed to the "ink bottle effect" where differing pore sizes control water drainage and imbibition (Bear, 1979). Since different pores sizes control the order pores empty or fill, capillary pressures tend to be larger on primary water drainage, at a given saturation, when compared to water imbibition. The "ink bottle effect" will also lead to differing pore water connectivity on drainage, when compared to imbibition, resulting in the observed differences in the shape of the capillary pressure/saturation curves.

The Leverett–Cassie equation was then fit to the intermediate-wet drainage and imbibition data (Figs. 2 and 3, respectively), and then these 'reference' capillary pressure parameters (α and n) were employed to yield the operative intermediate-wet receding and advancing contact angles listed in Table 3. Notice that the fitted receding contact angle, 82.3°, is larger than the corresponding receding contact angle measured on a coated smooth slide, 66.4°, (Table 3). However, the fitted advancing contact angle of 107.6° was similar to that measured on a smooth slide, 106.4° (Table 3). Previous studies have proposed the use of roughness and curvature corrections for

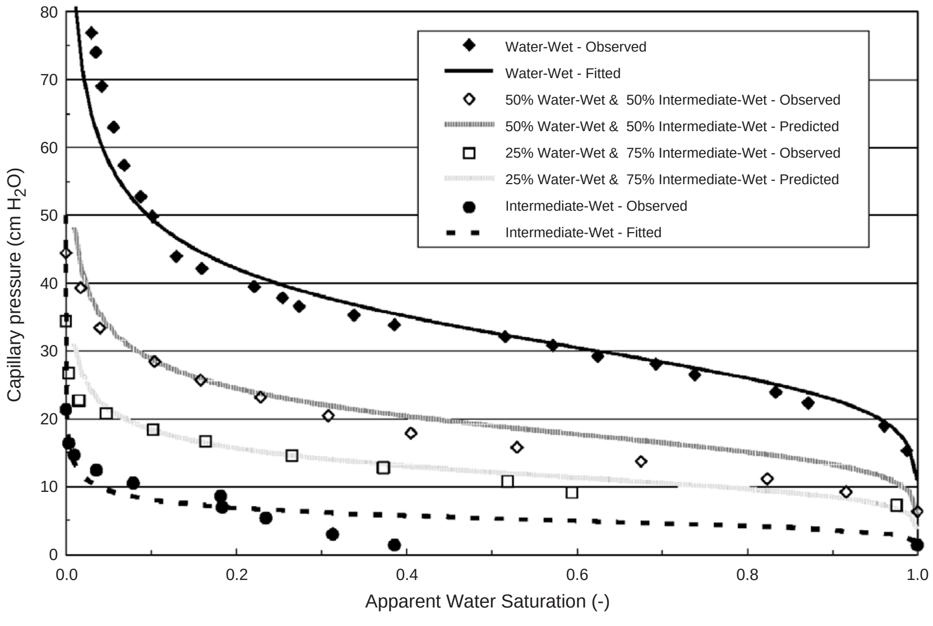

Fig. 2. Observed, fitted and predicted primary water drainage PCE/water capillary pressure/saturation relations for fractional water- and intermediate-wet F35/F50/F70/F110 sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)) and operative contact angles presented in Table 3.

contact angles in the prediction of capillary pressure/saturation data using Leverett scaling (Morrow, 1976; Demond and Roberts, 1991; Demond et al., 1994; Lord, 1999). For primary drainage these correction factors are typically less than one, effectively reducing the operative contact angle. Table 3, however, reveals that the operative contact angle in this system is greater than the measured contact angle. Thus the use of roughness or curvature corrections would worsen the discrepancy. The roughness correction factor was originally developed for roughened capillary tubes and the curvature correction factor was developed for ideal triangular and square sphere packings (Melrose, 1965; Morrow, 1975). As a result, these correction factors may not be directly applicable to porous media systems with random packings. Other studies have also found that effectively reducing the contact angle for primary drainage fails to consistently improve primary drainage retention function predictions (Morrow, 1976; Lord, 1999). The lack of consistency in the necessary correction factors found here does not support the use of a correction factor.

The 'reference' capillary pressure/saturation function parameters and the operative contact angles were then used in the Leverett–Cassie Eq. (4) to predict the 50% water/50% intermediate-wet and the 25% water/75% intermediate-wet drainage and imbibition curves. The shape and general magnitude of the predicted curves are consistent with the experimental data (Figs. 2 and 3). Based on the RMSE values of model predictions, presented in Table 6, the 25% water/75% intermediate-wet drainage curve prediction is good and the predicted 50% water/50% intermediate-wet curve is acceptable. Both

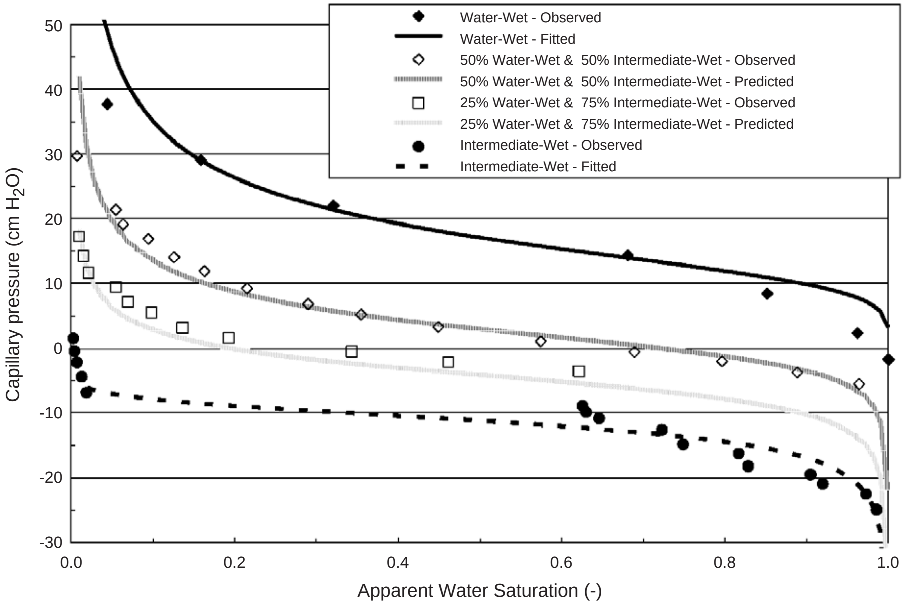

Fig. 3. Observed, fitted and predicted primary water imbibition PCE/water capillary pressure/saturation relations for fractional water- and intermediate-wet F35/F50/F70/F110 sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)) and operative contact angles presented in Table 3.

imbibition curve predictions provided good estimates of the experimental data based on the RMSE values (Table 6).

4.5. Water/organic-wet fractional wettability systems

Figs. 4 and 5 present experimental data from the water drainage and imbibition experiments respectively for the F35/F50 fractional water- and organic-wet systems. Similar to the behavior observed for the fractional water- and intermediate-wet systems, as

Table 5
Residual saturations

		S_{wr} (%)	S_{or} (%)
F35/F50/F70/F110	Water-wet	19	11
	50% Water/50% intermediate-wet	20	16[a]
	25% Water/75% intermediate-wet	19	16[a]
	Intermediate-wet	16	22[b]
F35/F50	Water-wet	4	19
	75% Water/25% organic-wet	2	11
	50% Water/50% organic-wet	4	8
	25% Water/75% organic-wet	9	7
	Organic-wet	12	4

[a] Assumed based on average of S_{or} for water- and intermediate-wet curves.
[b] Fit.

Table 6
RMSE values for predicted P_c/S relationships

		RMSE values for Leverett–Cassie equation				Imbibition RMSE values for model of Bradford and Leij (1996)
		Drainage		Imbibition		
F35/F50/F70/F110	50% Water/50% intermediate-wet	1.06×10^{-1}[a]		3.46×10^{-2}[a]		
	25% Water/75% intermediate-wet	8.99×10^{-2}[a]		8.08×10^{-2}[a]		
F35/F50	75% Water/25% organic-wet	1.89×10^{-1}[b]	1.01×10^{-2}[c]	3.20×10^{-2}[d]	1.18×10^{-1}[e]	1.72×10^{-1}
	50% Water/50% organic-wet	4.67×10^{-1}[b]	9.59×10^{-2}[c]	7.90×10^{-2}[d]	1.00×10^{-1}[e]	3.18×10^{-1}
	25% Water/75% organic-wet	5.17×10^{-1}[b]	2.53×10^{-1}[c]	8.23×10^{-2}[d]	9.78×10^{-1}[e]	4.35×10^{-1}

[a] Predicted using the Leverett–Cassie equation (Eq. (4)).
[b] Predicted using the Leverett–Cassie equation (Eq. (4)), the 'reference' drainage retention parameters and the fit receding operative contact angle for organic-wet sand.
[c] Predicted using the Leverett–Cassie equation (Eq. (4)), the 'reference' drainage retention parameters and the assumed receding organic-wet operative contact angle of 115.5°.
[d] Predicted using the Leverett–Cassie equation (Eq. (4)), the 'reference' retention parameters in conjunction with the fit operative advancing contact angle for organic-wet sand.
[e] Predicted using the Leverett–Cassie equation (Eq. (4)), the water-wet drainage retention parameters in conjunction with an assumed advancing contact angle of 60° in the water-wet sand the fit operative advancing contact angle for organic-wet sand.

the fraction of hydrophilic surfaces decreased, the capillary pressure also decreased at a given saturation. For water drainage, capillary pressures were positive for the water-wet, 75% water/25% organic-wet and 50% water/50% organic-wet systems. For the 25% water/75% organic-wet and completely organic-wet systems negative capillary pressures were observed at high water saturations. It should also be noted that these latter systems exhibited nearly identical drainage capillary pressure/saturation behavior. Water-wet water imbibition capillary pressures were positive over the entire saturation range, whereas the 75% water/25% organic-wet and 50% water/50% organic-wet systems exhibited both positive and negative capillary pressures. For the 25% water/75% organic-wet and completely organic-wet systems negative capillary pressures were observed over the entire saturation range.

Similar to the procedure for the water/intermediate-wet system, the van Genuchten (1980) capillary pressure/saturation model was fit to the water-wet primary water drainage and imbibition data (Figs. 4 and 5) to yield the values of α and n given in Table 4 for the reference system. The receding and advancing operative contact angles of 87.4° and 128.0° were found by fitting the Leverett–Cassie Eq. (4) to the organic-wet water drainage and imbibition data using the 'reference' capillary pressure/saturation parameters. The value of the receding operative contact angle in the organic-wet sand is consistent with experimental and simulation results of a 2D DNAPL infiltration study that suggested negligible capillary forces existed for the majority of primary water drainage in organic-wet systems (O'Carroll et al., 2004).

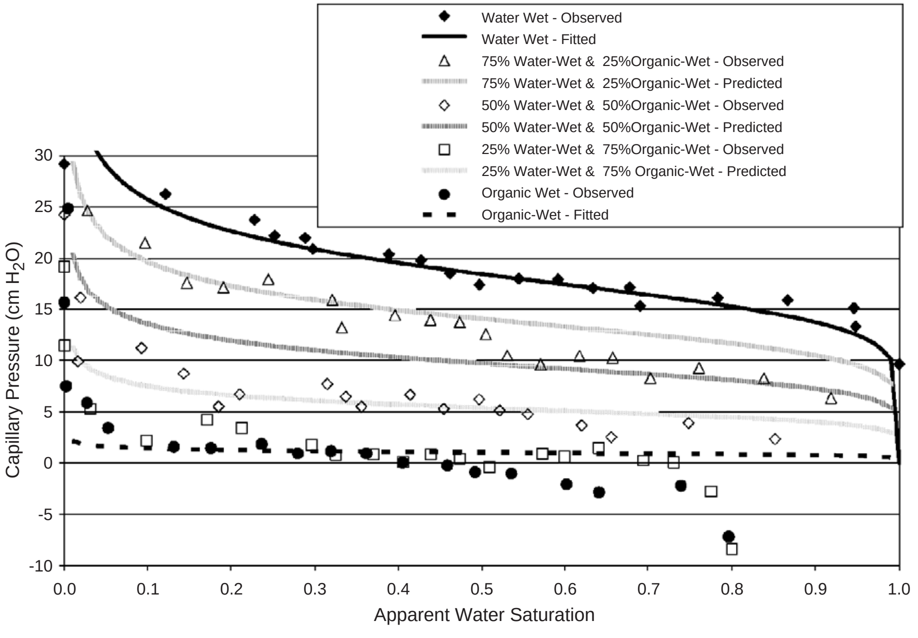

Fig. 4. Observed, fitted and predicted primary water drainage PCE/water capillary pressure/saturation relations for fractional water- and organic-wet F35/F50 sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)) and operative contact angles presented in Table 3.

The Leverett–Cassie Eq. (4) was then used to predict primary water drainage and imbibition in the fractional water/organic-wet sand system. Fig. 4 shows that the model tends to over predict the observed fractional water/organic-wet primary drainage capillary pressures, particularly as the fraction of organic-wet sands increases and the effect of the organic-wet operative contact angle increases (Fig. 4). This tendency is reflected in the RMSE values which indicate that the Leverett–Cassie Eq. (4), in conjunction with the fitted receding operative contact angle for the organic-wet sand, resulted in poor predictions of observed behavior, particularly as the fraction of organic-wet sand increases (Table 6). In an attempt to improve the predictions, the smallest measured receding contact angle was used as the operative receding contact angle. As previously discussed, this contact angle is considered the most representative measured receding contact angle, given the measurement difficulties. Use of this value dramatically improved the primary water drainage predictions, resulting in decreased RMSE values (Fig. 6 and Table 6). But the organic-wet capillary pressure data are under predicted using the receding contact angle of 115.5°. These results suggest that the Leverett–Cassie equation provides a reasonable prediction, using the minimum measured organic-wet receding contact angle, for water drainage in water- and organic-wet fractional wettability systems at organic-wet fractions below 75%. However, as the organic-wet fraction increased beyond 75%, observed capillary forces were close to zero, rather than negative as suggested by the measured contact angle. Note that the presence of capillary pressures close to zero at high organic-wet fractions are consistent with the 2D DNAPL infiltration experimental and simulation

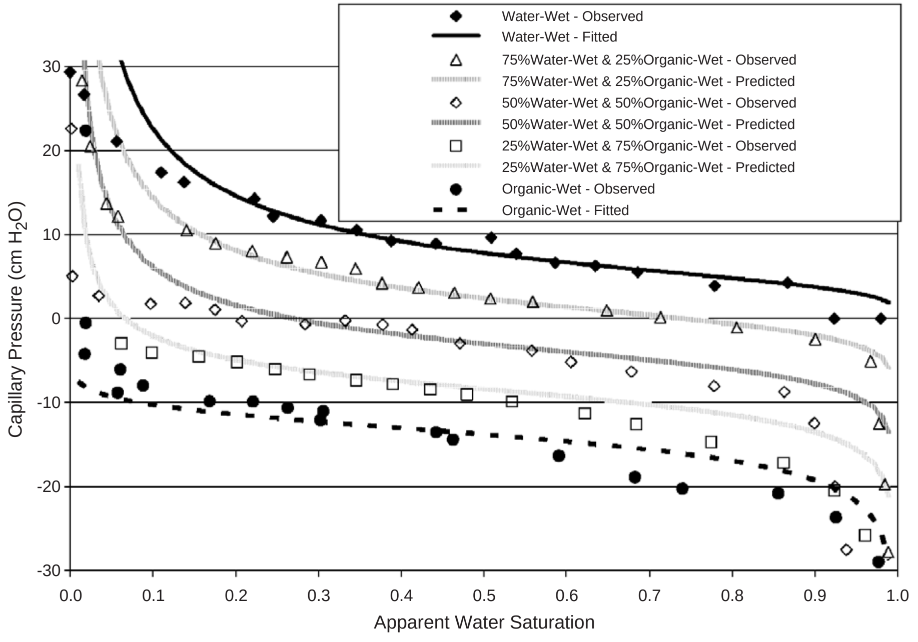

Fig. 5. Observed, fitted and predicted primary water imbibition PCE/water capillary pressure/saturation relations for fractional water- and organic-wet F35/F50 sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)) and operative contact angles presented in Table 3.

study mentioned previously (O'Carroll et al., 2004). Use of the 'reference' capillary pressure/saturation functions and the fitted advancing operative contact angles resulted in good predictions of the fractional water/organic-wet primary imbibition data for all fractions (Fig. 5 and Table 6).

In cases where the water-wet water imbibition capillary pressure/saturation parameters are unknown, the water drainage capillary pressure/saturation curve in water-wet sand has often been scaled by a factor of 0.5 to obtain the water imbibition capillary pressure/saturation curve for the same sand (e.g., Kool and Parker, 1987). Fig. 7 presents the water imbibition capillary pressure/saturation curve in F35/F50 water-wet sand, estimated using the fit water drainage water-wet sand van Genuchten (1980) model parameters, the Leverett–Cassie equation and a contact angle of 60°, consistent with the approach proposed by Kool and Parker (1987). Note that this assumed contact angle is larger than that measured on an untreated smooth glass plate (47.0°). The estimated water-wet imbibition curve, shown in Fig. 7, has a flatter slope than that of experiment observations, but results in an acceptable representation of the data (RMSE=$1.37\times10^{-1}<2.0\times10^{-1}$). This behavior is consistent with that observed by other researchers who have found that imbibition capillary pressure/saturation curves appear more 'graded' than drainage capillary pressure/saturation curves (Steffy et al., 1997). Use of a scaling factor of 0.5 assumes that differences in drainage and imbibition curves, due to both advancing and receding contact angle hysteresis and the "ink bottle effect" (Bear, 1979), are accounted for

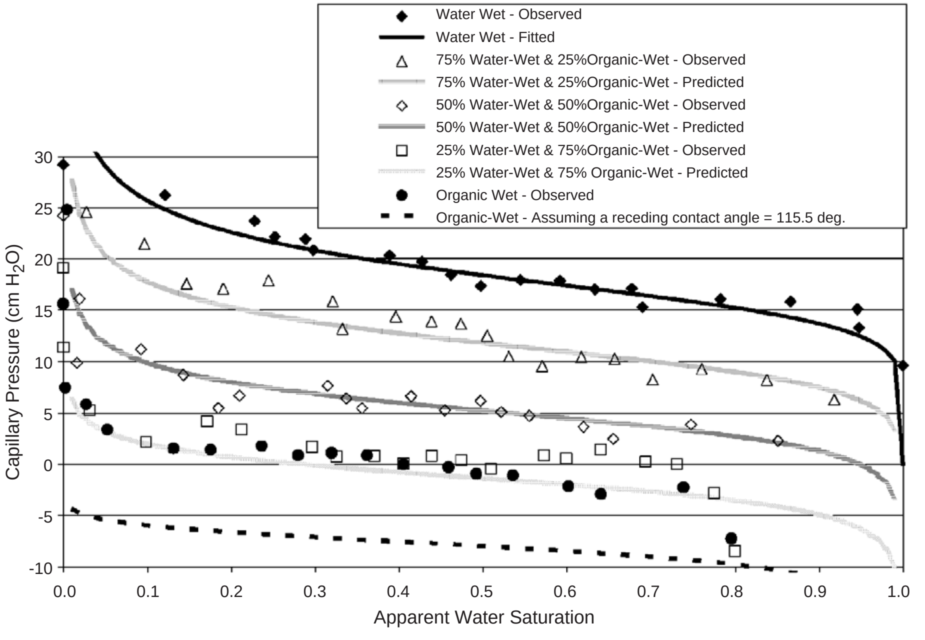

Fig. 6. Observed, fitted and predicted primary water drainage PCE/water capillary pressure/saturation relations for fractional water- and organic-wet F35/F50 Ottawa sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)), the receding water-wet operative contact angle presented in Table 3 and assuming organic-wet θ_{receding}=115.5°.

in the $\cos(\theta_{\alpha,i})$ term. Combining these phenomena may limit the ability of the assumed primary imbibition curve to closely replicate observed behavior. The Leverett–Cassie equation was then used in conjunction with the water drainage 'reference' retention function in water-wet sand, the assumed advancing contact angle of 60° in water-wet sand and the fit advancing contact angle of 128° in organic-wet sand to predict the fractional water- and organic-wet data. Although the fractional wettability data predictions were better when the water imbibition curve in water-wet sand was used as the "reference" retention function, using the assumed advancing contact angle of 60° yielded acceptable predictions of observed data (Fig. 7 and Table 6).

Leverett–Cassie model predictions were also compared with the predictions of the relationship presented by Bradford and Leij (1996) for the observed behavior of the fractional water/organic-wet water imbibition data. These investigators developed their model from data generated using sands coated with a similar OTS material, resulting in a similar surface hydrophobicity. For example, using Leverett scaling, they found an operative advancing contact angle of 146° for the water imbibition data in their OTS-coated sand system (Bradford and Leij, 1995b). This value is similar to the operative contact angle of 128.0° found here by fitting the Leverett–Cassie equation. Given that their model was generated based on experiments using similar materials, it was anticipated that it would have good predictive capability for the data generated in this study. Their model predictions, however, had a high RMSE, tending to over predict the water imbibition

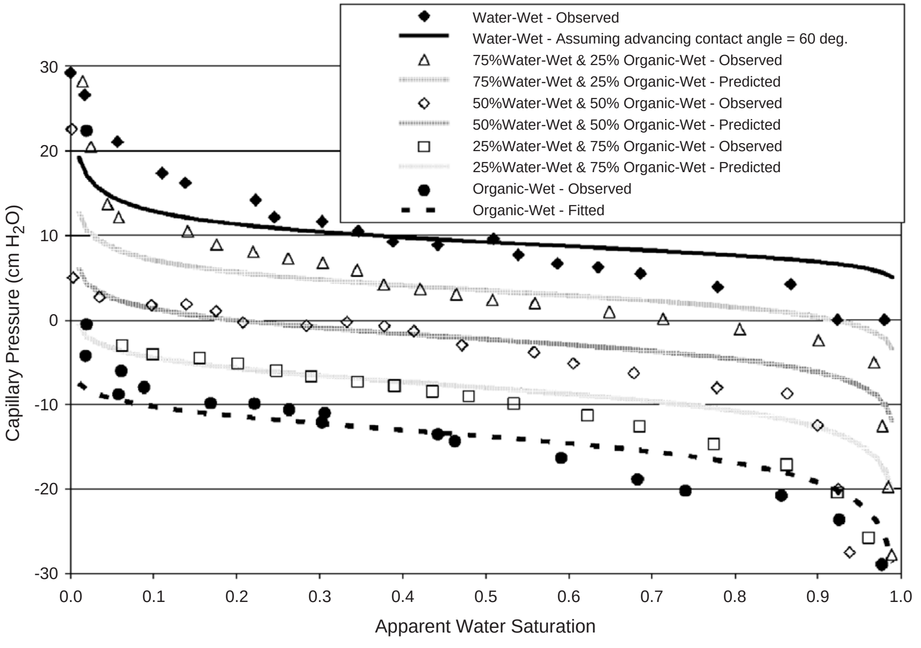

Fig. 7. Observed, fitted and predicted primary water imbibition PCE/water capillary pressure/saturation relations for fractional water- and organic-wet F35/F50 Ottawa sand. Predicted curves were found using the Leverett–Cassie equation (Eq. (4)), the advancing organic-wet operative contact angle presented in Table 3 and assuming water-wet $\theta_{advancing}$=60°.

capillary pressure, particularly as the fraction of organic-wet sand increases (Fig. 8 and Table 6). Note that their model was developed using a different grain size medium. These results suggest that their model may not be applied to other size fractions without further modification.

4.6. Extension of model to other studies

Other researchers have conducted capillary pressure/saturation experiments in fractional wettability systems (Bradford and Leij, 1995a; Ustohal et al., 1998). These studies present additional data sets that can be used to test the predictive abilities of the Leverett–Cassie equation. Bradford and Leij (1995a) measured capillary pressure/saturation data for a Soltrol 220/water system in untreated and OTS-coated blasting sands. Van Genuchten capillary pressure/saturation parameters (α=9.58×10^{-2} cm H_2O and n=4.92) were found by fitting the van Genuchten model to the untreated sand main drainage data and an operative water receding contact angle of 85.6° was estimated by fitting the Leverett–Cassie model to the OTS-coated sand main drainage data. These values were then used in the Leverett–Cassie model to predict the water and OTS-coated fractional wettability main drainage retention curves measured by Bradford and Leij (1995a) (Fig. 9). The Leverett–Cassie model predictions are classified as acceptable, based upon the RMSE. Since the fitted OTS main drainage

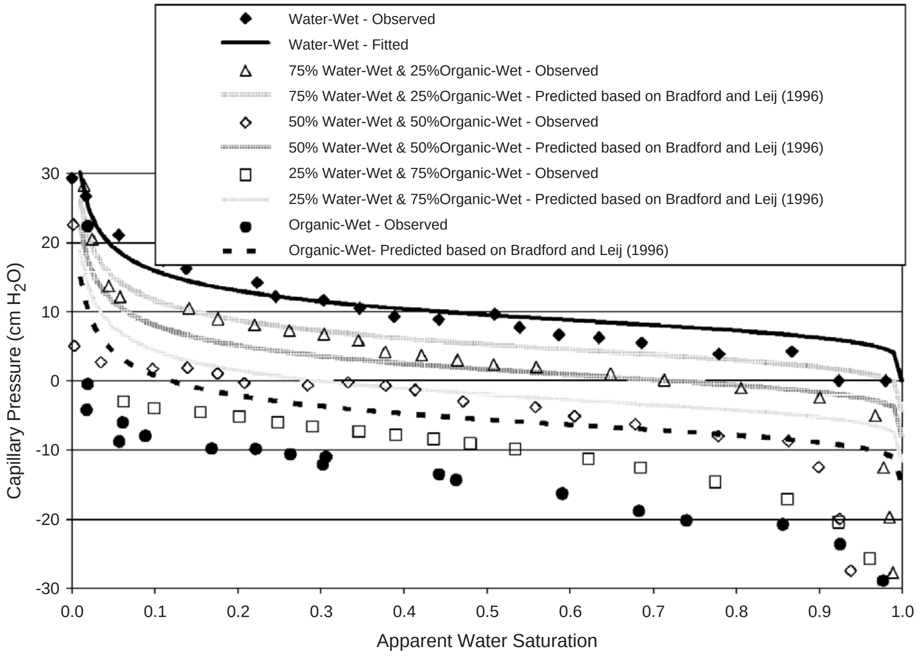

Fig. 8. Observed, fitted and predicted primary water imbibition PCE/water capillary pressure/saturation relations for water- and organic-wet fractional wettability F35/F50 Ottawa sand based on Bradford and Leij (1996).

curve fell below the measured capillary pressure at low apparent water saturations, the predicted curves underestimated the measured fractional wettability data at low water saturations. Although the model of Bradford and Leij (1996) yielded lower RMSE values than the Leverett–Cassie equation (an expected outcome since their model was calibrated to these data (Table 7)) these analyses suggest that the Leverett–Cassie model, developed in this work, is applicable to other water/NAPL fractional wettability systems.

Air/water main drainage and imbibition experiments were conducted by Ustohal et al. (1998) in quartz and silanized sand fractional wettability systems. To predict the observed main imbibition fractional wettability data using the Leverett–Cassie equation, the van Genuchten model was fit to both the water drainage and water imbibition data in quartz sand. The fitted water imbibition curve served as the 'reference' retention function for water imbibition in quartz sand. Since air was the wetting fluid for water imbibition in the silanized sand system, the main water drainage curve in water-wet sand served as a 'reference' capillary pressure/saturation function and an operative advancing contact angle of 139° was estimated using the Leverett–Cassie equation. Leverett–Cassie model predictions for imbibition in fractional wettability systems are presented in Fig. 10. Here capillary pressures are significantly under predicted, resulting in relatively large RMSE values (Table 8). These discrepancies can be attributed to the relatively large advancing contact angle obtained by fitting the Leverett–Cassie equation to the silanized sand system

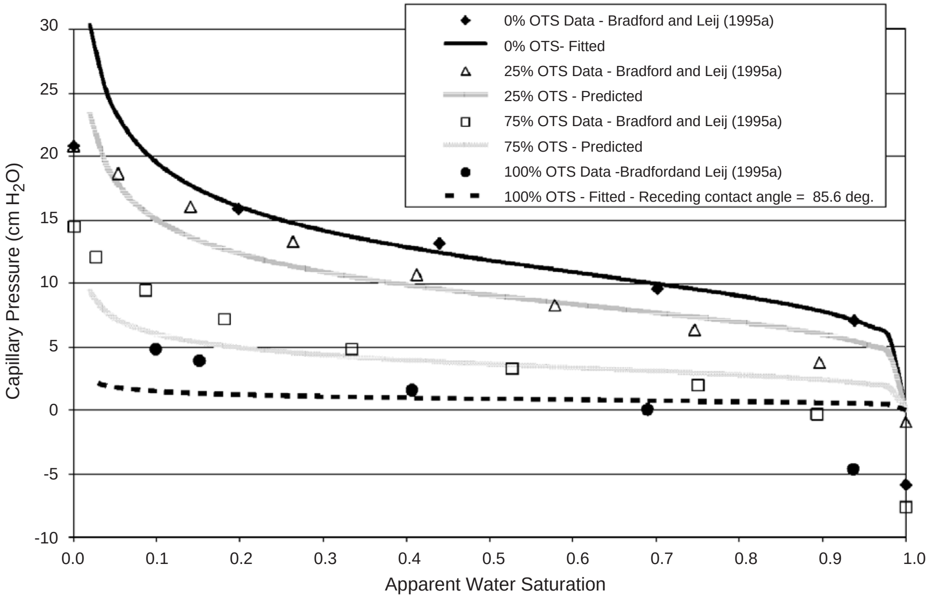

Fig. 9. Observed, fitted and predicted main water drainage capillary pressure/saturation relations for OTS fractional wettability sand (observed data from Bradford and Leij (1995a, 1996). Predicted curves were found using the Leverett–Cassie equation (Eq. (4)).

measurements. Ustohal et al. (1998) fit their model to the fractional wettability data and produced operative advancing contact angles of 30° and 110° for the quartz and silanized sands in their fractional wettability systems. Use of these values in the Leverett–Cassie equation significantly improved the main imbibition predictions in fractional wettability systems (Table 8). However the pure quartz and silanized sand imbibition data are still not well represented. The model of Bradford and Leij (1996) was extended to air/water systems to serve as another point of comparison. The fractional wettability and silanized sand predictions, using their model, are comparable to the estimates using the Leverett–Cassie equation and the operative contact angles of Ustohal et al. (1998) (Table 8). Here again the imbibition data in the silanized sand system is over predicted. This analysis suggests that the data of Ustohal et al. (1998)

Table 7
Comparison of RMSE values for Leverett–Cassie equation and the model of Bradford and Leij (1996) for the main drainage data reported by Bradford and Leij (1995a)

	RMSE	
	Leverett–Cassie equation	Model of Bradford and Leij (1996)
75% Water/25% organic-wet	6.86×10^{-2}	3.48×10^{-2}
50% Water/50% organic-wet	1.06×10^{-1}	1.96×10^{-2}
25% Water/75% organic-wet	1.02×10^{-1}	5.42×10^{-2}

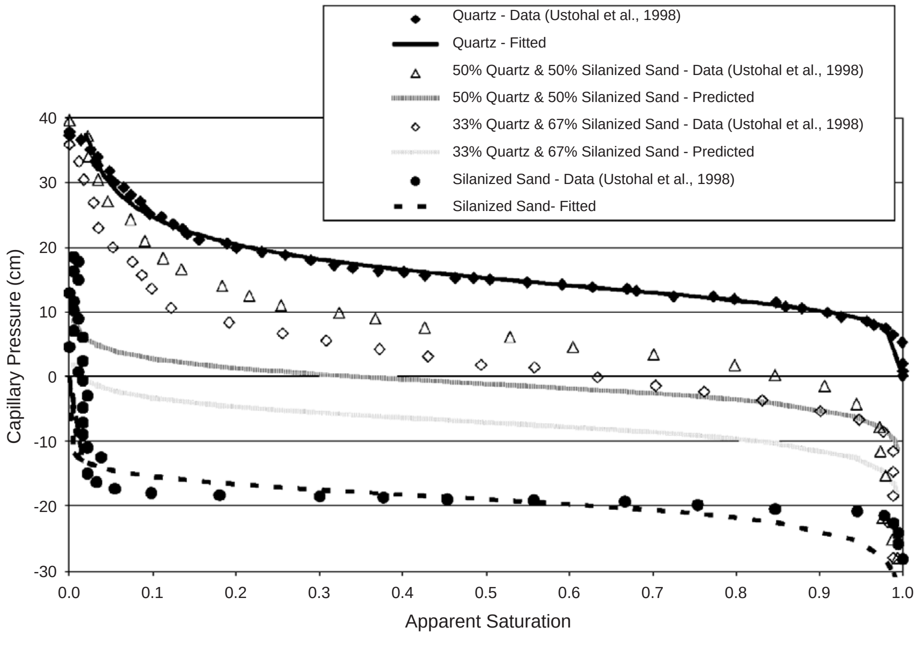

Fig. 10. Observed, fitted and predicted main water imbibition capillary pressure/saturation relations for quartz and silanized fractional wettability sand (observed data from Ustohal et al. (1998)). Predicted curves were found using the Leverett–Cassie equation (Eq. (4)). The fractional wettability data was predicted using the fit water imbibition curve in quartz sand as the 'reference' retention curve for water imbibition in quartz sand. For water imbibition in silanized sand the fit operative contact angle (139°) in the silanized sand system as well as the water drainage 'reference' curve in quartz sand were used.

are not consistent with behavior expected based on the scaling principles as incorporated in the Leverett–Cassie equation or the model of Bradford and Leij (1996). The reason for this discrepancy is not apparent.

Table 8
Comparison of RMSE values for Leverett–Cassie equation predictions and the model of Bradford and Leij (1996) to the main imbibition data reported by Ustohal et al. (1998)

	RMSE		
	Leverett–Cassie equation using fit 'reference' curves and an operative advancing contact angle of 139° for silanized sand	Leverett–Cassie equation using operative advancing contact angles of 30° and 110° for quartz and silanized sand, respectively	Model of Bradford and Leij (1996)
Water Wet	1.71×10^{-2}	2.98×10^{-1}	1.71×10^{-2}
50% Water/50% organic-wet	2.70×10^{-1}	1.15×10^{-1}	1.27×10^{-1}
33% Water/67% organic-wet	3.38×10^{-1}	2.01×10^{-1}	1.10×10^{-1}
Organic-wet	9.66×10^{-2}	4.27×10^{-1}	4.05×10^{-1}

5. Conclusions

A new model has been proposed to predict capillary pressure–saturation relationships in water-, intermediate- and organic-wet fractional wettability systems. This model represents a natural extension of the Leverett scaling approach to fractionally wet media. Model input parameters include the P_c/S parameters for drainage and/or imbibition of a strongly wetting fluid in the porous medium, surface area fractions of the component soils, fluid–fluid interfacial tensions and operative contact angles for component surfaces. The proposed model has advantages over others that have appeared in the literature. For example, it is applicable to a broader range of grain size distributions and wetting conditions than the model of Bradford and Leij (1996), and it is easier to implement with fewer input parameters than the model of Ustohal et al. (1998).

The model presented herein provides excellent predictions of the capillary data measured in this study and those measured by Bradford and Leij (1995a). Capillary measurements indicate that, as the fraction of strongly organic-wetting material increases, capillary forces along primary drainage become negligible even though the operative receding contact angle is greater than 90°. The proposed model was only able to adequately predict the fractional wettability data of Ustohal et al. (1998) when the operative advancing contact angle applied was significantly less than that obtained through Leverett scaling of the uniform wettability systems. Predictions based on the model of Bradford and Leij (1996) also over predicted the capillary pressure data in the organic-wet sand. These results are inconsistent with fundamental scaling principles. The reasons for this discrepancy cannot be assessed without further information pertaining to the experimental systems.

In this study relatively simple fractional wettability systems were selected representing a first step to understand more complex real-world systems. Contact angles measured here, on smooth slides of a given material, were not consistently in agreement with operative contact angles for a porous medium of the same material. To increase the utility of the proposed model, further work will be required to develop a predictive relationship between measured and operative contact angles. In addition further work is necessary to estimate operative contact angles at field sites. Field scale wettability is a complex phenomenon, dependent on a solid, aqueous, and NAPL chemistry. Knowledge of field sample mineralogy distribution and of pore fluid constituents would facilitate the measurement and prediction of operative contact angles. At this time, however, a limited number of studies have explored the prediction of contact angles based on sample mineralogy and pore fluid constituents. Further work is, therefore, necessary to quantify operative contact angles and implement the proposed model at field sites.

The proposed model was developed for fractional wettability media. Further work will be required to investigate applications of the model to mixed wettability conditions.

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