Fundamentals of Wettability

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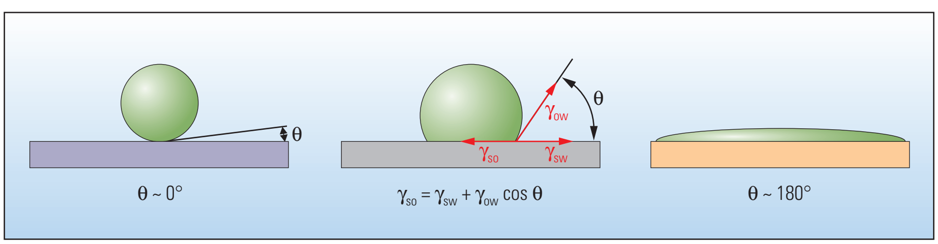
Understanding formation wettability is crucial for optimizing oil recovery. The oil-versus-water wetting preference influences many aspects of reservoir performance, particularly in waterflooding and enhanced oil recovery techniques. Making the assumption that a reservoir is water-wet, when it is not, can lead to irreversible reservoir damage.

Wetting forces are in play all around us. They have practical applications, such as making rain bead up on a freshly waxed car so it is protected from rust. And they provide whimsy: wetting forces bind sand grains to hold the shape of a child's sand castle.

Forces of wetting influence hydrocarbon reservoir behavior in many ways, including saturation, multiphase flow and certain log interpretation parameters. However, before getting into these details, it is best to first establish what wettability is.

Wettability describes the preference of a solid to be in contact with one fluid rather than another. Although the term "preference" may seem odd when describing an inanimate object, it aptly describes the balance of surface and interfacial forces. A drop of a preferentially wetting fluid will displace another fluid; at the extreme it will spread over the entire surface. Conversely, if a nonwetting fluid is dropped onto a surface already covered by the wetting fluid, it will bead up, minimizing its contact with the solid. If the condition is neither strongly water-wetting nor strongly oil-wetting, the balance of forces in the oil/water/solid system will result in a contact angle, θ, between the fluids at the solid surface (below).

In many oilfield applications, wettability is treated as a binary switch—the rock is either water-wet or oil-wet. This extreme simplification masks the complexity of wetting physics in reservoir rock. In a homogeneous, porous material saturated with oil and water, "strongly water-wetting" describes one end member of a continuum in which the surface strongly prefers contact with water. A strongly oil-wetting surface prefers contact with oil.[1] Degrees of wetting apply along the continuum, and if the solid does not have a marked preference for one fluid over the other, its condition is termed intermediate-wetting or neutral-wetting. Parameters that influence where on the continuum a system lies are discussed later.



^ Contact angle. An oil drop (green) surrounded by water (blue) on a water-wet surface (*left*) forms a bead. The contact angle θ is approximately zero. On an oil-wet surface (*right*), the drop spreads, resulting in a contact angle of about 180°. An intermediate-wet surface (*center*) also forms a bead, but the contact angle comes from a force balance among the interfacial tension terms, which are γ_{so} and γ_{sw} for the surface-oil and surface-water terms, respectively, and γ_{ow} for the oil-water term.

Reservoir rocks are complex structures, often comprising a variety of mineral types. Each mineral may have a different wettability, making the wetting character of the composite rock difficult to describe. Typically, the primary constituents of reservoirs—quartz, carbonate and dolomite—are water-wet prior to oil migration.

This brings up a further complexity: the saturation history of the material may influence surface wetting, such that pore surfaces that had been previously contacted by oil may be oil-wet, but those never contacted by oil may be water-wet. Various terms have been used to describe both of these conditions, including mixed-, fractional- and dalmation-wetting. In this article, the general term "mixed-wetting" will be used for any material with inhomogeneous wetting. It is important to note the fundamental difference between intermediate-wetting (lacking a strong wetting preference) and mixed-wetting (having a variety of preferences, possibly including intermediate-wetting) conditions.

Another important distinction is that a preferentially water-wetting surface can be in contact with oil or gas. Wettability does not describe the saturation state: it describes the preference of the solid for wetting by a certain fluid, given the presence of that preferred wetting fluid. Thus, a water-wet rock can be cleaned, dried and fully saturated with an alkane, while the surfaces in the pores remain water-wet. This can be easily seen: drop such an oil-saturated but water-wet rock into a beaker of water and it will spontaneously imbibe a significant quantity of water and expel oil.

Strictly speaking, the term imbibition refers to an increase in the saturation of the wetting phase, whether this is a spontaneous imbibition process or a forced imbibition process such as a waterflood in a water-wet material. Conversely, drainage refers to an increase in saturation of the nonwetting phase. However, in practice, the term imbibition is used to describe a process with increasing water saturation, and drainage is used to describe a process with increasing oil saturation. Care should be taken when reading the literature to determine which sense is being used.

This article outlines the effects of wettability in the oil field, and then describes the basic chemistry and physics of wetting that explain these effects. The emphasis here is on oil/water/solid interactions, but there are also gas/liquid/solid systems for which wettability is important. The measurement methods are briefly described. Two case studies from the Middle East and a North Sea chalk laboratory study describe scenarios that require an understanding of wettability. Laboratory methods with the potential to improve our ability to measure and model wettability conclude the article.

The Practical Importance of Wettability

The current, favorable oil price has improved the economics of waterflooding and some enhanced oil recovery methods. With multiple phases flowing in the reservoir, understanding wettability becomes important.[2] However, even during

1. Unless otherwise specified in this article, the terms "water-wet" and "oil-wet" are used to indicate "strong" preferences.
2. An extensive wettability literature survey was published in 1986 and 1987.

   Anderson WG: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *Journal of Petroleum Technology* 38 (October 1986): 1125–1144.

   Anderson WG: "Wettability Literature Survey—Part 2: Wettability Measurement," *Journal of Petroleum Technology* 38 (November 1986): 1246–1262.

   Anderson WG: "Wettability Literature Survey—Part 3: The Effects of Wettability on the Electrical Properties of Porous Media," *Journal of Petroleum Technology* 38 (December 1986): 1371–1378.

   Anderson WG: "Wettability Literature Survey—Part 4: Effects of Wettability on Capillary Pressure," *Journal of Petroleum Technology* 39 (October 1987): 1283–1300.

   Anderson WG: "Wettability Literature Survey—Part 5: The Effects of Wettability on Relative Permeability," *Journal of Petroleum Technology* 39 (November 1987): 1453–1468.

   Anderson WG: "Wettability Literature Survey—Part 6: The Effects of Wettability on Waterflooding," *Journal of Petroleum Technology* 39 (December 1987): 1605–1622.

primary recovery, wettability influences productivity and oil recovery.[3] The original wettability of a formation and altered wettability during and after hydrocarbon migration influence the profile of initial water saturation, S_{wi}, and production characteristics in the formation.

Most reservoirs are water-wet prior to oil migration and exhibit a long transition zone, through which saturation changes gradually from mostly oil with irreducible water at the top of the transition zone to water at the bottom. This distribution is determined by the buoyancy-based pressure difference between the oil and water phases, which is termed the capillary pressure, P_c (below). Oil migrating into an oil-wet reservoir would display a different saturation profile: essentially maximum oil saturation down to the base of the reservoir. This difference reflects the ease of invasion by a wetting fluid.

Layers within formations can also have different wetting states because of lithology variations. A tight zone may remain water-wetting if little or no oil migrates into it, while surrounding formations are converted to a more oil-wet state. Other wetting variations may not be so easily explained. Several carbonate reservoirs in the Middle East are thought to have variation of wettability by layer, but the cause is not yet understood.

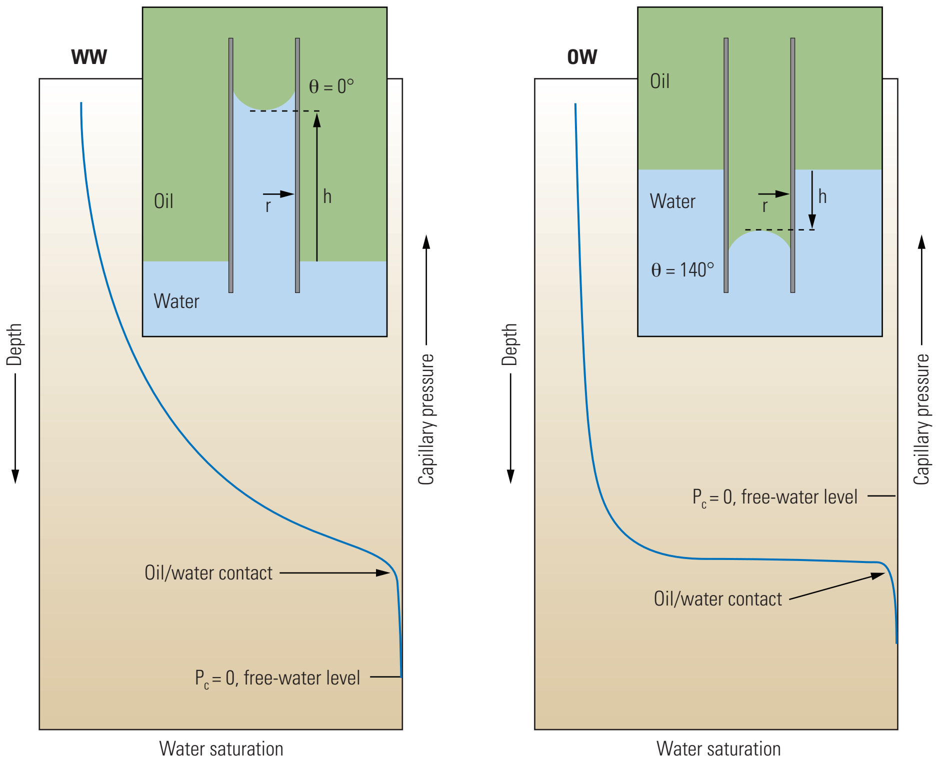
This wetting heterogeneity can affect recovery. For example, models using ECLIPSE reservoir simulation software incorporated parameters typical of a Middle East carbonate reservoir, with water-wet layers and oil-wet layers having similar permeabilities. Under waterflood, water penetrates the water-wet layers more readily than the oil-wet layers because of capillary effects. The simulation shows that little oil would be recovered from the oil-wet layers.

Wettability also affects the amount of oil that can be produced at the pore level, as measured after waterflood by the residual oil saturation, S_{or}. In a water-wet formation, oil remains in the larger pores, where it can snap off, or become disconnected from a continuous mass of oil, and become trapped. In an oil-wet or mixed-wet formation, oil adheres to surfaces, increasing the probability of a continuous path to a producing well, and resulting in a lower S_{or}.

Because the impact of wettability extends from pore scale to reservoir scale, wettability can affect project economics. Through the parameters S_{wi} and S_{or}, wettability influences oil recovery, one of the most important quantities in the E&P business. In addition, the relative permeabilities of oil and water vary with formation wettability. In projects with huge upfront capital expenditures for facilities, such as those in deepwater areas, failure to understand wettability and its ramifications can be costly.

Wettability affects waterflood performance, which also can involve significant upfront spending. Imbibition forces—the tendency of a formation to draw in the wetting phase—determine how easily water can be injected and how it moves through a water-wet formation. Water breakthrough occurs later in a waterflood, and more oil is produced before the water breaks through in a water-wet reservoir than in an oil-wet reservoir.

Wettability can also influence gasflood performance. The gasflood front or oil bank can move water, if it is mobile, again generating flow variation based on oil/water wetting preferences. In addition, if asphaltenes are present in the crude oil, contact by injected hydrocarbon gas alters the equilibrium condition and can lead to asphaltene precipitation. As discussed later, this precipitation can alter the wettability of the pore surfaces.



$P_c = P_{nw} - P_w$ where P_c = capillary pressure; h = height of capillary rise
$P_c = \rho g h$; P_{nw} = pressure in nonwetting phase; γ = interfacial tension
$P_c = 2\gamma\cos\theta/r$, P_w = pressure in wetting phase; θ = contact angle
ρ = density difference between phases; r = inner radius of capillary.
g = gravitational acceleration

^ Forming a transition zone. A homogeneous formation exhibits a zone of transition from high oil saturation at the top to high water saturation at the bottom (blue curves). This saturation transition has its origin in the capillary pressure, P_c, which is the difference between the water and oil pressures at the interface (equations, *above*). In a capillary tube, water-wetting (WW) surface forces cause water to rise (*left inset*), displacing oil, but if the tube inner surface is oil-wetting (OW), the oil will push water down (*right inset*). The wetting force, and therefore P_c, is inversely proportional to the capillary radius. The capillary rise, h, is determined by the balance of wetting forces and the weight of fluid displaced from the bulk-fluid interface. Translating this to a porous formation, there is a free-water level (FWL) defined where the capillary pressure between water and oil is zero. Since porous rocks have a distribution of pore and pore-throat sizes—similar to a distribution of capillary tubes—at any given height above the FWL, the portion of the size distribution that can sustain water at that height will be water-saturated. At greater height, the buoyancy of oil in water provides greater capillary pressure to force water out of smaller voids. In a water-wet formation (*left*), the oil/water contact is above the FWL, indicating that pressure must be applied to force oil into the largest pores. In an oil-wet formation (*right*), the contact is below the FWL, signifying that pressure must be applied to force the water phase into the largest pores. The oil/water contact divides the zone containing mostly oil from the one containing mostly water.

Even in a gas reservoir, wettability or its alteration can affect recovery. Condensate blockage near a wellbore decreases gas productivity. Some recovery methods use chemical means to alter the wettability around the wellbore to produce the oil and thereby clear the blockage.[4]

Some enhanced oil recovery processes are designed to overcome the wetting forces that trap oil. They aim either to alter the wetting preference of the formation to be more oil-wetting or to decrease the interfacial tension between the fluids, thereby decreasing the wetting forces.

Some logging methods are also dependent on wetting. Resistivity methods rely on a continuous electrical path through the rocks, which is provided by the water phase. In an oil-wet formation, the water may not be continuous. This influences the saturation exponent, n, in Archie's equation relating saturation and resistivity.[5] In water-wet conditions, n is ~2, but in oil-wet conditions, n is greater than 2. So if n is set to 2 in an oil-wet formation, a resistivity-based saturation assessment will likely be wrong.

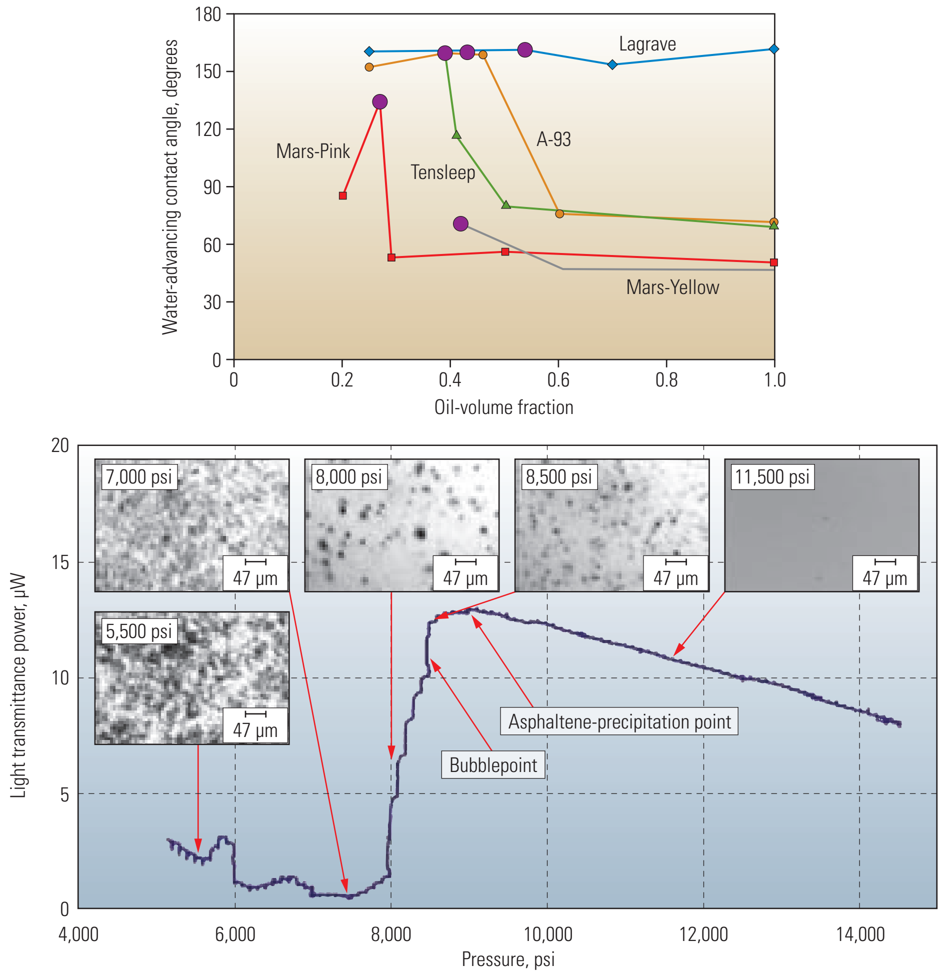
Nuclear magnetic resonance (NMR) responses also depend on the position of the fluids with respect to the pore surfaces. The nonwetting fluid exhibits relaxation rates similar to those of bulk fluid, because it sits in the middle of pores, while the wetting phase has shortened relaxation times because of surface interactions.[6]

Wettability is of vital importance to drilling-fluid formulation, particularly in oil-base muds. For example, surfactants are included to keep solids in suspension. An oil-external mud filtrate containing oil-wetting surfactants invades the near-well formation, potentially altering the wettability of the pores.[7] This can change the position of the fluids in the pore spaces, which may affect some logging responses. Because the alteration may not be permanent, different measurements may be obtained in subsequent logging runs.

Wettability Changes

Wetting forces lead to an equilibrium condition between at least three substances: a solid and two fluids.[8] The constituents and conditions for all three substances influence the wetting preference. Thus, we must consider the oil components, the brine chemistry and the mineral surface, as well as the system temperature, pressure and saturation history.[9]

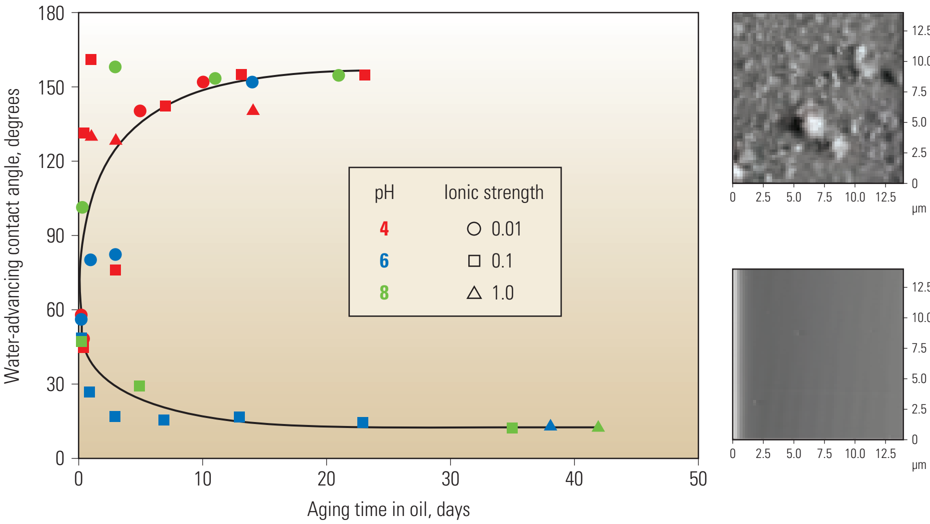
Oil composition is key to changing the wettability of a naturally water-wet surface, because any wettability-altering components are in the oil phase. These are polar compounds in resins and asphaltenes, both of which combine hydrophilic and hydrophobic characteristics. Bulk-oil composition determines the solubility of the polar components. A crude oil that is a poor solvent for its own surfactants will have a greater propensity to change wettability than one that is a good solvent (above).[10] Temperature,



^ Wettability alteration from asphaltene precipitation. Contact angles were measured after exposure to several crude oils diluted with n-heptane to various oil-volume fractions (*top*). The contact angle increased markedly near the asphaltene-precipitation point (large filled circles). Another way to induce asphaltene precipitation is by decreasing the pressure (*bottom*). In a PVT vessel, asphaltenes begin to flocculate, or clump together, as shown in high-pressure microscope photographs, as the pressure decreases to the asphaltene-precipitation point. As asphaltenes come out of solution, the light transmittance decreases (blue).

3. Morrow NR: "Wettability and Its Effect on Oil Recovery," *Journal of Petroleum Technology* 42, no. 12 (December 1990): 1476–1484.
4. For more on gas-condensate reservoirs: Fan L, Harris BW, Jamaluddin A, Kamath J, Mott R, Pope GA, Shandrygin A and Whitson CH: "Understanding Gas-Condensate Reservoirs," *Oilfield Review* 17, no. 4 (Winter 2005/2006): 14–27.

   For an example of wettability alteration in gas-condensate wells: Panga MKR, Ooi YS, Chan KS, Enkababian P, Samuel M, Koh PL and Chenevière P: "Wettability Alteration Used for Water Block Prevention in High-Temperature Gas Wells," *World Oil* 228, no. 3 (March 2007): 51–58.
5. Archie's equation can be expressed as $S_w = (R_t/R_o)^n$, where R_t is the formation resistivity at saturation S_w, and R_o is the formation resistivity at 100% water saturation.
6. For more on NMR logging: Alvarado RJ, Damgaard A, Hansen P, Raven M, Heidler R, Hoshun R, Kovats J, Morriss C, Rose D and Wendt W: "Nuclear Magnetic Resonance Logging While Drilling," *Oilfield Review* 15, no. 2 (Summer 2003): 40–51.
7. In an oil-external emulsion, surfactant molecules form clusters called micelles consisting of an aqueous core encapsulated in a surfactant monolayer, in which the hydrophilic parts of the molecules point inward toward the aqueous core and the hydrophobic parts point outward toward the oil phase.
8. Wetting preference also can involve three immiscible fluids, such as mercury, water and air.
9. Buckley JS, Liu Y and Monsterleet S: "Mechanisms of Wetting Alteration by Crude Oils," paper SPE 37230, *SPE Journal* 3, no. 1 (March 1998): 54–61.
10. Al-Maamari RSH and Buckley JS: "Asphaltene Precipitation and Alteration of Wetting: The Potential for Wettability Changes During Oil Production," paper SPE 84938, *SPE Reservoir Evaluation & Engineering* 6, no. 4 (August 2003): 210–214.



^ Effect of brine chemistry on film stability and contact angle. A glass surface was conditioned in water with a salt [NaCl] concentration of 0.01, 0.1 or 1.0 mol/m^3, and a pH of 4, 6 or 8. This water-wet surface was then aged in a crude oil known to contain components that can alter wettability. Contact-angle measurements showed oil-wetting behavior at low concentration and low pH, and water-wetting behavior at high concentration and high pH (*left*). The surface-water film retained its stability at high concentration and high pH. In related tests, freshly cleaved mica surfaces were aged in various NaCl solutions and then in the crude oil for 11 to 14 days. When the brine conditions (0.01 mol/m^3, pH = 4) allowed a change to oil-wetting state, a surface image from atomic-force microscopy (AFM) shows a complex of micron-sized surface irregularities deposited on the surface (*top right*). These were thought to be asphaltic material because the irregularities were insoluble in decane. A similar image of a mica surface aged in brine (1.0 mol/m^3, pH = 8) that retains a water-wetting surface film indicated no deposits (*bottom right*).

pressure and composition of the crude oil affect asphaltene stability (see "Asphaltenes—Problematic but Rich in Potential," *page 22*).

For components of an oil to alter wetting, the oil phase must displace brine from the surface. The surface of a water-wet material is coated by a film of the water phase.[11] The part of this water film that is closest to the surface forms an electrical double layer: excess charges on the solid surface are countered by electrolyte ions of opposite charge. The first layer of water with these ions is static, and the second layer exchanges ions with the bulk water.

When two interfaces—such as the solid-water and water-oil interfaces—are in proximity, the forces acting to keep them separated or draw them closer together include van der Waals, electrostatic, and structural or solvation interactions.[12] The net force is often expressed as a force per unit area, termed the disjoining pressure. A positive disjoining pressure holds the interfaces apart; a negative disjoining pressure between interfaces is attractive. The composition of crude oil, and the pH and composition of brine influence the disjoining pressure.

Measurements of these quantities have been used to predict water film stability, and the general trends are upheld by experiment. Atomic-force microscopy (AFM) has been used to image the solid surfaces after aging, providing graphic illustration of the complexity of surface interactions (above).[13] When the film destabilizes, polar components of the crude oil can adhere to the surface and make the surface more oil-wetting. Dissolved divalent ions, such as Ca^{2+}, can also destabilize the film.

Because of the presence and nature of ionized sites on the solid surface, the range of pH leading to instability is different for carbonates and sandstones. Silica surfaces are negatively charged above a pH of about 2, so positively charged ions (base chemical species) can adsorb. Conversely, calcite surfaces may be positively charged below pH 9.5, so negatively charged ions (acidic species) can adsorb.[14] Carbonate wettability is also influenced by specific interactions with carboxylic acids and by the reactivity of carbonate minerals.[15]

The existence of the double layers in the water phase explains why there is a difference between a material that is saturated with crude oil and one with surfaces that are wetted by oil. So long as the water film is stable, components of the crude oil cannot attach to the solid surface and alter the wetting tendency toward oil-wet. One result of this surface interaction is contact angle hysteresis. The water-advancing contact-angle, which is present when bulk water displaces bulk oil from a surface, can be much larger than the water-receding angle, which occurs when bulk oil displaces bulk water. Descriptions of the surface layers in these two conditions may be complex.[16]

This recalls another influence on the wetting preference of a surface, its saturation history. In an oil-bearing formation, the wettability can vary with depth, with a greater water-wetting preference near the bottom of the transition zone and a greater oil-wetting preference near the top.[17] The higher zones have a greater capillary pressure, which can counteract the disjoining pressure and destabilize the water film, allowing surface-active components in the oil to contact the solid. Lower in the structure, the solid surfaces mostly retain the water film.

However, saturation in a reservoir is not static. Multiple phases of oil migration, development of a gas cap, leakage of oil and gas from the reservoir and tectonic activity all can affect the saturation state of a reservoir. These changes will result in different fluid saturations based in part on the wettability of the surface at the time.

This dependence of saturation on history applies not only over geologic time, but also within drilling and production time scales. Drilling fluids, particularly oil-base muds, contain surfactants that can invade pore spaces. This invading fluid can alter wettability in the near-well region, affecting flow when the well is put on production. Fluids used in workover operations can have a similar near-well impact on wettability.

During production, the parameters already discussed in the context of primary production or waterflooding can also be changed by injected fluid that alters formation wetting either deliberately or inadvertently. This action may result in improved or damaged injectivity or productivity. An injected brine whose dissolved solid content or pH differs from those of the formation brine can induce wetting changes. Surfactants, including those generated by microbial action, can decrease the interfacial tension between fluids and change the contact angle. Quartz tends to become more oil-wet at higher temperatures, but calcite tends to become more water-wet.[18] Thus, thermal recovery methods can change wettability.[19]

As a reservoir is produced, pressure depletion can alter the composition of the crude, moving the asphaltene-precipitation point, which can lead to asphaltene deposition in the reservoir. This can also occur due to formation pressure or temperature decline, which, in addition to asphaltene dropout, can lead to wax formation, gas condensation, or formation of a gas cap; these affect the wettability distribution in a formation.

A Pore-Level View

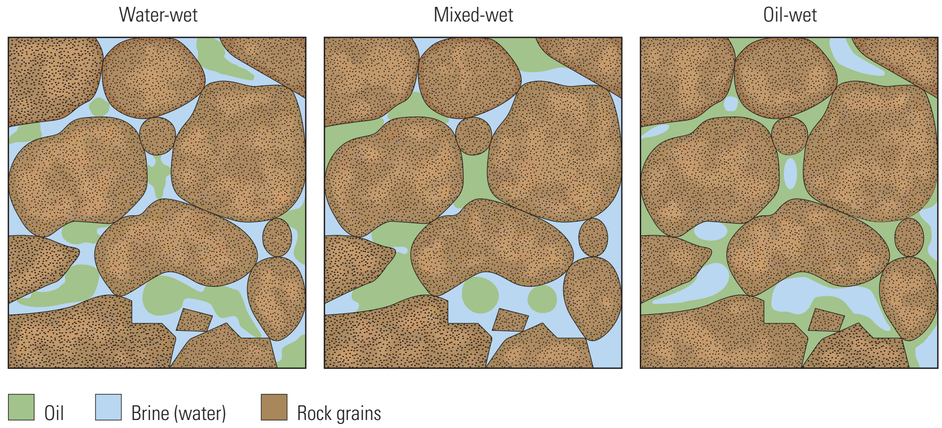
Pore geometry complicates the application of the wetting principles discussed above. A contact angle is easiest to understand when the surface is a smooth plane. However, pore walls are not smooth, flat surfaces, and typically more than one mineral species composes the matrix surrounding the pores.

Surface rugosity confounds visualization of a simple contact angle in a pore, because the apparent contact angle (based on the average plane of the surface) can differ markedly from the true contact angle, which is based on the local orientation of the surface (below). Sharp points, or asperities, on the surface can also be the loci for thinning of the water film coating the surface, leading to the potential for wetting alteration at these points.

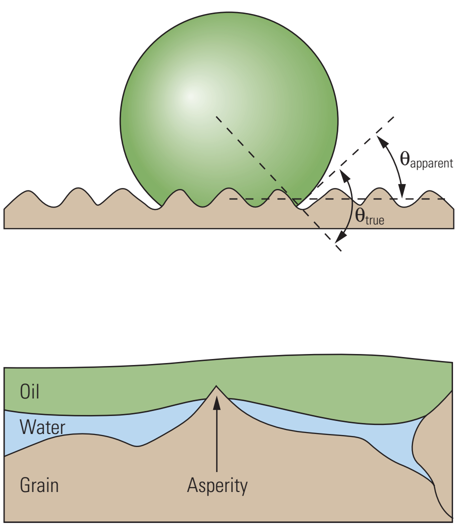
Conceptual or tutorial models of capillarity in porous media often refer to a "bundle of capillaries" model. The distribution of pore sizes is modeled by a distribution of capillaries with various radii. Each capillary is invaded by a nonwetting oil phase at a different capillary entry pressure, which is inversely proportional to that capillary's radius. Once the entry pressure is overcome, the whole cross section of the capillary is filled with oil.

In actuality, the complex geometry of a pore is defined by the grain surfaces surrounding it. The capillary entry pressure in this geometry relates to the inscribed radius of the largest adjacent pore throat. Although most of the pore body may fill with oil, the interstices where grains meet do not fill, because the capillary pressure is insufficient to force the nonwetting oil phase into those spaces.

Thus, depending on the pore and pore-throat geometry and the surface roughness, some parts of the pore space are oil-filled and the others are brine-filled (assuming no gas saturation). Some solid surfaces are in contact with oil, and for some or all of those surfaces, the water film may not be stable. Where the film is not stable, the surface wetting preference can be changed. This may lead to a situation of mixed wettability, where some parts of the pore surface are water-wetting and others are oil-wetting. The generally accepted theory is that because of the way this condition arose, the large pore spaces are more likely to be oil-wetting, and the small pore spaces and interstices within pores are more likely to be water-wetting (above).[20]



^ Wetting in pores. In a water-wet case (*left*), oil remains in the center of the pores. The reverse condition holds if all surfaces are oil-wet (*right*). In the mixed-wet case, oil has displaced water from some of the surfaces, but is still in the centers of water-wet pores (*middle*). The three conditions shown have similar saturations of water and oil.



^ Pore surface roughness. The apparent contact angle, measured from the average surface plane, can differ significantly from the true contact angle at a locally inclined surface (*top*). Even if a pore is water-wetting, the surface water may not be a double layer, but could be thicker due to pore rugosity (*bottom*). At an asperity, the surface forces are more favorable for displacing the double layer than elsewhere on the surface.

11. The double layer of water is almost always present on a water-wet material. It can be removed at high temperature, but soaking in water or condensation from humid air will replenish the double layer.
12. Hirasaki GJ: "Wettability: Fundamentals and Surface Forces," *SPE Formation Evaluation* 6, no. 3 (June 1991): 217–226.
13. Buckley JS, Takamura K and Morrow NR: "Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils," *SPE Reservoir Engineering* 4, no. 4 (August 1989): 332–340.

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17. Okasha TM, Funk JJ and Al-Rashidi HN: "Fifty Years of Wettability Measurements in the Arab-D Carbonate Reservoir," paper SPE 105114, presented at the 15th SPE Middle East Oil & Gas Show and Conference, Bahrain, March 11–14, 2007.

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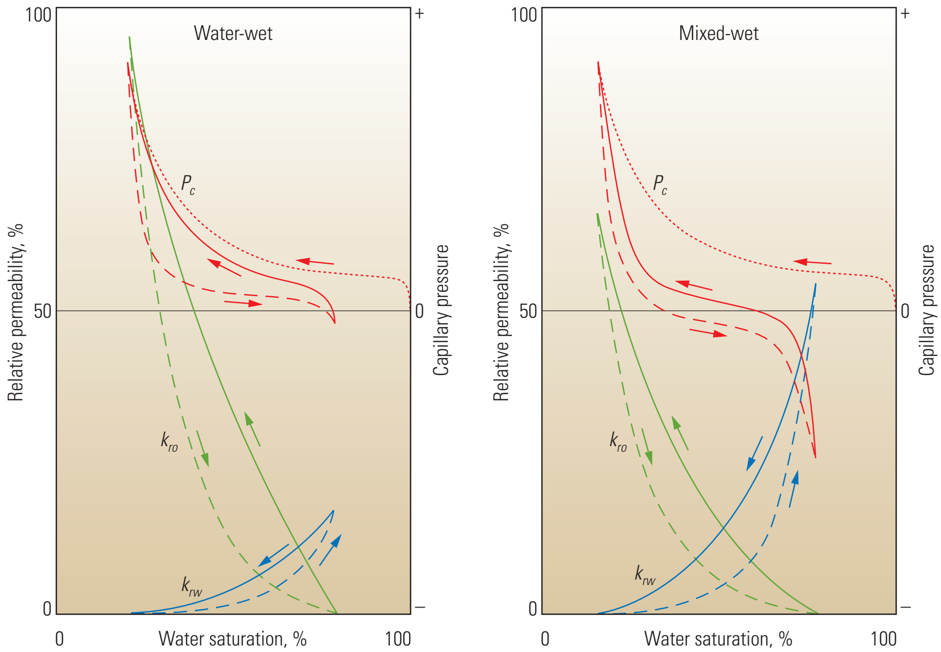


^ Capillary pressure and relative permeability for water-wet and mixed-wet conditions. This schematic representation contrasts possible capillary-pressure, P_c, (red) and relative-permeability curves for water, k_{rw}, (blue) and oil, k_{ro}, (green) for water-wet (*left*) and mixed-wet (*right*) reservoirs. The first curve to consider is the primary drainage P_c curve (dotted), which indicates a certain pressure in the oil phase that is required before a substantial displacement of water can occur. Since most reservoirs are considered to be water-wetting when oil first migrates, this curve is also used for the mixed-wet condition. The other curves (dashed = increasing water saturation, solid = increasing oil saturation) differ based on the wettability change due to oil contact with the surfaces in the large pore spaces. In the strongly water-wet situation, the capillary-pressure curve stays positive over most of the saturation range, while in the mixed-wet case its sign has both positive and negative portions, signifying that some parts of the surface imbibe water and others imbibe oil. The k_{ro} values are less at low water saturation in the mixed-wet case, because the oil is in competition with water in the large pores. Similarly, the k_{rw} at high water saturation is reduced in the water-wet case because the oil preferentially occupies the large pores.

This simple view assumes a homogeneous formation with oil migration from below. Most formations are more complex than this, and the lithological complexity must be taken into account when applying the migration history to the current wetting state.

In addition to this mixed wettability based on saturation history, there can be mineralogy-based mixed wettability. The pH and concentration conditions for a stable water film are different for quartz, dolomite and calcite surfaces, and for clays and other compounds within the pore space. Thus, different grains may have different wetting preferences.

Many experts today believe that most oil reservoirs have some mixed-wetting characteristics. The original, water-wet condition is altered to some extent by oil migration. In the following discussion, we examine the implications of the wetting condition on multiphase flow by examining the case of two-phase flow through a uniformly water-wet medium and then a mixed-wet medium (above).

Water-wet case—As the preferentially wetting phase, water will be in the small spaces that were not invaded by oil. Oil will be in the large pores. Before this formation is produced, both phases are continuous, although the connate water phase in the highest part of the formation may have such a low saturation that the relative permeability to water, k_{rw}, is essentially zero. Since electrical resistivity logging will respond to a continuous, conducting water phase, the use of an Archie saturation exponent, n, of around 2 is valid.

Under natural or induced waterflooding, both phases flow. The oil relative permeability, k_{ro}, is high, since oil flows through the largest pores, and decreases as oil saturation decreases. The water relative permeability, k_{rw}, starts low and increases as water saturation increases.

Water saturation increases preferentially in the smaller pore spaces first, due to wetting forces. As the displacement moves from smaller to larger pores, the water increasingly occupies pore throats that were formerly filled with oil. One pore or a group of pores containing oil can become cut off from the rest of the oil. Lacking sufficient driving pressure to overcome the capillary entry pressure for the now water-saturated pore throat, the oil is trapped in place.

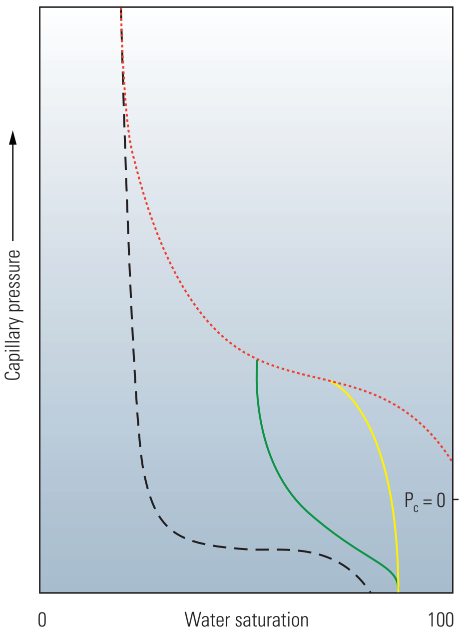
Eventually, all continuous flow paths are water-filled, and oil stops flowing. The final k_{rw} is lower than the original k_{ro} because of the oil trapped in large pores.

This trapped oil is one target of enhanced oil recovery methods. Some of these methods seek to mobilize the oil by lowering the interfacial tension or by changing the contact angle. Both have the effect of decreasing the capillary entry pressure. Another way to produce more oil is by increasing the pressure gradient, or viscous force, within the pore. The ratio of viscous force due to a drive pressure and capillary force at the driven interface is called the capillary number.[21] A high capillary number results in greater recovery; it can be increased by lowering the interfacial tension or making the pressure drop larger.

Mixed-wet case—In this case, the oil likely migrated into a water-wet formation, so the original water and oil saturation distribution may be macroscopically similar to the case described above. However, in a mixed-wet case, the oil occupying the large spaces of the pores has altered the wettability of the contacted pore surfaces.

As before, initially k_{ro} is high and k_{rw} is low. However, as the water saturation increases, it invades the largest pores first and remains in the center of those pores, because of the oil-wet condition of the surfaces surrounding those pores. This causes a more rapid decline in k_{ro} as the most permeable paths fill with water. However, the water does not trap the oil, because the oil-wet surfaces provide a path for the oil to escape from nearly water-filled pores. The flooded water may not be in contact with the connate water, which can yield an Archie saturation exponent, n, greater than 2.

In this mixed-wet condition, when water breaks through to a producing well, oil production continues for a long time, although the water cut increases. Laboratory tests on cores prepared with a procedure resulting in mixed-wet conditions of varying degrees show that maximum oil recovery is obtained for slightly water-wet samples.[22]



^ Hysteresis in capillary pressure. The primary drainage (red) and imbibition (black) curves bound the capillary-pressure behavior. If the direction of saturation change is reversed at an intermediate saturation, *Pc* will follow an intermediate path (green). Another reversal will take it back to the drainage curve (yellow). This behavior could occur in the middle of a transition zone, or as a result of oil banking during a waterflood.

In both water-wet and mixed-wet conditions, hysteresis in relative permeability and capillary pressure accompanies changes in saturation (above). This reflects the difference between water-advancing and water-receding contact angles, and the locations of oil and water in the pore spaces.

Oil-wet case—The extreme of a completely oil-wet reservoir is unlikely except in a reservoir that is its own source rock. In that case, the kerogen—organic solids that can yield oil upon heating—in place and the oil-maturation process could result in oil-wet surfaces.

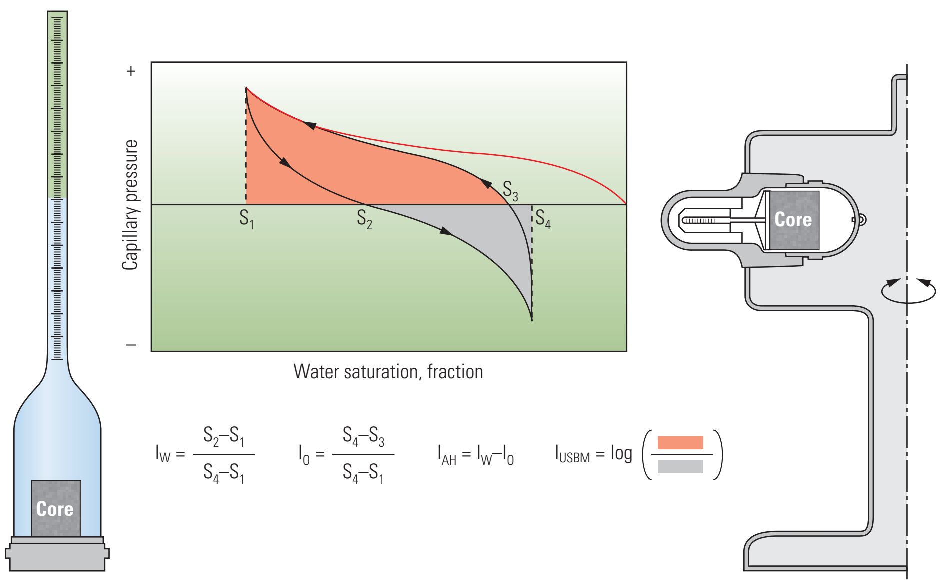
Measuring Wettability

Several methods are available to measure a reservoir's wetting preference. Core measurements include imbibition and centrifuge capillary-pressure measurements (below). An imbibition test compares the spontaneous imbibition of oil and water to the total saturation change obtained by flooding.

The Amott-Harvey imbibition test is commonly used.[23] A sample at irreducible water saturation, S_{wirr}, placed into a water-filled tube spontaneously imbibes water over a period of time—at least 10 days, and sometimes much longer. Then the sample is placed in a flow cell and water is forced through, with the additional oil recovery noted. The sample is now at residual oil saturation, S_{or}, and the process is repeated with an oil-filled imbibition tube, and then an oil-flooding apparatus. Separate ratios of spontaneous imbibition to total saturation change for water, I_w, and oil, I_o, are termed the water and oil imbibition indices, respectively. The Amott-Harvey index is the difference between the water and oil ratios. The result is a number between +1 (strongly water-wetting) and –1 (strongly oil-wetting).

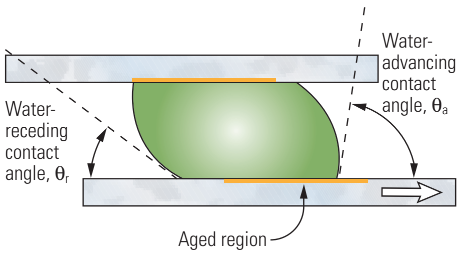
In a US Bureau of Mines (USBM) test, a centrifuge spins the core sample at stepwise-increasing speeds.[24] The sample starts at irreducible water saturation, S_{wirr}, in a water-filled tube. After periods at several spin rates, the sample reaches residual oil saturation, S_{or}, and it is placed into an oil-filled tube for another series of measurements. The areas between each of the capillary-pressure curves and the zero capillary-pressure line are calculated, and the logarithm of the ratio of the water-increasing to oil-increasing areas gives the USBM wettability index.[25] The measurement range extends from +∞ (strongly water wetting) to –∞ (strongly oil wetting), although most measurement results are in a range of +1 to –1. The centrifuge method is fast, but the saturations must be corrected because the centrifuge induces a nonlinear capillary-pressure gradient in the sample.

It is possible to combine the Amott-Harvey and USBM measurements by using a centrifuge rather than flooding with water and oil to obtain the forced flooding states. The Amott-Harvey index is based on the relative change in saturation, while the USBM index gives a measure of



^ Measurement of core wettability. An imbibition cell contains a sample at S_{wirr} in water (*left*). Expelled oil collects at the top of a graduated tube. A similar cell turned upside down can measure oil imbibition, starting at S_{or}. In a centrifuge, the graduated tube is at a larger radius than the core for collecting water (*right*), and in an opposite configuration to collect oil. The measurements are illustrated on a capillary-pressure curve (*center*). Spontaneous water imbibition is from S_1, which is S_{wirr}, to S_2 at zero capillary pressure. The core is waterflooded or spun in a centrifuge, moving along the negative capillary-pressure curve to S_4. Spontaneous oil imbibition is from S_4 to S_3, and then an oilflood takes the sample back to S_1, assuming there was no wettability change due to flooding. The imbibition index is the ratio of spontaneous saturation change to spontaneous plus driven saturation change, separately determined for water, I_w, and oil, I_o. The Amott-Harvey index is $I_w - I_o$. The USBM index uses the areas under the positive and negative capillary-pressure curves. This index is the logarithm of the ratio of the areas.

21. The Bond number is the ratio of gravitational force to capillary force and is useful in determining equilibrium conditions in thick reservoirs.
22. Jadhunandan PP and Morrow NR: "Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems," *SPE Reservoir Engineering* 10, no. 1 (February 1995): 40–46.
23. Amott E: "Observations Relating to the Wettability of Porous Rock," *Transactions, AIME* 216 (1959): 156–162.
    Boneau DF and Clampitt RL: "A Surfactant System for the Oil-Wet Sandstone of the North Burbank Unit," *Journal of Petroleum Technology* 29, no. 5 (May 1977): 501–506.
24. The USBM wettability index can also be determined using a porous-plate method.
25. Donaldson EC, Thomas RD and Lorenz PB: "Wettability Determination and Its Effect on Recovery Efficiency," *SPE Journal* 9 (March 1969): 13–20.



^ Contact-angle measurement. Crystals representative of pore surfaces are aged in simulated formation brine. After an oil drop is trapped between the crystals, the system is aged again. Then, the bottom crystal is displaced. Oil moves onto a water-wet surface (*lower left*) providing a water-receding contact angle (θ_r). Water moves onto the surface aged in contact with oil (*lower right*) providing a water-advancing contact angle (θ_a).

the energy needed to make the forced displacement, making them related but independent indicators of wettability.

Unfortunately, core wettability can be altered at any of several handling stages before the core reaches the laboratory, even when steps are taken to preserve its native wetting state. First, it can be contaminated by drilling mud. On its trip to surface, temperature and pressure changes can lead to fluid composition changes, possibly causing asphaltenes and waxes to precipitate and coat pore surfaces. Exposure to oxygen can alter the chemical composition of crude oil, generating surfactants that affect the core. These changes may also occur during storage and later handling.

The alternative to using preserved core is to restore the core condition. First, a vigorous cleaning renders a core water-wet, then it is saturated in simulated formation brine and aged. Next, it is flooded with crude oil—typically dead oil—and aged for approximately 40 days, typically at reservoir temperature and pressure. More complex methods are available that preserve sensitive clays. The assumption is that the result of this procedure approximates the in-situ wetting state. However, variations in brine or oil composition between the formation—throughout its history—and the laboratory can affect the resulting wetting state.

Measurements may also be made without using core material from the formation. One example is the contact-angle test (above). In this test, a crystal of quartz or calcite is cleaned, or a new mica surface is cleaved, and aged in a simulated formation brine. A drop of crude oil placed in contact with the surface is aged. Several methods are used for creating moving contact lines, from which the water-advancing and receding contact angles are measured. The assumption in this test is that the crude oil will change the model surface—under the conditions of the brine temperature, pH and salt concentrations—to that of the formation.

Wettability is often inferred from other measurements. Strongly water-wet and strongly oil-wet materials display certain characteristic relative-permeability curves, but intermediate-wetting and mixed-wetting states are not a simple extrapolation between the wettability extremes.

No method for measuring wettability gives an absolutely accurate result, which drives ongoing research, as discussed later in "News from the Laboratory."

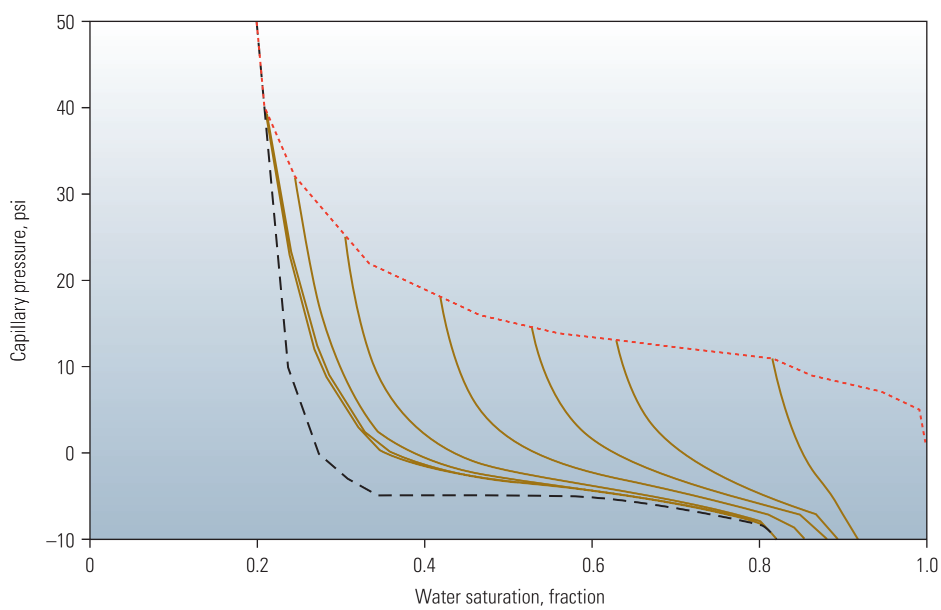
Production in Transition Zones

Predicting the production of oil and water in a transition zone can be difficult when the crude oil has altered formation wettability after migration. In its unperturbed state, a homogeneous formation would exhibit a smooth transition from dry oil production at the top of the transition zone, increasing water cut deeper in the formation, to no oil production at a point above the free-water level.

Unfortunately, drilling a well perturbs the fluid distributions in the near-well region unless the well is drilled underbalanced. Drilling-mud filtrate invasion into a formation can alter the near-well saturations, affecting shallow-reading well logs. It also can increase near-well formation pressure in a process termed supercharging.[26]

Measuring pressure gradients helps evaluate reserves and productivity. In the oil zone, oil density sets the pressure gradient; in the water zone, water density controls it. However, filtrate invasion can produce anomalous formation pressure measurements that, if misinterpreted, might condemn a prospect. Particularly troublesome for interpretation are gradients indicative of water but positioned high above the free-water level, substantial shifts in pressure potentials between the lower and upper parts of the transition zone that can result in negative pressure gradients, and gradients implying an oil density different from one that would normally be expected.

Significant anomalies in the gradients of transition zones of homogeneous limestone reservoirs are often found in the Middle East. In some of these formations, it is even possible to produce oil from zones in which both the pressure gradient and formation resistivity indicate a water zone. Schlumberger studied these phenomena using an ECLIPSE 100 finite-difference numerical-flow simulator. The engineers modeled drilling-fluid invasion and the effect of hysteresis in relative-permeability and capillary-pressure curves on resulting near-well pressure and water cut.[27]



^ Scanning curves for an intermediate-wet carbonate. Hysteresis between the primary drainage (red) and imbibition (black) curves can be represented by a series of scanning curves (gold). Each scanning curve represents a different starting saturation point on the drainage or imbibition curve, which would correspond to different heights in the transition zone.

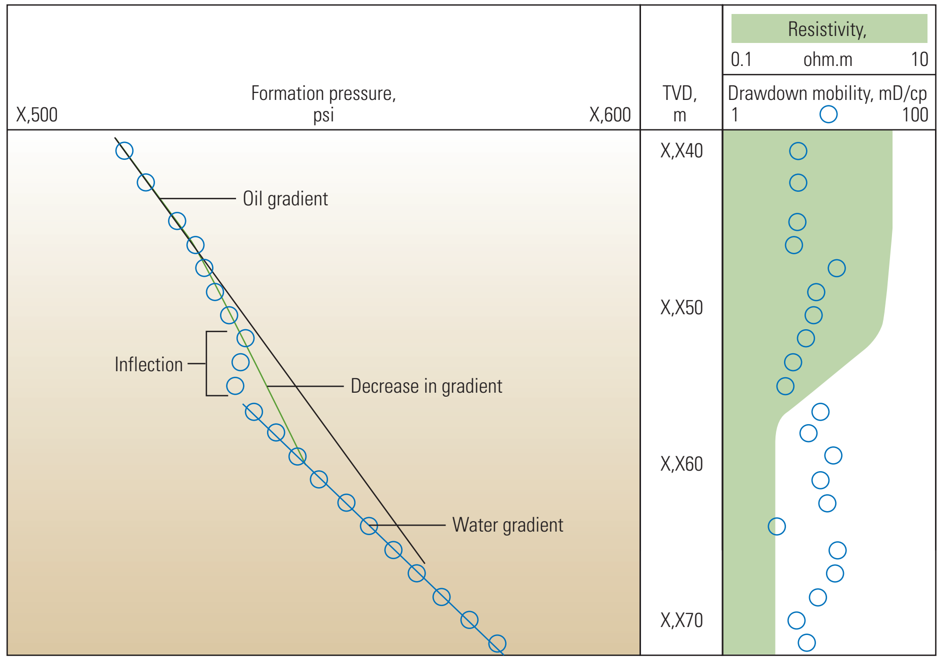
The wetting character, being dependent on original oil saturation, varies with height, with the greatest amount of oil-wet rock surface at the top of the transition zone and the water-wet state at the bottom. One manifestation of this situation is a variation with depth of capillary entry pressure, or threshold pressure, for water. In this case, above a water-base mud-filtrate saturation of 30%, the threshold pressure becomes significant: for the conditions of this model it was about 6 psi [40 kPa], similar to the value in the oil zone. The hysteresis in drainage and imbibition capillary pressure also depends on the initial saturation at each height. In the model, this hysteresis is represented by a series of capillary-pressure curves termed scanning curves (previous page, bottom).

There are three features of pressure measurements in these limestone reservoirs that the model sought to explain (right). First, the pressure gradient has an inflection with large curvature, which is not a result of differential supercharging. Second, significant amounts of oil can be produced below the inflection, in the zone with a water-like gradient. Finally, just above the inflection, the gradient decreases.

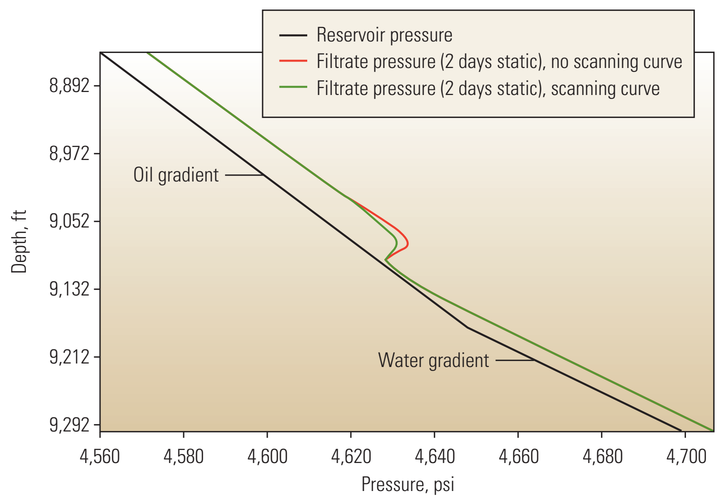
The study had several findings. The first was that the combination of all these features is best explained by the formation being mixed-wet, with the saturation and wetting characteristics described above. Using a water-wet assumption in the model did not result in the anomalies. The anomalies are seen in the simulations when the drilling mud used is water-base, but not when it is oil-base.

The production of oil below the inflection is also a result of the original saturation profile, according to the results of this model (right). Use of the scanning curves leads to predicting lower residual oil saturation when the initial water saturation is higher. Thus, oil at the bottom of the transition zone may have a low initial saturation, but some of it remains mobile because of its saturation history.

When faced with these apparent contradictions, an operator needs to know where the oil/water contact is within a transition zone, how much mobile oil and water are in the zone, and how these fluids flow. Such issues may be addressed to a certain degree with logging and formation tester data, and can be improved after matching observed measurements in single-well simulations. Resistivity logs will help identify likely transition zones and possible locations of contacts. Density and neutron logs help derive porosity and show similar locations of permeable lithology, which are then used to choose zones for subsequent wireline formation tests. Wireline



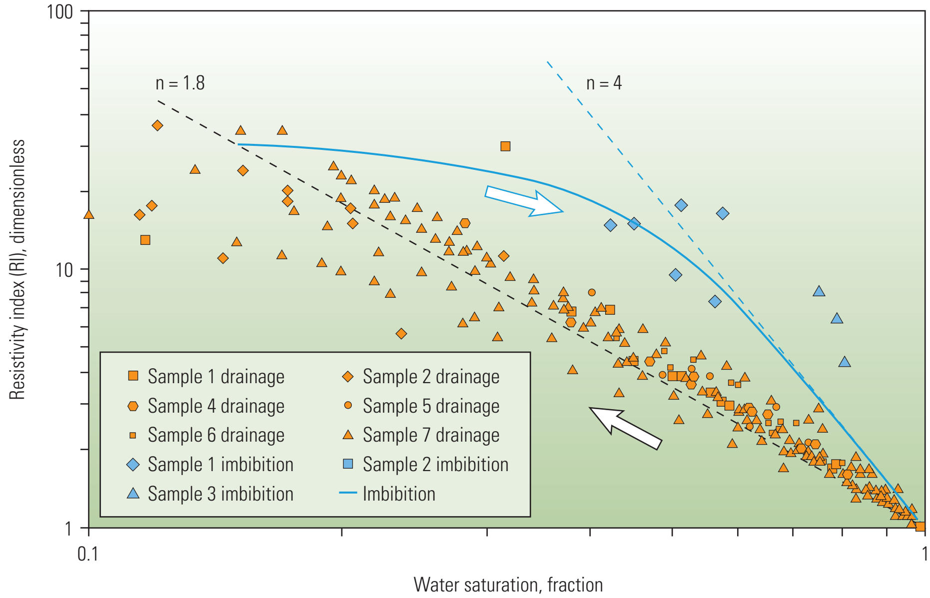
^ Transition-zone anomalies in Middle East carbonates. Pressure measurements (Track 1) in many Middle East carbonate transition zones have three unusual aspects: an inflection with large curvature; a decrease in gradient just above the inflection; and potential production of significant amounts of oil below the inflection. In this case, the pressure measurements are unlikely to be affected by supercharging, since the mobility is high, and the resistivity log indicates increasing oil saturation moving upward through this zone (Track 2).



^ Matching pressure anomalies. An ECLIPSE reservoir simulator can match the pressure anomalies using parameters typical of Middle East carbonate reservoirs and assuming mixed-wet conditions. Prior to invasion by drilling-mud filtrate, the reservoir pressure profile has distinct oil and water gradients (black). With hysteresis scanning curves in the model, the pressure decreases above the inflection, matching observations (green). Without hysteresis, the gradient above the inflection does not decrease (red).

26. Phelps GD, Stewart G and Peden JM: "The Analysis of the Invaded Zone Characteristics and Their Influence on Wireline Log and Well-Test Interpretation," paper SPE 13287, presented at the SPE Annual Technical Conference and Exhibition, Houston, September 16–19, 1984.

27. Carnegie AJG: "Understanding the Pressure Gradients Improves Production from Oil/Water Transition Carbonate Zones," paper SPE 99240, presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, April 22–26, 2006.



^ Calculating Archie's exponent from resistivity index (RI) for a Shuaiba carbonate formation. As core samples are drained (gold symbols), the cores behave as if they were water-wet. The Archie saturation exponent, *n*, is around 1.8 (dashed black line), given by the negative slope of the line on this logarithmic plot. For a water-imbibition process (blue symbols), the behavior departs significantly from the drainage case, with *n* equal to 4 or greater for water saturation above about 50% (dashed blue line). A curve indicating imbibition behavior is included to guide the eye (solid blue). For an RI of 10, this represents an interpreted saturation difference of about 25 saturation units.

formation testers can acquire openhole filtrate pressures, formation permeabilities, fluid pressures, oil densities and fluid samples.[28] NMR logging can be used to discriminate pore types to help refine the points for making formation tester measurements.[29]

Detecting Water Zones in a Mixed-Wet Carbonate

Petroleum Development Oman (PDO) operates an onshore field producing from the Shuaiba formation, a Cretaceous limestone with porosity around 30%. The field has been on production for more than 35 years, and recent infill drilling of horizontal wells exhibited logging anomalies that petrophysical experts sought to clarify. Some wells produced 100% water, even though the oil saturation determined from resistivity was in excess of 50%, which historically had been used as the limiting value for water-producing zones. PDO suspected some intervals had been flushed with water, which had not been seen in well logs because of hysteresis in electrical properties due to a mixed-wetting character.[30]

In a mixed-wet formation, resistivity from logs may not provide accurate saturation estimates, depending on the saturation history. There are two saturation conditions to consider: with original fluids and after waterflooding. Oil and brine in the original saturation configuration resulted from oil migration into a water-wet formation. The Archie saturation exponent, *n*, used to convert from resistivity to saturation is typically about 2; in this case it was 1.8.

However, laboratory studies have shown that the formation is mixed-wet, and that its Archie exponent is different when the water saturation increases compared with when it decreases (above). At an increasing water saturation above the 50% cutoff value, the exponent *n* equals 4, leading to a significant difference in the relationship between resistivity and saturation.

With this insight, PDO sought a method that would discriminate zones that had been waterflooded from those that were in the original state with high oil saturation. They achieved this by combining two logging methods for determining saturation: resistivity and pulsed-neutron capture (PNC) cross section, sigma.

Resistivity was measured as part of a standard LWD suite, and the pulsed-neutron capture device was in an RSTPro Reservoir Saturation Tool that was pumped inside the drillpipe to the bottom of the borehole. The two tools provide independent measures of water saturation. The RSTPro tool could also be used while stationary to measure water flowing in the well annulus; in a second pass of the tool, this WFL Water Flow Log measurement identified inflow of fluids into the borehole at a series of stations.

This approach is possible because the wells in this field are drilled underbalanced. In underbalanced drilling (UBD), the wellbore pressure while drilling is kept below the formation pressure. UBD avoids flushing the near-well region with drilling fluid: a distinct advantage for saturation measurement. Formation fluid inflow mixes with the drilling fluid, which in this case was crude oil from a neighboring field. The only source of water in the wellbore annulus was the formation.

In this favorable environment of high-salinity formation water and high porosity, the accuracy of the oil saturation determined by both sigma and resistivity is about 5 to 7% of the pore space. When comparing the two logs, a 10% difference was used as a conclusive indicator of saturation anomaly.

PDO logged 11 horizontal wells that were drilled underbalanced. Some wells produced only oil, and the resistivity and sigma logs matched within the 10% criterion. They examined two wells with no water production: the average difference between the methods was 0.1 and 0.2 saturation units, with a standard deviation of 4.5 saturation units. This agreement gave PDO confidence in the approach.

The logging results were used directly in making completion decisions for some wells, such as Well E (below). This flank well had a TD only 350 m [1,150 ft] away from a water-injection well. As soon as the well penetrated the reservoir, it started producing dry oil at a low rate. As drilling continued, water production began and increased rapidly with further drilling. Two more water inflow zones were found, with no other zones flowing oil.

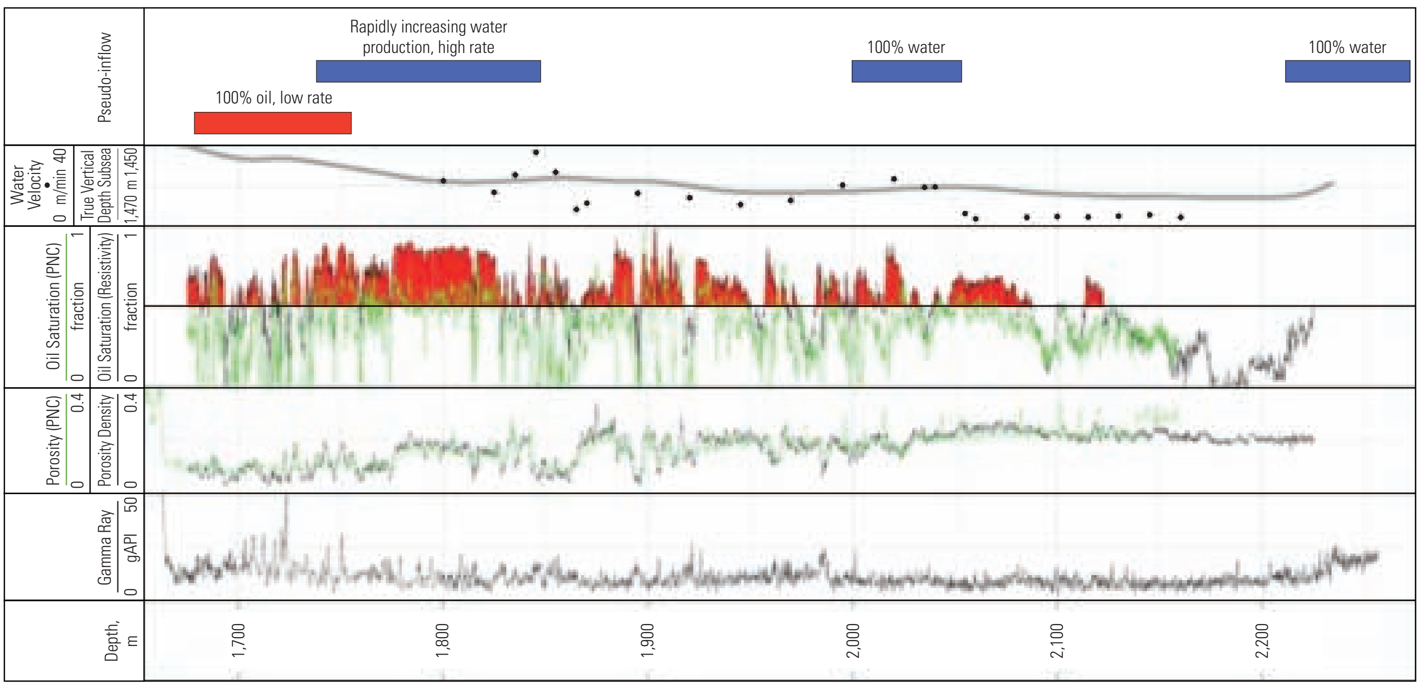
Without the additional information obtained through the new method, several zones would have been completed in this well, and it would have been a prolific water producer. Instead, PDO abandoned the well beyond 1,850 m [6,070 ft] MD and left an openhole completion between 1,775 and 1,825 m [5,824 and 5,988 ft] MD, with the possibility of water shutoff later. A postcompletion production test delivered a gross rate of 225 m^3/d [1,415 bbl/d] with a 50% water cut.[31]

PDO feels this method, combining UBD and resistivity, sigma and WFL logging, provides a high-confidence approach to identify water-producing intervals in this mixed-wet formation. The basis of the problem was resistivity hysteresis that is dependent on the most recent displacing phase. The key to the solution was combining resistivity- and sigma-based logging in an UBD environment in which there is no invaded zone, so shallow- and deep-reading measurements are both measuring undisturbed formation.

Flow Across Fractures

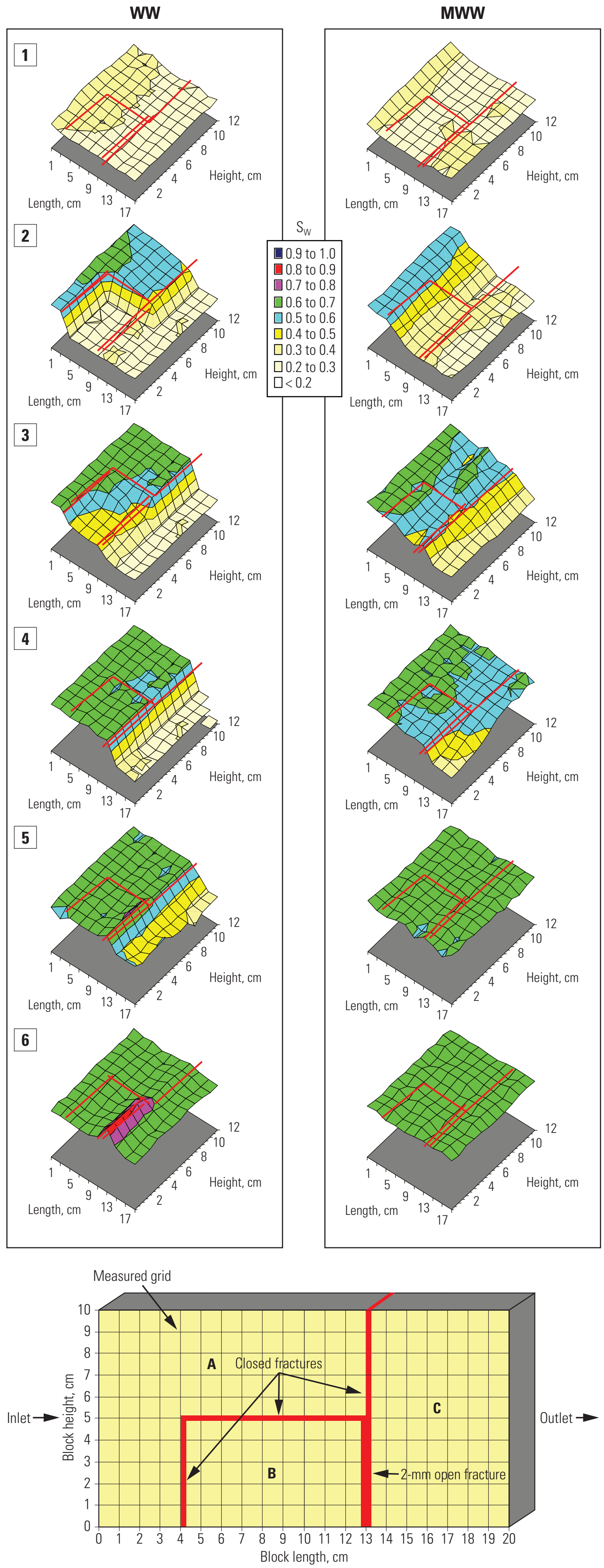
Chalks in the North Sea can vary in wettability from strongly water-wet to intermediate-wet.[32] Since many of these chalks are fractured and the fields undergo waterflooding, researchers at the University of Bergen, Norway, investigated the effect of wettability on flow through fractured chalk.[33]

A block of outcrop chalk approximately 20 cm long by 10 cm high by 5 cm thick [7.9 by 4 by 2 in.] was tested in the original condition and compared with a similar block that had been aged in crude oil. Water-imbibition tests on plugs from the same material and treated the same as the slabs had I_w values of 1 and 0.7, respectively, indicating strongly and moderately water-wet conditions. Water saturation was determined in these tests by 2D nuclear tracer imaging, with a sodium-22 [^{22}Na] tracer in the water phase. In addition, after the flow tests, plugs were cut from the blocks for imbibition tests to confirm wettability.



^ Comparison of sigma and resistivity logging for saturation. Shuaiba horizontal Well E was drilled underbalanced. Both resistivity-based saturation measurements (black) and pulsed-neutron saturation measurements (green) were calculated (Track 3). The resistivity measurement beyond the typical 50% cutoff level, where oil production is expected, is shaded (red). Without the new method, these zones would be completed, but the WFL results (Track 5) show water influx in three zones beginning at 1,750 m [5,740 ft]. Dry oil flows only near the heel of the well above about 1,750 m. The water-influx zones correspond to regions with large differences between the two saturation measurements, indicating the log differences are a good discriminator of a saturation anomaly.

28. Carnegie, reference 27.
29. Gomaa N, Al-Alyak A, Ouzzane D, Saif O, Okuyiga M, Allen D, Rose D, Ramamoorthy R and Bize E: "Case Study of Permeability, Vug Quantification, and Rock Typing in a Complex Carbonate," paper SPE 102888, presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, September 24–27, 2006.
30. Gauthier PJ, Hussain H, Bowling J, Edwards J and Herold B: "Determination of Water-Producing Zones While Underbalanced Drilling Horizontal Wells—Integration of Sigma Log and Real-Time Production Data," paper SPE 105166, presented at the 15th SPE Middle East Oil and Gas Show and Conference, Bahrain, March 11–14, 2007.
31. Gauthier et al, reference 30.
32. Andersen, reference 17.
33. Graue A and Bognø T: "Wettability Effects on Oil Recovery Mechanisms in Fractured Reservoirs," paper SPE 56672, presented at the SPE Annual Technical Conference and Exhibition, Houston, October 3–6, 1999.
Graue A, Viksund BG, Baldwin BA and Spinler EA: "Large Scale 2D Imaging of Impacts of Wettability on Oil Recovery in Fractured Chalk," paper SPE 38896, presented at the SPE Annual Technical Conference and Exhibition, San Antonio, October 5–8, 1997.



Both slabs were sawn into three pieces, with the saw cuts representing fractures (left). The blocks were butted together, except for one cut, where the chalk pieces were separated by 2 mm [0.8 in.]: this represented an open fracture, while the other cuts represented closed fractures. The waterflood tests began with the material at S_{wirr}.

The strongly water-wet blocks filled to 1-S_{or} before the front crossed the fractures, regardless of whether the chalk pieces abutted. The flood front in the moderately water-wet material, in contrast, crossed closed fractures almost as easily as it moved though the adjacent intact material, and thus transferred a viscous pressure gradient into the adjacent matrix block. However, the open fracture was more of a barrier than the closed fractures in the moderately water-wet system.

Bergen researchers examined the fracture-bridging phenomenon in a second set of tests.[34] Chalk core plugs from the same outcrop were cut to 3.8-cm [1.5-in.] diameter. To alter wettability, crude oil was continuously flooded through the plugs for an extended period.[35] For each wetting condition, two core plugs were placed in series with a 2-mm [0.4-in.] spacer between the adjacent ends to represent an open fracture (next page). A magnetic resonance imaging (MRI) tomography method imaged the fluid-saturation distribution in the fracture at the end of the upstream core. Additional scans produced a saturation profile along the core length.

< Waterflooding a fractured chalk block. An outcrop chalk slab was cut into three pieces and reassembled (*bottom*). Part A was abutted to both parts B and C, representing closed fractures, but a 2-mm gap representing an open fracture separated part B from part C. The scan maps (*top*) indicate saturation at increasing injected volumes from top to bottom for a strongly water-wet (WW) slab (*left sequence*) and a moderately water-wet (MWW) slab (*right sequence*). The sharp flood front in WW Image 2 shows that part A filled to its maximum water saturation, which is 1-S_{or}, before water crossed the closed fracture, but MWW Image 2 shows water already in part B. Again, in WW Image 4 there is a sharp front at the fracture, and then part C fills first from the open fracture and then from both A and B in the WW Image 5. In MWW Images 3 and 4, part C filled across the closed fracture from A before filling from the open fracture.

The cores at S_{wirr} were waterflooded. The less strongly water-wetting the material, the sooner water appeared in the open fracture. For the moderately water-wet case, beads formed at the fracture face that bridged the 2-mm open fracture. With additional flow, the bridging beads expanded and eventually filled the fracture. In contrast, the strongly water-wet material achieved a high saturation throughout the upstream core before any water entered the fracture, and then it filled the fracture from the bottom up. Only then did water begin flowing into the downstream core. A wider fracture gap of 3.5 mm [0.14 in.] prevented most bridging, even in the moderately water-wet case, with most water filling from the bottom of the fracture upward.

These results showed that wetting-phase bridges form through a combination of viscous forces, which control the growth of the water droplets making up the bridge, and interfacial tension between the water and oil phases, which controls the droplet contact angle. Thus, open fractures in a chalk reservoir will have different effects on waterflood efficiency, depending on the wettability of the chalk matrix.

News from the Laboratory

Laboratory techniques beyond the simple Amott-Harvey imbibition test have the potential to expand our understanding of wettability. Surface examination by atomic-force microscopy and the fractured chalk blocks examined by 2D nuclear tracer imaging are but two examples of current laboratory techniques. Many other techniques have been used, and updates of these and other new approaches are being tested in today's laboratories.

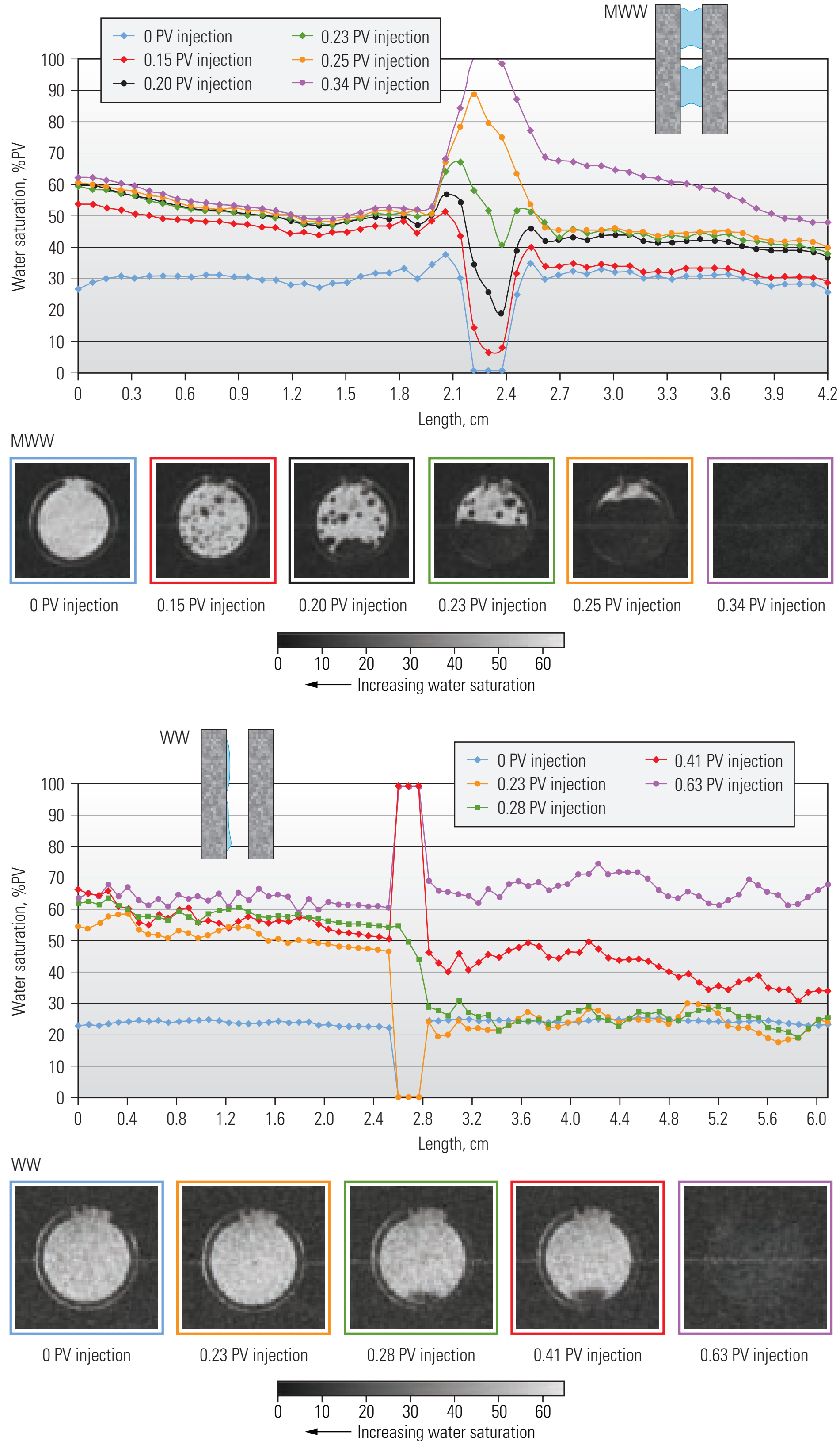
For example, although there is variation in both water-wet and oil-wet rocks, the Archie saturation exponent tends to be greater for oil-wet rocks. Recent work using ideas from

34. Aspenes E, Graue A, Baldwin BA, Moradi A, Stevens J and Tobola DP: "Fluid Flow in Fractures Visualized by MRI During Waterfloods at Various Wettability Conditions—Emphasis on Fracture Width and Flow Rate," paper SPE 77338, presented at the SPE Annual Technical Conference and Exhibition, San Antonio, September 29–October 2, 2002.

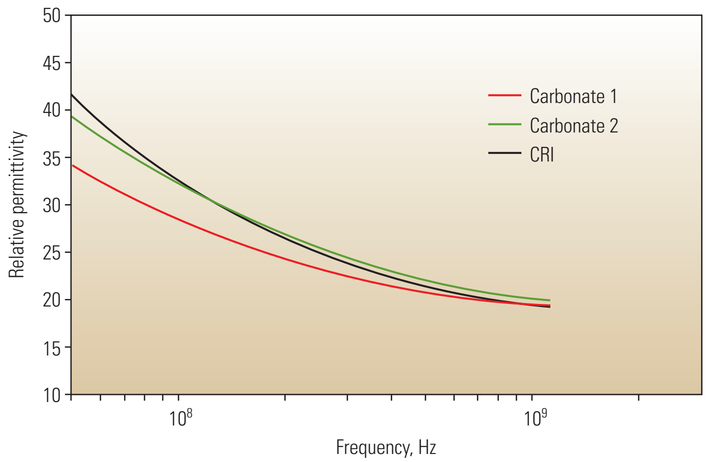
Graue A, Aspenes E, Moe RW, Baldwin BA, Moradi A, Stevens J and Tobola DP: "MRI Tomography of Saturation Development in Fractures During Waterfloods at Various Wettability Conditions," paper SPE 71506, presented at the SPE Annual Technical Conference and Exhibition, New Orleans, September 30–October 3, 2001.

35. Graue A, Aspenes E, Bognø T, Moe RW and Ramsdal J: "Alteration of Wettability and Wettability Heterogeneity," *Journal of Petroleum Science and Engineering* 33, no. 1–3 (April 2002): 3–17.

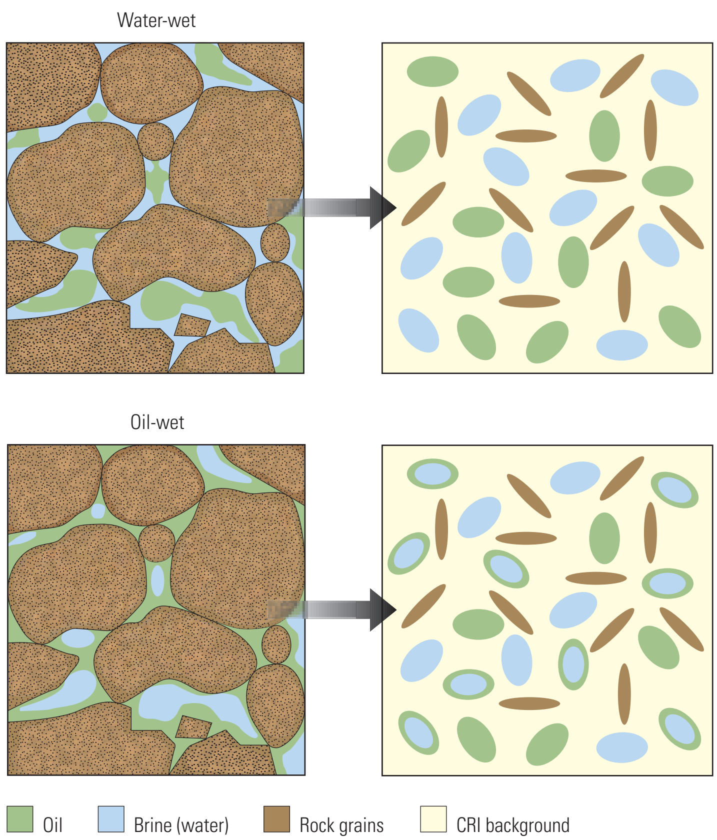
Aspenes E, Graue A and Ramsdal J: "In-Situ Wettability Distribution and Wetting Stability in Outcrop Chalk Aged in Crude Oil," *Journal of Petroleum Science and Engineering* 39, no. 3–4 (September 2003): 337–350.



^ Bridging across an open fracture. Two core samples in a waterflooding cell were separated by a 2-mm gap. One was moderately water-wet (MWW, *upper sequence*) and the other strongly water-wet (WW, *lower sequence*). Saturations at various pore-volumes (PV) injected were measured along the core (plots) and in 2D cross section at the upstream core face (photographs) using MRI. The MWW core had earlier breakthrough, with water forming beads on the core face. The beads coalesced and eventually bridged the gap (*inset schematic*). Saturation profiles along the core length show that water is transported across the open fracture before S_{or} is reached. In the WW core, saturation scans show that no water enters the open fracture before the upstream core reaches S_{or}. The drops on the core face did not bridge across the gap, until the gap filled from the bottom up (*inset schematic*).



^ Permittivity dispersion for two carbonate rocks. The two brine-saturated samples with similar mineralogy and porosity have a similar permittivity at 1 GHz. The CRI model (black) matches dispersion for Carbonate 2, but rock textural differences result in separation of the lower frequency response for Carbonate 1.



^ The textural model. Water-wet pores filled with oil and water (*top left*) are represented in the textural model as randomly distributed oblate spheroids placed in a background of a CRI medium (*top right*). In an oil-wet rock, oil is in contact with the grains and surrounds conductive brine (*bottom left*). Brine is predominantly situated in the center of the pores. In the textural model, this is represented as spheroids with oil surrounding water (*bottom right*).

percolation theory provides a new approach to the resistivity and saturation relationship. As an example, one of these models introduces only two parameters.[36] One is an exponent, similar to the Archie saturation exponent n. The other new parameter is the water connectivity correction index, which can be related to the oil-wet fraction of the pore surfaces. When this index is zero, the model reduces to Archie's relationship. The new model matches the relationship seen in core measurements on oil-wet limestones.[37]

Archie's equation uses resistivity, which is a DC, or zero-frequency, measurement. At high frequency, materials exhibit a complex dielectric response, including both conductivity—the inverse of resistivity—and permittivity. Measurements of the formation permittivity are sensitive to the formation water content because at ambient conditions the permittivity of water is at least an order of magnitude higher than the permittivity of oil or the rock matrix. When total formation porosity is known, water saturation can be determined directly, avoiding the need for often unknown cementation and saturation exponents in the Archie equation, which is used to interpret resistivity measurements.

Dielectric measurement interpretation requires that a relationship be established between the dielectric properties of rocks and their constituents. Multiple mixing models have been proposed to predict rock's dielectric constant based on its volumetric composition. Experimental data obtained on carbonate rocks saturated with both oil and brine showed that a complex refractive index law (CRI) worked better than other mixing laws at a frequency of 1 GHz.[38]

However, permittivity is also influenced by factors other than mineralogy and water content, especially at lower frequencies (above left). Although CRI is the best simple mixing model at 1 GHz, it fails to accurately reconstruct dielectric and permittivity dispersion of rocks over a wide frequency range. A new model that includes rock texture matches rock dielectric properties over a wide frequency range more successfully.[39] This new model has an average or background behavior described by the CRI model, then incorporates ellipsoidal grains and pores to reflect the influence of texture on dielectric dispersion (left).

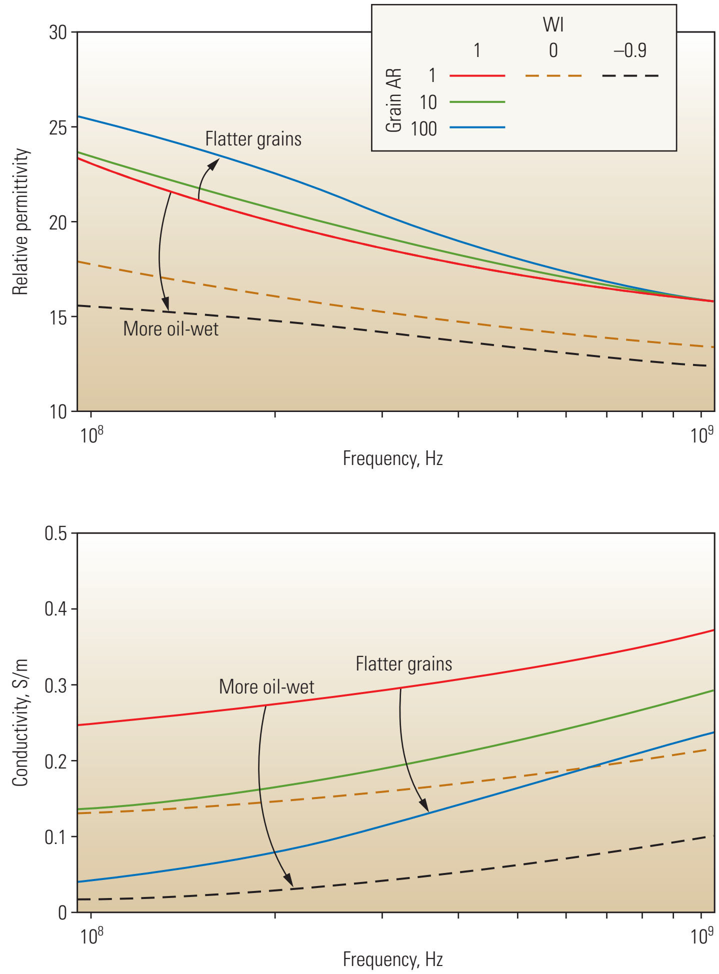
Pores, grains and oil inclusions can be represented in a simple way as oblate spheroids—ellipsoids with two longer axes of equal length. An advantage of using ellipsoids is that the model can be calculated analytically. One additional geometrical parameter is added for each phase:

the aspect ratio, or the ratio of the long to the short axis of the oblate spheroid. Rocks with thinner insulating regions—flatter grains with higher aspect ratio—exhibit greater dielectric and conductivity dispersion (right).

Wettability influences the rock dielectric response.[40] It strongly affects the spatial distribution of conductive and nonconductive phases—brine and hydrocarbon, respectively—within the pore space and, therefore, the rock's dielectric properties. In a strongly water-wet rock, the hydrocarbon phase is predominantly in the center of the pores surrounded by the conductive brine. The fluid-phase distribution is the opposite in a strongly oil-wet sample, with the hydrocarbon phase next to the pore walls. This reverse distribution of the conductive and nonconductive phases has several effects. In oil-wet rocks, the conductive brine phase does not form a continuous, connected network with increasing brine isolation as the oil wettability increases. This leads to a large decrease in rock conductivity.

Another laboratory technique that has a considerable potential to aid in characterizing wettability and pore geometry is NMR.[41] The NMR signal is a measure of the degree of relaxation of magnetic moments after an initial polarization.[42] Fluids in direct contact with a rock surface undergo enhanced relaxation because of the presence of paramagnetic ions or magnetic impurities on the rock surface.[43] The wetting preference of the surface determines which of two available fluids will be in contact, and therefore, which will be influenced by the surface.

When a single fluid phase is present in the rock, the relaxation time, or T_2 distribution, is dominated by surface relaxation effects. However, when two phases are present, the NMR response can vary considerably, depending on the rock wettability. After drainage with a laboratory oil, the rock remains water-wet with a remnant layer of water coating the rock surface.



^ Dispersion in a textural model. Two series are shown here, one with varying aspect ratios (AR) and the other with varying wettability indices (WI). The water-wet case (WI = 1.0) with spherical grains (AR = 1) is the base case (red). In one series, the grain AR increases to 10 (green) and 100 (blue) while remaining water-wet. As grains become flatter, or AR increases, rock conductivity (*bottom*) decreases significantly and relative permittivity (*top*) increases. This provides a crucial link between dispersion properties and rock texture. A second series maintains spherical grains (AR = 1), but wettability changes from water-wet (red) to intermediate-wet (orange) to oil-wet (black). Increasing oil-wetting character leads to a strong decrease in the rock conductivity. The wettability index here is based on the fraction of oil-wet pores relative to the total pore volume, and ranges from 1 for strongly water-wet, to –1 for strongly oil-wet. The pores in these models are spherical (AR = 1), with porosity of 30%, water saturation of 80%, and brine conductivity of 5 S/m.

36. Montaron B: "A Quantitative Model for the Effect of Wettability on the Conductivity of Porous Rocks," paper SPE 105041, presented at the 15th Middle East Oil and Gas Show and Conference, Bahrain, March 11–14, 2007.

37. Sweeney SA and Jennings HY: "The Electrical Resistivity of Preferentially Water-Wet and Preferentially Oil-Wet Carbonate Rock," *Producer's Monthly* 24, no. 7 (1960): 29–32.

38. Seleznev N, Boyd A, Habashy T and Luthi S: "Dielectric Mixing Laws for Fully and Partially Saturated Carbonate Rocks," *Transactions of the 45th SPWLA Annual Logging Symposium*, Noordwijk, The Netherlands, June 6–9, 2004, paper CCC.

39. Seleznev N, Habashy T, Boyd A and Hizem M: "Formation Properties Derived from a Multi-Frequency Dielectric Measurement," *Transactions of the 47th SPWLA Annual Logging Symposium*, Veracruz, Mexico, June 4–7, 2006, paper VVV.

40. Bona N, Rossi E and Capaccioli S: "Electrical Measurements in the 100 Hz to 10 GHz Frequency Range for Efficient Rock Wettability Determination," *SPE Journal* 6, no. 1 (March 2001): 80–88.

41. Allen D, Flaum C, Ramakrishnan TS, Bedford J, Castelijns K, Fairhurst D, Gubelin G, Heaton N, Minh CC, Norville MA, Seim MR, Pritchard T and Ramamoorthy R: "Trends in NMR Logging," *Oilfield Review* 12, no. 3 (Autumn 2000): 2–19.

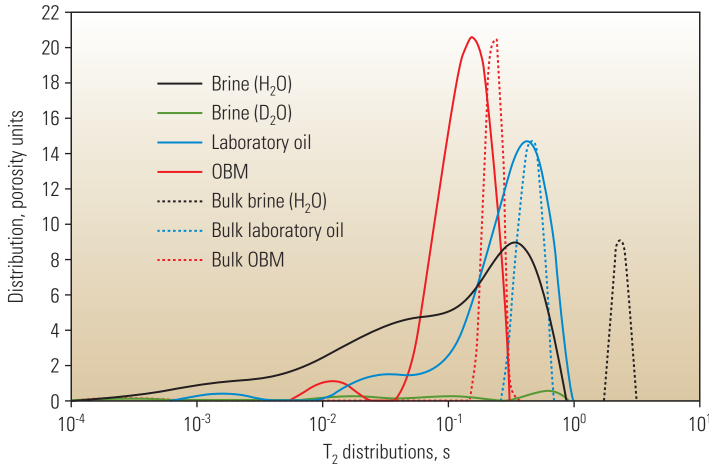
Chen J, Hirasaki GJ and Flaum M: "NMR Wettability Indices: Effect of OBM on Wettability and NMR Responses," *Journal of Petroleum Science and Engineering* 52, no. 1–4 (June 2006): 161–171.

42. The typical sequence for polarization and detection is the Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo method: Meiboom S and Gill D: "Modified Spin-Echo Method for Measuring Nuclear Relaxation Times," *The Review of Scientific Instruments* 29, no. 8 (1958): 688–691.

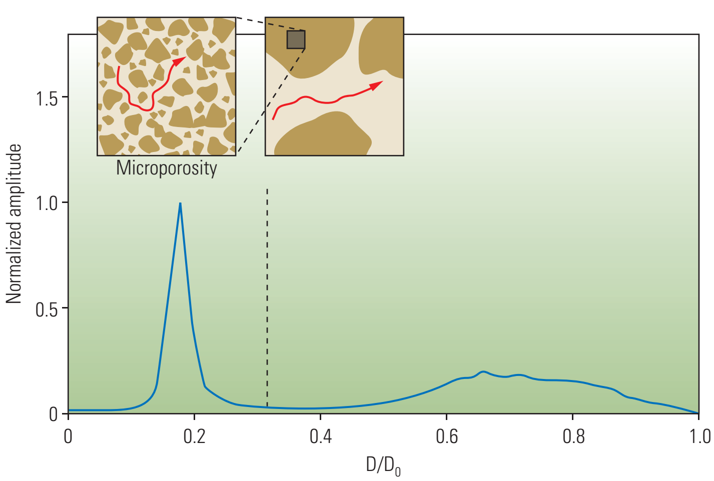
43. Brown RJS and Fatt I: "Measurements of Fractional Wettability of Oilfield Rocks by the Nuclear Magnetic Relaxation Method," *Transactions*, AIME 207 (1956): 262–264.

Foley I, Farooqui SA and Kleinberg RL: "Effect of Paramagnetic Ions on NMR Relaxation of Fluids at Solid Surfaces," *Journal of Magnetic Resonance, Series A* 123, no. 1 (November 1996): 95–104.

The T_2 oil peak value is close to bulk value (below). In contrast, drainage with oil-base mud (OBM) results in shorter T_2 values than for bulk OBM. This is an indication that the OBM, which was made by adding substances, including asphaltenes, to the same laboratory oil, is contacting the rock surface and, therefore, wetting the core.



^ T_2 decay-time distributions. The T_2 distribution for a carbonate sample fully saturated with brine (H_2O) (solid black) is shifted to shorter time than the bulk-brine signal (dotted black) due to surface interactions. The brine is replaced with a brine made from deuterated water (D_2O), which has no NMR signal other than a small amount of residual H_2O (green). After the deuterated sample is flushed with OBM, the peak (solid red) is shifted from the bulk OBM (dotted red), indicating that the OBM wets the rock. The sample was cleaned and prepared again in the deuterated state, then flushed with laboratory oil. The main peak (solid blue) aligns with the bulk-oil signal (dotted blue), and so with laboratory oil, the surface remains water-wet.



^ Distinguishing microporosity. The mean normalized diffusion coefficient, D/D_0, indicates the presence of two populations of diffusing molecules (blue). The measured diffusion coefficient is smaller in micropores (*inset, left*) because the diffusion path of molecules (red) is more tortuous. The peak at large values is a measurement of molecules in larger pores (*inset, right*) that have D values closer to the bulk D_0 value. The sharper peak at smaller D represents molecules in micropores. The area under the curve to the left of the fixed cutoff line (black), relative to the total area under the curve, is the microporosity: 44% of the pore space in this example.

The wetting character can vary with pore size, often with microporosity remaining water-wet. Therefore, determining the microporous fraction can be crucial for analyzing formations exhibiting complex wetting character. In the field, T_2 NMR logs are commonly used for estimating microporosity fraction. However, this approach can fail due to variations in surface relaxivity or pore geometry.

A different method, called restricted diffusion NMR, is unaffected by surface relaxivity and is sensitive to pore sizes, connectivity and tortuosity. The diffusion coefficient in a bulk fluid, D_0, is a constant that measures how rapidly a concentrated group of molecules diffuses. However, inside a restricted space, such as in the pores of a rock, the diffusion, D, may be reduced from the bulk value because molecules are restricted in their motion by the pore walls.

The diffusion coefficient is determined by analysis of the NMR echo decay in the presence of a nonhomogeneous magnetic field.[44] An example for a carbonate rock shows the normalized D/D_0 distribution at early diffusion times (below left).[45] The distribution has a peak at small diffusion coefficients, which corresponds to molecules in restricted microporous space, and a second peak at higher diffusion coefficients closer to D_0, which corresponds to those in less restricted areas, or larger pores. Applying an empirical cutoff to the distribution separates the microporosity: the percentage of the population at D/D_0 values less than the cutoff gives the microporosity, which is in good agreement with mercury porosimetry data and irreducible water saturation after centrifugation.

Some of these new methods are providing input for pore-network modeling, which has emerged as an effective way to investigate the capillary, flow and transport properties of porous

44. Stejkal EO and Tanner JE: "Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient," *Journal of Chemical Physics* 42, no. 1 (1965): 288–292.

45. Hürlimann MD and Venkataramanan L: "Quantitative Measurement of Two-Dimensional Distribution Functions of Diffusion and Relaxation in Grossly Inhomogeneous Fields," *Journal of Magnetic Resonance* 157, no.1 (July 2002): 31–42.

46. Valvatne PH and Blunt MJ: "Predictive Pore-Scale Modeling of Two-Phase Flow in Mixed Wet Media," *Water Resources Research* 40, no. 7, W07406 (2004): doi:10.1029/2003WR002627.

47. Picard G and Frey K: "Method for Modeling Transport of Particles in Realistic Porous Networks: Application to the Computation of NMR Flow Propagators," *Physical Review E* 75 (2007): 066311.

48. Knackstedt MA, Arns CH, Limaye A, Sakellariou A, Senden TJ, Sheppard AP, Sok RM, Pinczewski VW and Bunn GF: "Digital Core Laboratory: Properties of Reservoir Core Derived from 3D Images," paper SPE 87009, presented at the SPE Asia Pacific Conference on Integrated Modelling for Asset Management, Kuala Lumpur, March 29–30, 2004.

media.[46] Modeling the pore space with a network of nodes and bonds enables a numerically efficient calculation of the flow properties and provides detailed understanding of processes such as miscible and immiscible displacement that are important in enhanced oil recovery.

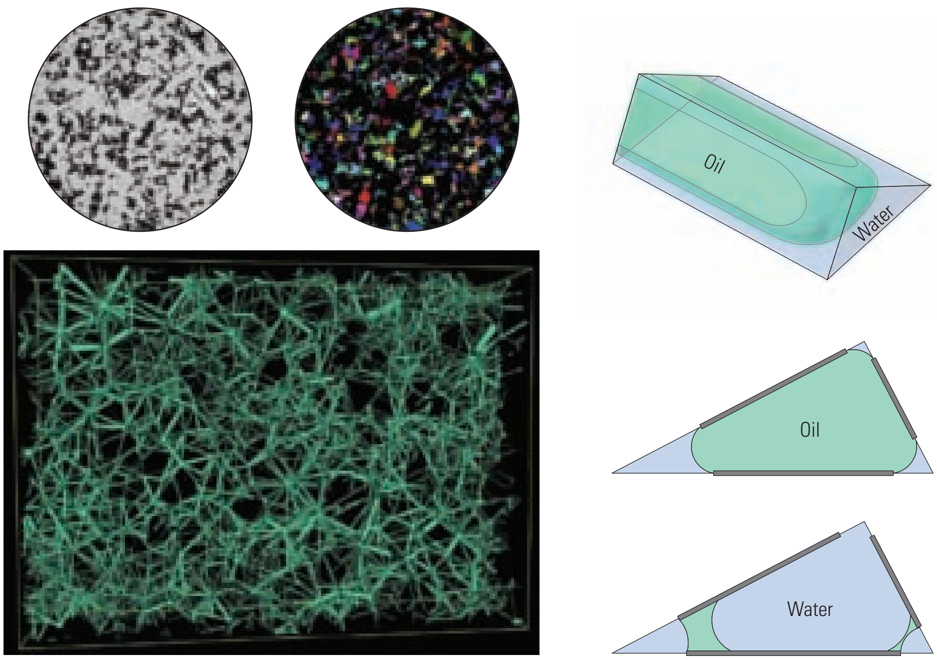
A pore-network model is an idealized pore space, generally incorporating a pore-scale description of the medium and of the physical pore-scale events. Complex multiphase flow and transport processes in porous media can be simulated using pore-network models.[47] For such processes, pore-network models are faster to run on a computer than other approaches using more exact models.

Although pore-network models are traditionally employed in qualitative studies, they have the potential to become predictive if pore-structure parameters are properly assigned. Significant advances have recently been made in predictive pore-network modeling, where geologically realistic networks are constructed by analyzing 3D images that may be generated by 3D reconstruction of X-ray microtomograms (left).[48]

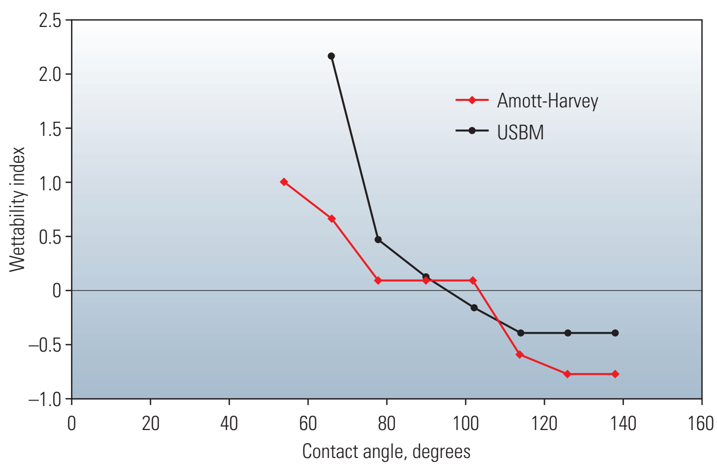
However, the resolution of X-ray microtomograms is currently limited to several microns and, therefore, a proper description of microporosity with pore-network models is a challenge. Several techniques, such as NMR restricted diffusion, confocal microscopy—useful for optical imaging of thick specimens—and scanning electronic microscopy, have potential to extend applicability of pore-network models to microporous rocks.

Pore-network modeling is useful for studying the impact of wettability on oil recovery. Petrophysical parameters, such as capillary pressure, relative permeability and resistivity, are calculated under different wetting conditions. These conditions are given by contact angles that are randomly assigned based on selected distributions, providing the fluid distribution and interface configurations in the network for multiple realizations. Quasi-static drainage and imbibition simulations can be conducted to examine the result of the wetting conditions (left).

These laboratory techniques point the way to the future of wettability application. Fields around the world are maturing, and the industry will extract as much of the hydrocarbon resource as is economically possible before they are abandoned. All systems will need to be optimized to achieve this goal, and that requires continued improvement in applying a fundamental parameter underlying recovery: rock wettability. —MAA



^ Pore-network modeling. Microtomogram slices of a carbonate (*top left*) are partitioned (*top middle*) into grains (black) and pores (individually colored). Many slices form a 3D microtomogram that is converted to a pore network (*bottom left*). A small subset of a model is shown; the pores are not to scale. The network comprises spheres and more complex shapes, such as tubes with triangular cross sections. Displacement from these structures is piston-like (*top right*). In this water-wet condition, oil is in the middle of the tube and water is at the apexes, as also shown in cross section (*middle right*). The model can allow oil to touch surfaces and alter the contact angle toward oil-wetting (shading on surface). In a subsequent waterflood, oil layers may remain in the elements with high value of contact angle (*bottom right*).



^ Pore-model results after a wettability shift. A micromodel had an initial distribution of contact angles between 50° and 60°. In simulations, contact angle in 95% of the network elements shifts to higher values as a result of wettability alteration. Simulated drainage and imbibition cycles allowed calculation of the Amott-Harvey (red) and USBM (black) wettability indices, shown as a function of the altered contact angle.