The Use of Capillarity Surfaces to Predict Phase Distributions In Mixed-Wet Porous Media.

MCDUGALL, Steven R, Heriot-Watt University Edinburgh, UK

DIXIT, Ashok B, Heriot-Watt University Edinburgh, UK

SORBIE, Kenneth S, Heriot-Watt University Edinburgh, UK

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ABSTRACT

Pore-scale network models have been used to study a range of nonuniformly-wet systems, their associated capillary pressure curves, imbibition characteristics and waterflood recovery efficiencies. Recent research has demonstrated that wettability alteration depends upon a variety of factors, including; ageing temperature, brine pH/composition, crude oil composition, and connate water saturation. The premise here, however, is that the net result of these parameters is to produce a particular *distribution* of contact angles within the pore system. Consequently, the ageing process characterising a particular wettability experiment produces oil-wet pores with effective contact angles in the range $\theta_{o1} < \theta_o < \theta_{o2}$ and water-wet pores with $\theta_{w1} < \theta_w < \theta_{w2}$. The underlying pore-scale physics has been further explored by defining a *capillarity surface* which, when examined in conjunction with percolation theory, can be used to predict phase distributions for any contact angle range. Indeed, results show that a sample containing pores with a *range* of effective contact angles can imbibe up to 50% more water than one that is strongly water-wet. A number of apparently contradictory experimental observations have also been successfully reproduced and interpreted in light of this new theory.

1 INTRODUCTION

Numerous reports of experimental work relating to the role of non-uniform wettability in various aspects of oil recovery have been published, although a precise taxonomy of wettability is still lacking. Ageing temperature, brine pH/composition, crude oil composition, and connate water saturation have all been shown to play an important role in determining the ultimate wettability state of a system (Dubey and Waxman, 1989; Hirasaki *et al.*, 1990; Dubey and Doe, 1991; Jadhunandan and Morrow, 1991; Wolcott *et al.*, 1991, 1993; Buckley, 1993; Kovscek *et al.*, 1993). Unfortunately, variations in laboratory procedure and experimental materials make generalised conclusions almost impossible and the precise wettability conditions prevailing at the end of a conditioning procedure are frequently difficult to deduce. Moreover, there are even

serious doubts concerning the cross-correlation of the two main experimental methods used to determine core wettability, i.e. Amott and USBM tests. Indeed, until some clear theoretical interpretation of such matters is available, it is difficult to see how results from different laboratories can be adequately reconciled and understood.

To this end, the work presented here focuses upon the systematic investigation of wettability alteration at the pore-scale and its subsequent impact upon waterflood displacement efficiency. Pore-scale models have been used to study a range of nonuniformly-wet systems, their associated capillary pressure curves, spontaneous water imbibition characteristics and waterflood recovery behaviour. The models are capable of simulating the full flooding cycle characteristic of laboratory wettability tests (primary drainage, "ageing", water imbibition, water drive, oil imbibition, oil drive).

The first part of the cycle (primary drainage of water by oil from a water-wet system) is followed by an "ageing" process, whereby wettability alterations occur at the pore-scale. As noted earlier, in a physical system, wettability alteration depends upon a variety of factors. The premise here, however, is that the net result of these parameters is to produce a particular distribution of contact angles within the system. Consequently, the simulated ageing process produces oil-wet pores with contact angles in the range $\theta_{o1} < \theta_o < \theta_{o2}$ and water-wet pores with $\theta_{w1} < \theta_w < \theta_{w2}$. Of course, the precise range operating during an experiment depends upon complex interactions amongst the factors mentioned above. Thus, instead of quantifying the effects of contact angle range for one particular case, the model has been used to examine the *sensitivities* of a cycle of displacements running under a number of different wettability scenarios. The results have been illuminating and have led to the concept of a **capillarity surface**, which can be used to predict phase distributions for any contact angle range. A number of contradictory experimental observations have been reproduced and interpreted using this new approach.

2. FLOW SIMULATIONS IN SYSTEMS OF NON-UNIFORM WETTABILITY

2.1 Generation of Model and the Flooding Cycle

A 3-D pore-scale model of average co-ordination number four ($z=4$) has been used for the simulations. For simplicity, a uniform pore size distribution has been assumed: radii in the range of 0.1 to 100 μm are assigned to pore elements by using a random number generator. All pores are assumed to be of equal length (100 μm) and have a cylindrical geometry. Note, however, that these are *not* limitations of the model, as any other pore size distribution and/or volume function can be included in order to mimic alternative geometries. Such sensitivities have been carried out and overall trends are very similar to those reported later. The full five-flood cycle described above, including wettability alterations, is performed on all networks. The detailed algorithms corresponding to each stage of the cycle have been presented elsewhere (McDougall et al, 1995) and only the most important details are reported here.

The **primary drainage** simulation begins with a strongly water-wet network ($\theta=0^\circ$ in all pores) at 100% water saturation. The capillary pressure is increased step by step from zero to a value at which the continuity of water is lost (hydraulic discontinuity). At each pressure step, water and oil saturations are evaluated and the primary drainage capillary pressure curve constructed.

The experimental work of various researchers indicate that components of the crude oil interact differently with different mineral substrates in the rock e.g. quartz, feldspars, clays, etc (Jordan et al, 1994). Therefore, we believe that the wettability alterations that have occurred in actual reservoirs, as well as those associated with core ageing experiments, are non-uniform; i.e. contact angles are not identical for all water-wet or oil-wet pores. These pore level wettability variations are incorporated in the network model as a result of **ageing**. It is assumed that the pores occupying initial water remain strongly water-wet ($\theta=0^\circ$) as they are not in contact with oil. However, the effective contact angles of the pores occupying oil after primary drainage may change during the ageing process. In the present study, a mixed-wet model of non-uniform wettability is considered as being most realistic: this is a system where the *largest* pores containing oil after primary drainage preferentially become oil-wet (Figure 1). This assumption is rigorously true for cylindrical pore elements and a heuristic argument based upon surface asperities can be invoked to generalise the assumption to pores of random geometry. The argument is outlined in Figure 2.

In the oil-wet pores, effective contact angles are distributed randomly from 91 to 180°. Note that

the remaining fraction of pores occupying oil after primary drainage remain water-wet (by definition, $\theta < 90^\circ$) and therefore, contact angles are distributed randomly between 0 and 89° in this region. We would like to emphasise two things: (i) no experimental techniques are currently available to measure such contact angle distributions in natural porous media and thus, the pore-scale simulator presented here provides an ideal theoretical tool to investigate and predict the expected *consequences* of various wettability/contact angle variations; (ii) the term "*effective contact angle*" is used here to include the effects of pore geometry — wall curvature and measured fluid/solid contact angles combine to give an effective meniscus curvature that we characterise using the effective contact angle).

The subsequent steps in the flooding cycle, namely **water imbibition, forced water drive, oil imbibition and forced oil drive** are simulated using this modified/aged network.

Many researchers have observed film-flow via thin wetting films in multiphase flow experiments using glass micromodels. In the present model, a realistic partial film-flow mechanism is implemented during all four stages of the cycle following ageing. Note, that film-flow affects not only the imbibition of a phase *into* the network but also its escape *from* it during other parts of the flooding cycle. The details of the partial film-flow mechanism are as follows:

Both water-wet and oil-wet pores are subdivided into two categories, depending upon their contact angle: (i) it is assumed that water can invade by film flow only in pores with contact angles in the range 0 to θ_{cw} (strongly water-wet), whilst oil can only escape through films in pores having contact angles between θ_{co} and 180° (strongly oil-wet). θ_{cw} and θ_{co} are critical cut-off values; (ii) a continuous path of water-filled pores is essential for the remaining weakly water-wet pores ($\theta_{cw} < \theta < 89^\circ$) to become available for invasion. Similarly, oil-wet pores with $91^\circ < \theta < \theta_{co}$ require a continuum of oil to the outlet of the system in order to escape. Analogous arguments hold when oil is the invading phase. In the present study, the values of θ_{cw} and θ_{co} have been taken as 45° and 135°, respectively. The partial film-flow mechanism is considered by the authors to be the most realistic mechanism operating in natural porous media

It is well known that the advancing contact angle is usually higher than the receding contact angle (Morrow, 1975). This experimentally observed phenomenon is also incorporated in the model. A

distribution of advancing contact angles is used during imbibition processes whereas receding contact angles are employed for drainage processes. In all the simulations presented here, the receding contact angle was taken to be 20% less than the corresponding advancing angle (broadly in line with experimental data).

3 RESULTS AND DISCUSSION

The more "severe" the ageing conditions under which wettability alteration occurs, the greater the number of those pores occupied by oil after primary drainage that will become oil-wet. In the present study, a number of different ageing conditions are simulated simply by converting different fractions of oil-filled pores from a water-wet to an oil-wet state after the primary drainage simulation. Note that the pores occupied by initial water remain strongly water-wet ($\theta=0^\circ$) even after ageing and therefore, for a finite initial water saturation, the fraction of oil-wet pores in the network (α) is always less than one. In the present study, primary drainage is terminated at water hydraulic discontinuity. According to percolation theory, in an infinite network of a given co-ordination number (z), hydraulic discontinuity would be observed when the fraction of water-occupied pores in the network is slightly less than the corresponding percolation threshold (P_T) of the system (Stauffer and Aharony, 1994). Therefore, for this study, the maximum value of α ($\alpha_{\max}$) is equal to $1-P_T$. For $z=4$, this corresponds to $\alpha \approx 0.625$. We note that it is possible to have, $\alpha_{\max} > 1-P_T$, if we continue to allow water to escape via thin films along water-wet clusters after hydraulic discontinuity has been reached. This work is currently in progress.

Although a wide range of sensitivities has been performed during this work (using different film-flow mechanisms, different co-ordination numbers, mixed- and fractionally-wet systems), discussion will be restricted here to the role played by distributed contact angles during oil/water displacements. Results from systems containing pores with **distributed** contact angles (i.e. water-wet pores with $0^\circ < \theta < 90^\circ$ and oil-wet pores with $90^\circ < \theta < 180^\circ$), will be compared with those from systems containing pores with **single-valued** contact angles (i.e. *all* water-wet pores having $\theta=0^\circ$ and *all* oil-wet pores having $\theta=180^\circ$, say).

3.1 Capillary Pressure Curves

Single-Valued Contact Angles: Simulated capillary pressure curves for a variety of networks with single-valued contact angles are presented in Figure 3. Consider first the strongly water-wet network ($\alpha=0$, Figure 3a). Following the imbibition curve downwards from the end of primary drainage, it is found that about

30% of the total pore volume is occupied by water after water imbibition. The third and fourth parts of the flooding cycle (forced water drive and oil imbibition), produce curves that are completely vertical: this is due to the absence of any oil-wet pores in the network. The final stage of the procedure, oil-drive, is characterised by its hysteresis with the water imbibition curve.

An immediate observation from Figure 3 is that the amount of water imbibed decreases with an increase in α . This is due to: (i) a reduction in the number of water-wet pores in the network, which cuts down the number of possible imbibition paths, and (ii) the connectivity of the system ($z=4$), which means that the number of *isolated* water-wet clusters present after ageing also increases with α . These isolated water-wet clusters are effectively shielded from the invading water by oil-wet pores during imbibition.

The water saturation at the end of water-drive is found to remain almost constant up to $\alpha=0.375$, because no connected path of oil-wet pores is yet available to transfer oil via film-flow. Only after $\alpha > 0.375$ should any difference be seen, as this is the percolation threshold for oil-wet pores. This has been borne out by simulation — for $\alpha=0.469$ and 0.625 , the water saturations after forced water drive are found to be much higher than those with $\alpha=0.156$ and 0.313 .

A continuous oil-wet cluster from the surface is also essential for oil imbibition during stage four of the cycle: no imbibition of oil is observed for $\alpha=0.156$ and 0.313 as expected. For $\alpha > 0.375$, however, the extent of oil imbibition increases rapidly, as the oil-wet pores aggregate to form larger spanning clusters.

When $\alpha=0.625$ (i.e. when all oil-filled pores at the end of primary drainage have become oil-wet), no imbibition of water takes place at all because all of the water-wet pores are associated with disconnected irreducible water (Figure 3c): no oil drainage occurs for the same reason. Note also, that the end-of-cycle water saturation is slightly higher than the connate water saturation, which implies that water ultimately remains trapped in both oil-wet and water-wet pores. These observations are consistent with experimental results reported by Salathiel (1973).

Distributed Contact Angles: Having outlined the typical behaviour of single-valued contact angle systems, compare now the results obtained from systems with distributed contact angles. The corresponding capillary pressure curves are shown in Figure 4. The extent of water imbibition differs significantly from that obtained from single-valued contact angle systems. Compare the results for $\alpha=0$ (note that although $\alpha=0$ means that no oil-wet pores exist, weakly water-wet pores - $0^\circ < \theta < 89^\circ$ - are present). The extent of spontaneous water imbibition increases by $\sim 55\%$ to 0.384 PV when the contact angles are distributed between 0° and 89° . This compares with only 0.248 PV imbibed with single-valued contact angles ($\theta=0^\circ$). Moreover, for $\alpha < 0.375$ (percolation threshold), the water saturations at the end of the *forced* water drive

decrease significantly with α when contact angles are distributed. Remember that this effect was absent after waterflooding systems characterised by single-valued contact angles. *These results clearly indicate that a distribution of contact angles at the pore-scale plays a crucial role in determining recovery in systems of non-uniform wettability.* In fact, it will now be shown that it is the actual range of contact angles that is of primary importance.

Table 1 shows water saturations and % OOIP (original oil in place) recovered after water imbibition for various effective contact angle ranges in a 100% water-wet system. Notice that the extent of water imbibition with distributed contact angles up to 30° is almost identical with that resulting from single-valued contact angles. Even with $\theta=0-60^\circ$, the water saturation is only marginally higher than that obtained with all $\theta=0^\circ$. Only when contact angles are assigned from the range $0-89^\circ$ is water imbibition substantially enhanced — implying something special about the range $60-89^\circ$. This has been confirmed by distributing the contact angles within the restricted ranges $45-89^\circ$ and $60-89^\circ$ (see Table 1). This has major implications for laboratory wettability tests: *these results show that a sample containing pores with a range of contact angles can imbibe up to 50% more water than one that is strongly water-wet ($\theta=0^\circ$).* What is even more surprising, is that this is even true for a system that would appear to be neutrally-wet on the basis of contact angle measurements ($\theta=60-89^\circ$). So, what are the reasons for this intriguing behaviour?

3.2 Contact Angle Distributions and Capillarity Surfaces

Consider the simple example of five oil-filled cylindrical capillary tubes of differing radii. When the oil/water contact angle is the same in each tube, the imbibition filling sequence is entirely governed by pore radius through the Young-Laplace equation — the smallest tube fills first, and so on (Figure 5a). With distributed contact angles, however, this need no longer be the case, as shown in Figure 5b; the filling sequence can be altered dramatically, because some of the smaller pores may now possess large contact angles and can only be filled at very low capillary pressures. This is rather intuitive and not too surprising, but the next example highlights a less-obvious effect. What happens to the filling sequence if the contact angle of each tube is simply halved; i.e. if the set of contact angles is changed from $\{9^\circ, 15^\circ, 50^\circ, 76^\circ, 88^\circ\}$ to $\{4.5^\circ, 7.5^\circ, 25^\circ, 38^\circ, 44^\circ\}$? On the face of it, the filling sequence should be the same as before, as all angles have simply been reduced by a factor of 2 and their rank order remains the same. The new filling sequence, shown in Figure 6c, demonstrates that this need not be the case, however. This rather surprising result is due to the nonlinearity of the cosine function and its implicit nonlinear effect upon capillary pressure. The combined effects of contact angle and capillary entry radius can perhaps best be understood by defining a **capillarity surface**. This is a three-dimensional plot of capillary pressure as a function of both contact angle and capillary entry radius; i.e. the surface:

$$P_c(r, \theta) = \frac{2\sigma \cos \theta}{r} \dots\dots\dots(1)$$

A typical example is shown in Figure 6a — the nonlinearity is self-evident. An important consequence of such a plot is that approximate phase distributions can be predicted for any array of capillary elements (including interconnected networks) simply by examining the associated surface in the light of percolation theory. This is best illustrated with reference to a fully connected 3D water-wet network ($z=6$), which remains free of additional topological complications.

By taking a number of sequential horizontal cross-sections through the capillarity surface (i.e. planes of constant P_c), the progress of the imbibition floods can be studied as capillary pressure decreases (note that drainage floods can also be analysed, but accessibility has to be taken into account). Pores lying on the flat plateau of the sliced surface must have capillary entry pressures greater than that corresponding to the horizontal cut-off value and, if accessible, must be filled with water. Those pores not lying on the flat plateau must therefore be filled with oil as shown in Figure 6b. Capillarity surfaces for any range of contact angles or capillary entry radii can easily be plotted and sensitivities analysed. Such an analysis will now be conducted and used to examine two issues arising from the simulation results described earlier.

The first issue relates to the effect of contact angle range upon the early stages of water imbibition. To investigate this, four ranges are considered and a constant capillary pressure cut-off is used to slice all four capillarity surfaces at the same point during the displacement. The results are given in Figure 7. They clearly show that the amount of water *initially* imbibed *reduces* considerably once the contact angle range incorporates weakly water-wet pores ($60^\circ < \theta < 90^\circ$).

The second, more important, issue arising from the simulation studies, concerns the reduction seen in residual oil once weakly water-wet pores are incorporated into the system. By examining the capillarity surface in light of percolation theory, the reasons for this behaviour become clear. For a well-connected network with $z=6$, the percolation threshold is approximately 0.25 (Stauffer and Aharony, 1994), so at the end of water imbibition, about 75% of the pores will contain water. Hence, the residual oil saturation can be estimated for all four cases by slicing the corresponding capillarity surface at a capillary pressure value that leaves 75% of the pores lying in the plateau region. The unshaded regions in Figure 8 therefore show the distributions of oil-filled pores at the end of water imbibition. Although the unshaded regions all have the same area (approximately 25% of the square), their shapes differ: it can therefore be concluded from the figure that residual oil should be maximum when the contact angles are all 0° and minimum when they range from 0° to 90° .

The two sets of sensitivities just described mean that the capillary pressure curves from the four systems must actually cross one another. The implication for petrophysical practice is that wettability-imbibition trends depend entirely upon the capillary pressure cut-off employed in the laboratory. Moreover, the results presented here demonstrate that the contact angle *range* plays a major role in determining the form of capillary pressure curves and residual saturations.

3.3 Oil Production During Water Imbibition

The water imbibition capillary pressure curves as functions of produced OOIP from single-valued and distributed contact angle networks are given in Figure 9. The imbibition curve for the single-valued water-wet system ($\theta=0^\circ$ for all pores in the network) is also given in Figure 9b for reference. With single-valued contact angles, imbibition is maximum in a 100% water-wet system ($\alpha=0$) and diminishes monotonically with an increase in the fraction of oil-wet pores. In the case of distributed contact angles, however, oil production for $\alpha=0$ and $\alpha=0.156$ is actually *higher* than that obtained from the strongly water-wet system. For larger α , production again decreases.

These results, when viewed in light of the earlier theoretical discussion, may go some way towards a clearer interpretation of many contradictory experimental results of the past. Jadhunandan (1990) has reported similar experimental trends from cores aged using various brines at 26°C. For a brine composition of 4% NaCl and 0.2% CaCl₂, for example, the oil produced by water imbibition was found to be higher than that observed in a strongly water-wet core: no explanation was given. The work reported here would suggest that the increase in water imbibition in the aged core is probably due to a distribution of contact angles at the pore-scale; such anomalous behaviour cannot be explained by assuming single valued contact angles. Other experimental examples (Graue et al, 1994, Ma et al, 1994) are also consistent with the theory developed here. Such experimental evidences provide useful support for the physics underpinning the pore-scale simulator. A great deal of additional experimental data has been interpreted using a regime-based framework based upon the network model described here. Details can be found in Dixit et al (1996).

4. CONCLUSIONS

Capillary pressure curves from mixed-wet systems have been analysed using a 3-D pore-scale simulator which takes into account many pore level flow processes: non-uniform wettability alterations, partial film flow, trapping of wetting and non-wetting phases, variations in advancing and receding contact angles, etc.

It has been proposed that the ageing of cores produces pores with a *distribution of effective contact angles*; i.e. oil-wet pores in the range $\theta_{o1} < \theta_o < \theta_{o2}$ and water-wet pores with $\theta_{w1} < \theta_w < \theta_{w2}$.

Simulations predict that final waterflood recoveries from weakly water-wet (or even weakly oil-wet) systems can often exceed those from strongly water-wet systems (even though *initial* imbibition rates may lead to the opposite conclusion).

The underlying pore level physics has been explored by defining a *capillarity surface* which incorporates the combined effects of both contact angle and pore dimension during the imbibition process.

Theoretical models derived in this paper, in conjunction with pore-scale simulation, have led to the development of a new analytical framework within which apparently contradictory wettability experiments can be reconciled.

NOMENCLATURE

P_T = Percolation threshold

S_{wi} = Initial water saturation

z = Mean co-ordination number

α = Fraction of oil-wet pores in the network

α_{cr} = Critical fraction of oil-wet pores

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Table 1. Effect of Contact Angle Range Upon Imbibition and Oil Recovery

Contact Angle Range	Sw After Imbibition	%OIP Produced After Imbibition
0-0°	0.31	26.13
0-15°	0.31	26.13
0-30°	0.299	25.22
0-45°	0.327	28.21
0-60°	0.337	29.28
0-89°	0.446	40.9
45-89°	0.408	36.85
60-89°	0.411	37.17

Figure 1. Schematics of mixed-wet pore size distribution

Figure 2. Heuristic argument showing why the largest oil-filled pores may become oil-wet after aging — regardless of pore geometry. Consider two triangular pores of equal length but differing cross-sectional area. Applying thin film theory to this system would result in both pores becoming oil-wet at the same time (critical disjoining pressure is exceeded in both pores simultaneously). However, pore surfaces are rough, so consider a distribution of asperity heights arranged as a regular lattice on the pore surface. As disjoining pressure increases, wetting films rupture at the highest asperities first (largest negative interfacial curvatures here). Hence, problem becomes one of percolation upon the pore wall itself — an oilwet pathway exists across the pore once sufficient asperities have become oil-wet and this will occur first in the widest pore (the thinner pore has a smaller width/length aspect ratio and the percolation problem becomes more and more 1-dimensional as the pore aspect ratio decreases).

Figure 3. Capillary pressure curves from five systems with single-valued contact angles: (a) $\alpha=0$; (b) $\alpha=0.469$; (c) $\alpha=0.625$

Figure 4. Capillary pressure curves from five systems with distributed contact angles: (a) $\alpha=0$; (b) $\alpha=0.469$; (c) $\alpha=0.625$.

Figure 5. Tube filling sequences during imbibition for 5 tubes of differing radii: (a) all contact angles= 45° ; (b) contact angles distributed from 0° - 90° ; (c) contact angles half those in (B).

Figure 6. (a) Schematic example of a capillarity surface, $P_c(r, \theta)$ (θ in radians); (b) water and oil pore occupancy for imbibition

Figure 7. Capillarity surfaces, $P_c(r, \theta)$, for various ranges of water-wet contact angle; the water-filled pores are shown shaded for each contact angle range (a) $\theta = 0^\circ$, (b) $\theta = 0-45^\circ$, (c) $\theta = 0-60^\circ$ (d) $\theta = 0-90^\circ$.

Figure 8. Distribution of water and oil filled pores at residual oil; the water-filled pores are shown shaded for each contact angle range; (a) $\theta = 0^\circ$, (b) $\theta = 0 - 45^\circ$, (c) $\theta = 0 - 60^\circ$ (d) $\theta = 0 - 90^\circ$.

Figure 9 Spontaneous water imbibition curves from mixed-wet systems; (a) single valued contact angles (b) distributed contact angles. NB the values of α shown here actually correspond to the fraction of *oil-filled* pores that become oil-wet after primary drainage. To obtain the fraction of *total* pores that are oil-wet, multiply these values by 0.625.