Wetting Alteration of Silicate Surfaces by Brine and Crude Oil

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ABSTRACT

Contact with crude oils can alter the wetting of initially water-wet surfaces. If those surfaces are flat, the effect of wetting alteration can be observed directly by changes in oil/water contact angles. In porous media, changes in wetting must be inferred from indirect measurements. The wetting conditions established either on flat surfaces or in porous media depend on the surface mineralogy, compositions of both oil and brine phases, and aging conditions (time and temperature), but as yet no clear connection between surface measurements and wetting of crude oil/brine/rock ensembles has been made. To bridge that gap, we compare the effects of a well established wetting transition that occurs with changes in aqueous phase pH on the wetting of flat surfaces and two types of cores, a synthetic silicate material and Berea sandstone.

Two sodium chloride solutions (pH 4 and 8) were found to produce a clear distinction in wetting. Tests with identical fluid properties, differing only in wetting conditions, were compared. On flat surfaces, tests included adhesion and oil/water contact angles measured on altered surfaces. Imbibition and waterflood tests were conducted in cores. Imbibition rates confirm the relationship between wetting in the synthetic cores and on flat surfaces. Oil recovery efficiency is shown to depend on pore structure as well as on the wettability.

INTRODUCTION

It is now widely accepted that oil reservoirs can have a range of wetting conditions that depends not only on the oil and rock, but also on the composition and amount of the brine phase. Crude oil/brine/rock (COBR) interactions have been used to create wetting conditions in laboratory samples that may be more representative of wetting in an oil reservoir than either the strongly water-wet or strongly oil-wet extremes.[1]

Factors that can influence the extent of wetting alteration in COBR ensembles include the chemical compositions of the crude oil, brine, and mineral surfaces, as well as the duration of contact between these phases and the temperature during the aging period. In cores, the brine saturation is important as well.[2] Moreover, the additional complexities of rough surfaces, converging and diverging pore shapes, and heterogeneous mineralogy can all contribute to generation of complicated wetting conditions. Contact angle hysteresis, associated with both the physical and chemical heterogeneities of surfaces,[3] and pinning of three-phase contact lines can produce further contact angle hysteresis.[4] Superimposed on all these sources of heterogeneity and hysteresis in natural porous media, is the ability of crude oil components to adsorb onto mineral surfaces, changing surface wetting properties. Circumstances under which adsorption occurs, the extent to which wetting is changed, and the possibility that adsorption of crude oil components is reversible, have been reported for smooth surfaces.[5] What remains to be established is how the changes in wetting observed on flat surfaces correspond to the wetting alteration that occurs in a core.

Wetting transitions that depend on pH have been widely observed for crude oils.[6-11] Valat, *et al.*[9] determined adhesive (pH 2) and nonadhesive conditions (pH 11) for a French crude oil and glass using the adhesion test.[10] Waterflood displacements from bead packs under adhesive conditions produced less oil than did a similar flood with the nonadhesive brine. Early breakthrough of water and extended production of oil suggested more oil-wet conditions in the adhesive case, whereas the waterflood with the nonadhesive fluids was more typical of a water-wet displacement. IFT's were not reported, but may be significantly affected at these extremes of pH.

Skauge and Fosse[11] also used pH to vary wetting. A crude oil with 4.7% asphaltenes was tested on quartz surfaces and Berea sandstone cores. At higher pH (8.6), nonadhesion was observed and the water receding angle (θ_r) was 18°. At lower pH (5.4), adhesion occurred and θ_r increased to 42°. Decreasing endpoint relative permeabilities to water indicated more water-wet conditions as the pH of the waterflood solution increased. Better oil recovery was observed for less water-wet conditions, which is consistent with the findings of Jadhunandan and Morrow,[2] but in contrast to the bead-pack results.[9]

In this study, pH of low ionic strength NaCl solutions (buffered with weak acids and bases) is used to control wetting of crude oil on glass surfaces and in porous media. The aim is to investigate wetting alteration of porous media in the low ionic strength regime where DLVO theory successfully predicts stability of the water layer between oil and flat solid surfaces.

EXPERIMENTAL METHODS

Glass: Clean borosilicate glass microscope slides were used for tests of flat silicate surfaces.[5]

Synthetic core: Cylindrical cores were cut from a block of Aerolith-10. X-ray fluorescence showed that the Aerolith is composed of silica (90.6%) and alumina (4.25%), with minor amounts of other oxides and trace metals. Core dimensions and properties of the both Aerolith and Berea cores are included in Table 1.

Table 1. Properties of Aerolith and Berea Core Samples.

Core Material	Core ID	Length (cm)	Diameter (cm)	K_{N2} (md)	K_{brine} (md)	Porosity (%)
Aerolith	A2	4.43	3.59	4800	1520	43.45
Aerolith	A3	5.61	3.60	4500	1390	43.33
Aerolith	A4	5.14	3.58	4340	1960	44.46
Aerolith	A5	5.98	3.61	4725	1860	44.96
Berea	Q70	6.33	3.61	1060	270	21.44
Berea	Q71	5.31	3.60	1100	267	22.15

Brines: The brine phase was one of two low ionic strength solutions of 0.1 *M* NaCl in solutions buffered with either acetic acid (pH ≈ 4) or phosphate salts (pH ≈ 8). Solutions were degassed and passed through a Millipore AP25 inline prefilter prior to entry into cores.

Oils: An asphaltic crude oil from Alaska (A-93) was used in this study. Light ends were evaporated off before the flow experiments. Results of previous wetting studies with this crude oil have been published showing wetting alteration on flat surfaces[5] and in cores.[12] A refined oil mixture (referred to as Mix-1) of toluene and a viscous paraffinic oil (180-190 Saybolt Viscosity Paraffin Oil), was used to replace crude oil in the imbibition studies. This mixture does not cause precipitation upon mixing with A-93 crude oil. Physical properties of the brine and oil samples are included in Table 2. There is little change in IFT over the pH range of this study.

Table 2. Fluid Properties at 25°C (after evacuation).

	Composition	Density (g/cm^3)	Viscosity (cp)	IFT (dyn/cm)	
				Mix-1	A-93
low pH brine	pH=4; $[Na^+]$=0.1*M*	1.0026	1	30	23.5
high pH brine	pH=8; $[Na^+]$=0.1*M*	1.0051	1	30	20.3
A-93 (cyl-1)	10.7% asphaltenes	0.9016	52		
A-93 (cyl-2)	not measured	0.9025	70		
Mix-1	1/5 Toluene + 4/5 paraffin oil	0.8630	12		

Adhesion and Adsorption: Interactions between oil, brine, and flat glass surfaces were observed by adhesion[10] and adsorption[5] methods, reported previously.

Core Preparation: Cores were dried for several days at 80°C and N_2 permeabilities were measured. The cores were then saturated with either low or high pH brine and allowed to equilibrate for one week at room temperature. Fresh brine was injected into the core and the permeability to brine was measured. Effluent pH was monitored for the first four pore volumes produced and variations were observed to be small. At least 20 PV of brine were flushed through each of the cores. Porosity was calculated gravimetrically. Cores were then flooded with 20 PV of A-93 crude oil to establish initial water saturation (S_{wi}), aged in crude oil for two weeks at 80°C, cooled to room temperature, and reflooded with either fresh A-93 (waterflood) or Mix-1 (imbibition). Permeability to oil at initial water saturation, $K_{o(Swi)}$, was measured after aging. Similar measurements were repeated for Berea sandstone cores.

Imbibition and Waterfloods: Rates of spontaneous imbibition of both water and oil were recorded from observations of the change in weight.[13] Aerolith cores at S_{wi} were submerged in brine of the same composition as that initially saturating the core. Tests continued until no further oil production could be discerned. The cores were then waterflooded to provide endpoint saturation values for Amott indices. The process was repeated for cores submerged in oil (Mix-1), to establish oil imbibition indices. Constant flow-rate waterfloods were performed at low and high flow rates using a standard experimental set-up.[14] Differential pressure and fluid volumes produced were recorded as a function of time. Waterfloods were simulated with a one-dimensional coreflood model.

RESULTS AND DISCUSSION

Wetting Alteration on Flat Surfaces: Fig. 1 shows the adhesion map of A-93 crude oil under NaCl brines of varying pH and ionic strength, at 80°C. A transition from adhesion to nonadhesion occurred between pH 4 and 6 for 0.1 *M* NaCl solutions. Changes that occur during longer periods of crude oil contact were evaluated by the adsorption test, as shown in Fig. 2. Both the adhesion and adsorption tests predict that more water-wet conditions should be expected in siliceous porous media saturated with the pH 8 solution and less water-wet for those saturated with pH 4 solutions.

Wetting Alteration in Synthetic Cores: Wetting was altered in cores using the same fluids (pH 4 and 8 NaCl solutions and A-93 crude oil) as were used in the flat surface tests. Test conditions and results are summarized in Table 3. The rates of water imbibition (Fig. 3) demonstrate that

(1) wetting has been changed by contact with crude oil,
(2) neither high nor low pH case is strongly water-wet, and
(3) the high pH case is significantly more water-wet (I_w = 0.97) than the core equilibrated with the low pH solution (I_w = 0.49).

The strongly water-wet case, shown for comparison, was measured in a larger Aerolith core, contacted only with brine and mineral oil.[15] The inset to Fig. 3 shows the three imbibition rates compared on the basis of dimensionless time.[16] Almost no oil imbibes into either core.

Table 3. Summary of Core Tests

Core material	Core ID	pH	Oils	Flow rate (cm^3/hr)	V_{front} (ft/day)	S_{wi} (%)	$K_o(S_{wi})$ (md)	S_{or} (%)	Final Rec. (%OOIP)	I_w
Aerolith-10	A3	4	A-93	4 70	1.4 20	18.8 16.5	1510 1750	30.8 21.4	63.3 74.4	
Aerolith-10	A2	8	A-93	4 70	1.15 19	18.1 23.5	3600 3000	11.8 9.9	85.6 87.0	
Aerolith-10	A5	4	A-93; Mix-1			18.6	3480	25.6	68.6	0.49
Aerolith-10	A4	8	A-93; Mix-1			21.0	3800	14.3	81.8	0.97
Berea	Q70	4	A-93	4.5 70	2.3 53	21.5 33.0	74 70	20.0 19.9	74.0 70.3	
Berea	Q71	8	A-93	4.3 70	3.9 75	19.7 30.1	350 660	41.6 37.5	48.1 46.3	

Oil Recovery by Waterflooding: Waterfloods were performed in crude oil-aged cores at two flow rates. A low rate flood at about 1 ft/day was followed by a second waterflood at a rate about 20 times higher than the first. The results are shown in Fig. 4. In the high-rate waterfloods of Aerolith, the pH 8 case was significantly more efficient in recovering oil (final recovery = 87% OOIP) than the pH 4 flood (final recovery = 74% OOIP). Extended production was observed to some extent for both cores. Displacement efficiency was better for low-rate floods. Fits to the high-rate waterfloods gave the relative permeabilities shown in Fig. 5. It was not possible, however, to use these k_r values to fit the low rate floods. Subsequent measurements with decane showed that absolute permeability is not constant in Aerolith, but varies with flow rate from about 3000 md at 300 cm^3/hr to 4500 md at about 80 cm^3/hr. Evidently there are loose particles (initially water-wet) that can reversibly impede flow. The existence of these particles makes comparisons between high and low flow rate waterfloods less useful, but does not interfere with the wettability study.

For Berea cores, the oil recovery trends are reversed (Fig. 6): better recovery in the pH 4 waterfloods and very poor displacement efficiency in the pH 8 tests, in agreement with Skauge and Fosse.[11] The high-rate waterfloods in Berea are not entirely comparable to the low-rate floods because initial water saturations were consistently and substantially higher on secondary drainage than they had been for primary drainage (Table 3). Trapping of additional water on secondary drainage is characteristic of cores that develop mixed wetting during aging.[17,18] Trapping was not in evidence during secondary drainage of Aerolith, probably because of the highly porous, well-connected, and unconstricted nature of the pore networks. Sandstones typically have more contrast between pore and throat dimensions and thus more constrictions that promote trapping.

Pore lining minerals may also be an important difference between the Aerolith and Berea cores. Aerolith is made from crystalline silica and silicic acid and contains some alumina. Berea has a framework of silica grains, but it also contains other minerals, including clays, which have different surface properties than silica. Clays may also provide a source of multivalent ions by ion exchange. If so, changes in brine compositions would also have an impact on oil-solid interactions. Finally, rock-brine interactions may cause changes other than wetting.[19] The produced water in the pH 8 test was milky in appearance after passing through the Berea core, although permeability damage was not observed.

Optimal Oil Recovery Efficiency: What should be the best wetting conditions for oil recovery is the subject of continuing debate. For Berea sandstone with wetting altered by aging in crude oils, optimal oil recovery was observed in weakly water-wet cores that imbibed a little water and no oil, with a combined Amott index ($WI = I_w - I_o$) of about 0.3.[2] This result challenged the commonly held view that the best recovery occurs under strongly water-wet conditions. Measurements in Berea were not pursued with the low ionic strength brines in this study because rock-brine interactions may interfere, but the preliminary results showing better recovery for low pH brine are consistent with the trend of optimal recovery in weakly water-wet systems.

In Aerolith, as in bead packs,[9] more water-wet conditions appear to give better recovery efficiency. This trend is also consistent with previously published waterflood results in Aerolith (Fig. 7).[20] Gauchet's strongly water-wet case was measured with mineral oil, like the most rapidly imbibing case shown in Fig. 3. In our work, the more water-wet case has an Amott index of one, but the rate of water imbibition is suppressed. Wetting distinctions are indicated in Fig. 7 by shading of the bars. No shading is used for the case where the core has never been in contact with crude oil. The lightest shading indicates the case where $I_w=1$, but the imbibition rate is suppressed. Closer inspection of Fig. 7 shows that there may be a small improvement in recovery efficiency over strong water-wetting, although the recovery is already quite high. Lower, rate-dependent displacement efficiencies are found for the less water-wet (pH 4 case) and weakly oil-wet[20] conditions.

An important distinction between these two classes of porous media is the extent to which capillary trapping can occur. The interrelationships between wetting and pore geometry and their combined effects on two-phase flow have been demonstrated in micromodels with converging and diverging pores.[21] Earlier observations in simpler micromodels of intersecting capillary tubes, with minimal capillary trapping, led to the conclusion that strongly water-wet conditions were optimal for maximizing oil recovery,[22] but in strongly trapping porous media like Berea sandstone, displacement efficiency is poor under strongly water-wet conditions and improves as conditions become less strongly water-wet. Much less improvement would be expected in the case, like Aerolith, where there was less trapping at the outset. Strong oil-wetting would lead to poor recovery efficiency in both high- and low-trapping media. Intermediate wetting resulted in poorer recovery in the simple capillary tube micromodel because of the formation of viscous fingers. Growth of viscous fingers is opposed by strong capillary forces and thus is more of a problem when capillary forces are weak. In Aerolith, especially with a viscous oil, bypassing of oil may reduce recovery efficiency when water imbibition is suppressed, whereas in the highly trapping media, recovery is improving because of the suppression of snapoff events that cause oil to be trapped.

Strong oil-wetting has not been encountered in any of the work reported here, nor is it reported in the references cited on alteration of wetting by crude oils. Even when contact angles on flat surfaces exceed 150°, as they do for A-93 and pH 4 brine on glass aged at elevated temperatures, cores were altered to weakly water-wet, not oil-wet conditions. In part, the expression of high contact angles as weakly water-wet conditions in a core may be related to development of mixed-wet conditions, with some surfaces altered and others, protected by thick water films, remaining water-wet. Slow desorption of adsorbed components[5] may also play a role in cores with altered wetting that imbibe water, but very slowly.

CONCLUSIONS

- Wetting alteration of silica surfaces by interactions with an asphaltic crude oil from Alaska can be controlled by changing the pH of low ionic strength solutions of monovalent salts.

- Wetting changes observed in porous media show the same trends as measurements of wetting alteration on flat glass surfaces by adhesion and adsorption techniques, if cores and flat surfaces have similar surface chemistry.

- With high pH salt solution (pH 8, [NaCl] = 0.1 *M*) more water-wet conditions were observed, whereas with a lower pH solution (pH 4, [NaCl] = 0.1 *M*), wetting was less water-wet for cores of Aerolith-10 aged in Alaska-93 crude oil.

- Better oil recovery efficiency, found for more water-wet Aerolith cores, illustrates the combined effects of wetting and pore geometry. The opposite trend in Berea sandstone is consistent with this explanation, but interpretation is hindered by the possibility of rock/brine interactions that may change properties other than wetting.

NOMENCLATURE

CSC	critical salt concentration	$K_{o\,(Swi)}$	permeability to oil with initial water saturation in the core (md)
I_o, I_w	Amott wettability indices to oil and water	k_{rw}	relative permeability to water
WI	combined wettability index ($WI=I_w-I_o$)	$k_{rw(Sorw)}$	relative permeability to water with waterflood residual oil
OOIP	original oil in place (%)	k_{ro}	relative permeability to oil
IFT, σ	interfacial tension (dynes/cm)	t	imbibition time (min)
K, K_{N2}	absolute permeability to nitrogen (md)	T_d	dimensionless time
K_{brine}	absolute permeability to brine (md)	θ_a, θ_r	contact angle, water advancing and receding (degrees, °)

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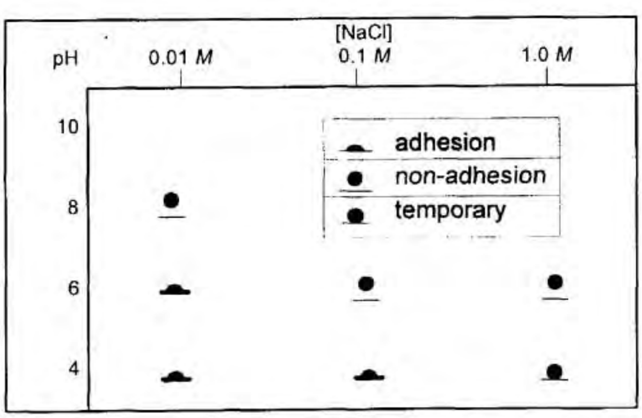

Figure 1. Adhesion of A-93 crude oil with NaCl brines on glass at 80°C.

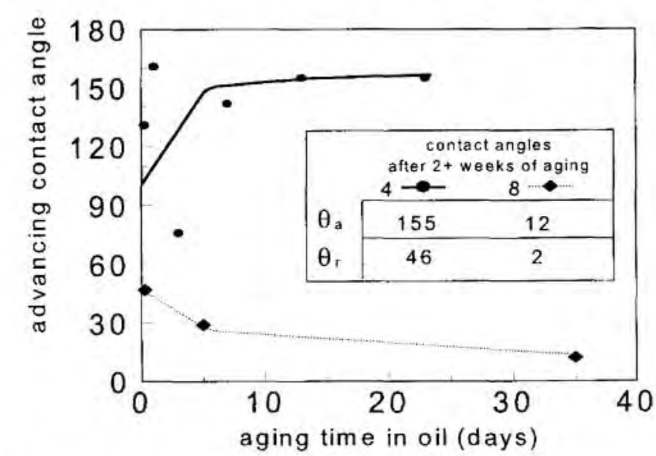

Figure 2. Adsorption of A-93 crude oil with 0.1 *M* NaCl brines on glass at 80°C.

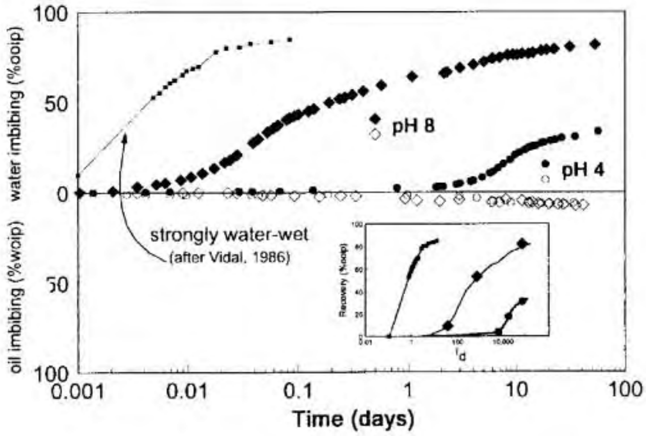

Figure 3. Imbibition into Aerolith-10 cores.

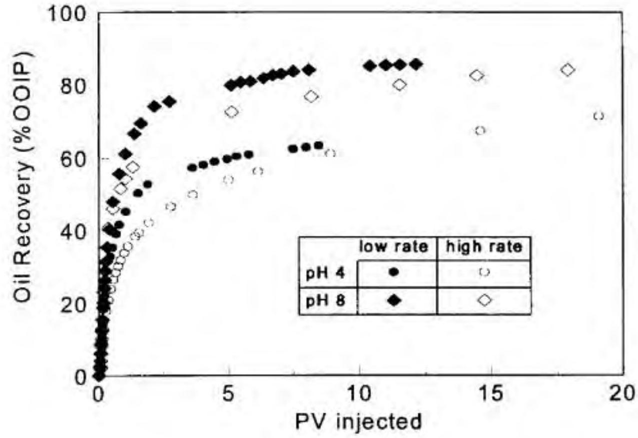

Figure 4. Waterfloods of Aerolith-10 cores.

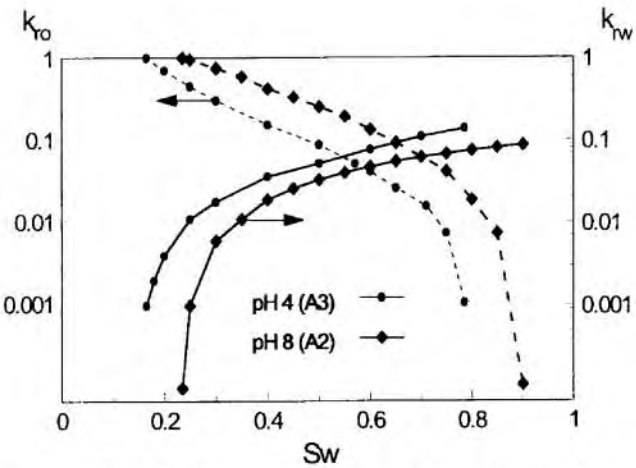

Figure 5. Relative permeabilities from fits to high rate waterfloods of Aerolith-10.

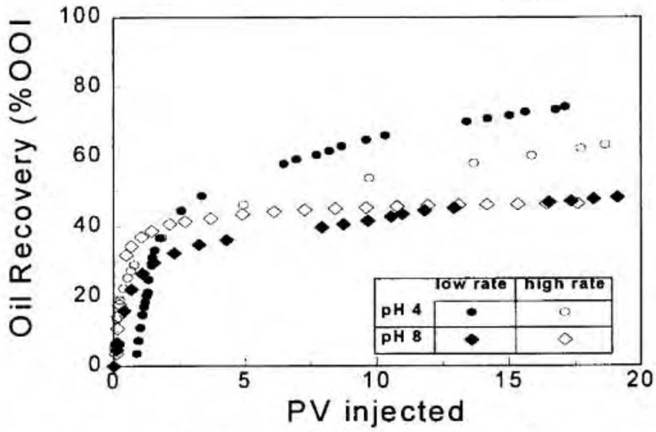

Figure 6. Waterflood of Berea sandstone.

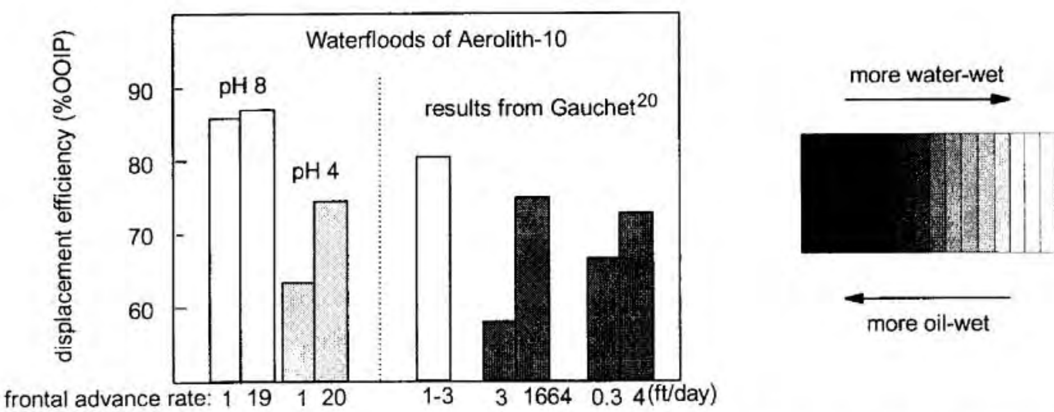

Figure 7. Waterflood displacement efficiency for different wetting conditions and frontal advance rates in Aerolith-10.