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AIR-WATER INTERFACIAL AREA AND CAPILLARY PRESSURE: POROUS-MEDIUM EXTURE EFFECTS AND AN EMPIRICAL FUNCTION

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Abstract

The relationship between air-water interfacial area and capillary pressure under higher water-content conditions is investigated for four natural porous media. The results show that the magnitude of the air-water interfacial area increases with increasing capillary pressure, consistent with the decrease in water saturation. The maximum observed air-water interfacial areas are dependent upon the magnitude of residual water saturation, which itself is condition dependent. The more well-sorted porous medium exhibited a greater rate of change of air-water interfacial area with capillary pressure than the more poorly-sorted porous media. The observed relationship between air-water interfacial area and capillary pressure was quantified by coupling an empirical equation describing the air-water interfacial area vs. water saturation relationship with the van Genuchten equation relating water saturation and capillary pressure. This equation produced reasonable simulations of the measured data.

INTRODUCTION

The air-water interface in unsaturated porous media is an important factor influencing fluid flow, contaminant transport, and mass and energy transfer in the vadose zone. Potential relationships between air-water interfacial area and capillary pressure are of interest for example in modeling water flow. Such relationships have been investigated in prior theoretical and modeling based research [e.g., Gvirtzman and Roberts, 1991; Hassanizadeh and Gray, 1993; Reeves and Celia, 1996; Or and Tuller, 1999; Dalla et al., 2002; Niemet et al., 2002; Schroth et al., 2008].

Examination of air-water interfacial phenomena and potential relationships with physical properties and conditions has been constrained by a lack of means by which to measure air-water interfacial areas. Recent advances in tracer [e.g., Karkare and Fort, 1996; Brusseau et al., 1997; Kim et al. 1997, 1999; Costanza and Brusseau, 2002] and imaging [e.g., Culligan et al., 2004; Brusseau et al., 2006, 2007] methods have relaxed this constraint. Concomitantly, experiment-based investigations of the relationship between air-water interfacial area and capillary pressure have begun to be reported [Cheng et al., 2004; Culligan et al., 2004; Brusseau et al., 2006; Chen et al., 2007; Pyrak-Nolte et al., 2008].

The objective of this study was to investigate the influence of porous-medium texture on the relationship between air-water interfacial area and capillary pressure. An empirical equation was developed to describe the observed relationships.

MATERIALS AND METHODS

Four porous media were used in this study: accusand sand, granusil sand, Vinton soil, and Hayhook soil. The accusand and granusil sands are commercially available, well-sorted natural sands (Unimin Corporation, Lesueur, MN and Unimin Corporation, Cleburne, TX). Vinton soil (sandy, mixed thermic Typic Torrifluent) and Hayhook soil (coarse loamy, mixed, superactive, thermic Typic Haplocambids) were collected locally in Tucson, Arizona and were sieved to remove the >2 mm fraction prior to use. The relevant physical properties of these media are presented in Table 1.

The interfacial area data used for this study (see Figure 1) were reported by Peng and Brusseau [2005]. The gas-phase tracer method [Brusseau et al., 1997; Kim et al., 1999; Costanza-Robinson and Brusseau, 2002] was used to measure volume-normalized air-water interfacial areas (A_{ia} , cm^{-1}). See Peng and Brusseau [2005] for more detailed information about these experiments. It is critical to note that areas obtained with this method represent total areas, in that both capillary-associated and film-associated interfacial areas are included in the measurements. In addition, they incorporate interfacial area associated with microscopic surface roughness [Brusseau et al., 2006, 2007, 2008]. It is useful when comparing data for multiple porous media to normalize the measured A_{ia} values by the specific solid surface area (s) measured using a method such as N_2 /BET. With this approach, the relative A_{ia} values (A_{ia}/s) will scale from 0 to 1 as shown in Figure 1.

For the current work, soil-water drainage experiments were conducted using the hanging water column method to characterize the relationship between water saturation (S) and capillary pressure (P_c) for the selected media [e.g., Warrick, 2003]. These measurements were conducted using tap water and at a temperature of approximately 23 C. The van Genuchten equation [van Genuchten, 1980] was calibrated to the measured data using the computer code RETC 4 [van Genuchten et al., 1991].

The measured A_{ia} - S and S - P_c data sets were integrated to obtain the A_{ia} - P_c relationships. For cases where water saturations did not correspond exactly between the two data sets, A_{ia} values were interpolated. Multiple water saturations and phase configurations can exist for a given capillary pressure dependent upon the wetting or drying history. However, to simplify the study, the focus was on primary drainage, and hysteresis was not incorporated into the analysis. The A_{ia} - P_c data for the Vinton soil were previously reported by Brusseau et al. [2006]; the A_{ia} - P_c data for the other three media have not been previously reported.

RESULTS AND DISCUSSION

Influence of Texture

The results of the water-drainage experiments are presented in Figure 2. Inspection of Figure 2 reveals that accusand, the coarsest medium, has the smallest air-entry value, as expected. Hayhook, Vinton, and granusil have residual water saturations of approximately 20%, 15%, and 10%, respectively, while accusand has a significantly smaller value (1%). The capillary pressures associated with the residual water saturations, defined as the water entry value (P_{cw}) herein, are estimated to range from 20–30, 80–120, 160–200, and 250 cm H_2O , for accusand, granusil, Vinton, and Hayhook, respectively. It is recognized that residual water saturation is condition dependent and may vary with measurement method. The residual water saturations reported herein correspond to gravity-drainage conditions. The van

Genuchten equation provides reasonable fits to the soil-water characteristic curve data, as shown in Figure 2.

The relationships between air-water interfacial area and capillary pressure are shown in Figure 3. The total A_{ia} is observed to increase with increasing P_c , as reported in prior studies [e.g., Or and Tuller, 1999; Dalla et al., 2002; Brusseau et al., 2006]. The change in A_{ia} with capillary pressure is greater at lower P_c and smaller at higher P_c . This is due to the different rates of change in water saturation for different P_c ranges (e.g., greater change at lower P_c), coupled with the relationship between A_{ia} and water saturation (as illustrated in Figure 1).

As previously discussed, A_{ia} values measured using the gas-phase tracer test method for conditions of very low water saturation are similar to specific solid surface areas measured with methods such as N_2 /BET (Costanza-Robinson and Brusseau, 2002; Peng and Brusseau, 2005; Brusseau et al., 2007). For accusand, the condition-dependent maximum A_{ia} value is essentially identical to the specific solid surface area determined using N_2 /BET. For the granusil medium, the condition-dependent maximum A_{ia} value is approximately 40% of the specific solid surface area. Conversely, the condition-dependent maximum A_{ia} values are much smaller than the corresponding specific solid surface areas for Vinton and Hayhook (~6% and ~2%, respectively). The disparity between the results for accusand and granusil versus the other two media is due in part to the lower residual water saturations associated with the accusand and granusil media (closer to mono-layer equivalent saturations), which have narrower grain-size distributions. It should be noted that the maximum observed A_{ia} will be condition dependent, given that the magnitude of residual water saturation will be condition dependent (e.g., measurement method, initial conditions, drainage-imbibition history).

Inspection of Figure 3 reveals that Vinton and Hayhook soils, which have wider particle-size distributions, exhibit more gradual changes of A_{ia} . Conversely, accusand, which has the narrowest particle-size distribution, has the sharpest change. A given change in capillary pressure will generally cause a larger change in water saturation for a well-sorted porous medium than for a poorly sorted porous medium. Thus, the more well-sorted porous medium will experience a greater change in A_{ia} , given the relationship between A_{ia} and water saturation.

Quantifying the A_{ia} - P_c Relationship

The results of the experiments reported by Peng and Brusseau [2005] showed that the magnitude of the air-water interfacial areas increased nonlinearly with decreasing water saturation (see Figure 1), and approached that of the specific solid surface areas, s . An empirical equation patterned after the van Genuchten equation was developed to describe the observed relationship between air-water interfacial area and water saturation:

$$A_{ia} = s[1 + (\alpha(S - S_m))^n]^{-m} \quad (1)$$

where S is water saturation ($S = V_v / V_p$); V_v is volumetric water content; V_p is porosity; S_m is the monolayer water saturation; s is the normalized specific surface area of the porous medium, which is determined using the surface area measured with the N_2 /BET method; and α , n , and m are coefficients, where $n = 1/(2-m)$. The coefficients α and m were found to correlate to the porous-medium uniformity coefficient, U , as follows [Peng and Brusseau, 2005]:

$$\alpha = 14.3 \ln(U) + 3.72 \quad (2)$$

$$m = \begin{cases} -0.098U + 1.53 & , U < 3.5 \\ 1.2 & , U \geq 3.5 \end{cases} \quad (3)$$

Equation 1 can be combined with a function describing the $S - P_c$ relationship, such as the van Genuchten equation:

$$S = S_r + (1 - S_r)(1 + (\alpha_v P_c)^{n_v})^{-m_v} \quad (4)$$

where α_v , n_v , and m_v are undetermined parameters, and $m_v = 1 - 1/n_v$; S_r is the residual water saturation.

Combining Equations 1 and 4 yields an empirical relationship for A_{ia} vs. P_c as:

$$A_{ia} = s \{ 1 + [\alpha ((S_r + (1 - S_r)(1 + (\alpha_v P_c)^{n_v})^{-m_v}) - S_m)]^n \}^{-m} - C \quad (5)$$

Equation 5 was used to simulate A_{ia} values as a function of capillary pressure, employing the parameter values reported in Table 2. Parameters in Table 2 are listed in two subsets: parameters for the A_{ia} - S equation (Equation 1) and parameters for the $S - P_c$ equation (Equation 4). Parameters for Equation 4 were obtained through calibration to the soil-water characteristic curve data, while parameters for Equation 1 were obtained through calibration to measured A_{ia} - S_w data (see details in Peng and Brusseau, 2005). For the more typical case wherein A_{ia} - S_w data are not available, the correlations presented in equations 2 and 3 would be used to parameterize equation 1. Parameter C is a coefficient to force A_{ia} to equal zero at full saturation.

The results of using equation 5 to simulate A_{ia} as a function of capillary pressure are shown in Figure 3. It is observed that Equation 5 provides a reasonable representation of the measured data. This suggests that Equation 5 may be useful estimating interfacial areas as a function of capillary pressure.

SUMMARY

The magnitude of air-water interfacial area was observed to increase with increasing capillary pressure, approaching a maximum value dependant upon specific solid surface area and residual water saturation. The more well-sorted porous medium exhibited a greater rate of change of air-water interfacial area with capillary pressure than the more poorly-sorted porous media. The observed relationship between air-water interfacial area and capillary pressure was quantified by coupling an empirical equation describing the relationship between air-water interfacial area and water saturation and the van Genuchten equation relating water saturation and capillary pressure. It is recognized that there is uncertainty associated with such empirical equations. However, the ability to produce estimates based on relatively simple system measurements (soil-water characteristic curve, texture analysis) provides a useful advantage in accessibility.

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Figure 1. Measured and simulated relationships between relative specific air-water interfacial area (A_{ia}/s) and water saturation for the porous media.

Figure 2. Measured and simulated soil-water characteristic curves for the porous media used in the study.

Figure 3. Measured relationships between air-water interfacial area (A_{ia}) and capillary pressure (P_c). Comparison of measured and simulated (Equation 5) air-water interfacial area vs. capillary pressure.

Table 1

Relevant properties of the porous media used in the experiments.

Sand	Median diameter (mm)	Uniformity coefficient, U_1	Specific surface area ² (m^2/g)	Porosity	Bulk density (g/cm^3)
Accusand	0.677	1.16	0.14	0.42 ± 0.02	1.55 ± 0.04
Granusil	0.172	1.77	0.43	0.43 ± 0.01	1.54 ± 0.03
Vinton	0.234	2.4	3.54	0.46 ± 0.02	1.46 ± 0.04
Hayhook	0.26	16	8.8	0.39 ± 0.01	1.64 ± 0.03

¹ $U = d_{60}/d_{10}$, where d_{60} and d_{10} are the diameters for which 60% and 10% of the sample are finer by weight, respectively.

² measured with the N_2 /BET method by Quantachrome Instruments (Boynton Beach, FL) and Micromeritics Corporation (Norcross, GA).

Table 2

Coefficients used in Equation 5 to predict the A_{ia} - P_c relationship (for analysis presented in Figure 3).

Sand	Parameters in A_{ia} - S_w equation					Parameters in van Genuchten equation				
	s	m	n	S_m	$C(\text{cm}^{-1})$	S_r	ν	m_ν	n_ν	
Accusand	2046	4.24	1.5	2.01	0	24	0.005	0.09	0.87	7.81
Granusil	6677	8.72	1.28	1.39	0	133	0.05	0.026	0.83	5.85
Vinton	51330	19.78	1.36	1.55	0	104	0.07	0.025	0.71	3.43
Hayhook	145200	42.3	1.2	1.25	0.01	529	0.078	0.024	0.56	2.26

Values for s and S_m are measured; the others are calibrated as noted in the text.