Oil Recovery by Surface Film Drainage In Mixed-Wettability Rocks

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Introduction

Material-balance data on the East Texas reservoir indicate that a very efficient water-oil displacement is being attained. Also, cores recovered with a pressure-retaining core barrel from watered-out parts of this reservoir indicate very low (less than 10 percent) residual oil saturations. This paper describes a systematic examination of mechanisms and conditions that can lead to such an unusually efficient displacement of oil by water. Experimental studies conducted to test a postulated mechanism are reported, and the significance and applicability of the mechanism are discussed.

A High-Efficiency Waterflood

Richardson *et al.*[1] observed that waterflood tests on core samples from the Woodbine reservoir, East Texas field, behaved very differently when the cores were extracted rather than tested "fresh" from the core barrel or in a preserved condition. For example, they found that restored-state waterfloods on fresh East Texas cores normally leave 15 to 18 percent pore volume (PV) of oil after about 40 PV of water injection. This compared with oil residuals of about 30 percent PV in extracted cores after flooding. Values for average residual oil saturation in the reservoir estimated by material balance also fell in the range of 15 to 18 percent PV. Judging from this average range, even lower local residual saturations might occur in some parts of the reservoir. This expectation was later verified when many of the pressure cores recovered from 20 ft or more below the present water/oil contact were found to contain less than 10 percent PV of oil.

In subsequent laboratory displacement tests, it was found that residual oil saturations in preserved East Texas Field cores could be reduced to less than 10 percent PV by either of two methods — extended waterflooding (several hundred to several thousand pore volumes) or extended centrifuging under brine. Results of these tests showed that a small but finite permeability to oil exists even at very low oil saturations.

This unusual flow behavior appears to depend on the wetting condition existing in this formation, since extracting fresh cores altered their flow behavior greatly. Causes for this flow behavior in fresh cores can be postulated by considering types of wetting conditions that might provide paths for oil to flow at low saturation, especially types of wetting that might occur naturally in a typical reservoir.

Known Effects of Wettability on Displacement

In waterflooding strongly water-wet core samples, except for high oil/water viscosity ratios, most of the recoverable oil is typically displaced before water breakthrough, and oil production ceases, or almost ceases, soon thereafter. The residual oil (the nonwetting phase) remains trapped by capillary forces as discontinuous droplets or irregular bodies of oil separated by continuous water.

Tests with both fresh cores and treated outcrop samples suggest that there is a special kind of mixed wettability in which parts of the rock surfaces are strongly oil-wetted and parts are water-wetted. In some rocks, the oil-wetted surfaces are distributed in such a way that oil can move along them readily, permitting drainage to very low residual oil saturations.

In laboratory waterfloods on strongly oil-wet cores, on the other hand, an early breakthrough of flood water occurs, with appreciable oil production continuing for a number of pore volumes. In this case, a moderate residual oil saturation (corresponding to the irreducible water saturation of a water-wet sample) remains after extended flooding, and much of the residual oil (the wetting phase) is retained by capillary forces in the smaller pores and at grain contacts.

Many different assumptions have been made with regard to the "wettability" of a porous medium, the degree of preferential water wetting or oil wetting, and the effect of wettability on flooding behavior. For simplicity it has often been assumed that pore surfaces within a reservoir rock are uniformly wetted. However, many authors do not accept this view. The dye adsorption method of Holbrook and Bernard[2] for determining wetting in reservoir solids purports to measure the ratio of oil-wet to water-wet pore surface area. Obviously, these authors assumed that wetting of reservoir solids was heterogeneous rather than uniform. In a more recent publication, Schmid[3] showed, by means of data on capillary pressure vs saturation, that in preserved cores the fine pores were water wet, whereas the larger pores were much less water wet. Heterogeneous wettability as a normal condition in oil sands has also been suggested by Iwankow,[4] Brown and Fatt,[5] and Gimatudinov.[6] It is generally recognized that different types of wettability can result in wide variations in the residual oil saturations remaining after waterflooding. In some heterogeneous wettability systems, the residual saturation will be higher[5] than that measured for either a uniformly water-wet or a uniformly oil-wet system. This paper presents results of a study of a nonuniform, or mixed wettability, system for which the residual oil saturation is less than for either type of uniform wettability. This system closely resembles that believed to exist in the East Texas field.

Postulated Effects of Mixed Wettability

While neither strongly water-wet nor strongly oil-wet porous rocks can be flooded by water to unusually low oil saturations, we may visualize a *mixed-wettability condition* that will provide paths for oil to flow even at very low saturations. In this condition the fine pores and grain contacts would be preferentially water-wet and the surfaces of the larger pores would be strongly oil-wet. If oil-wet paths were continuous through the rock, water could displace oil from the large pores and little or no oil would be held by capillary forces in small pores or at grain contacts. This type of mixed wettability condition could account for the very low residual oil saturations observed in the East Texas field.

The type of heterogenous mixed wettability just described should be distinguished from another type, sometimes termed "fractionally wetted," in which oil-wet and water-wet sands are packed in different proportions to provide a porous matrix.[5]

Postulated Development of Mixed Wettability

We can visualize as follows the generation of a mixed wettability condition like that described above: As oil accumulates in a reservoir, water present in the initially water-wet rock is displaced from the larger pores while capillary forces retain water in small capillaries and at grain contacts. After extended periods of exposure to this fluid distribution, the required mixed-wettability condition could develop if some organic material from the oil were deposited onto those rock surfaces that are in direct contact with oil, thus making those surfaces strongly oil-wet.

This process by which heterogeneous wettability conditions might occur in reservoirs should be affected by crude oil composition. This dependence has, in fact, been shown by several workers.[7,10,11] All crude oils contain surface-active materials. However, crudes can differ greatly with respect to the kinds, concentrations, and states of aggregation of surface-active materials present. That surface-active materials occur in crude oils is evidenced by the fact that interfacial tension between oil and water or oil and brine is lower with crude oils than with refined oils. The presence of surface-active agents in crudes is also evidenced by effects on contact angle between mineral solid surfaces and oil and brine.[7] The behavior of some crude oils at quartz/oil/water contacts is very similar to that of refined oils. Other crudes, however, may exhibit contact angle behavior drastically different from that of refined oils.

Wettability of mineral surfaces may be altered not only by adsorbed monolayers of surface-active components, but also by much thicker layers of deposited organic materials. Several workers have reported the formation of stable films on solid surfaces when they stand in contact with certain crude oils. Reisberg and Doscher[8] describe deposition on glass or quartz surfaces of highly stable and appreciably thick films of strongly oil-wet material from Ventura crude oil. A substantial period of time was required for films to become stably attached to the solid surfaces. The film deposited only where oil stood in contact with the glass and not in adjacent areas where glass was in contact with brine. Reisberg and Doscher believe the film attached to the glass surface was similar to, if not identical with, the semisolid film ("prune skin" film) that formed at the oil/brine interface. Strassner[9] discusses the influence of the composition of crude oils on the formation of semisolid films at the oil/brine interface and on oil-wetting of glass.

Even with oils that deposit stable, strongly oil-wet films, the surface drainage behavior would develop only when *continuous* oil-wet paths of appreciable length develop through the porous rocks. Consequently, the pore geometry of the reservoir rock should affect drainage. Similarly, the connate water saturation present during the deposition of an oil-wet film should also affect the degree of development of continuous oil-wetting paths by controlling the degree of contact of crude oil with solid surfaces.

Extraction with strong solvents should be expected to dissolve away the strongly oil-wet surface coating of deposited organic material and thereby alter the wetting condition. This dissolution (and perhaps redistribution of the coating substances) is in agreement with the observation that extraction alters the fluid displacement behavior of many fresh or preserved cores.

Laboratory procedures designed to test these hypotheses are described in the next section.

Laboratory Procedures

Rock Samples

Several factors influenced the selection of the porous rock used in different tests. Outcrop-rock samples offer several advantages for laboratory investigations. For one thing, sufficient samples are available; and what is more important, they closely resemble adjacent samples in the same bedding plane. Reliable conclusions regarding the effects of different variables can thus be drawn from fewer tests. For these reasons outcrop samples were used in most of the tests.

Although drainage of oil to very low saturation had already been observed in East Texas field Woodbine sandstone, an outcrop Woodbine sandstone from near Mansfield, Tex., was used for one series of tests. Since it seemed desirable to test for this behavior in other rocks, cores from several other outcrops were also tested. A well consolidated and highly permeable outcrop sandstone from near Boise, Idaho, was employed in a number of laboratory tests. This mostly angular-grained sandstone is silica consolidated. Test pieces of the rock varied in permeability from 930 to 2,110 md and in porosity from 28 to 31 percent.

More limited tests were made on two other sandstones (Lissie and Upper Austin), a limestone (Upper Noodle), and a glass bead pack.

Photomicrographs

Pore spaces of samples of the test rocks were evacuated and filled with Woods metal. Photographs of polished cross-sections of the metal-filled rocks were taken by reflected light. The pictures were examined to obtain information on size, shape, and continuity of pore spaces.

Generation of Mixed Wettability

To evaluate the mechanism proposed to explain low residual oil saturation, a method was developed for generating in the laboratory the type of mixed wettability inherent in that mechanism. Experiments conducted with East Texas crude oil revealed that, upon long standing at reservoir temperatures, it will deposit a film of strongly oil-wetted material on surface contacted directly by the oil. However, the oil-wet film deposited (on a glass or quartz surface) by "stabilized" (evacuated) East Texas Field crude during several days of contact is not highly stable — that is, brine will displace the film after a rather brief contact. Thus, it appeared at first that to generate a stable, mixed-wettability system it would be necessary to contact the rock with oil at reservoir temperature and pressure —an approach similar to that described by Mungan.[11]

However, in subsequent experiments it was found that a mixture of evacuated East Texas crude oil and heptane will deposit a stable, strongly oil-wet film on initially water-wet glass or fused quartz in direct contact with the oil mixture; but adjacent areas (of the same solid surface) in contact with brine will remain preferentially water wet. When the film (of organic material) was deposited on the surface of a glass vial, it was visible as a somewhat darkened zone where the oil contacted the glass. When this film was covered with brine and contacted with oil, the oil spread freely over the brine-covered film and then drained across the film with no apparent tendency to accumulate into flattened drops or lenses (as would occur if oil wetting were less than perfect). Strongly oil-wet films deposited in this way on glass remained stable after standing covered with brine for more than a year.

In adapting this phenomenon to a procedure for developing mixed wettability in cores, we reasoned that the film-depositing oil, when placed in cores containing connate water, should behave much as it does in a glass vial. That is, at points where oil contacts the solid surfaces of pore spaces, a film of strongly oil-wet organic material should become firmly attached, and where water, rather than oil, remains in contact with the pore surfaces, no film should be deposited. Rock surface with no film should remain preferentially water-wet.

On a smooth, perfectly oil-wet surface of low curvature, such as the glass vial, oil may drain as a uniform, thin film. However, where the strongly oil-wet surfaces have a very irregular geometry, such as exists in porous rocks, the oil should not be expected to drain uniformly. We would expect, rather, that capillary forces would tend to concentrate oil flow into rivulets or streams. Consequently, mathematical flow relations applicable to uniform, thin films are not directly applicable to the surface drainage effect in naturally occurring porous media.

Core Test Procedures

The preparation of rock samples, the fluids used, and the procedures followed in displacement tests are described in the Appendix.

Test Results

Boise Core Displacement Tests

Waterflood Behavior. Waterfloods of oil in mixed-wettability cores showed characteristic results: oil saturation continued to decline as long as water was injected. With the same oil in a water-wet core, however, oil saturation quickly reached a constant value. Fig. 1 shows data from a water displacement in a strongly water-wet Boise core and sequential displacements of an 0.8-cp heptane-crude oil solution and a 2.5-cp refined oil after a mixed-wettability condition has been established. The oil saturation at the beginning of the 0.8-cp test was 85.2 percent — 13.1 percent higher than that for the 2.5-cp test.* The water saturation present at the beginning of the water-wet flood was midway between these two values. The difference between the floods of the water-wet system and that of the mixed-wettability system is striking.

*As discussed in more detail later, this increase in the "irreducible water saturation" after the initial mixed-wettability waterflood is characteristic of mixed-wettability systems such as that occurring in the East Texas field. The irreducible water saturation for mixed-wettability systems is frequently somewhat higher than for the same rock when it is completely water-wet or when the mixed-wettability condition was originally generated. In order to achieve the same initial water saturation, it is usually necessary to extract and then muffle the core to restore its water-wet condition, reduce the water saturation to the desired value of initial water saturation, and then regenerate the mixed-wettability condition.

Little oil was produced from the water-wet core after water breakthrough. For the mixed-wettability core, on the other hand, oil production continued for many pore volumes after water breakthrough and resulted in lower oil saturations for both the 0.8-cp and the 2.5-cp floods than could be reached in the water-wet flood.

Since oil continues to be produced for many pore volumes in these mixed-wettability waterfloods, it is convenient to present the data as a log-log plot of residual oil saturation vs pore volumes of water injected, as shown in the insert to Fig. 1. It should be noted that the production curves after 1 PV of water injected can be represented by two straight lines.* Straight-line log-log relationships such as these were frequently observed in this study. Although it was found that some of the production curves would ultimately flatten out and approach a small but finite residual saturation, the straight-line relationship was usually valid for several hundred pore volumes of water injected.

A striking similarity to the mixed-wettability waterflood data is exhibited by waterflood data on preserved cores from the East Texas field, Woodbine reservoir, Fig. 2. Like the mixed-wettability flood results shown in Fig. 1, these data do not indicate the lower limit to which oil saturation might go if flooding were continued, even though almost 5,000 PV of water was injected during these extended waterfloods.

Different "connate" water saturations were established in a group of Boise cores before they were contacted with an oil that deposits an oil-wet film. The differences in water saturation were intended to expose different fractions of the pore surface to direct contact with oil and thus cause different fractions of the pore surface to become strongly oil-wet. Data from waterfloods on this group of cores are presented in Table 1, and selected data are plotted in Figs. 3 through 5.

The amount of oil remaining after various amounts of flood water were injected was found to depend on the connate water saturation present in a core during contact with film-depositing oil. Data presented in Fig. 3 show the residual oil saturations remaining in several tests after flooding with 20 PV of water (brine). As shown, residual oil saturations were least (16 to 17 percent) where connate water saturations (the water saturations at time of contact with film-depositing oil) were in the range of 13 to 20 percent. Much higher residual oil saturations will remain after waterflooding a muffled, strongly water-wet Boise sandstone core containing white oil. The value of about 33.5 percent obtained for one of the cores described above is typical. Results of waterflooding oils of different viscosities from each of the several cores were similar, except that more flood water was required to attain equivalent saturations with the more viscous oil.

Drainage Exponents. For waterflood data such as those presented in the insert of Fig. 1 and in Fig. 2,

*The horizontal separation between the two straight lines is approximately equal to the viscosity ratio of the oils used in the two floods.

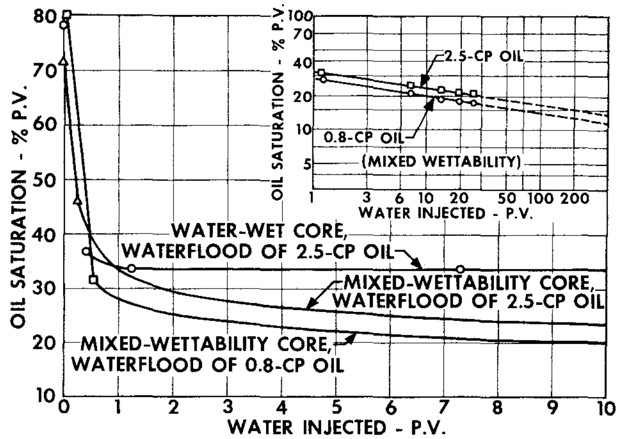


Fig. 1—Comparison of waterflood behavior for mixed-wettability and water-wet cores (insert shows extension of mixed-wettability flooding data).

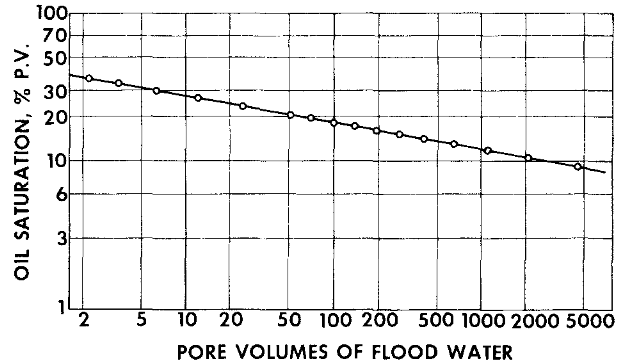


Fig. 2—Extended waterflood data on a preserved East Texas Field core.

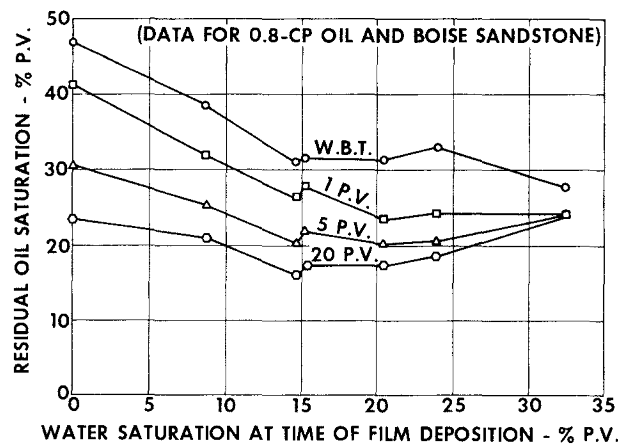


Fig. 3—How water saturation during deposition of oil-wet film affects saturations left by waterfloods.

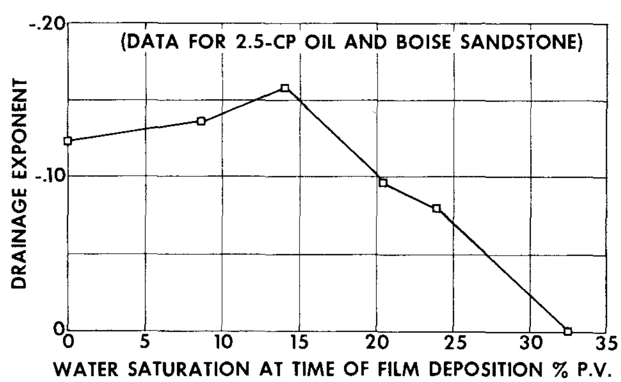


Fig. 4—How water saturation during deposition of oil-wet film affects drainage exponents for waterfloods.

TABLE 1—WATERFLOOD DATA ON BOISE SANDSTONE CORES IN WHICH PART OF THE PORE SURFACES WERE MADE VERY OIL WET BY DEPOSITS FROM CRUDE OIL

				Initial Waterflood of 0.8-cp Oil						Waterflood of 2.5-cp Oil				
				S_o (percent PV) After Various Volumes Flooded						S_o (percent PV) After Various Volumes Flooded				
Core Designation	Porosity (percent)	Permeability (md)	"Contact"* S_{wr} (percent PV)	WBT**	1 PV	5 PV	20 PV	Drainage Exponent	S_{wr} By Oil Flood After First Waterflood	WBT**	1 PV	5 PV	20 PV	Drainage Exponent
BO-4-Um	29.0	957	0	47.1	41.5	30.7	23.6	−0.190	16.9	51.8	40.0	32.7	27.6	−0.123
BO-5-Um	31.0	1,910	8.8	38.6	32.0	25.6	21.3	−0.135	28.8	42.9	34.6	27.8	23.1	−0.135
BO-3-Mm	28.2	958	14.8	31.0	26.1	20.8	16.3	−0.155	27.9	49.0	33.0	25.8	21.1	−0.153
BO-3-Um	29.3	1,094	15.4	31.6	28.0	22.0	17.8	−0.152	29.3	46.1	32.5	25.2	20.3	−0.155
BO-3-Mm†	28.2	958	20.5	31.4	23.5	20.2	17.5	−0.106	24.0	46.0	31.0	23.3	21.0	−0.095
BO-4-Mm	28.9	933	24.0	33.2	24.5	20.7	18.8	−0.074	23.6	45.4	30.0	23.7	20.7	−0.078
BO-5-Mm	28.6	1,493	32.5	28.0	24.5	24.2	24.0	0.00	21.8	37.6	28.4	24.8	24.5	0.00
Muffled				35.0	34.0	33.5	33.5			38.0	33.8	33.5	33.4	
Extracted				29.5	26.8	26.0	25.8			41.3	29.5	26.5	23.4	

*Refers to water saturation when film depositing oil contacted the core.
**WBT = Water breakthrough.
†Muffled and re-treated at a higher "contact" S_{wf}.

the relationship between the average oil saturation $\overline{S}_o$, and pore volumes of water injected, w_i, is expressed by Eq. 1, where m is the slope and n is the intercept value from the graph.

$$\overline{S_o} = n\,(w_i)^m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Thus, the flood data of Fig. 2, obtained for a preserved East Texas Field core, may be expressed as Eq. 2.

$$\overline{S_o} = 42\,(w_i)^{-0.183} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The value of m, the drainage exponent, is independent of viscosity (Fig. 1) and thus is a convenient parameter for characterizing the drainage behavior whenever the production curves can be represented by the straight-line log-log relationship.

Variations of the drainage exponent with the initial connate water saturation are given in Fig. 4 for waterfloods of 2.5-cp oil from Boise cores. For this core material the drainage exponent was maximum when the initial connate water saturation was about 15 percent. For higher connate water saturations, the drainage exponent decreased, becoming zero at 32.5 percent.

Oil Floods After Waterfloods. After the initial waterflood, each of the Boise cores used in the above experiments was flooded with 13 PV of 21-cp oil at 300 psi/ft differential pressure. Although the oil-flooding treatment was the same in each case, the residual water saturation remaining after these oil floods varied. Maximum values were obtained for cases in which the connate water saturations at time of contact with the film-depositing oil were in the range of 9 to 15 percent (Fig. 5). This occurrence of higher residual water saturations resembles the behavior commonly observed when core samples (from a number of fields other than the East Texas field) are oil flooded in preparation for "restored state" waterfloods.[1]

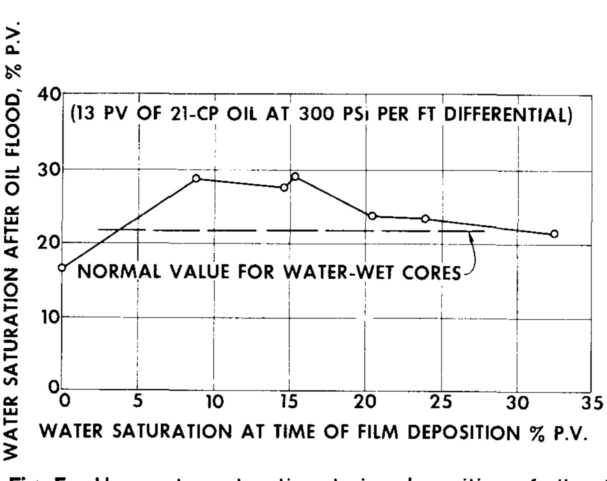


Fig. 5—How water saturation during deposition of oil-wet film affects water saturation remaining after a standardized oil flooding step.

Centrifuge Displacements of Oil by Water. A Boise core, in which mixed wettability had been established at a "connate" water saturation of 17.2 percent PV, was flooded with 25 PV of brine to displace refined oil having a viscosity of 2.5 cp. The 2-in.-long core was then covered with brine and centrifuged at a constant rate; oil displacement was observed as a function of time. The waterflood was performed at a constant, 3-psi differential pressure. In the centrifuging step, the differential pressure between oil and water across the core was 7.4 psi. For oil saturations above 9.5 percent, linear log-log relations describe both the waterflood and the centrifuge drainage (Fig. 6). For oil saturations below 9.5 percent, the drainage relation flattens, possibly indicating loss of continuity of some of the oil-wet drainage paths.

Similar flood and centrifuge tests were made on a preserved field core. In these tests, the pressure differential driving oil through the core was 10 psi for both the flooding and centrifuging steps. Linear log-log relations describe both the flooding and the centrifuging steps (Fig. 7). No change in the drainage relationship is apparent in the centrifuge data, suggesting that loss of oil-wet drainage path continuity did not occur during this experiment. This result is consistent with the low oil saturation typical of East Texas cores. (Different drainage exponents are expected for the centrifuge and constant-pressure flood curves, since the driving force mechanisms are different. The same water/oil relative permeability data can be used to predict the oil production curves for either type of experiment.)

Waterflood Behavior of Other Rock Samples

Waterflood data on other porous rocks indicate that the effects of generating mixed wettability depend on rock properties. Tests on a Woodbine outcrop sandstone were made after the rock samples were contacted with film-depositing oil at several levels of connate water saturation. Tests were also made on two other sandstones and a limestone after the cores were contacted with the film-depositing oil. The initial "connate" water saturations used in these tests were established by an oil-flooding procedure (injecting 20 PV of 145-cp white oil at a differential pressure of 3,000 psi/ft) that led to pronounced mixed-wettability drainage behavior in the Boise and Woodbine outcrop sandstones. Data from comparable flooding tests on the five rock samples are presented graphically in Fig. 8.

Residual oil saturations after 25 PV of waterflooding in both the water-wet and the mixed-wettability conditions are given in Table 2. Initial water saturation as well as porosity and permeability values for the rock samples are also listed in Table 2.

When these cores were strongly water-wet, very little oil production was obtained from any of the cores after the first pore volume of flood water. In the mixed-wettability floods, the cores continued to produce significant amounts of oil even after many pore volumes of waterflooding. This continued drainage was most pronounced in the Boise and Upper Austin tests. Flooding data from Boise, Upper Austin, and Woodbine tests indicated no lower limit to ultimate residual oil saturation for the injection volumes used. On the other hand, data from tests on the Upper Noodle (limestone) and the Lissie (sandstone) did indicate limits (20 and 26 percent, respectively) below which oil saturation could not be reduced. Note that only for the Woodbine outcrop material was the residual oil saturation after flooding 25 PV of water higher for the mixed-wettability than for the water-wet condition. For this rock also, however, mixed wettability would probably provide the lower residual oil saturation with continued flooding (see Fig. 8).

Exponential drainage relationships for these mixed-wettability floods are presented in Table 3. It is apparent from these relationships that waterflood behavior in mixed-wettability cores depends on rock properties. Two properties likely to affect waterflood behavior are pore geometry and the mineral composition of the rocks.

Effect of Pore Geometry. Continuous, strongly oil-wet paths along pore surfaces are necessary to the proposed mechanism for oil drainage to low oil saturation. Hence, pore structure can be expected to influence drainage behavior. A simplified description of the relationship of pore geometry to recovery is illustrated by Fig. 9.

In Fig. 9a, two spheres are shown in contact after having been treated to generate mixed wettability. As indicated, the oil-wetted surfaces of the two spheres are separated by a barrier where a "pendular ring" of connate water rather than oil remains in contact with the solid surface.

In a pack of water-wet, spherical particles, water will be retained near points of contact between spheres. In such a pack we would not expect a generated mixed wettability to create continuous paths of oil wetting. For one test, a pack was prepared using glass beads of approximately 110-micron diameter. This 3,200-md, 37.3-precent-porosity bead pack was contacted with a film-depositing oil at a connate

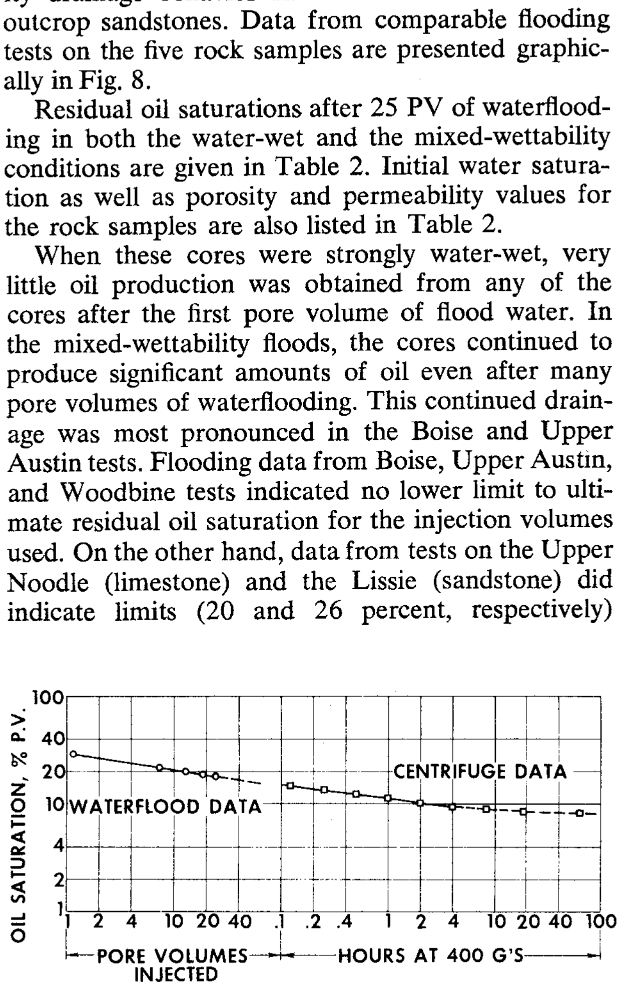


Fig. 6—Waterflooding followed by centrifuging of a mixed-wettability core.

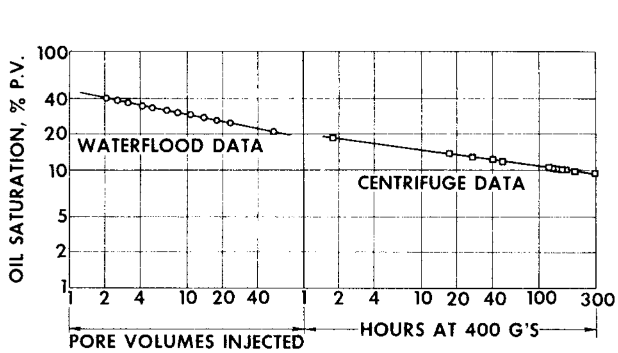


Fig. 7—Waterflooding followed by centrifuging of a preserved East Texas Field core.

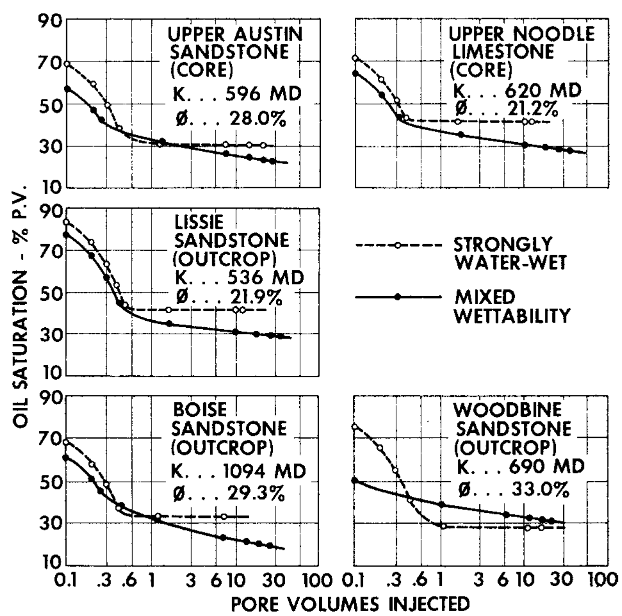


Fig. 8—Comparison between waterfloods under strongly water-wet conditions and waterfloods under mixed-wettability conditions in several porous rocks.

TABLE 2—RESIDUAL OIL SATURATIONS AFTER 25 PV WATERFLOODING (FIVE CORES)

Rock Sample	Permeability (md)	Porosity (percent)	S_w at Time of "Contact" (percent PV)	S_o After 25 PV Waterflooding	
				Water Wet	Mixed Wettability
Boise (SS)	1,094	29.3	13.5	33.5	20.5
Upper Austin (SS)	596	28.0	20.0	30.0	22.9
Woodbine Outcrop (SS)	690	33.0	17.0	27.3	30.7
Upper Noodle (LS)	620	21.2	18.9	40.5	28.1
Lissie (SS)	536	21.9	7.2	42.5	29.1

TABLE 3—DISPLACEMENT EQUATIONS FOR MIXED-WETTABILITY WATERFLOODS

Rock Sample	Equation
Boise	$\bar{S}_o = (32.4)\,(w_i)^{-0.155}$
Upper Austin	$\bar{S}_o = (32.3)\,(w_i)^{-0.112}$
Woodbine Outcrop	$\bar{S}_o = (40.0)\,(w_i)^{-0.082}$
Upper Noodle	$\bar{S}_o = 20 + (16.3)\,(w_i)^{-0.217}$
Lissie	$\bar{S}_o = 26 + (10.5)\,(w_i)^{-0.37}$

water saturation of 8.3 percent before waterflooding. Recovery of 2.5-cp oil from the pack was markedly higher (residual oil saturation was 8.8 percent) than from an otherwise similar but strongly water-wet pack (for which residual oil saturations was 15.3 percent). However, flow of oil from the pack essentially ceased after the first few pore volumes of flooding. This result supports the above view that water-wetted areas between oil-wetted parts of adjacent spheres should prevent the drainage of oil to continue to extremely low oil saturations.

In Fig. 9b, two spheres that have been cemented together by a mineral deposit are pictured. When the cementation material fills the pendular ring area, so that water is no longer held between the grains, a continuous oil-wet path can develop from one pore space to the next. Of course, porous rocks differ from packs of uniform spheres in that rock grains are neither spherical nor uniform in size or shape. Furthermore, porous rocks usually contain substantial amounts of mineral solids deposited or recrystallized near the original grain contacts and along pore channels. These differences in sphere packing and porous rocks may explain how continuous paths of oil wetting can develop in fluid-bearing rocks.

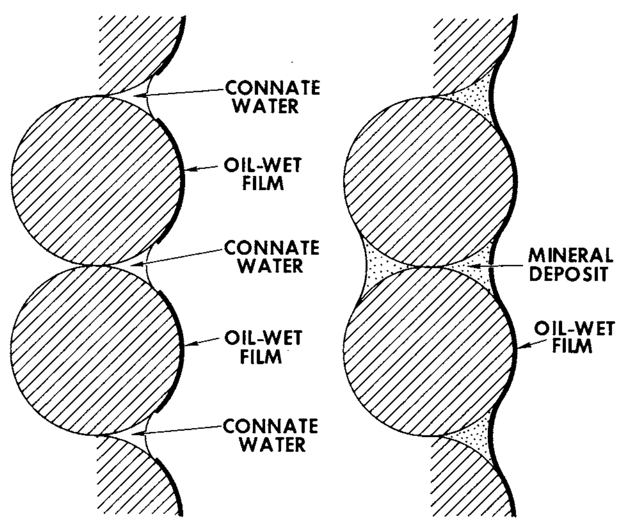
Insight as to both shape and size of pore spaces in the various rocks can be obtained from photomicrographs of polished cross-sections in which pores are filled with Woods metal. It is rather easy, by using these polished cross-sections, to classify rocks according to the distribution of pore sizes and the "average" pore size. It is much more difficult to rate the effectiveness of the flow channels connecting the large pore openings from such a photograph.* Nevertheless, microscopic examination of the pore structure of the different rock samples provided a valuable source of information that qualitatively confirmed the importance of pore "continuity" in determining the residual oil saturations attainable in mixed-wettability cores.

Effect of Mineral Composition. Some differences in drainage behavior among the mixed-wettability rocks might have resulted from variations in mineral composition. The more limited drainage of oil from the Upper Noodle limestone and from the Lissie sandstone, which contains carbonate crystals, could be explained by assuming that the deposited oil-wet film was less stable on carbonate surfaces than on silicate surfaces.

Discussion

We have seen that by waterflooding mixed-wettability porous rock samples, unusually low residual oil saturations can be attained. However, as evidenced in Fig. 2, many pore volumes of flood water, with extremely high water/oil producing ratios, are required to reach these low saturations. Nonetheless, oil saturations remaining in cores taken from several reservoirs, including the East Texas Woodbine, are much lower than would be predicted by one-dimensional Buckley-Leverett calculations for flow along the bedding planes only. However, cross-section calculations using relative permeability data obtained (using either extended waterfloods or centrifuge tests) from preserved East Texas cores and the rate of rise of the East Texas Field water table confirm the plausibility of unusually low residual oil saturations. These calculations show that oil tends to drain upward (across bedding planes) and accumulate at the top of

*The scanning electron microscope is a much more powerful tool for use in this type of study but none was available at the time this work was completed.



(A) CONNATE WATER MAY ISOLATE OIL-WETTED SURFACES

(B) MINERAL DEPOSITS BETWEEN GRAINS PROMOTE CONTINUOUS OIL-WETTED PATHS

Fig. 9—Relationship of pore geometry to oil recovery.

each stringer.* Subsequent flow updip then depends primarily upon the somewhat higher relative permeability to oil that corresponds to the "sand-top" saturations rather than upon the average oil saturation contained in the sand.

While there is strong evidence that surface drainage of oil occurs in the East Texas field, we should not expect migration of oil by this mechanism to occur in all reservoirs. Waterflood behavior resembling that found in preserved East Texas cores has, however, been observed by Esso Production Research Co. in preserved cores from other reservoirs both under simulated reservoir conditions and at room temperature and moderate pressure. In still other reservoirs, core tests fail to show significant differences in water-oil displacement behavior on preserved cores before and after extractive cleaning, thus indicating that surface drainage does not occur. Furthermore, it may be that surface drainage of oil does not occur under actual reservoir conditions, even though it is indicated by the results of conventional "restored-state" floods using refined oil at ambient temperature and pressure. Consequently, only tests using reservoir fluids at reservoir temperature and pressure with preserved cores are likely to give consistently reliable results with regard to surface drainage. To be useful, test results should indicate both how rapidly oil drains and how low a saturation can be attained.

Oil drainage over oil-wet paths along pore surfaces will be a useful mechanism primarily where gravity drainage can make a significant contribution to the over-all displacement process. Whether or not economic advantage may be taken of surface drainage in specific reservoirs will depend not only upon the rate of such drainage, but also upon reservoir characteristics such as continuity of vertical permeability, reservoir geometry, and time allowed for depletion. For the East Texas field, the drainage of oil along continuous oil-wet paths appears to be significant.

Conclusions

Laboratory tests described in this paper support the postulate that in some reservoirs where conditions are favorable for significant gravity drainage, a mixed-wettability condition permits drainage of oil to low saturations. Following are a number of more specific conclusions based on the investigation:

1. A condition of mixed wettability can be generated in laboratory cores and leads to water displacement behavior similar to that of some preserved reservoir cores.
2. In the laboratory method for generating a stable and reproducible mixed-wettability condition, surfaces of the larger pores should become strongly oil-wetted, whereas surfaces in the smaller pores and near grain contacts (pendular regions) should remain preferentially water-wet.
3. In mixed-wettability porous rocks, permeability to oil can persist to low oil saturations. It is postulated that the flow of oil (surface drainage) occurs in films or rivulets over strongly oil-wetted pore surfaces, forming continuous oil-wet paths extending through the pore structure.
4. The drainage behavior of laboratory-prepared, mixed-wettability cores depends on the "connate" water saturation present when an oil-wet film is deposited by the oil. Thus, drainage behavior appears to depend on the fraction of the pore surface that is strongly oil-wetted.
5. Both the pore structure and the mineral composition of porous rocks appear to affect the surface drainage of oil from mixed-wettability laboratory cores.
6. Since surface drainage of oil depends on the composition of reservoir fluids and on rock properties, the process will occur in some, but not all, reservoirs.
7. In those reservoirs where surface drainage can occur, it will usually be possible to attain very low residual oil saturations, practically, only when depletion times are long enough for gravity drainage or segregation to be effective.

*The ratio of viscous to gravitational forces in the East Texas field is generally less than 1/6. Consequently, gravity segregation in the East Texas field is a major factor in the unusually high displacement efficiency of the waterflood.

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APPENDIX

Core Test Procedures

Preparation of Rock Samples for Tests

Before they were used in tests, most of the samples of various rocks were prepared in the following manner to assure uniform initial wetting conditions and to prevent accidental wettability changes. Cores were muffled at 350° to 400°C, and then stored several days in moist air before being dried at 110°C. This treatment assured an initial strongly water-wet condition. For flooding tests, cores were fitted with metal wire screens and connectors and given a cast coating of low-melting-point alloy (138°C mp bismuth-tin eutectic). For centrifuging tests, cores were left uncoated.

The East Texas Field Woodbine cores were cut, preserved, and prepared for "restored-state" tests by conventional procedures.

Fluids for Displacement Tests

Brine employed for saturating and for flooding cores was "synthetic" East Texas Field brine. This chloride brine, which matched the Na, Ca, and Mg ion content of field brine, was lightly buffered to pH 7 with Na borate.

Although 21-cp and 145-cp white oils were used in establishing various initial water saturations, other oils were displaced by water in flood and centrifuge drainage tests. In most cases water displaced a 2.5-cp refined oil (Bayol 35), but in other specified cases the oil was an 0.8-cp mixture of *n*-heptane and evacuated ("stabilized") East Texas Field crude oil.

Procedures for Displacement Tests

The water-wet mounted cores were saturated with brine and reduced to selected "connate water" saturations by, in most cases, flooding with viscous white oils. (For a given rock the water saturation attained is controlled by the volume and the viscosity of the oil injected and by the pressure differential applied.) The viscous white oil was then replaced by 2.5-cp refined oil (Bayol 35). To attain lower water saturations than was possible by oil flooding,* the water content was decreased first by air flooding and then by repeated intervals of evacuation to evaporate water as uniformly as possible before filling up the remaining pore space with Bayol 35.

Some cores were flooded in the above condition. More commonly, other steps preceded the displacement of oil by water. Usually, the Bayol 35 was replaced by a warm, freshly prepared mixture of three parts *n*-heptane and one part stabilized East Texas Field crude oil. The saturated core was allowed to stand 3 days. This step generates a condition of mixed wettability in cores. The first waterflood of mixed-wettability cores usually displaced the 0.8-cp-viscosity mixture of heptane and crude oil. Next, the core was flooded with viscous oil to a residual water saturation. Then, after the viscous oil was replaced with 2.5-cp refined oil, another waterflood was performed. This last flooding step corresponds, in core treatment, to "restored-state" flooding on fresh or preserved reservoir cores. In some cases, the mixture of heptane and crude oil was replaced with the 2.5-cp refined oil before being waterflooded. After the waterflooding, oil saturation was determined by an extraction procedure. This extraction provided a check on saturation values found by volumetric balance.

The "restored-state" flooding on preserved East Texas Field Woodbine cores was followed by either "extended" flooding or by centrifuging under brine. The normal restored-state floods terminated after about 40 PV of water had been injected. For extended waterfloods, flooding continued for several hundred to several thousand pore volumes. Centrifuging tests ordinarily followed an initial waterflooding step. The core was placed under brine and centrifuged at constant rate, and the oil displacement was observed as a function of time. **JPT**

*The residual oil saturation for an oil-wet core should be the same as the irreducible water saturation in a water-wet core obtained either by an oil flood or in a drainage capillary pressure test. Either or both of these tests were used on some of the cores to provide the "end-point" residual oil saturation for a waterflood of a completely (uniformly) oil-wet rock.

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