

Wettability Literature Survey— Part 5: The Effects of Wettability on Relative Permeability

William G. Anderson,* SPE, Conoco Inc.

Summary. The wettability of a core will strongly affect its waterflood behavior and relative permeability. Wettability affects relative permeability because it is a major factor in the control of the location, flow, and distribution of fluids in a porous medium. In uniformly or fractionally wetted porous media, the water relative permeability increases and the oil relative permeability decreases as the system becomes more oil-wet. In a mixed-wettability system, the continuous oil-wet paths in the larger pores alter the relative permeability curves and allow the system to be waterflooded to a very low residual oil saturation (ROS) after the injection of many PV's of water. The most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. Serious errors can result when measurements are made on cores with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants.

Introduction

This paper is the fifth in a series of literature surveys covering the effects of wettability on core analysis.¹⁻⁵ Wettability has been shown to affect waterflood behavior, relative permeability, capillary pressure, irreducible water saturation (IWS), ROS, dispersion, simulated tertiary recovery, and electrical properties. Earlier, but less complete, reviews covering the effects of wettability on waterflood and relative permeability can be found in Refs. 6 through 16.

Relative permeability is "a direct measure of the ability of the porous system to conduct one fluid when one or more fluids are present. These flow properties are the composite effect of pore geometry, wettability, fluid distribution, and saturation history."⁶ Wettability affects relative permeability because it is a major factor in the control of the location, flow, and spatial distribution of fluids in the core. Craig⁶ and Raza *et al.*¹⁰ have given good summaries of the effects of wettability on the distribution of oil and water in a core. Most experimental studies that examined fluid distribution as a function of wettability used bead packs or other micromodels,¹⁷⁻²⁴ although some more recent studies have used reservoir rock and fluids such as epoxy or Wood's metal that can be solidified in situ (e.g., see Yadav *et al.*²⁵).

Consider a strongly water-wet rock initially at IWS. Water, the wetting phase, will occupy the small pores and form a thin film over all the rock surfaces.^{19,20,22,26,27} Oil, the nonwetting phase, will occupy the centers of the larger pores. This fluid distribution occurs because it is the most energetically favorable. Any oil placed in the small pores would be displaced into the center of the large pores by spontaneous water imbibition, because this would lower the energy of the system.

During a waterflood of a water-wet system, water moves through the porous medium in a fairly uniform front.⁶ The injected water will tend to imbibe into any small- or medium-sized pores, moving oil into the large pores where it is easily displaced. Only oil is moving ahead of the front. In the frontal zone, each fluid moves through its own network of pores, but with some wetting fluid located in each pore.⁶ In this zone, where both oil and water are flowing, a portion of the oil exists in continuous channels with some dead-end branches, while the remainder of the oil is trapped in discontinuous globules. Fig. 1a, taken from Raza *et al.*,¹⁰ shows water displacing oil from a water-wet pore. The rock surface is preferentially wetted by the water, so water will advance along the walls of the pore, displacing oil in front of it. At some point, the

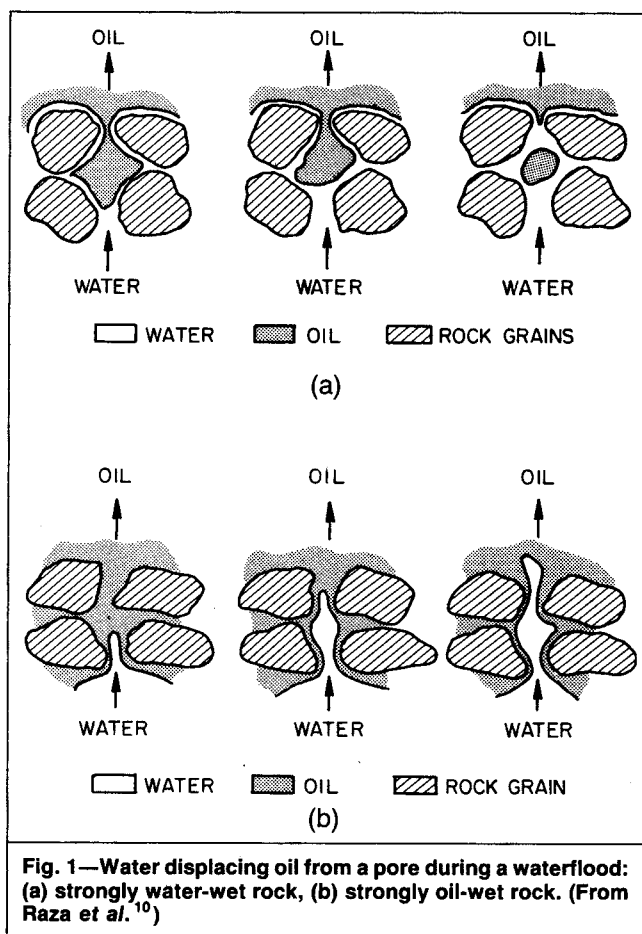
neck connecting the oil in the pore with the remaining oil will become unstable and snap off, leaving a spherical oil globule trapped in the center of the pore. After the water front passes, almost all the remaining oil is immobile. Because of such immobility in this water-wet case, there is little or no production of oil after water breakthrough.^{6,18-20,22,23,26} The disconnected, residual oil exists in two basic forms: (1) small, spherical globules in the center of the larger pores, and (2) larger patches of oil extending over many pores that are completely surrounded by water.

In a strongly oil-wet rock, the rock is preferentially in contact with the oil, and the location of the two fluids is reversed from the water-wet case. Oil generally will be found in the small pores and as a thin film on the rock surfaces, while water will be located in the centers of the larger pores. The interstitial water saturation appears to be located as discrete droplets in the centers of the pore spaces in some strongly oil-wet reservoirs.¹⁰ A waterflood in a strongly oil-wet rock is much less efficient than one in a water-wet rock. When the waterflood is started, the water will form continuous channels or fingers through the centers of the larger pores, pushing oil in front of it (see Fig. 1b¹⁰). Oil is left in the smaller crevices and pores. As water injection continues, water invades the smaller pores to form additional continuous channels, and the WOR of the produced fluids gradually increases. When sufficient water-filled flow channels form to permit nearly unrestricted water flow, oil flow practically ceases.⁶ The remaining oil is found (1) filling the smaller pores, (2) as a continuous film over the pore surfaces, and (3) as larger pockets of oil trapped and surrounded by water.^{19,20,26} Because much of this oil is still continuous through the thin oil films and can be produced at a very slow rate,^{19,22,23,26} the ROS is not well-defined.

In this paper, the terms "wetting" and "nonwetting" will be used in addition to water-wet and oil-wet. This will more easily enable us to draw conclusions about a system with the opposite wettability. For example, a waterflood in a system of one wettability will behave in the same manner as an oilflood in the same system with the wettabilities reversed. Relative permeability curves will also show that the fluids can exchange positions and flow behavior.^{28,29} Because relative permeability is a function of saturation history, hysteresis in the relative permeability curves is often observed when comparing relative permeabilities measured with increasing vs. decreasing wetting-phase saturations. "Imbibition" is often used to refer to flow that results in increasing wetting-phase saturations, while "drainage" refers to flow with decreasing wetting-phase saturations.⁶ For example, waterflooding a water-wet rock is an imbibition process, while waterflooding an oil-wet rock is a drainage process.

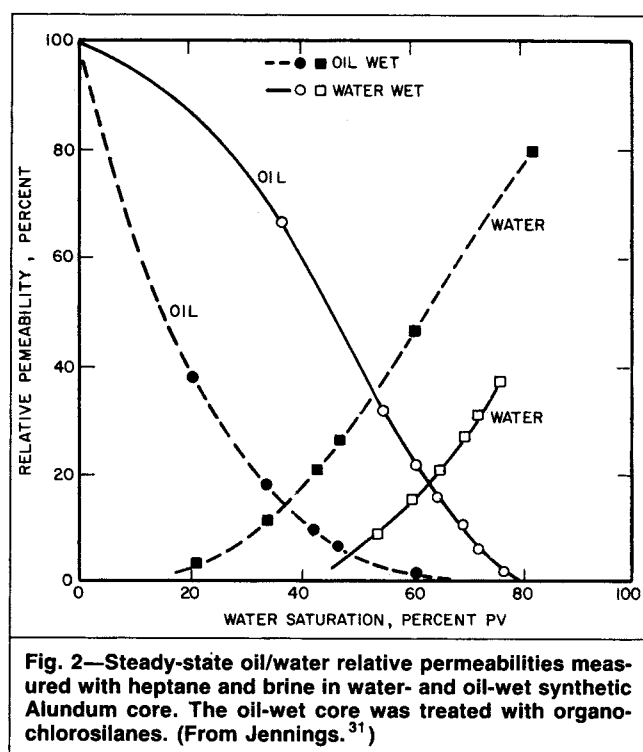
*Now with Particulate Solids Research Inc.

Copyright 1987 Society of Petroleum Engineers



Relative Permeability Curves in Strongly Wetted Systems

Before discussing how changes in wettability affect relative permeability, we will examine relative permeability curves measured on strongly water-wet and strongly oil-wet systems. The wetting fluid in a uniformly wetted system generally will be located in the smaller pores and as a thin film in the larger pores, while the non-wetting fluid is located in the centers of the larger pores. In general, at a given saturation, the relative permeability of a fluid is higher when it is the nonwetting fluid. For example, the water relative permeability is higher in an oil-wet system than it would be if the system were water-wet. This occurs because the wetting fluid tends to travel through the smaller, less permeable pores, while the non-wetting fluid travels more easily in the larger pores. In addition, at a low nonwetting-phase saturation, the nonwetting phase will become trapped as discontinuous globules in the larger pores. These globules block pore throats, lowering the wetting-phase relative permeability. On the other hand, the nonwetting-phase relative permeability is high because the nonwetting phase flows through the centers of the larger pores. At low wetting-phase saturations, the



nonwetting-phase effective permeability will often approach the absolute permeability, demonstrating that the wetting phase does not greatly restrict the flow of the nonwetting phase.^{6,10,28,30}

Jennings³¹ measured steady-state relative permeabilities in water-wet and oil-wet synthetic AlundumTM (sintered aluminum oxide) cores with brine and heptane. The water-wet Alundum core was fired at 1,832°F [1,000°C] to remove any adsorbed materials, while the oil-wet core was prepared by treating it with organochlorosilanes. Wettability was measured with imbibition tests.² Both cores were then saturated with heptane, and steady-state relative permeabilities were measured with increasing brine saturations. The results are shown in Fig. 2, with the relative permeabilities normalized to the absolute oil permeability at 100% oil saturation. At any given saturation, the water permeability is higher and the oil permeability is lower in the oil-wet core when compared with the water-wet one. The water relative permeability at ROS for the oil-wet core is roughly 80%, while it is less than 40% for the water-wet core. The crossover point, where the water and oil relative permeabilities are equal, occurs at a water saturation of about 35% PV for the oil-wet core and about 65% PV for the water-wet one. Note that the relative permeability curves for the oil-wet and water-wet cores are in good agreement if they are plotted vs. wetting-phase saturation (oil for the oil-wet system, water for the water-wet system), indicating the reversal of the positions and flow behavior of the oil and water.²⁹

Craig⁶ presented several rules of thumb, given in Table 1, that indicate the differences in the relative permeability characteristics of strongly water-wet and strongly oil-wet cores.^{10,29,32} These

TABLE 1—CRAIG'S⁶ RULES OF THUMBS FOR DETERMINING WETTABILITY

	Water-Wet	Oil-Wet
Interstitial water saturation	Usually greater than 20 to 25% PV.	Generally less than 15% PV. Frequently less than 10%.
Saturation at which oil and water relative permeabilities are equal.	Greater than 50% water saturation.	Less than 50% water saturation.
Relative permeability to water at the maximum water saturation (i.e., floodout); based on the effective oil permeability at reservoir interstitial water saturation.	Generally less than 30%.	Greater than 50% and approaching 100%.

rules are demonstrated in Fig. 3, taken from Craig,⁶ which shows examples of relative permeability curves in strongly wetted systems. Fig. 2 also shows the effects of wettability on the crossover point and the maximum water relative permeability (nothing can be said about the interstitial water saturation because the measurements started at 100% oil saturation). A further example is shown in Fig. 4, taken from Donaldson and Thomas.¹⁹ Core 1 is strongly water-wet, while Core 5 is strongly oil-wet. Treiber *et al.*³³ generally found good agreement between contact angle and relative permeability measurements in obtaining a qualitative indication of reservoir wettability. Additional measurements on strongly water-wet and strongly oil-wet systems in agreement with Craig's rules can be found in Refs. 28, 29, 34 (see Refs. 35 and 36), and 37 through 45.

The differences in relative permeabilities measured in strongly water-wet and strongly oil-wet systems are caused by the differences in the fluid distributions. Consider a strongly water-wet core. At the IWS, the water is located in the small pores, where it has very little effect on the flow of oil. Because the water does not significantly block the oil flow, the oil effective permeability is relatively high, often approaching the absolute permeability.^{10,28} In contrast, the effective water permeability at ROS is very low, because some of the residual oil is trapped as globules in the centers of the larger pores, where it is very effective in lowering the water permeability. Therefore, the water permeability at ROS is much less than the oil permeability at IWS, with a ratio of less than 0.3 for a strongly water-wet core. In a strongly oil-wet core, the positions of the two fluids are reversed. The oil permeability at IWS is relatively low because the residual water blocks the oil flow. The water permeability at ROS is high because the residual oil is located in the small pores and as a film on the surface, where it has little effect on the water flow. Consequently, the ratio of the two permeabilities can approach 1 or be even greater. The exact value is variable because waterflooding an oil-wet core is very inefficient, and the ROS and water relative permeability at ROS depend on how many PV's of water are injected.

Craig's second rule of thumb is that the water saturation at which the water and oil relative permeabilities are equal is greater than 50% in a strongly water-wet core and less than 50% in a strongly oil-wet one. The effective (and relative) permeability of a fluid is a function of the mobility of that phase at a given saturation. In turn, the mobility is a function of the wetting properties and of the average cross-sectional area of the fluid channels—i.e., of saturation.²⁷ The wetting fluid has a relatively low mobility compared with the nonwetting fluid because the wetting fluid is located next to the pore walls, while the nonwetting fluid is located in the centers of the pores. Consequently, the cross-sectional area (saturation) of the wetting fluid must be higher at the relative-permeability crossover point to compensate for its lower mobility.²⁷

Craig's final rule of thumb was that the interstitial water saturation was generally less than 15% PV in an oil-wet system and greater than 20 to 25% PV in a water-wet one. For a water-wet rock, the interstitial water saturation fills the small pores and forms a thin film over the rock surfaces; hence, the water saturation is relatively high. On the other hand, the interstitial water saturation in some uniformly, strongly oil-wet rocks is found as discrete droplets in the centers of the larger pores.¹⁰ Because there is no requirement that the water cover the pore surfaces, the interstitial water saturation is usually much lower. Raza *et al.*,¹⁰ however, state that they have found exceptions to this general rule. In addition, the interstitial water saturation is also a function of permeability and pore structure, particularly for water-wet rocks.^{2,10}

Craig's rules of thumb generally give an indication of the rock wettability, but there are exceptions.¹⁰ One reason is that the relative permeability is also dependent on initial saturation and pore geometry. Caudle *et al.*⁴⁶ found that relative permeability curves measured on a water-wet sandstone were dependent on the initial water saturation. Decreasing the initial water saturation changed the location and shape of the curves. Craig⁶ states that the initial water saturation strongly influences relative permeability curves in strongly water-wet rocks, but has little effect on curves measured on oil-wet rocks as long as the initial water saturation is less than approximately 20%.

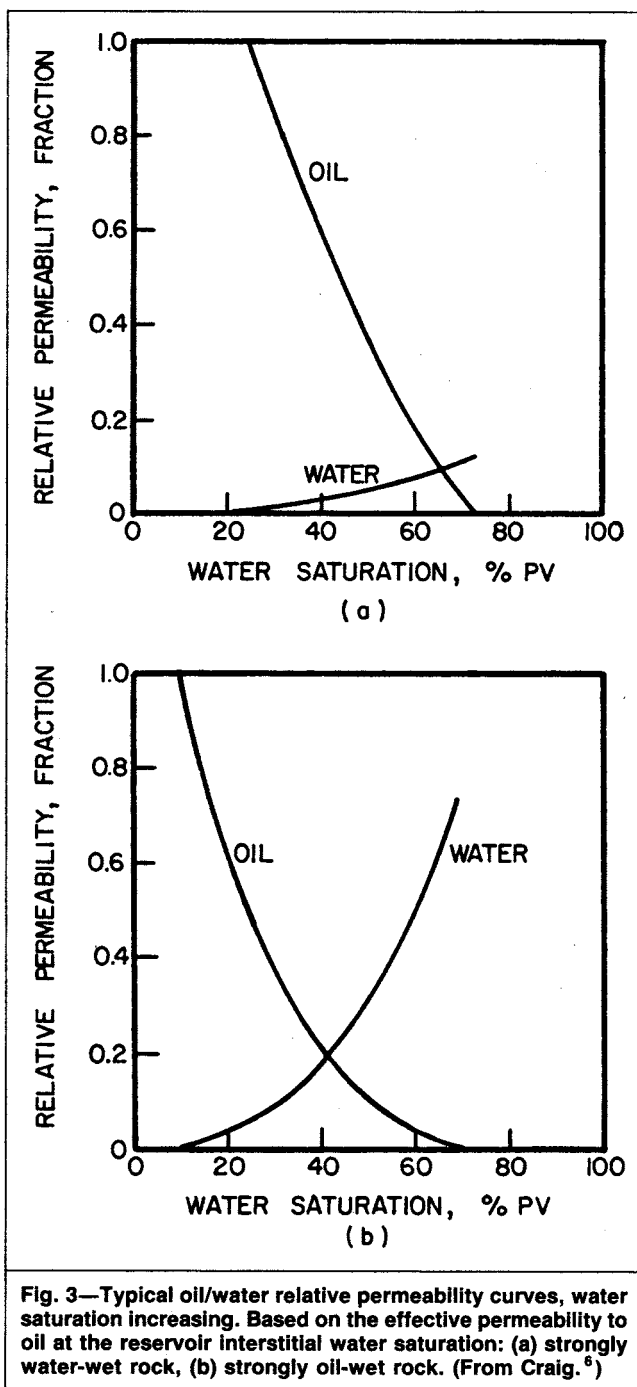


Fig. 3—Typical oil/water relative permeability curves, water saturation increasing. Based on the effective permeability to oil at the reservoir interstitial water saturation: (a) strongly water-wet rock, (b) strongly oil-wet rock. (From Craig.⁶)

Pore geometry can also have a strong effect on the measured relative permeability curves, including such factors as the crossover point and the IWS. Morgan and Gordon⁴⁷ measured relative permeabilities in cleaned, water-wet cores and found significant differences in rocks with large, well-interconnected pores when compared with rocks containing more numerous, smaller, less-well-interconnected pores. In these water-wet cores, the smaller pores are filled with water, which increases the IWS but contributes very little to water flow. When comparing two samples with the same absolute permeability, the rock containing more numerous but smaller pores had a larger IWS and the crossover point for the relative permeabilities occurred at a higher water saturation. Because factors other than wettability can have a similar influence on relative permeability curves, it is preferable to make independent measurements of wettability rather than to rely solely on Craig's rules of thumb to evaluate wettability.

Drainage and Imbibition Relative Permeabilities. In many strongly wetted systems, the wetting-phase relative permeability is primarily a function of its own saturation; i.e., the hysteresis between the

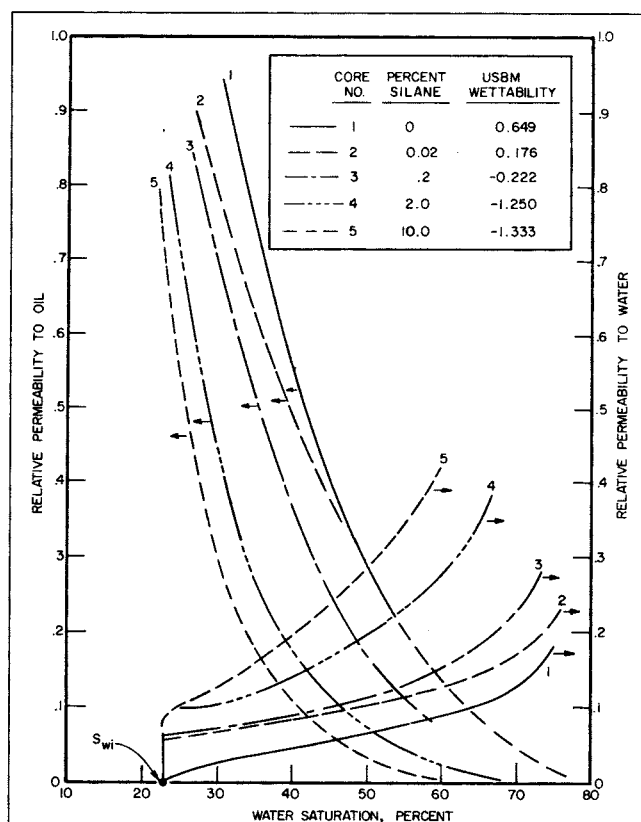


Fig. 4—Effects of wettability on relative permeability using brine, Squirrel crude oil, and organochlorosilane-treated outcrop Torpedo sandstone. Relative permeabilities are based on the absolute water permeability of the 100% brine-saturated core. (From Donaldson and Thomas.¹⁹)

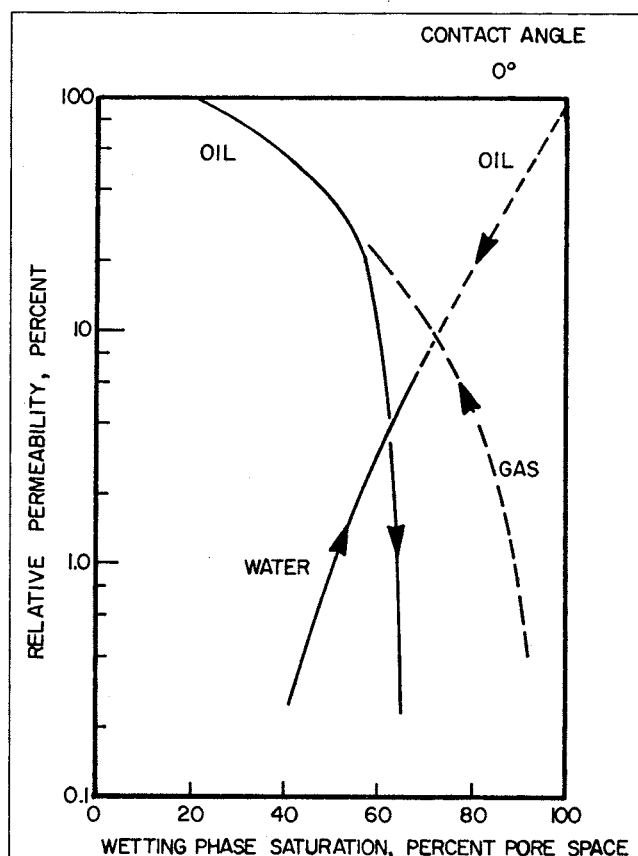


Fig. 5—Comparison of gas/oil drainage and water/oil imbibition relative permeability relationships—strongly water-wet Torpedo sandstone. (From Owens and Archer.⁵¹)

wetting-phase drainage and imbibition relative permeabilities is much smaller than the nonwetting-phase hysteresis.^{33,48-53} In addition, wetting-phase relative permeabilities are very similar for both two- and three-phase relative permeability measurements in strongly wetted systems at a given wetting-phase saturation. In Fig. 5, Owens and Archer⁵¹ compare unsteady-state gas/oil drainage with steady-state water/oil imbibition relative permeabilities in a strongly water-wet Torpedo sandstone core. The oil/water measurements used a refined mineral oil and brine with a small amount of Orvus KTM liquid (a water-wetting detergent) added. The water/oil contact angle measured on a quartz crystal was 0°, indicating that the oil/brine/Torpedo-sandstone system was strongly water-wet. (Note that “water-wet” refers to the wetting preference of the rock for water over oil. Gas is almost always a nonwetting phase for both gas/brine and gas/oil relative permeability measurements.) The gas/oil drainage relative permeabilities, where oil is the strongly wetting fluid, are shown as dotted lines in Fig. 5. The water/oil relative permeabilities, where water is the strongly wetting fluid, are shown as solid lines. Note that the water relative permeability, where the wetting-fluid saturation is increasing, is a continuation of the oil relative permeability, where the wetting-fluid saturation is decreasing.

Treiber *et al.*³³ also compared steady-state water/oil and unsteady-state gas/oil relative permeabilities and found good qualitative agreement with wettabilities measured by contact angles. In a water-wet system, they found good agreement between the wetting-phase relative permeabilities: water in the water/oil tests and oil in the gas/oil tests. The water saturation increased during the water/oil tests (imbibition), and the oil saturation decreased during the gas/oil tests (drainage), so they found little hysteresis in the wetting-phase relative permeability. The two curves did not agree for intermediate or oil-wet systems. Geffen *et al.*²⁸ compared steady-state gas/brine and oil/brine relative permeability ratios and found that they agreed in a strongly water-wet Alundum core.

Schneider and Owens⁵² compared steady-state oil/water relative permeabilities in a water-wet Torpedo sandstone core for increasing oil saturation (drainage) and increasing water saturation (imbibition). They found essentially no hysteresis in the water (wetting-phase) relative permeability. In a second set of experiments, Schneider and Owens⁵³ measured steady-state oil/water relative permeabilities on native-state San Andres and Grayburg cores, which are oil-wet as shown by contact-angle measurements. Starting at the initial water saturation, steady-state oil/water relative permeabilities with water saturation increasing (drainage in an oil-wet core) were followed by steady-state oil/water relative permeabilities with the water saturation decreasing (imbibition). In one plug, there was essentially no hysteresis in the oil (wetting-phase) relative permeability. Two other plugs showed some hysteresis in the oil relative permeability, although it is possible that the plugs were not strongly oil-wet.

McCaffery,⁴⁹ McCaffery and Bennion,⁵⁰ and Morrow and McCaffery⁵⁴ found essentially no hysteresis in the wetting-phase relative permeability when the wetting was sufficiently strong. They measured steady-state relative permeabilities in a teflon core with nitrogen as the nonwetting phase and heptane ($\theta = 20^\circ$ [0.35 rad]) or dodecane ($\theta = 42^\circ$ [0.73 rad]) as the wetting phase. They found that the wetting-phase relative permeability was not dependent on the prior saturation history or the direction of displacement. (These experiments, shown in Figs. 6 and 7, are discussed in more detail later.)

The experiments discussed above, which showed little or no relative permeability hysteresis in the wetting phase, used steady-state methods to determine oil/water relative permeability. Amaefule and Handy⁵⁵ measured steady-state imbibition and drainage relative permeabilities using brine and a refined oil in a fired, strongly water-wet Berea core, and found some hysteresis in the water relative permeability. Recently, several unsteady-state relative permeability measurements have shown significant hysteresis in the wetting-

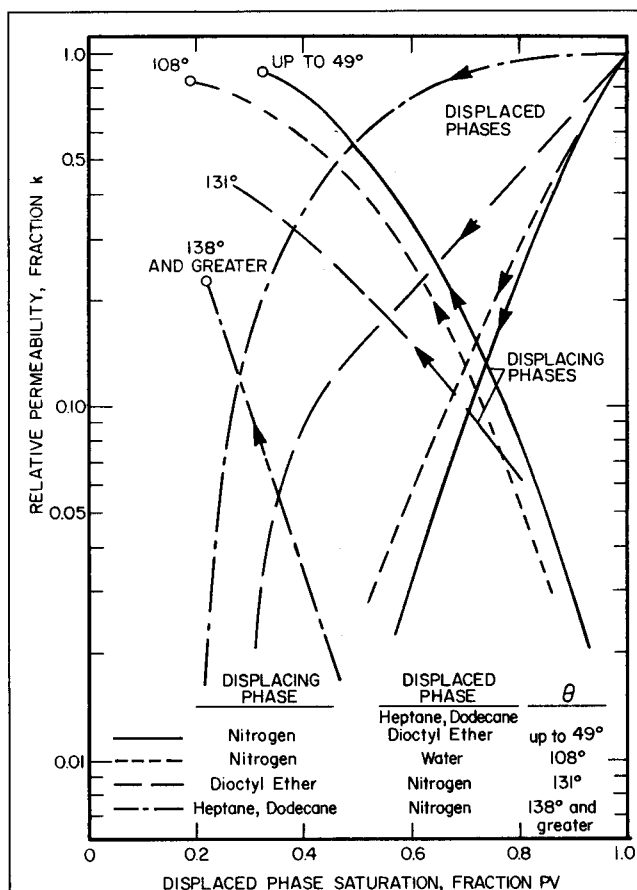


Fig. 6—Effect of wettability on relative permeability—artificial teflon plug, nitrogen, and pure fluids. Relative permeabilities are normalized with the absolute permeability. The plug was initially 100% saturated with the displaced phase. The contact angle, θ , was measured through the displaced phase on a smooth, flat plate. (From McCaffery.⁴⁹)

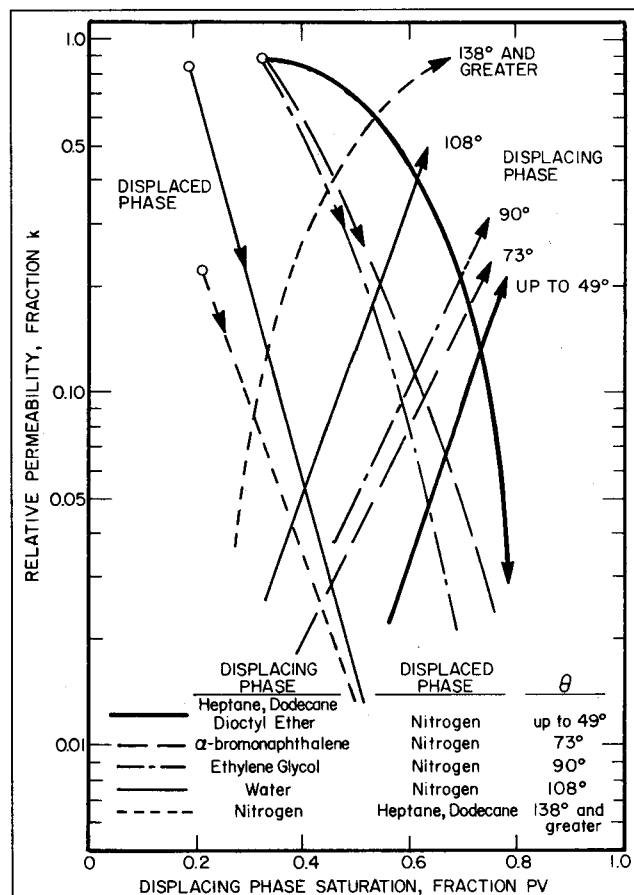


Fig. 7—Effect of wettability on relative permeability—artificial teflon plug, nitrogen, and pure fluids. The saturation of the displacing phase was initially at the irreducible value. The contact angle, θ , is measured through the displacing phase. (From McCaffery.⁴⁹)

phase relative permeability. Jones and Roszelle⁵⁶ and Sigmund and McCaffery⁵⁷ measured drainage and imbibition relative permeabilities in water-wet plugs. In both experiments, the plugs were initially at the IWS. The core was waterflooded, and the imbibition relative permeabilities (wetting phase increasing) were calculated from the pressure drop and production data. After the ROS was reached, the core was oilflooded and the drainage relative permeabilities were calculated. Both experiments found significant hysteresis in the wetting-phase (water) relative permeabilities, but very little hysteresis in the nonwetting-phase (oil) relative permeabilities. The reason for this discrepancy is not known. Craig⁶ and other researchers believe that problems occur with unsteady-state relative permeability measurements in strongly wetted systems with the wetting-phase saturation increasing (i.e., calculating unsteady-state relative permeabilities from a waterflood in a strongly water-wet system).

Effects of Wettability on Relative Permeability. The experiments discussed below examine the effects of wettability on relative permeability using cores with two different types of surfaces: uniform and heterogeneous. In uniformly wetted systems, the wettability of the entire surface is varied from water-wet to oil-wet, while attempting to keep the wettability of the entire surface as uniform as possible. Additional wettability effects will occur if the core has fractional or mixed wettability, where portions of the rock surfaces are water-wet but the remainder are oil-wet.

Relative permeability curves can be normalized with either (1) the absolute permeability of the core saturated with a single phase, usually brine or air, or (2) the effective permeability of the core at a specified initial saturation, such as the oil permeability at IWS. Although the absolute permeability is not affected by the wettability,

TABLE 2—EFFECTIVE OIL PERMEABILITIES AT AN INITIAL WATER SATURATION OF 20% AS A FUNCTION OF CONTACT ANGLE
Taken from Owens and Archer⁵¹

Effective Oil Permeability (md)	Contact Angle (degrees)
571	Air permeability
561	0—water-wet
472	47
459	90
380	138
357	180—oil-wet

the effective oil permeability at IWS decreases as a core becomes more oil-wet. An example is given in Table 2, taken from Owens and Archer.⁵¹ The choice of normalizing permeability affects how the shape of the plotted relative permeability curves will change as the wettability changes. As shown in Fig. 4, relative permeability curves normalized with the absolute permeability explicitly show the decline in relative (effective) oil permeability as the core becomes more oil-wet.¹⁹ On the other hand, relative permeability curves normalized with the effective oil permeability have already factored out this wettability effect; hence, all the curves will start at the same point, even though the wettability is changed (see Fig. 8).

Uniformly Wetted Systems

Fig. 8, taken from Owens and Archer,⁵¹ shows the effects of wettability on relative permeability measured with the Penn State steady-

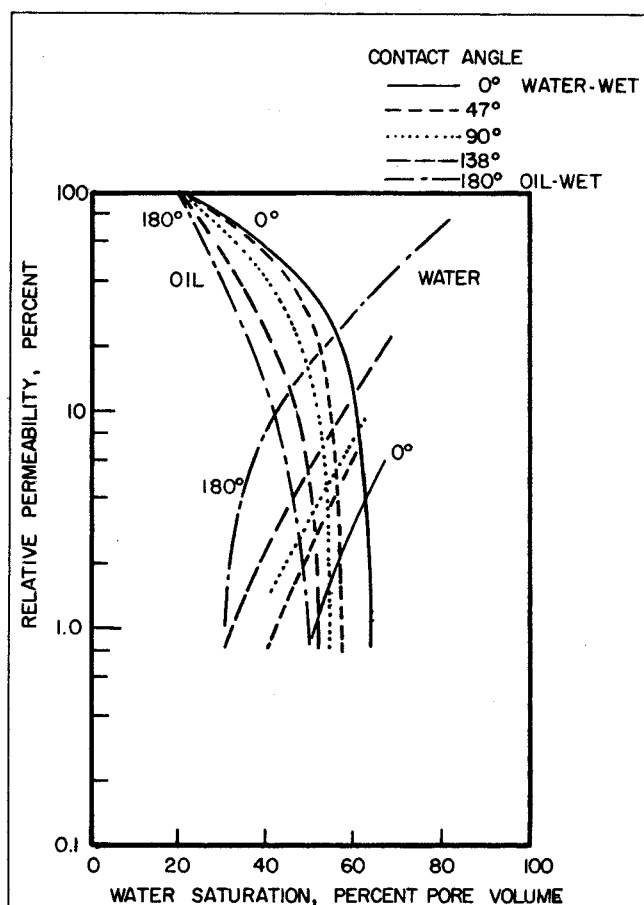


Fig. 8—Effects of wettability on relative permeability—outcrop Torpedo sandstone, brine, and BDNS-treated mineral oil. The contact angle, θ , was measured through the water. Relative permeabilities are based on the effective oil permeability at the initial water saturation. (From Owens and Archer.⁵¹)

state method. A mild NaCl brine and a 1.7-cp [1.7-mPa·s] refined mineral oil were used in an outcrop Torpedo sandstone that was fired before the experiments to stabilize clay minerals. The wettability of the system was controlled by adding either (1) various amounts of barium dinonyl-naphthalene sulfonate (BDNS) to the refined mineral oil, which made the system more oil-wet, or (2) Orvus K liquid (a detergent) to the brine to achieve a strongly water-wet system with a 0° contact angle through the brine. Wettability was monitored by contact-angle measurements on a quartz crystal. All the relative permeability tests started at an initial water saturation of about 20%. This was achieved by saturating the dry core with brine, then flooding it with a viscous mineral oil to the initial water saturation. Finally, the viscous mineral oil was replaced with the 1.7-cp [1.7-mPa·s] refined mineral oil containing the desired amounts of detergent or BDNS.

Fig. 8 shows that at any given water saturation, the water relative permeability increases as the system becomes more oil-wet. The oil relative permeability simultaneously decreases, causing a

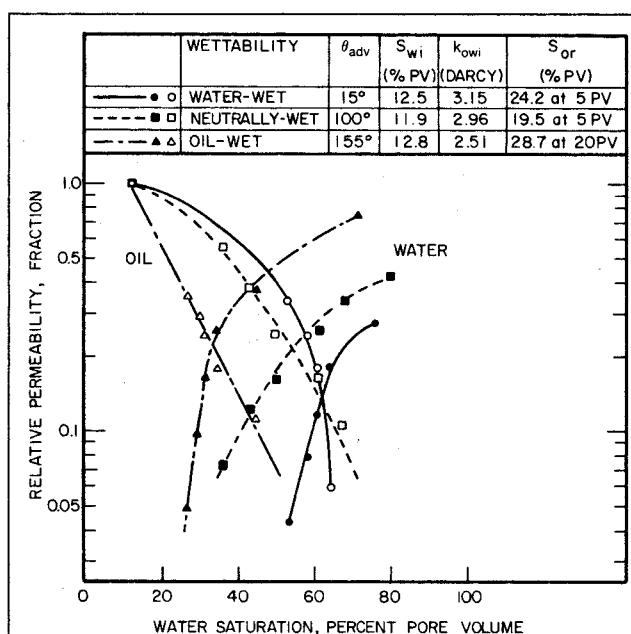


Fig. 9—Effects of wettability on relative permeability—dolomite pack, water, and oil treated with octanoic acid. Relative permeabilities are normalized with the effective oil permeability at the initial water saturation. (From Morrow et al.⁶²)

gradual reduction in the waterflooding efficiency. Owens and Archer normalized their curves with the effective oil permeability at the initial water saturation (see Table 2). The effective oil permeability decreases as the wettability is varied from water-wet to oil-wet. At a contact angle of 0° (measured through the water), the water has only a small influence on the effective oil permeability, which is almost equal to the absolute (air) permeability. The reason is that the initial 20% water saturation in the water-wet core is close to the IWS. At this condition, the water is present in the smallest pores and as a thin film on the rock surfaces, allowing the oil to flow through the larger pores. At 180° [3.14 rad] contact angle, water will be present in the form of blobs that can block the pore throats of the larger pores, substantially reducing the effective oil permeability.

Fig. 4 shows the results from unsteady-state relative permeabilities run in outcrop Torpedo sandstone cores using crude oil and brine and calculated by the Johnson-Bossler-Naumann⁵⁸ (JBN) method. Wettability was varied by treating the cores with different concentrations of organochlorosilanes and monitored with the U.S. Bureau of Mines (USBM) wettability method, where +1 indicates a strongly water-wet core, -1 a strongly oil-wet core, and 0 a neutrally wet core (see Table 3).^{2,59-61} The relative permeability curves are based on the absolute water permeability at 100% brine saturation. As the core becomes more oil-wet, the relative oil permeability decreases and the relative water permeability increases. However, in contrast to Fig. 8, which was normalized with the effective oil permeability, this set of curves shows how the oil permeability at the initial water saturation also decreases.

TABLE 3—APPROXIMATE RELATIONSHIP BETWEEN WETTABILITY, CONTACT ANGLE, AND THE USBM AND AMOTT WETTABILITY INDICES

	Water-Wet	Neutrally Wet	Oil-Wet
Contact Angle, degrees			
Minimum	0	60 to 75	105 to 120
Maximum	60 to 75	105 to 120	180
USBM Wettability Index	Near 1	Near 0	Near -1
Amott Wettability Index			
Displacement-by-water ratio	Positive	Zero	Zero
Displacement-by-oil ratio	Zero	Zero	Positive

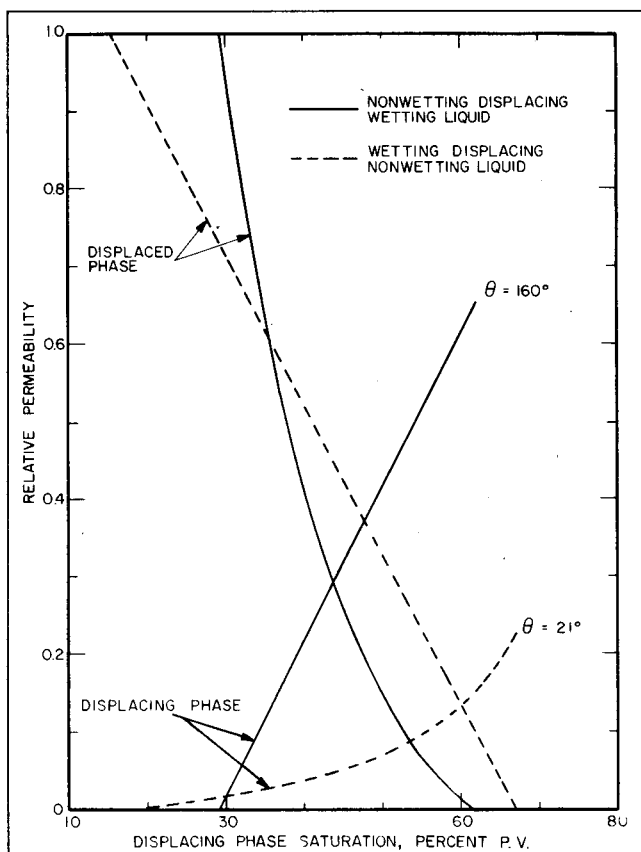


Fig. 10—Effect of wettability on relative permeability—sintered teflon core, refined mineral oil, and water or a sucrose solution. The contact angle, θ , is measured through the displacing phase on a flat teflon plate. (From Mungan.⁶³)

Morrow *et al.*⁶² measured steady-state relative permeabilities with water and a refined mineral oil, using packings of powdered dolomite as the porous medium. Wettability was controlled with different concentrations of octanoic acid in the oil. Water-advancing contact angles were measured on a smooth dolomite crystal. Relative permeabilities were measured at three different wettabilities: (1) water-wet, $\theta_{adv} = 15^\circ$ [0.26 rad], (2) neutrally wet, $\theta_{adv} = 100^\circ$ [1.75 rad], and (3) oil-wet, $\theta_{adv} = 155^\circ$ [2.7 rad]. All three tests started with initial water saturations of $12 \pm 1\%$ PV. The results are shown in Fig. 9, normalized with the effective oil permeability at the initial water saturation, which was 20% less for the oil-wet case than for the water-wet one. As the system becomes more oil-wet, the water relative permeability increases, while the oil relative permeability decreases. The crossover point, where the two relative permeabilities are equal, occurs at lower water saturations. The final water permeabilities at ROS of the water-wet and neutrally wet systems were measured after flowing 5 PV of brine through the system, after which no more oil was produced. For the oil-wet core, after 20 PV of brine were injected, a small amount of oil was still being produced. As discussed in more detail in Ref. 5, ROS's in oil-wet systems are less well defined when compared with water-wet systems.

Several researchers^{49,50,54,63,64} have used polytetrafluoroethylene (teflon) cores and pure fluids without surfactants to study the effects of wettability on relative permeability. The advantages of teflon are that it is chemically inert and has a low surface energy, allowing a wide range of contact angles to be obtained with various pairs of pure fluids that do not contain surfactants. The uniform composition of the core and the absence of surfactants combine to give a constant, uniform, and reproducible wettability, avoiding problems with nonuniform wettability or possible wettability alteration during the experiments.¹ The wettability of the teflon/fluid system is determined by contact-angle measurements on smooth

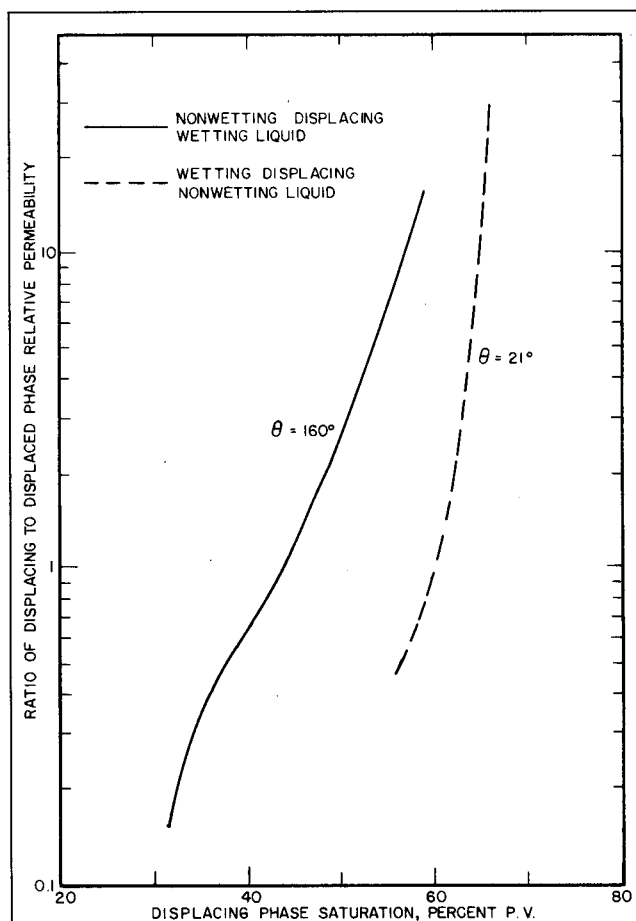


Fig. 11—Effect of wettability on relative permeability ratio—sintered teflon core, refined mineral oil, and water or a sucrose solution. (From Mungan.⁶³)

teflon plates. The advancing and receding contact angles are essentially equal because the measured contact angle generally has little or no hysteresis.

Stegemeier and Jessen⁶⁴ measured gas/liquid relative permeabilities using nitrogen and pure fluids in a teflon particle pack. The changes in relative permeability as the liquid phase became less wetting are consistent with the experiments discussed earlier. However, the changes are relatively small, possibly because of the homogeneous nature and high permeability (16 darcies) of the teflon pack.

Mungan⁶³ measured unsteady-state relative permeabilities in a sintered, consolidated teflon core with oil as the wetting fluid. A refined mineral oil and water or a sucrose solution were used, where the viscosity ratio was maintained constant by varying the sucrose concentration in the water. Typical results are shown in Fig. 10. For the wetting/displacing/nonwetting case (oilflood), the core was saturated with oil, driven to the ROS with sucrose solution, then oilflooded. Relative permeabilities were calculated by the JBN method and normalized with the water relative permeability at ROS. A similar procedure was used for the nonwetting/displacing/wetting case (waterflood). The contact angle was measured through the displacing phase on a smooth teflon plate. The changes in relative permeability for the two displacements are consistent with the other experiments discussed earlier. When the wetting fluid displaces the nonwetting one, the crossover point occurs at a higher displacing-phase saturation, and the displacing-phase relative permeability at floodout is lower.

Mungan also calculated relative permeability ratios, shown in Fig. 11. When the wetting fluid displaces the nonwetting one, the relative permeability ratio (displacing to the displaced phase) is nearly vertical and extends over a relatively short saturation interval. In contrast, when the nonwetting fluid displaces the wetting one, the relative permeability ratio is higher at a given saturation and ex-

tends over a greater saturation range. In reservoir systems, the slope of the relative permeability ratio (k_w/k_o) vs. S_w curve can sometimes be used as a qualitative indicator of the wettability.¹⁰ If the entire curve is nearly vertical and extends over a small saturation interval, the rock is strongly water-wet. Conversely, the rock is oil-wet if the ratio has a gentle slope and extends over a larger saturation interval. Note that while the relative permeability ratios in Fig. 9 do not cross, they may cross at very high relative permeability ratios if the oil-wet system has a lower ROS (e.g., see Raza *et al.*¹⁰).

McCaffery,⁴⁹ McCaffery and Bennion,⁵⁰ and Morrow and McCaffery⁵⁴ studied the effects of wettability on steady-state relative permeabilities using sintered teflon cores and various pairs of pure fluids (nitrogen and liquids). The first set of tests, shown in Fig. 6,⁴⁹ were primary drainage and imbibition tests. The core was initially saturated with one of the fluids, which will be referred to as the "displaced" liquid. The contact angle, measured through this displaced phase, ranged from 20° [0.35 rad] (nitrogen displacing heptane) to 160° [2.8 rad] (heptane displacing nitrogen). Steady-state relative permeabilities were measured at a series of decreasing saturations of the displaced phase, starting from 100% saturation. Primary-drainage relative permeabilities were measured when the contact angle through the displaced phase was less than 90° [1.57 rad], and primary imbibition measurements were made when the contact angle was greater than 90° [1.57 rad].

For example, one set of primary-drainage relative permeabilities was measured for nitrogen displacing dodecane. The teflon core was first saturated with dodecane; then the absolute permeability was measured with 100% dodecane flowing. Relative permeabilities were subsequently measured by increasing the flow rate of nitrogen and decreasing the flow rate of dodecane in a series of steps, while measuring saturation and pressure drop. During the final measurement, only nitrogen is flowing at the irreducible dodecane saturation. The reverse set of measurements, with dodecane displacing nitrogen from an initially 100% nitrogen-saturated core, were also made. These measurements were primary-imbibition relative permeabilities.

In Fig. 6, the relative permeabilities are normalized with the absolute permeability. The results are plotted vs. the displaced-phase saturation, and the contact angle was measured through the displaced phase on a flat teflon plate. As the contact angle increases and the displaced phase becomes less wetting, the displaced-phase relative permeability increases and the displacing-phase relative permeability decreases. The set of relative permeability curves marked "Up to 49°" are for a nonwetting fluid (nitrogen) displacing a wetting fluid (heptane, dodecane, or dioctyl ether) from the core. McCaffery and coworkers found essentially no effect of contact angle on relative permeability when one of the fluids wet the core strongly enough. The nitrogen (nonwetting phase) relative permeability at the irreducible wetting-phase saturation is high, roughly 90% of the absolute permeability. The relative permeability curves for a contact angle of 49° [0.86 rad] or less are analogous to water/oil relative permeability curves measured in a strongly oil-wet core, with the water saturation increasing. Comparing these curves with Figs. 2 and 3, we can see that the behavior is qualitatively similar. (Note that the curves are reversed because McCaffery's curves are plotted vs. displaced-phase saturation.)

As the displaced phase becomes less strongly wetting, its relative permeability increases while the relative permeability of the displacing phase decreases, as shown by the shift in the relative permeability curves for nitrogen displacing water ($\theta = 108^\circ$ [1.88 rad]) and dioctyl ether displacing nitrogen ($\theta = 131^\circ$ [2.29 rad]). The curves marked "138° and Greater" are for a wetting fluid (heptane or dodecane) displacing a nonwetting fluid (nitrogen). Again, McCaffery and coworkers found no effect of contact angle on relative permeability when the wetting is strong enough. These relative permeability curves are analogous to water/oil relative permeability curves measured in a strongly water-wet core, with the water saturation increasing. The wetting-phase relative permeability at the residual nonwetting-phase saturation is low, about 25% of the initial permeability, and the crossover point has shifted.

At the end of the steady-state relative permeability tests shown in Fig. 6, the core was left with an irreducible saturation of the

displaced phase in the core. McCaffery and coworkers then made a second set of steady-state relative permeability tests starting from this irreducible saturation. For example, in the first set of tests, nitrogen displaced dodecane from an initially 100% dodecane-saturated core in a series of steps, until only nitrogen was flowing at an irreducible dodecane saturation (primary drainage). During the second set of measurements, the nitrogen flow was decreased and the dodecane flow was increased in a series of steps, until finally only dodecane was flowing at an irreducible nitrogen saturation (secondary-imbibition measurements for this pair of fluids).

The results are shown in Fig. 7, normalized with the absolute permeability.⁴⁹ Note that the results are plotted vs. the displacing-phase saturation and the contact angle is measured through the displacing phase. This is done so that the two sets of relative permeability measurements in Figs. 6 and 7 can be compared easily, because the displaced and displacing phases have now been reversed. As the wetting tendency of a phase increases, its relative permeability decreases. In Fig. 7, for example, the relative permeability of the displaced phase decreases as the contact angle drops from 138° to 49° [2.4 to 0.86 rad]. However, as with the initially 100%-saturated measurements, McCaffery and coworkers found little effect of contact angle on wettability when the wetting was sufficiently strong. The curves marked "Up to 49°" are for a wetting phase (heptane, dodecane, or dioctyl ether) displacing a nonwetting phase (nitrogen), with a low relative permeability of the wetting phase at the nonwetting-phase residual saturation. Again, note the similarity to water/oil relative permeability curves measured in a water-wet core with water saturation increasing. As the wetting of the displacing phase gradually decreases, the curves shift, with the displacing-phase relative permeability increasing while the displaced-phase relative permeability decreases. The curve marked "138° and Greater" is for a strongly nonwetting phase (nitrogen) displacing a wetting phase (heptane, dodecane, or dioctyl ether) from the core. Note that these experiments start at different values of the irreducible saturation, in contrast to the work by Owens and Archer.⁵¹ The differences in starting saturation may also affect the relative permeability curves.⁴⁶

McCaffery and coworkers found essentially no hysteresis in the wetting-phase relative permeability when wetting was sufficiently strong. The relative permeability of heptane ($\theta = 20^\circ$ [0.35 rad]) or dodecane ($\theta = 42^\circ$ [0.73 rad]) measured with nitrogen as the second fluid was not dependent on prior saturation history or the direction of displacement. A comparison of the four heptane/dodecane curves ("Up to 49°" and "138° and Greater") in Figs. 6 and 7 shows that they are essentially identical. Two of the curves are reversed because heptane and dodecane were used as both displacing and displaced fluids in both figures.

These results are generally consistent with the other experiments discussed earlier.^{19,51,62} The most notable difference is that McCaffery and coworkers found that relative permeability is insensitive to changes in wettability and contact angle when the system is strongly wetted, with large changes occurring only when the system is near neutral wettability. Similarly, Morrow and McCaffery,⁵⁴ Morrow and Mungan,⁶⁵ and Morrow⁶⁶ found that capillary pressure curves measured in teflon plugs were also insensitive to changes in wettability when wetting was sufficiently strong. In contrast, Owens and Archer⁵¹ found changes in the relative permeability curves when the contact angle varied from 0° to 47° [0 to 0.82 rad] (see Fig. 8). The reason for this disagreement is unknown.

Effects of Core Cleaning and Handling

The experiments discussed above attempted to vary wettability systematically. In this section, we will review some experiments that show how core cleaning and handling can drastically affect relative permeability by altering the wettability of core. Note that some of these experiments were made on reservoir core, which may have nonuniform wettability.

Fig. 12, taken from Mungan,⁶⁷ shows native-state, cleaned, and restored-state relative permeabilities measured on a single core using the unsteady-state JBN⁵⁸ technique. All curves are based on the effective oil permeability at IWS. Native-state core was cut from a Pennsylvanian sandstone reservoir with lease crude oil, then stored

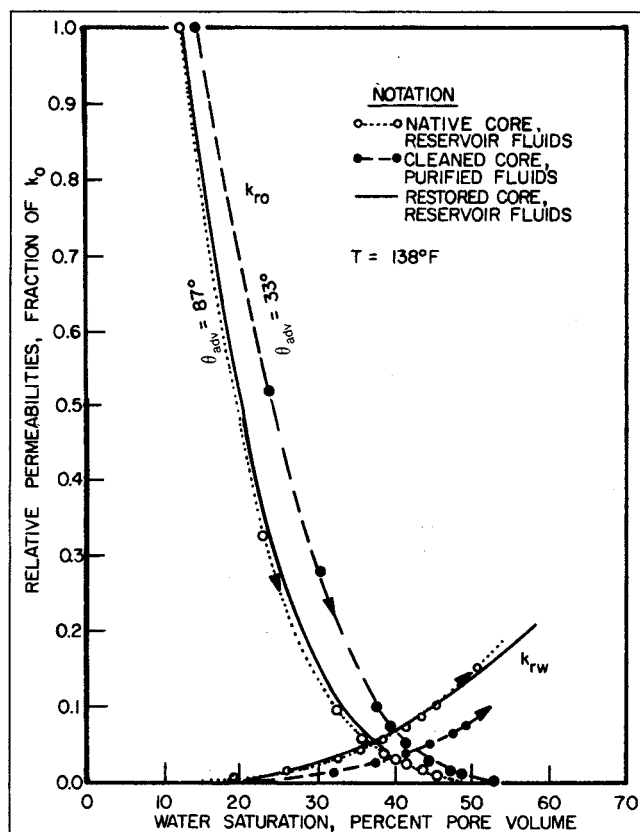


Fig. 12—Effect of wettability on relative permeability with a reservoir core in the native, cleaned, and restored states. The advancing contact angle, θ_{adv} , measured on a flat quartz surface, was 87° for the reservoir fluids and 33° for brine and the refined oil. (From Mungan.⁶⁷)

in lease crude to preserve wettability. Relative permeability was measured on the native-state core with brine and live crude oil at reservoir temperature (138°F [59°C]) and a pressure high enough to keep all gases in solution. The core was cleaned with benzene, followed by toluene, and then dried. Relative permeabilities were remeasured on the cleaned core using synthetic formation brine and a refined oil. Based on Craig's rules of thumb for wettability (see Table 1), the cleaned core is significantly more water-wet than the native-state one. This is confirmed by contact-angle measurements. The water-advancing contact angle, θ_{adv} , was 33° [0.58 rad] for the refined oil and brine and 87° [1.52 rad] for live reservoir fluids on a quartz surface. Finally, the cleaned core was saturated with brine, driven to IWS with crude, and aged at the reservoir temperature for 6 days to restore wettability. The relative permeability for the core in the restored state was then measured. Fig. 12 shows that it is very similar to the native-state relative permeability, implying that the wettability was successfully restored. Mungan then repeated the cleaning, restoration, and relative permeability measurements on the same core and obtained identical results.

Mungan's experiments show the importance of measuring relative permeability on native-state or restored-state cores, rather than on cleaned ones. At any water saturation, the relative oil permeabilities were lower and the relative water permeabilities were higher for the native- and restored-state core when compared with the more water-wet cleaned core. If a cleaned core were used to predict water-flood behavior, it would predict higher recovery efficiencies and later breakthrough than the actual behavior. Similar results comparing native-state vs. cleaned relative permeabilities can be found in Refs. 47, 68, and 69.

Wendel *et al.*⁷⁰ measured unsteady-state water/oil relative permeabilities on Hutton plugs in their contaminated, cleaned, and restored states (see Fig. 13). Contamination by surfactants in the invert-oil-emulsion mud used to drill the well rendered the cores

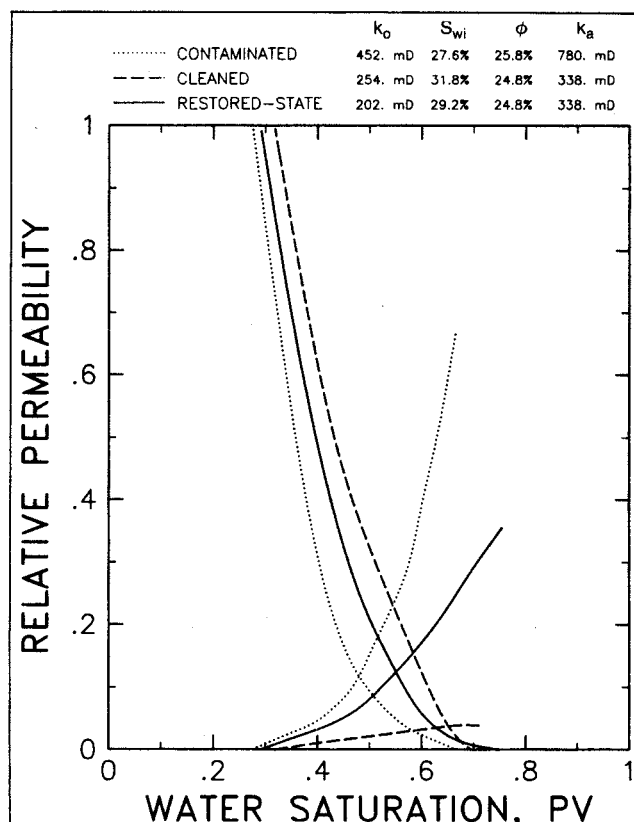


Fig. 13—Comparison of oil/water relative permeabilities measured on contaminated, cleaned, and restored-state plugs, Hutton massive sand zone: (1) contaminated, oil-wet plug, Well H3/21, 10,092 ft; (2) cleaned, strongly water-wet plug, Well H5/13, 10,077 ft; (3) restored-state measurements on the cleaned plug after saturation with formation fluids and aging. (From Wendel *et al.*⁷⁰)

oil-wet, as shown by relative permeability and USBM wettability measurements. Craig's rules of thumb (Table 1) show that the contaminated plug shown in Fig. 13 is strongly oil-wet. The crossover point for the oil and water relative permeabilities occurs at a water saturation of 48%, while the water relative permeability at floodout is about 67%. Wendel *et al.* were able to clean the cores and remove the drilling-mud surfactants using three successive Dean-Stark extractions with toluene, glacial acetic acid, and ethanol. In general, the cleaned cores were strongly water-wet. (Some cores could be cleaned only to neutral wettability, possibly because of the presence of coal, which is naturally neutrally wet.) Fig. 13 shows oil/water relative permeabilities measured on a second plug after cleaning, with a USBM wettability index of $+0.64$ after cleaning. The crossover point for the oil and water relative permeabilities occurs at a water saturation of 65% PV, while the water relative permeability at floodout is only 8%. Finally, Wendel *et al.* restored the wettability of the cleaned, water-wet cores by saturating the cores with formation fluids and aging the cores at reservoir temperature for 1,000 hours. The restored-state cores were neutrally wet, with relative permeability characteristics intermediate between measurements in the contaminated, strongly oil-wet state and the cleaned, strongly water-wet state. The restored-state relative permeabilities shown in Fig. 13 were measured on the cleaned plug after saturation and aging. The crossover point occurred at a water saturation of 56% PV, whereas the water relative permeability at floodout was 42%.

Keelan⁷¹ also compared unsteady-state oil/water relative permeabilities measured in a contaminated, oil-wet core vs. the same core after it had been cleaned and rendered strongly water-wet (see Fig. 14). Measurements were first made on an oil-wet, weathered core taken with wettability-altering chemicals in the mud. The core was then cleaned and rendered water-wet by firing at 572°F [300°C] in an oxygen/ CO_2 atmosphere to remove all adsorbed, wettability-

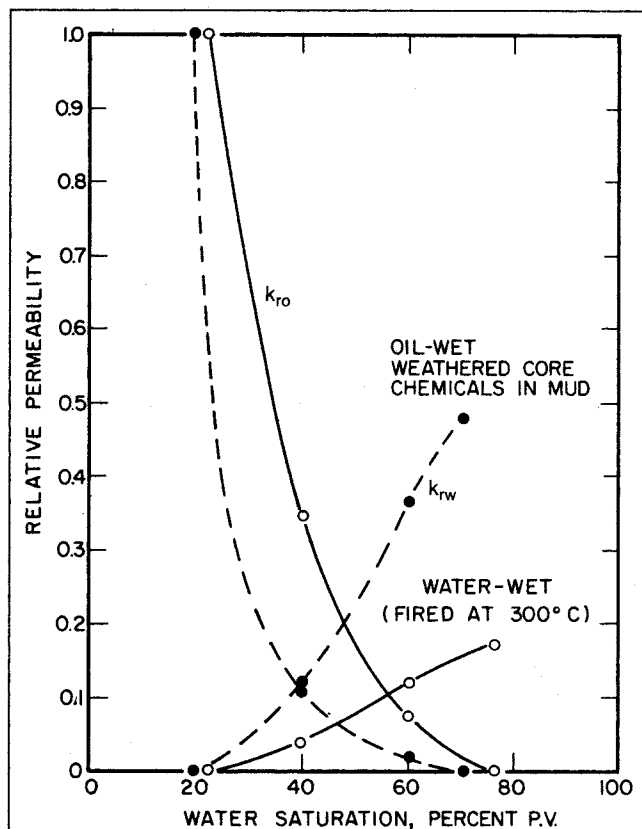


Fig. 14—Contaminated vs. cleaned oil/water relative permeabilities—sandstone plug. (From Keelan.⁷¹)

altering compounds. The changes in the relative permeability curves are similar to those observed by Wendel *et al.*

Wang⁶⁹ saturated a Berea core with brine, oilflooded it with dead Loudon crude, and then waterflooded it to ROS. The core was flushed with Loudon crude to IWS and allowed to age at 160°F [71°C] for 1 year before steady-state water/oil relative permeability was measured. The core was significantly less water-wet after aging. The ROS was initially 42.5% PV, but decreased to less than 17% PV after aging. Waterflood tests indicated that the aged core probably had mixed wettability.^{69,72} Wang compared the steady-state water/oil relative permeabilities of the aged Berea core with relative permeabilities measured without aging in an adjacent Berea core using brine and dead Loudon crude. According to Craig's rules of thumb, the unaged core was significantly more water-wet: (1) crossover saturation without aging was roughly 50% PV vs. 60% PV for the aged core; (2) water relative permeability at ROS for the unaged core was roughly 5% vs. 30% after aging; and (3) ROS without aging was roughly 47% PV vs. 17% PV for the aged core.

Grist *et al.*⁷³ showed how different cleaning methods could alter the effective permeability and wettability of cleaned cores. Similar cores were cleaned by several currently used methods and then waterflooded before the ROS and endpoint effective water permeability were measured. The ROS was very similar for all cleaning methods. However, the endpoint effective permeability varied by more than a factor of 3 between cleaning methods. Their explanation for this behavior was that some methods were able to extract more of the adsorbed, wettability-altering compounds, leaving the rock more water-wet. In the more water-wet cores, the residual oil had a greater tendency to form trapped droplets, blocking pore throats and lowering effective water permeability. The least effective of the three methods was an overnight reflux extraction with toluene. A reflux extraction with toluene followed by extraction with a mixture of chloroform and methanol for 2 days was more effective. Finally, the most effective method used reflux extrac-

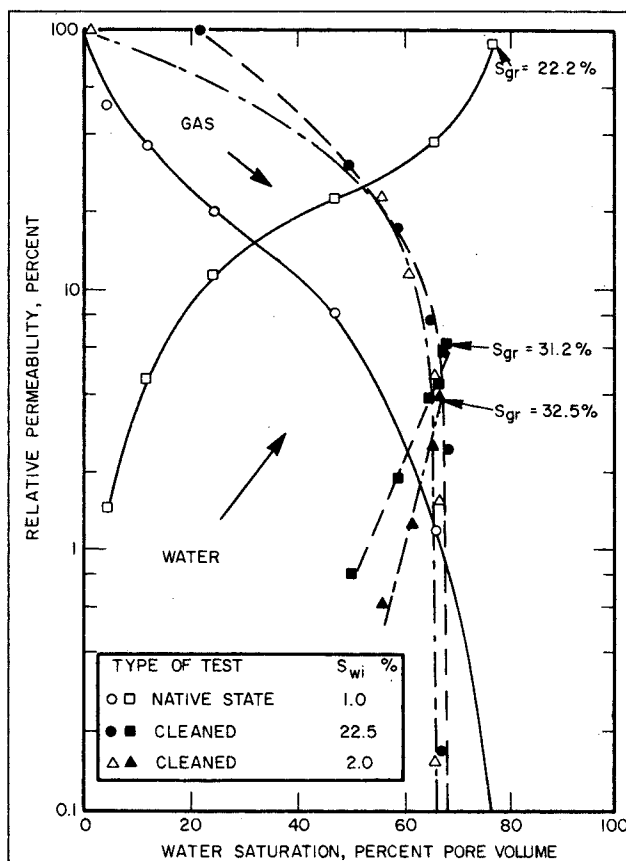


Fig. 15—Comparison of native-state and cleaned water/gas relative permeabilities—San Andres plug. $k_{gi} = 135$ md, $\phi = 20.3\%$. (From Schneider and Owens.⁵³)

tion with toluene followed by extraction with chloroform and methanol for 3 weeks. In the final stage of the cleaning, methanol alone was used.

Although the authors cited above have found that the cleaned cores were more water-wet, it is also possible for cleaning to change a core from water-wet to oil-wet, either by deposition of compounds from the oil⁷⁴ or by adsorption of the cleaning solvents.⁷⁵ In any case, cleaning the core can introduce serious errors in the relative permeability measurements.

Jennings⁷⁶ used toluene extraction to clean cores from different reservoirs and found that the wettabilities and relative permeabilities were not changed. The initial wettabilities of the cores before cleaning ranged from water-wet to oil-wet. Jennings stated that his results indicated that toluene-extracted cores retained the reservoir wettability and could be used for relative permeability measurements. In general, however, this is not the case, except for strongly water-wet reservoirs where there are no adsorbed wettability-altering compounds to be removed during cleaning. Although it is often less efficient than other solvents, toluene extraction can alter the wettability and relative permeabilities of a core.^{1,69,77} In some cases, we have found that neutrally wet or mildly oil-wet native-state core becomes strongly water-wet after extraction with toluene. The relative permeability curves also shift. Amott⁷⁷ has also found that toluene extraction can clean some cores, while it has little effect on others, such as the strongly oil-wet Bradford cores. Wang⁶⁹ found that extracting native-state Loudon cores with toluene made them more water-wet and altered the relative permeability curves. Therefore, since toluene extraction will alter the wettability and relative permeability of many native-state cores, measurements should be made on native-state cores before toluene extraction.

Based on recent work,^{70,75} it is possible that Jennings was not able to alter the wettability with toluene because many of his cores were taken with either oil-based or surfactant/emulsion drilling fluids. The surfactants in drilling muds, which can render core oil-wet, are very difficult to remove. For example, Wendel *et al.*⁷⁰

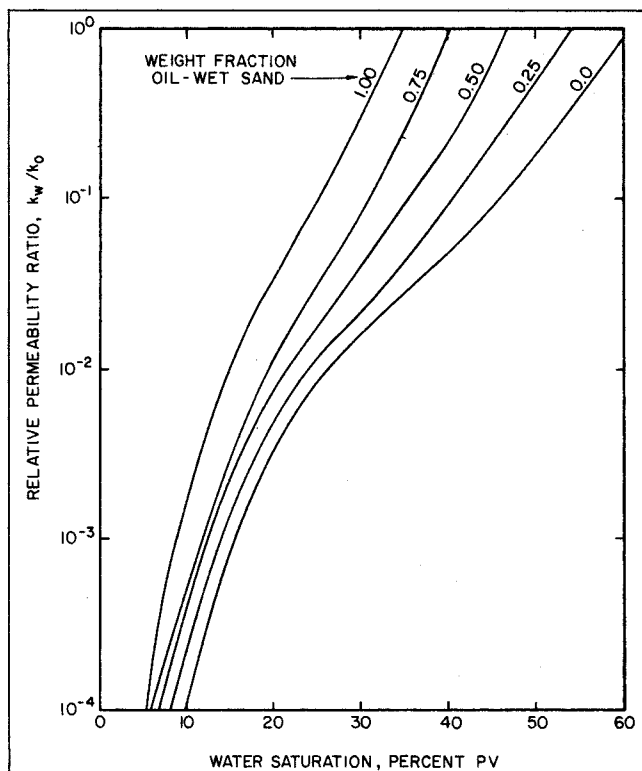


Fig. 16—Water/oil relative permeability ratio curves for fractionally wetted sandpacks. (From Fatt and Klirkoff.⁷⁹)

found that toluene extraction would not remove the surfactants deposited on Hutton core by an invert-oil-emulsion mud. It was necessary to remove the surfactants by three successive Dean-Stark extractions using toluene, glacial acetic acid, and ethanol.

Schneider and Owens⁵³ examined the effects of cleaning on steady-state, gas/water relative permeabilities measured in a San Andres carbonate core taken from an oil reservoir. Oil/water contact-angle measurements indicated that the reservoir was moderately oil-wet. The experiments were designed to study the late stages of a miscible flood. In a miscible flood, a gas such as CO₂ is injected into the reservoir to displace the oil, followed by water injection to displace the gas and oil. In areas swept by gas, the gas saturation is high and the water saturation is relatively low before water injection. The gas/water relative permeability curves measured in the direction of increasing water saturation are needed to predict the behavior of the injected water.

The native-state core used in the experiments was prepared by flushing with pentane under backpressure to remove the crude, followed by nitrogen to remove the pentane, leaving a core containing only brine and gas. It was assumed that this procedure did not significantly alter the wettability. Steady-state gas/water relative permeability was measured on the flushed, native-state core in the direction of increasing water saturation. The native-state gas/water relative permeabilities, shown in Fig. 15, indicate that the core is behaving as if it is oil-wet (more accurately, as if it is water-repellant, since the oil saturation is zero). The crossover point at which the gas and water relative permeabilities are equal occurs at a water saturation of about 30%. The water relative permeability at the residual gas saturation is more than 90% of the initial gas relative permeability. Note that the initial water saturation is only 1%, which is extremely low. It is not known whether the reservoir water saturation is this low or whether the water saturation was lowered during the pentane flush and subsequent evaporation of the pentane.

After native-state gas/water relative permeability measurements were made, the core was cleaned and dried, and gas/water relative permeabilities were measured on the cleaned core with two different initial water saturations. In the first set of measurements, an initial water saturation of 22.5% was established with a centrifuge technique. In the second set, a special low-salinity brine was used

TABLE 4—ROS AT WOR = 100, FRACTIONALLY WETTED SANDPACKS⁷⁹

Oil-wet Sand (%)	ROS (%)
0	28
25	35
50	40
75	45
100	48

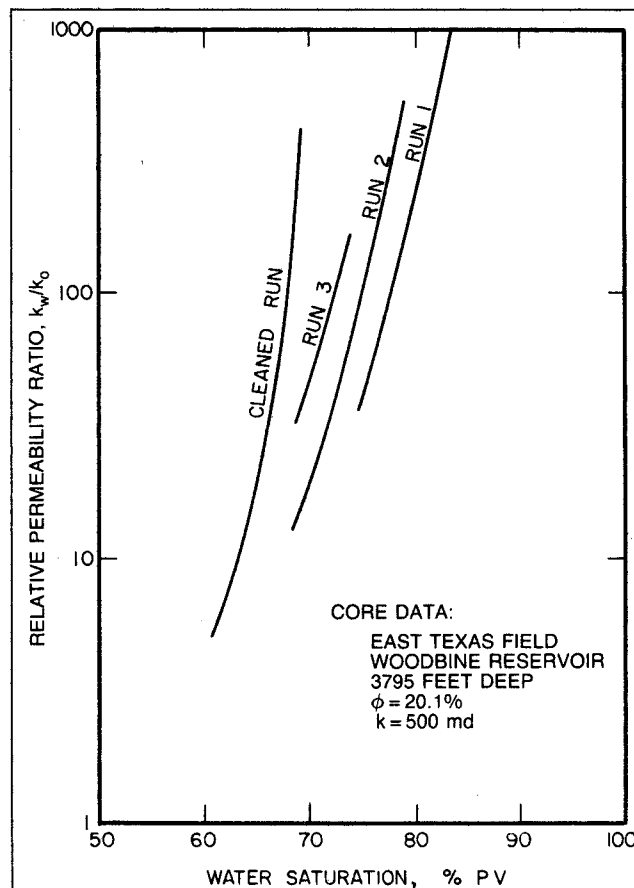


Fig. 17—Unsteady-state water/oil relative permeability ratios, k_w/k_o , measured during a series of waterfloods of a native-state East Texas Woodbine core that initially had a mixed wettability. (From Richardson et al.⁸⁴)

and dry nitrogen was injected to reduce the water saturation to 2%, in close agreement with the initial water saturation in the native-state test. The measurements, shown in Fig. 15, are completely different from the native-state ones. The residual gas saturation is higher and the water endpoint relative permeability is much lower at less than 10% of the initial permeability, indicating that the residual gas strongly interferes with the water flow. Based on their previous work, Schneider and Owens⁵² believe that the native-state core is oil-wet, while the cleaned core is water-wet. This is consistent with the gas/liquid relative permeability measurements made by McCaffery⁴⁹ and McCaffery and Bennion⁵⁰ (see Figs. 6 and 7). Schneider and Owens conclude that gas/water relative permeability data for tertiary oil recovery processes should be measured on native-state core, where the reservoir wettability is maintained.

In summary, the most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. When such core is unavailable, restored-state core should be used, where the wettability is restored by a three-step process: (1) cleaning the core to remove all adsorbed compounds, (2) saturating with formation fluids, and (3) aging at reservoir conditions. Serious errors can result when measurements are made on

core with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants. For example, if the reservoir is oil-wet or intermediate-wet and a clean, water-wet core is used, the water relative permeability will be underestimated and the oil relative permeability will be overestimated. More water and less oil will flow at any given saturation than what the clean core would predict.

Fractional and Mixed-Wet Systems

In the experiments in uniformly wetted porous media, the wettability of the core was varied, while the wettability of the entire surface was kept as uniform as possible. For example, all the rock surfaces in a neutrally wet system should have little preference for oil or water. However, many reservoir rocks have heterogeneous wettability, with variations in wetting preference on different surfaces. Additional wettability effects will occur when the system has nonuniform wettability (either fractional or mixed) where portions of the surface are strongly water-wet, while the remainder is strongly oil-wet.^{1,72,78} Salathiel⁷² introduced the term "mixed" wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The small pores remain water-wet, containing no oil. Note that the main distinction between mixed and fractional wettability is that the latter does not imply either specific locations for the oil-wet and water-wet surfaces or continuous oil-wet paths. In fractionally wetted systems, the individual water-wet and oil-wet surfaces have sizes on the order of a single pore.

Fractional Wettability. Fatt and Klikoff⁷⁹ measured the relative permeability ratio (k_w/k_o) in fractionally wetted sandpacks that were formed by mixing treated and untreated sand grains together. The untreated sand grains were strongly water-wet. The remaining sand grains were treated with Drifilm™, an organochlorosilane, to render them oil-wet. During mixing, some Drifilm may have been transferred to some of the water-wet sand grains, probably giving them a nonzero contact angle.⁷⁹ The absolute permeability of the sandpacks was roughly 3.2 darcies. The fractionally wetted sandpacks were saturated with water and then driven to IWS with a refined mineral oil.

Fig. 16 shows the relative permeability ratios calculated from constant-rate waterflood data by Welge's method.⁸⁰ The changes in the relative permeability ratio are similar to the changes observed when the wettability of a uniformly wetted core is changed from water-wet to oil-wet (see Fig. 11). In Fig. 11, the relative permeability ratio for the nonwetting fluid displacing the wetting fluid (analogous to a waterflood in an oil-wet core) is above the ratio for the reverse displacement. Similarly, in Fig. 16 the relative permeability ratio for waterflooding the oil-wet pack lies above the ratio for the water-wet one. The remaining curves lie between the two extremes. Fatt and Klikoff state that the relatively small difference in position of the curves for the 100% water-wet and 100% oil-wet sandpacks results from the relatively narrow pore-size distribution of the sandpack when compared with the pore-size distribution in reservoir sandstones. Table 4 gives the ROS measured at WOR=100. The oil recovery decreases as the system becomes more oil-wet.

Singhal *et al.*⁸¹ measured unsteady-state relative permeabilities in fractionally wetted bead packs where the fractional wettability was altered by changing the percentages of water-wet (glass) and oil-wet (teflon) beads. Distilled water and a series of refined organic liquids were used, which gave contact angles measured through the water that ranged from 40 to 77° [0.70 to 1.34 rad] for glass and 83 to 157° [1.45 to 2.74 rad] for the teflon. The glass was always the more strongly water-wet surface, while the teflon was always more oil-wet for all the fluid pairs used. The dry bead pack was first saturated by water, then flooded with an organic liquid to the residual water saturation. Relative permeabilities were calculated by the JBN method.⁵⁸ After cleaning, the dry bead pack was saturated with the organic liquid and waterflooded, and unsteady-state relative permeabilities were again calculated by the JBN method. The fact that the core was initially 100% saturated with the nonwetting fluid may have influenced the relative permeability.^{6,10,82,83}

Generally, Singhal *et al.* found that the ratio of relative permeability of the injected phase to the displaced phase, k_i/k_d , at a given injected-phase saturation increased as the fraction of surface wetted by the injected phase was decreased, although there were some exceptions. This is consistent with the behavior observed by Mungan⁶³ for uniformly wetted systems (Fig. 11), and by Fatt and Klikoff⁷⁹ for fractionally wetted systems (Fig. 16). Singhal *et al.* were not able to determine a definite trend in the individual oil (organic liquid) and water effective permeabilities at a given saturation as the wettability was altered. The scatter in their data probably resulted at least partly from changes in the pore-size distribution as the fractional wettability was altered. Unfortunately, the alterations in the wettability also changed the bead-size (and pore-size) distribution because the glass beads were roughly eight times larger in diameter than the teflon beads.

Mixed Wettability. Richardson *et al.*⁸⁴ measured unsteady-state oil/water relative permeabilities on native-state East Texas Woodbine cores. These cores were later shown by Salathiel⁷² to have mixed wettability, where continuous oil-wet paths in the larger pores allow oil drainage to occur until very low oil saturations are obtained after the injection of a very large number of PV's of water. The waterflood behavior is discussed in more detail in Ref. 5. Native-state Woodbine cores were oilflooded with kerosene until brine production stopped. The cores were then waterflooded and the relative permeability ratio was calculated. This procedure was repeated through several additional cycles of oilflooding followed by waterflooding. Finally, the cores were extracted with benzene and methanol, dried, saturated with brine, and then oilflooded. The relative permeability ratio of the cleaned core was then measured by waterflooding with brine.

Fig. 17, taken from Richardson *et al.*,⁸⁴ shows the changes in the relationship between water saturation and relative permeability ratio, k_w/k_o , as a core was repeatedly oilflooded and waterflooded. Run 1, the initial waterflood of the native-state core, had a very low ROS. Note that substantial oil is produced at very high water/oil ratios. ROS averaged about 12% PV for the nine native-state samples tested after the injection of roughly 40 PV of water.^{72,84} Three of the cores had very low ROS's, on the order of 2% PV. During the repeated cycles of oilflooding followed by waterflooding, the water/oil relative permeability ratio increased for a given water saturation (see Runs 2 and 3 in Fig. 17). In addition, the ROS increased. The relative permeability ratio for the extracted core increased even more, with an average ROS after extraction of 30% PV. Imbibition tests showed that the cleaned core was more water-wet than the native-state core because it imbibed water more rapidly.

The behavior of the relative permeability ratio as the core was cleaned and rendered water-wet contrasts with the behavior for uniformly and fractionally wetted systems (see Figs. 11 and 16). In these cases, the relative permeability ratio at a given water saturation was lowest for a strongly water-wet system (wetting fluid displacing nonwetting fluid), and the more oil-wet curves were to the left of the strongly wet curve. In Fig. 17, the water-wet curve lies to the left of the native-state curve. This behavior occurs because the native-state core has mixed wettability.

At the same time that the residual oil was increasing during the repeated floods, the IWS was decreasing. The native-state core generally had a high IWS after the first oilflood, with an average value of 40% PV. After the second oilflood, the average IWS decreased to 34% PV. After cleaning, the IWS was only 20% PV. The changes in the relative permeabilities, IWS, and ROS during the repeated oil- and waterflooding before cleaning are probably caused either by hysteresis effects or by alterations in wettability. Richardson *et al.* found similar increases in the ROS when a second set of native-state plugs was exposed to oxygen during storage. In many cases, oxidation of crude has been shown to alter wettability.¹ Cores were stored under four different procedures: (1) wrapped in metal foil and sealed in paraffin; (2) stored in deaerated formation brine; (3) stored in aerated formation brine; and (4) stored in cloth core bags. Samples were flooded to IWS with kerosene and then waterflooded. The ROS of cores stored by the first two methods was about 13%, while cores stored by the sec-

ond two methods (and exposed to oxygen) had ROS's of roughly 25%.

Burkhardt *et al.*⁸⁵ also made unsteady-state relative permeability measurements on preserved East Texas Woodbine plugs and compared them with relative permeability measurements on the same plugs after they had been cleaned and rendered water-wet. Burkhardt *et al.* also found a significant shift in the relative permeability ratio after cleaning. At low relative permeability ratios, the preserved-state relative permeability ratio was higher at a given water saturation. It appears that the two curves would cross at higher relative permeability ratios (higher water saturations), with a lower ROS for the preserved plugs. This would be consistent with Richardson *et al.*'s results (see Fig. 17). Unfortunately, Burkhardt *et al.* did not waterflood the plugs to very high water/oil ratios. In addition, the plugs were sealed with aluminum foil and paraffin, then stored for 3½ years before testing. It is possible that some wettability alteration occurred during this time, either from oxidation of the crude or evaporation of the brine and crude.

Unsteady-State Relative Permeability

Relative permeabilities can be measured either by steady- or unsteady-state methods.^{7,86} In the various steady-state methods, oil and water are injected at constant rates into the core until the saturations reach equilibrium values. The pressure drop across the core is then measured to determine the relative permeabilities. The main difference in the various steady-state methods is the procedure used to minimize outlet end effects. Steady-state methods are generally very slow, taking days or weeks, because the saturations must reach equilibrium after each change in the injection flow rates. The unsteady-state (external-drive) method is much more rapid, requiring only hours to determine the entire relative permeability curve, and for this reason it is usually used. A core is first flooded with oil and driven to IWS. Water is then injected into the core at a steady rate, and the relative permeability is calculated from the pressure drop and produced fluids using the JBN method.^{58,80,87} Viscous oils are normally used to increase the period of two-phase production, because the flow before breakthrough gives no information about the relative permeability. If low-viscosity oils are used in a water-wet core, the displacement is pistonlike and the relative permeabilities can be found only for the IWS and ROS using the unsteady-state method.⁸⁸

Craig⁶ and others^{10,89-91} recommend that the unsteady-state method not be used with strongly water-wet cores. They believe that the combination of high velocities and high viscosities that are commonly used in the unsteady-state measurements will cause a strongly water-wet core to behave as if it were oil-wet during a waterflood because of insufficient time for the fluids to come to equilibrium. Note that they are not referring to the increased two-phase production after breakthrough with a higher-viscosity oil, but instead to changes in the calculated relative permeability curves.

When a waterflood is conducted at a sufficiently slow rate with a low-viscosity oil, the distribution of the oil in the pores will change as the waterfront passes. If the system is strongly water-wet, the water will displace the oil from the smaller pores and the pore surfaces. However, Craig⁶ states that the water wetness of the core will be masked when viscous oils and high displacement rates are used because the viscous oil will not have enough time to adjust to the waterflood. The high rates are necessary to stabilize the flow and to minimize outlet end effects.^{6,92} The injected water will tend to move rapidly through the larger pores, causing early breakthrough and making the waterflood behave as if the core were oil-wet. In comparison with steady-state relative permeabilities, the calculated unsteady-state relative permeabilities will also appear more oil-wet (see Table 1).⁶

Unsteady-state relative permeabilities will appear more oil-wet when measurements are made on strongly water-wet systems initially 100% saturated with oil.^{82,93} Newcombe *et al.*⁸³ waterflooded water-wet sandpacks initially 100% saturated with a 1.3-cp [1.3-mPa·s] refined mineral oil and obtained significant amounts of simultaneous oil and water production after breakthrough. Generally, there is little or no production after water breakthrough in a strongly water-wet core with a low oil/water viscosity ratio, so this core behaved as if it were somewhat oil-wet.^{6,10,51,59,94} Leach *et*

*al.*⁸² pointed out that this behavior was caused by a lack of wetting equilibrium during the waterflood. During a waterflood of a water-wet, initially 100% oil-saturated core, water will displace oil from the pore surfaces. However, achieving wetting equilibrium is a relatively slow process. If water is injected at too high a rate, wetting equilibrium will not be achieved and the system will appear more oil-wet. Leach *et al.* presented results comparing the effects of water injection rate on ROS in water-wet packs with and without an initial water saturation. They found that the apparent oil-wetness of packs without an initial water saturation increased as the water injection rate increased.

Unfortunately, there are very few data in the literature either to prove or to disprove the hypothesis for strongly water-wet systems initially at the IWS, where the system should be in wetting equilibrium. Most of the early work comparing the steady- and unsteady-state methods used either gas drives, where oil was the wetting fluid, or cores that were treated to make them oil-wet. In both cases, the nonwetting fluid displaces the wetting fluid (drainage) during the measurement. In addition, much of the work used sandpacks, which have a fairly uniform pore-size distribution. The effect of viscosity and flow rate on the trapping of residual oil is probably much less important in these homogeneous packs than in consolidated cores.⁹⁵

Johnson *et al.*⁵⁸ compared steady- and unsteady-state oil/water relative permeabilities in a Weiler sandstone and found good agreement. The plug was initially at IWS and appears to have been strongly water-wet. Unfortunately, the viscosity of the oil is not given. Amaefule and Handy,⁵⁵ however, found significant differences between steady- and unsteady-state imbibition relative permeabilities in a fired, strongly water-wet Berea core with the low oil/water viscosity ratio of 1.28. The unsteady-state relative permeabilities appeared to be more oil-wet than the steady-state ones, which supports Craig's hypothesis. In the unsteady-state runs, the crossover point of the water and oil relative permeability curves shifted toward lower water saturations. In addition, the unsteady-state water relative permeabilities were higher than the steady-state water permeabilities at the same water saturation. As shown in Table 1, this indicates that the unsteady-state relative permeabilities acted more oil-wet. Another factor indicating differences in steady- and unsteady-state relative permeabilities is the difference in hysteresis in the wetting phase during drainage and imbibition. As discussed earlier, many steady-state measurements show little or no hysteresis in the wetting-phase relative permeability, while unsteady-state experiments by Jones and Roszelle⁵⁶ and Sigmund and McCaffery⁵⁷ showed relatively large amounts of hysteresis.

Three-Phase Relative Permeabilities

Wettability is a controlling factor in determining three-phase relative permeability characteristics through its effect on the spatial distribution of the three phases.⁵² As discussed in the Introduction, when the wetting is sufficiently strong, the wetting-phase relative permeability is primarily a function of its own saturation and is very similar for both two- and three-phase systems.^{48-50,52,96} This occurs because the wetting phase occupies the small pores and occurs as a thin film on the pore surfaces. The two nonwetting phases, one of which is always the gas, compete for the larger pores. In an oil-wet system, the presence of the trapped gas will affect the water relative permeability because of the interference of these two nonwetting phases. Similarly, in a water-wet system, the trapped gas will usually lower the oil relative permeability by interference and competition for the large flow channels, while the water relative permeability will be relatively unaffected.

Schneider and Owens⁵² examined the effects of a trapped, immobile gas saturation on water/oil relative permeabilities measured in oil-wet Grayburg carbonate and Tensleep sandstone samples. They found almost no effect on the oil (wetting-phase) relative permeability when comparing the two- and three-phase measurements. The water relative permeability was lowered by the trapped gas, showing the interaction between the two nonwetting fluids. Similar results were reported by Emmett *et al.*⁹⁷

Leverett and Lewis⁴⁸ measured three-phase, gas/oil/water relative permeabilities in water-wet sandpacks and found that the relative permeability of the wetting phase (water) was only a function

of water saturation and not dependent on oil or gas saturations. Saraf and Fatt⁹⁸ reported similar results for the water relative permeability during three-phase flow measurements in water-wet Boise sandstone. Schneider and Owens⁵² measured two- and three-phase relative permeabilities on oil-wet Tensleep and water-wet Torpedo sandstone samples and found good agreement between the two- and three-phase relative permeabilities for the wetting phase.

There have been some experiments, however, where the wetting-phase relative permeability depends on the other saturations. Schneider and Owens⁵² studied the effects of trapped gas saturation on a Tensleep plug that was fired at 1,000°F [538°C] to remove all adsorbed compounds and to render it water-wet. They found that the trapped gas saturation affected both the water and oil relative permeabilities. Other experiments have also found that the wetting-phase relative permeability was affected by the nonwetting-phase saturations in water-wet systems.^{28,46,99} It is possible that some of these systems were not strongly water-wet.^{96,98} As an example, Snell⁹⁹ states that polar compounds in the diesel/lubricating-oil mixture that he used may have altered the wettability of his system.

The effect of wettability on the nonwetting-phase relative permeabilities is more complicated because saturation and saturation history are also important. In many cases, the two nonwetting phases will interfere with each other. Schneider and Owens⁵² found that trapped gas in oil-wet Tensleep sandstone and Grayburg carbonate plugs reduced the water relative permeability when compared with two-phase water/oil measurements at the same water saturation. This was expected because the trapped gas and the nonwetting water would be expected to interfere with each other. Schneider and Owens then fired the Tensleep sandstone plug at 1,000°F [538°C] to render it strongly water-wet and measured steady-state water/oil relative permeabilities in the presence of a trapped gas. They found that the nonwetting-phase (oil) relative permeability at high wetting-phase (water) saturations was increased by the presence of trapped gas. This observation remains unexplained.

Conclusions

1. Relative permeabilities are a function of wettability, pore geometry, fluid distribution, saturation, and saturation history. Wettability affects relative permeability by controlling the flow and spatial distribution of fluids in a porous medium.

2. In a uniformly wetted core, the effective oil permeability at a given initial water saturation decreases as the wettability is varied from water-wet to oil-wet. In addition, the water relative permeability increases and the oil relative permeability decreases as the core becomes more oil-wet.

3. In fractionally wetted sandpacks, where the size of the individual water- and oil-wet surfaces are on the order of a single pore, relative permeabilities appear to be similar to those in uniformly wetted systems. The water relative permeability increases and the oil relative permeability decreases as the fraction of oil-wetted surfaces increases.

4. In a mixed-wettability core, the larger, oil-filled pores are oil-wet, while the smaller, water-filled pores are water-wet. The continuous oil-wet paths in the larger pores change the relative permeability curves when compared with a uniformly or fractionally wetted system, and allow the mixed-wettability system to be water-flooded to a very low ROS by the injection of many PV's of water.

5. The most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. When such core is unavailable, the core should be cleaned and restored. Serious errors can result when measurements are made on core with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants.

6. The effective water permeability of a cleaned core at the ROS will vary, depending on the effectiveness of the core cleaning method.

7. The wetting-phase drainage and imbibition relative permeabilities show little hysteresis in many strongly wetted systems. However, several unsteady-state experiments have shown little hysteresis in the nonwetting phase, but significant hysteresis in the wetting phase.

8. In many strongly wetted systems, the wetting-phase relative permeability is primarily a function of its own saturation and is very

similar for both two- and three-phase relative permeability measurements.

9. Some researchers recommend that the unsteady-state JBN relative permeability method not be used in strongly water-wet cores because of insufficient time for the fluids to come to wetting equilibrium. Unfortunately, very few data are available either to prove or to disprove this hypothesis.

Nomenclature

- k_a = air permeability, md (Fig. 13)
- k_d = permeability of the displaced phase, md
- k_i = permeability of the injected phase, md
- k_o = oil permeability, md
- k_{owi} = effective oil permeability at initial water saturation, md
- k_{ro} = relative oil permeability
- k_{rw} = relative water permeability
- S_{gr} = residual gas saturation, %PV
- S_{or} = residual oil saturation, %PV
- S_w = water saturation, %PV
- S_{wi} = irreducible water saturation, %PV
- T = temperature, °F [°C]
- θ = contact angle, degrees [rad]
- θ_{adv} = advancing contact angle, degrees [rad]
- ϕ = porosity, %

Acknowledgments

I am grateful to Jeff Meyers, Don Blankenship, and Jeff Hawkins for their many helpful comments and suggestions. I also thank the management of Conoco Inc. for permission to publish this paper.

References

1. Anderson, W.G.: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions, and the Effects of Core Handling on Wettability," *JPT* (Oct. 1986) 1125-49.
2. Anderson, W.G.: "Wettability Literature Survey—Part 2: Wettability Measurement," *JPT* (Nov. 1986) 1246-62.
3. Anderson, W.G.: "Wettability Literature Survey—Part 3: The Effects of Wettability on the Electrical Properties of Porous Media," *JPT* (Dec. 1986) 1371-78.
4. Anderson, W.G.: "Wettability Literature Survey—Part 4: The Effects of Wettability on Capillary Pressure," *JPT* (Oct. 1987) 1283-1300.
5. Anderson, W.G.: "Wettability Literature Survey—Part 6: The Effects of Wettability on Waterflooding," to be published in *JPT* (Dec. 1987).
6. Craig, F.F.: *The Reservoir Engineering Aspects of Waterflooding*, Monograph Series, SPE, Richardson, TX (1971) 3.
7. Dullien, F.A.L.: *Porous Media: Fluid Transport and Pore Structure*, Academic Press, New York City (1979).
8. Marsden, S.S.: "Wettability—Its Measurement and Application to Waterflooding," *J. Jpn. Assoc. Pet. Tech.* (Jan. 1965) 30, No. 1, 1-10.
9. Marsden, S.S.: "Wettability: The Elusive Key to Waterflooding," *Petroleum Engineer* (April 1965) 37, No. 4, 82-87.
10. Raza, S.H., Treiber, L.E., and Archer, D.L.: "Wettability of Reservoir Rocks and Its Evaluation," *Prod. Monthly* (April 1968) 32, No. 4, 2-7.
11. Hjelmeland, O. and Torsaeter, O.: "Wettability, The Key to Proper Laboratory Waterflooding Experiments," *Proc., Intl. Energy Agency Workshop on Enhanced Oil Recovery*, Bartlesville Energy Technology Center, April 24, 1980, U.S. DOE, CONF-8004140 (Feb. 1981) 1-24.
12. Honarpour, M., Koederitz, L., and Harvey, A.H.: *Relative Permeability of Petroleum Reservoirs*, CRC Press, Boca Raton, FL (1986).
13. Mungan, N.: "Enhanced Oil Recovery Using Water as a Driving Fluid: Part 2—Interfacial Phenomena and Oil Recovery: Wettability," *World Oil* (March 1981) 192, No. 4, 77-83.
14. Mungan, N.: "Enhanced Oil Recovery Using Water as a Driving Fluid: Part 3—Interfacial Phenomena and Oil Recovery: Capillarity," *World Oil* (May 1981) 192, No. 5, 149-58.
15. Schönberger, K.: "The Role of Wettability in Oil Reservoir Recovery," *Erdöl-Erdgas Zeitschrift* (April 1982) 98, No. 4, 130-35. English translation available from the John Crerar Library, U. of Chicago, Translation No. 85-10244 (*BLL) 48A.
16. Taber, J.J.: "Research on Enhanced Oil Recovery: Past, Present, and Future," *Surface Phenomena in Enhanced Oil Recovery*, D.O. Shah (ed.), Plenum Press, New York City (1981).

17. Chatenever, A. and Calhoun, J.C.: "Visual Examinations of Fluid Behavior in Porous Media—Part 1," *Trans., AIME* (1952) **195**, 149–56.
18. Chatenever, A.: "Microscopic Behavior of Fluids in Porous Systems—Final Report on Research Project 47b," *Research on Occurrence and Recovery of Petroleum*, API, New York City (1955) 69–80.
19. Donaldson, E.C. and Thomas, R.D.: "Microscopic Observations of Oil Displacement in Water-Wet and Oil-Wet Systems," paper SPE 3555 presented at the 1971 SPE Annual Meeting, New Orleans, Oct. 3–6.
20. Donaldson, E.C. and Crocker, M.E.: "Review of Petroleum Oil Saturation and Its Determination," Bartlesville Energy Research Center, U.S. DOE, report BERC/RI-77/15 (Dec. 1977).
21. Hornof, V. and Morrow, N.R.: "Flow Visualization of the Effects of Interfacial Tension on Displacement," paper SPE 14930 presented at the 1986 SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, April 20–23.
22. Mattax, C.C. and Kyte, J.R.: "Ever See a Waterflood?" *Oil & Gas J.* (Oct. 16, 1961) **59**, No. 42, 115–28.
23. Morris, E.E. and Wieland, D.R.: "A Microscopic Study of the Effect of Variable Wettability Conditions on Immiscible Fluid Displacement," paper SPE 704 presented at the 1963 SPE Annual Meeting, New Orleans, Oct. 6–9.
24. Wardlaw, N.C.: "The Effects of Geometry, Wettability, Viscosity, and Interfacial Tension on Trapping in Single Pore-Throat Pairs," *J. Cdn. Pet. Tech.* (May–June 1982) **21**, No. 3, 21–27.
25. Yadav, G.D. et al.: "Microscopic Distribution of Wetting and Non-wetting Phases in Sandstones During Immiscible Displacements," *SPERE* (May 1987) 137–47.
26. Moore, T.F. and Slobod, R.L.: "The Effect of Viscosity and Capillarity on the Displacement of Oil by Water," *Prod. Monthly* (Aug. 1956) **20**, No. 10, 20–30.
27. Pirson, S.J.: *Oil Reservoir Engineering*, McGraw-Hill Book Co. Inc., New York City (1958).
28. Geffen, T.M. et al.: "Experimental Investigation of Factors Affecting Laboratory Relative Permeability Measurements," *Trans., AIME* (1951) **192**, 99–110.
29. Kamath, I.S.K. and Marsden, S.S.: "A Wettability Scale for Porous Media," preprint 14D presented at the 1966 AIChE Natl. Meeting, Dallas, Feb. 6–9.
30. Von Engelhardt, W. and Lübken, H.: "Study of the Influence of Interfacial Stress and Contact Angle on the Displacement of Oil by Water in Porous Materials. I. Theoretical Principles and Performance of Tests," *Erdöl und Kohle* (Nov. 1957) **10**, No. 11, 747–52. English translation available from the John Crerar Library, U. of Chicago, Translation No. 62-14556.
31. Jennings, H.Y. Jr.: "Surface Properties of Natural and Synthetic Porous Media," *Prod. Monthly* (March 1957) **21**, No. 5, 20–24.
32. Bobek, J.E., Mattax, C.C., and Denekas, M.O.: "Reservoir Rock Wettability—Its Significance and Evaluation," *Trans., AIME* (1958) **213**, 155–60.
33. Treiber, L.E., Archer, D.L., and Owens, W.W.: "A Laboratory Evaluation of the Wettability of Fifty Oil Producing Reservoirs," *SPEJ* (Dec. 1972) 531–40; *Trans., AIME*, **253**.
34. Babalyan, G.A.: *Questions on Mechanism of Oil Recovery*, Aznefteizdat Press, Baku, USSR (1956).
35. Chilingar, G.V. and Yen, T.F.: "Some Notes on Wettability and Relative Permeabilities of Carbonate Reservoir Rocks," *Energy Sources* (1983) **7**, No. 1, 67–75.
36. Sinnokrot, A.A. and Chilingar, G.V.: "Effect of Polarity and Presence of Carbonate Particles on Relative Permeability of Rocks: A Review," *The Compass of Sigma Gamma Epsilon* (Jan. 1961) **38**, No. 2, 115–20.
37. Graham, J.W., Monaghan, P.H., and Osoba, J.S.: "Influence of Proping Sand Wettability on Productivity of Hydraulically Fractured Oil Wells," *Trans., AIME* (1959) **216**, 324–29.
38. Shankar, P.K.: "Experimental Investigation of Two-Phase (Oil-Brine) Relative Permeability Characteristics in Mixed Wet Sandstone Systems With Reference to Oil Recovery Efficiency," PhD thesis, U. of Waterloo, Waterloo, Ont. (1979).
39. Shankar, P.K. and Dullien, F.A.L.: "Experimental Investigation of Two-Liquid Relative Permeability and Dye Adsorption Capacity Versus Saturation Relationships in Untreated and DRIFILM®-Treated Sandstone Samples," *Surface Phenomena in Enhanced Oil Recovery*, D.O. Shah (ed.), Plenum Press, New York City (1981) 453–77.
40. Coley, F.H., Marsden, S.S., and Calhoun, J.C.: "A Study of the Effect of Wettability on the Behavior of Fluids in Synthetic Porous Media," *Prod. Monthly* (June 1956) **20**, No. 8, 29–45.
41. Donaldson, E.C., Lorenz, P.B., and Thomas, R.D.: "The Effects of Viscosity and Wettability on Oil and Water Relative Permeabilities," paper SPE 1562 presented at the 1966 SPE Annual Meeting, Dallas, Oct. 2–5.
42. Henderson, J.H. and Yuster, S.T.: "Relative Permeability Studies," *Prod. Monthly* (Jan. 1948) **12**, No. 3, 13–20.
43. Henderson, J.H. and Meldrum, A.H.: "Progress Report on Multiphase-Flow Studies," *Prod. Monthly* (March 1949) **13**, No. 5, 12–17.
44. Morse, R.A., Terwilliger, P.L., and Yuster, S.T.: "Relative Permeability Measurements on Small Core Samples," *Oil & Gas J.* (Aug. 23, 1947) **46**, No. 16, 109–25.
45. Sarem, A.M.: "Significance of Water-Oil Relative Permeability Data Calculated From Displacement Tests," *Proc., Conference on the Theory of Fluid Flow in Porous Media*, U. of Oklahoma, Norman (March 23–24, 1959) 191–209.
46. Caudle, B.H., Slobod, R.L., and Brownscombe, E.R.: "Further Developments in the Laboratory Determination of Relative Permeability," *Trans., AIME* (1951) **192**, 145–50.
47. Morgan, J.T. and Gordon, D.T.: "Influence of Pore Geometry on Water-Oil Relative Permeabilities," *JPT* (Oct. 1970) 1199–1208.
48. Leverett, M.C. and Lewis, W.B.: "Steady Flow of Gas-Oil-Water Mixtures Through Unconsolidated Sands," *Trans., AIME* (1941) **142**, 107–16.
49. McCaffery, F.G.: "The Effect of Wettability on Relative Permeability and Imbibition in Porous Media," PhD thesis, U. of Calgary, Calgary, Alta. (1973).
50. McCaffery, F.G. and Bennion, D.W.: "The Effect of Wettability on Two-Phase Relative Permeabilities," *J. Cdn. Pet. Tech.* (Oct.–Dec. 1974) **13**, No. 4, 42–53.
51. Owens, W.W. and Archer, D.L.: "The Effect of Rock Wettability on Oil-Water Relative Permeability Relationships," *JPT* (July 1971) 873–78; *Trans., AIME*, **251**.
52. Schneider, F.N. and Owens, W.W.: "Sandstone and Carbonate Two- and Three-Phase Relative Permeability Characteristics," *SPEJ* (March 1970) 75–84; *Trans., AIME*, **249**.
53. Schneider, F.N. and Owens, W.W.: "Relative Permeability Studies of Gas-Water Flow Following Solvent Injection in Carbonate Rocks," *SPEJ* (Feb. 1976) 23–30; *Trans., AIME*, **261**.
54. Morrow, N.R. and McCaffery, F.G.: "Displacement Studies in Uniformly Wetted Porous Media," *Wetting, Spreading, and Adhesion*, G.F. Padday (ed.), Academic Press, New York City (1978).
55. Amaefule, J.O. and Handy, L.L.: "The Effect of Interfacial Tensions on Relative Oil/Water Permeabilities of Consolidated Porous Media," *SPEJ* (June 1982) 371–81.
56. Jones, S.C. and Roszelle, W.O.: "Graphical Techniques for Determining Relative Permeability From Displacement Experiments," *JPT* (May 1978) 807–17; *Trans., AIME*, **265**.
57. Sigmund, P.M. and McCaffery, F.G.: "An Improved Unsteady-State Procedure for Determining the Relative-Permeability Characteristics of Heterogeneous Porous Media," *SPEJ* (Feb. 1979) 15–28.
58. Johnson, E.F., Bossler, D.P., and Naumann, V.O.: "Calculation of Relative Permeability From Displacement Experiments," *Trans., AIME* (1959) **216**, 370–72.
59. Donaldson, E.C., Thomas, R.D., and Lorenz, P.B.: "Wettability Determination and Its Effect on Recovery Efficiency," *SPEJ* (March 1969) 13–20.
60. Donaldson, E.C. et al.: "Equipment and Procedures for Fluid Flow and Wettability Tests of Geological Materials," Bartlesville Energy Technology Center, U.S. DOE, report DOE/BETC/IC-79/5 (May 1980).
61. Donaldson, E.C.: "Oil-Water-Rock Wettability Measurement," *Preprints*, American Chemical Soc., Div. of Petroleum Chemistry, Atlanta (March 29–April 3, 1981) **26**, No. 1, 110–22.
62. Morrow, N.R., Cram, P.J., and McCaffery, F.G.: "Displacement Studies in Dolomite With Wettability Control by Octanoic Acid," *SPEJ* (Aug. 1973) 221–32; *Trans., AIME*, **255**.
63. Mungan, N.: "Interfacial Effects in Immiscible Liquid-Liquid Displacement in Porous Media," *SPEJ* (Sept. 1966) 247–53; *Trans., AIME*, **237**.
64. Stegemeier, G. and Jessen, F.W.: "The Relationship of Relative Permeability to Contact Angles," *Proc., Conference on the Theory of Fluid Flow in Porous Media*, U. of Oklahoma, Norman (March 23–24, 1959) 213–29.
65. Morrow, N.R. and Mungan, N.: "Wettability and Capillarity in Porous Media," Report RR-7, Petroleum Recovery Research Inst., Calgary, Alta. (Jan. 1971).
66. Morrow, N.R.: "Capillary Pressure Correlations for Uniformly Wetted Porous Media," *J. Cdn. Pet. Tech.* (Oct.–Dec. 1976) **15**, No. 4, 49–69.
67. Mungan, N.: "Relative Permeability Measurements Using Reservoir Fluids," *SPEJ* (Oct. 1972) 398–402.
68. Schmid, C.: "The Wettability of Petroleum Rocks and Results of Experiments to Study the Effects of Variations in Wettability of Core Samples," *Erdöl und Kohle-Erdgas-Petrochemie* (1964) **17**, No. 8, 605–09. English translation available from the John Crerar Library, U. of Chicago, Translation No. TT-65-12404.

69. Wang, F.H.L.: "Effect of Wettability Alteration on Water-Oil Relative Permeability, Dispersion, and Flowable Saturation in Porous Media," paper SPE 15019 presented at the 1986 SPE Permian Basin Oil and Gas Recovery Conference, Midland, TX, March 13-14.
70. Wendel, D.J., Anderson, W.G., and Meyers, J.D.: "Restored-State Core Analysis for the Hutton Reservoir," paper SPE 14298 presented at the 1985 SPE Annual Technical Conference and Exhibition, Las Vegas, Sept. 22-25.
71. Keelan, D.K.: "A Critical Review of Core Analysis Techniques," *J. Cdn. Pet. Tech.* (April-June 1972) **11**, No. 2, 42-55.
72. Salathiel, R.A.: "Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks," *JPT* (Oct. 1973) 1216-24.
73. Grist, D.M., Langley, G.O., and Neustadter, E.L.: "The Dependence of Water Permeability on Core Cleaning Methods in the Case of Some Sandstone Samples," *J. Cdn. Pet. Tech.* (April-June 1975) **14**, No. 2, 48-52.
74. Duyvis, E.M. and Smits, L.J.M.: "A Test for the Wettability of Carbonate Rocks," *SPEJ* (March 1970) 3-4.
75. Gant, P.L. and Anderson, W.G.: "Core Cleaning for Restoration of Native Wettability," paper SPE 14875 presented at the 1986 SPE Rocky Mountain Regional Meeting, Billings, MT, May 18-20.
76. Jennings, H.Y. Jr.: "Effects of Laboratory Core Cleaning on Water-Oil Relative Permeability," *Prod. Monthly* (Aug. 1958) **22**, No. 10, 26-32.
77. Amott, E.: "Observations Relating to the Wettability of Porous Rock," *Trans., AIME* (1959) **216**, 156-62.
78. Brown, R.J.S. and Fatt, I.: "Measurements of Fractional Wettability of Oilfield Rocks by the Nuclear Magnetic Relaxation Method," *Trans., AIME* (1956) **207**, 262-64.
79. Fatt, I. and Klikoff, W.A.: "Effect of Fractional Wettability on Multiphase Flow Through Porous Media," *Trans., AIME* (1959) **216**, 426-32.
80. Welge, H.J.: "A Simplified Method for Computing Oil Recovery by Gas or Water Drive," *Trans., AIME* (1952) **195**, 91-98.
81. Singhal, A.K., Mukherjee, D.P., and Somerton, W.H.: "Effect of Heterogeneous Wettability on Flow of Fluids Through Porous Media," *J. Cdn. Pet. Tech.* (July-Sept. 1976) **15**, No. 3, 63-70.
82. Leach, R.O., Geffen, T.M., and Berry, V.J.: "Discussion of Wettability Versus Displacement in Waterflooding in Unconsolidated Sand Columns," *JPT* (March 1956) 61-63.
83. Newcombe, J., McGhee, J., and Rzaa, M.J.: "Wettability Versus Displacement in Waterflooding in Unconsolidated Sand Columns," *Trans., AIME* (1955) **204**, 227-32.
84. Richardson, J.G., Perkins, F.M., and Osoba, J.S.: "Differences in the Behavior of Fresh and Aged East Texas Woodbine Cores," *Trans., AIME* (1955) **204**, 86-91.
85. Burkhardt, J.A., Ward, M.B., and McLean, R.H.: "Effect of Core Surfacing and Mud Filtrate Flushing on Reliability of Core Analysis Conducted on Fresh Cores," paper SPE 1139-G presented at the 1958 SPE Annual Meeting, Houston, Oct. 5-8.
86. Scheidegger, A.E.: *The Physics of Flow Through Porous Media*, third edition, U. of Toronto Press, Toronto, Ont. (1974) 248-60.
87. Buckley, S.E. and Leverett, M.C.: "Mechanism of Fluid Displacement in Sands," *Trans., AIME* (1942) **146**, 107-16.
88. Archer, J.S. and Wong, S.W.: "Use of a Reservoir Simulator to Interpret Laboratory Waterflood Data," *SPEJ* (Dec. 1973) 343-47.
89. Bentsen, R.G.: "Conditions Under Which the Capillary Term May Be Neglected," *J. Cdn. Pet. Tech.* (Oct.-Dec. 1978) **17**, No. 4, 25-30.
90. Loomis, A.G. and Crowell, D.C.: "Relative Permeability Studies: II. Water-Oil Systems," *Prod. Monthly* (Aug. 1959) **23**, No. 10, 18-24.
91. Loomis, A.G. and Crowell, D.C.: "Relative Permeability Studies: Gas-Oil and Water-Oil Systems," USBM Bulletin 599, San Francisco Petroleum Research Laboratory, U.S. Government Printing Office, Washington, DC (1962).
92. Kyte, J.R. and Rapoport, L.A.: "Linear Waterflood Behavior and End Effects in Water-Wet Porous Media," *Trans., AIME* (1958) **213**, 423-26.
93. Garrison, A.D.: "Selective Wetting of Reservoir Rock and Its Relation to Oil Production," *Drill. & Prod. Prac.*, API, New York City (1936) 130-40.
94. Kyte, J.R., Naumann, V.O., and Mattax, C.C.: "Effect of Reservoir Environment on Water-Oil Displacements," *JPT* (June 1961) 579-82; *Trans., AIME*, **222**.
95. Handy, L.L. and Datta, P.: "Fluid Distributions During Immiscible Displacements in Porous Media," *SPEJ* (Sept. 1966) 261-66; *Trans., AIME*, **237**.
96. Donaldson, E.C. and Kayser, M.B.: "Three-Phase Fluid Flow in Porous Media," Bartlesville Energy Technology Center, report DOE/BETC/IC-80/4, U.S. DOE (April 1981).
97. Emmett, W.R., Beaver, K.W., and McCaleb, J.A.: "Little Buffalo Basin Tensleep Heterogeneity—Its Influence on Drilling and Secondary Recovery," *JPT* (Feb. 1971) 161-68.
98. Saraf, D.N. and Fatt, I.: "Three-Phase Relative Permeability Measurement Using a Nuclear Magnetic Resonance Technique for Estimating Fluid Saturation," *SPEJ* (Sept. 1967) 235-42; *Trans., AIME*, **240**.
99. Snell, R.W.: "Three-Phase Relative Permeability in an Unconsolidated Sand," *J. Inst. Pet.* (March 1962) **48**, No. 459, 80-88.

SI Metric Conversion Factors

degrees	× 1.745 329	E-02 = rad
ft	× 3.048*	E-01 = m
°F	(°F - 32)/1.8	= °C

*Conversion factor is exact.

JPT

Original SPE manuscript (SPE 16323) received for review Nov. 3, 1986. Paper accepted for publication April 7, 1987. Revised manuscript received June 1, 1987.