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Oil Recovery by Sequential Waterflooding of Mixed-Wet Sandstone and Limestone

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Duplicate tests on mixed-wet sandstone cores have been shown to give closely reproducible results. For studies with reservoir cores, duplicate tests are often precluded because of the limited availability of cores and their heterogeneity. In repeat flooding tests for recovery of crude oil, it has been found that each test affects the outcome of a subsequent test. Some consistent trends of increase in recovery have been observed. In this paper, results are presented for up to four cycles of flooding between initial water saturation and residual oil for reservoir sandstone, outcrop sandstone, and outcrop oolitic limestone. A single crude oil was used for most of the tests. Sequential flooding was also tested for low- and high-viscosity mineral oils. The brine was synthetic seawater for all but one of the floods. Each consecutive flood for the sandstones resulted in a systematic increase in the recovery of crude oil. Crude oil was sometimes produced as an emulsion of about 2% water. Trends for carbonate cores were comparable except that, for one of four of the tested cores, reduced recovery was observed for the second cycle. Implications for establishing baseline results for assessment of processes, such as low-salinity water flooding, are discussed.

Introduction

Mixed wettability, whereby the distribution of connate water determines the areas of rock surface exposed to adsorption from crude oil, is now the most widely accepted model of reservoir wettability.[1-9] Laboratory core tests are commonly made to evaluate the microscopic displacement efficiency of oil recovery from the swept zone of a waterflood. Various approaches are taken to simulate reservoir performance, ranging from preservation or restoration of wettability and testing cores at full reservoir conditions to measurement of recovery for cleaned cores and mineral oil at ambient conditions.[10]

Duplicate tests on mixed-wet sandstone cores have been shown to give closely reproducible results.[11-13] However, in parametric studies with reservoir cores, costs of core recovery and heterogeneity between cores can necessitate repeat tests on individual cores. An advantage of such tests on individual cores is that the pore geometry might be expected to remain unchanged for consecutive tests.

When crude oil is displaced from a rock by brine of different compositions, laboratory tests show that changes in the crude oil/brine/rock properties can occur. For example, in previously reported tests of waterflood recovery by low-salinity flooding of reservoir sandstone, the original recovery behavior given by injection of seawater could not be reproduced.[14] For the results presented in Figure 1a, a reservoir core, LK 1, was cleaned, aged at elevated temperature, flooded with seawater, and then taken back to initial brine saturation. The process of cleaning, establishing an initial water saturation, and aging is referred to as restoration (R). Waterflooding followed by re-establishment of initial water saturation by flow of oil is referred to as a flooding cycle (C). The first recovery curve is indicated as R1/C1 (restoration 1/cycle 1) in Figure 1a. The core was restored by cleaning and re-aging, and the test was repeated, except that the injection brine was 0.1 seawater (i.e., 10 times dilution). Recovery increased from 51% for R1/C1 to 68% for R2/C2. After the third restoration with seawater as the initial brine, the core was flooded with 0.01 seawater. Recovery for R3/C3 was 80%. As a test for possible changes in core properties that affect oil recovery, after the fourth cleaning and restoration, the core was again flooded with seawater. However, the recovery with seawater (R4/C4) was much higher than given by R1/C1 and also higher than that given by flooding with 0.1 seawater. Such observations raise questions as to the effect of the history of core treatment on wettability states that result from adsorption from crude oil.

Tests at reservoir conditions are commonly used to predict reservoir performance at the early stages of development. These tests are expensive and technically difficult; very little

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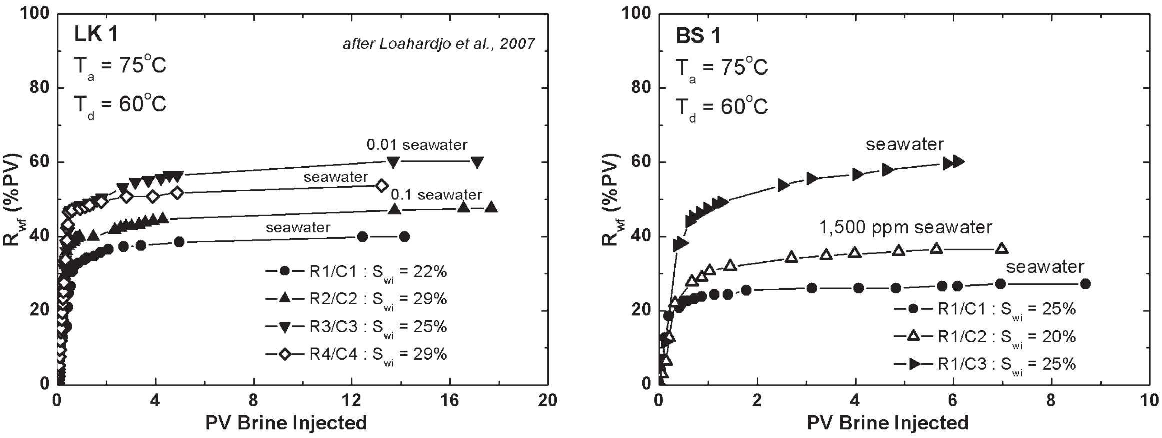

(a) cleaned and re-aged between cycles (b) no cleaning and re-aging between cycles

Figure 1. Consecutive flood cycles on individual cores with changes in salinity.

Table 1. Crude Oil Properties

crude oil	WP
C_6 asphaltenes (wt %)	6.3
acid number (mg of KOH/g of oil)	1.46
base number (mg of KOH/g of oil)	2.49
ρ at 22 °C (g/cm^3)	0.9125
μ of oil at 22 °C (cP)	111.2
μ of oil at 60 °C (cP)	20.1

Table 2. Brine Composition

composition (g/L)	seawater
NaCl	28
KCl	0.935
$CaCl_2$	1.19
$MgCl_2$	5.368
NaN_3	0.1
total dissolved solid/L	35.493

Table 3. Rock Properties

rock type	core ID	L (cm)	d (cm)	φ (%)	k_g (md)
sandstone LK reservoir	LK 1	7.12	3.19	23	479
	LK 2	6.14	3.88	20	886
sandstone outcrop	BS 1	7.24	3.78	21	611
	BS 2	6.34	3.82	20	297
	BS 3	7.28	3.78	21	708
	BS 4	7.21	3.78	20	615
	BS 5	7.45	3.78	20	622
	BS 6	7.45	3.79	21	643
	BS 7	7.08	3.79	21	777
limestone outcrop	EdGc 1	7.24	3.80	22	26
	EdGc 2	7.26	3.80	24	46
	EdGc 3	7.21	3.79	22	23
	EdGc 4	7.35	3.86	20	27

information is available on their reproducibility. Richardson et al.[15] investigated the cyclic recovery behavior of fresh cores (not cleaned) from the East Texas Field and reported that recovery of kerosene decreased from 98% for consecutive floods. Apart from one test, reported by Tang and Morrow,[16] the question of reproducibility of recovery of crude oil for sequential mixed-wet floods on individual core samples does not appear to have been addressed.

This study concerns sequential floods on individual cores at conditions of reduced complexity compared to those for the example shown in Figure 1a. The tests usually involved only one initial aging step, no cleaning between cycles, and except in one case, no change in brine composition. They include a comparison of recovery of mineral oil versus crude oil with no initial aging. In general, for production of crude oil, the outcome of a flood was affected by the previous flood.

Experimental Section

Refined Oil. Soltrol 220 of 3.9 cP viscosity [designated as low-viscosity oil (LVO)] and a 173 cP white mineral oil [designated as high-viscosity oil (HVO)], with densities of 0.782 and 0.872 g/cm^3, respectively, were used in tests with refined oils. Polar contaminants were removed by flow of LVO through a packed column of alumina and silica gel and, for HVO, by forming a suspension of alumina and silica gel followed by filtration.

Crude Oil. An asphaltic crude, designated as WP crude oil, was used for all tests with crude oil. Properties of the oil are given in Table 1. The crude oil was filtered to remove particulate matter and then vacuumed for 2 h at room temperature to minimize the possibility of gas production during the course of tests run at elevated temperature. The vapor pressure of the crude oil at 60 °C was 1.4 psi.

Brine. Brines were based on the composition of synthetic seawater, given in Table 2. The brine was degassed by vacuum. The viscosities of the brines were about 0.6 cP at 60 °C. The density of seawater was 1.0233 g/cm^3 at 22 °C.

Cores. The cores were reservoir sandstone, Berea sandstone, or an oolitic outcrop limestone referred to, respectively, as LK 2, BS, and EdGc (Edwards formation, Garden City, TX) (see Table 3). Permeability to nitrogen, k_g, ranged from 479 to 886 md for the sandstones and from 26 to 46 md for the limestone. Porosity, φ, ranged from 20 to 26% for the sandstones and from 20 to 24% for the limestone.

Thin section and scanning electron microscope (SEM) images for LK reservoir sandstone and EdGc limestone, an outcrop oolitic limestone, have been presented previously.[9,14] The reservoir sandstone is rich in chert and kaolinite and has good sorting. The limestone is mostly composed of calcite.

Core Cleaning. Reservoir cores were set in core holders at 300 psi confining pressure. They were first flushed with 200 cm^3 of toluene at 2 cm^3/min to remove crude oil. The cores were then flushed with 10 PV of methanol at 2 cm^3/min to remove salts and then flushed again with toluene. If the effluent was not clear, the cores were flooded with methanol, followed again by toluene. Outcrop cores were cut from quarried blocks. They were dried

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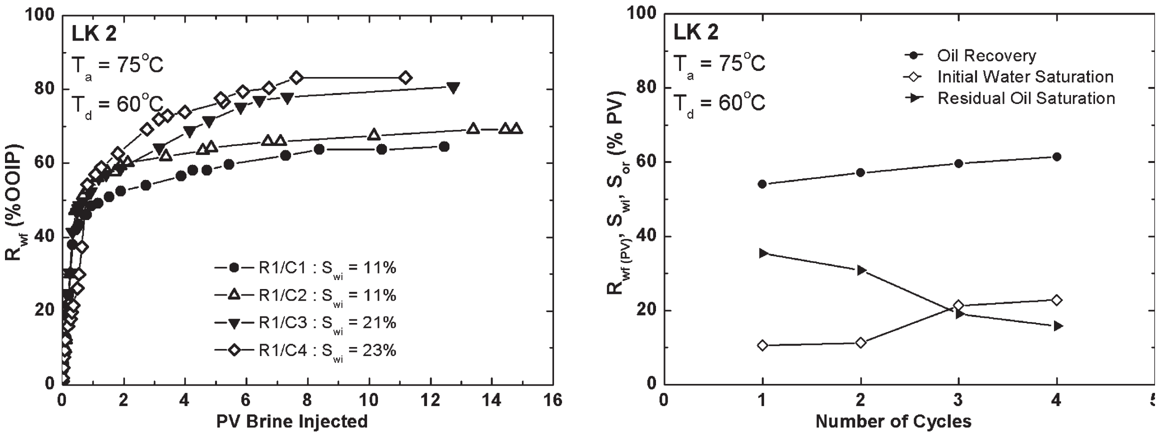


(a) oil recovery (b) % PV, S_{wi} and S_{or} at 6PV

Figure 2. Sequential seawater floods on a reservoir core with no cleaning and re-aging between cycles.

by evaporation at elevated temperature. After drying, the air permeability to nitrogen for each core was measured.

Establishing Initial Water Saturation. The cores were saturated with synthetic seawater (Table 2) and left for 14 days at room temperature to establish ionic equilibrium. The cores were then flooded with about 80 cm^3 of crude oil at 2 cm^3/min (or 150 psi pressure drop for limestone) at room temperature to establish the initial water saturation. The cores then were flooded with 20 cm^3 of crude oil in the reverse direction to reduce end effects.

For an experiment in which low-viscosity mineral oil was the initial oil phase, the initial water saturation was established by displacing brine with air using a porous plate. The core was then evacuated and saturated with the mineral oil.

Aging. After an initial brine saturation, S_{wi}, was established at ambient temperature by displacement with crude oil (μ = 171.2 cP), the core was submerged under crude oil in sealed pressure vessels and aged at 75 °C for 14 days.

Waterfloods. Identification of core floods by the restoration and cycle numbers is also applied to outcrop cores. Tests on each core are identified according to the sequence of restoration and the overall sequence with respect to the number of flooding cycles. For most of the tests, core preparation involved only one aging step, denoted for both reservoir and outcrop samples as restoration, R1. The sequence of flood cycles is then identified as R1/C1, R1/C2, etc.

After aging, a core was set in a core holder containing brine. For the first flood, all lines were initially filled with brine. For subsequent floods, the initial saturation was established by the flow of oil and the volume of produced oil was reduced by the volume of oil in the connecting lines. Waterfloods were run at 0.25 cm^3/min, at either ambient (~22 °C) or elevated temperature (60 °C) as indicated. After each flood, the core was left for 12 h at residual oil before re-establishing initial water saturation. Any variance from these procedures is described with the results.

Produced Crude Oil. Produced crude oil was checked for the presence of brine by measurement of the oil density and centrifuge separation. Corrections to the volume of produced oil were based on the average of the two methods.

Results

Sandstones. *Berea BS 1: Change in Salinity without Cleaning and Re-aging between Floods*. Tests of cyclic flooding with the change in the injection brine composition but without cleaning and re-aging were made on Berea sandstone core BS 1. After establishing an initial seawater saturation of 25% and aging at elevated temperature, the core was flooded with seawater to give the recovery curve shown in Figure 1b as R1/C1. An initial water saturation of 20% was re-established with crude oil, and the core was flooded with diluted seawater of 1500 ppm (R1/C2); recovery increased by about 8% original oil in place (OOIP). The low-salinity brine was displaced by seawater with the core at residual oil saturation, and an initial saturation of 25% was established by flow of crude oil. In the subsequent flood (R1/C3), oil recovery by seawater injection was much higher than for the low-salinity brine. Observations, such as those presented in Figure 1, make identification of the baseline recovery problematic with respect to assessment of improved secondary recovery by low-salinity flooding for consecutive floods on individual cores. The effect of cyclic flooding without a change in salinity, referred to as sequential waterflooding, needs to be tested.

Reservoir Sandstone LK 2: High-Temperature Aging and High-Temperature Flooding. Because of the many possibilities of wettability alteration during core recovery and storage, reservoir cores are usually cleaned and restored prior to running displacement tests. After LK 2 was cleaned by the alternate flow of toluene and methanol, an initial water saturation of 11% was established and the core was aged at 75 °C. The core cleaning procedure does not necessarily result in the core being completely free of adsorbed hydrocarbons. Cycles of seawater flooding were performed at 60 °C without cleaning or restoration between the cycles. The core was highly friable and was handled with care to minimize the loss of sand grains. Once mounted, the core was not removed from the core holder during the course of the tests. Recovery, expressed as a percentage of OOIP, showed a consistent increase with each cycle (see Figure 2a). Values of initial brine saturation, expressed as a percentage of rock pore volume (PV) oil recovery, $R_{wf(PV)}$, and residual oil, S_{or}, at 6 PV injected (by either interpolation or, in some cases, minor extrapolation of the recovery curves), are shown in Figure 2b.

Berea BS 2: Refined Mineral Oil. For core BS 2, 4 cycles of flooding with seawater were performed for recovery of LVO and HVO (see Figure 3a). In preparation for cycle 1, an initial water saturation of 23.1% was established by porous-plate displacement of brine by air followed by saturation with LVO. The waterflood recovery curve showed a clean breakthrough, except for very slight later production. For cycle 2, the core was flushed with the LVO and an initial water saturation of 23.8% was established before waterflooding. Cycle 2 closely reproduced cycle 1.

The residual LVO remaining after cycle 2 was flushed with HVO mineral oil, and an initial water saturation of 24.5% was established. Waterflood recovery for the HVO (cycle 3)

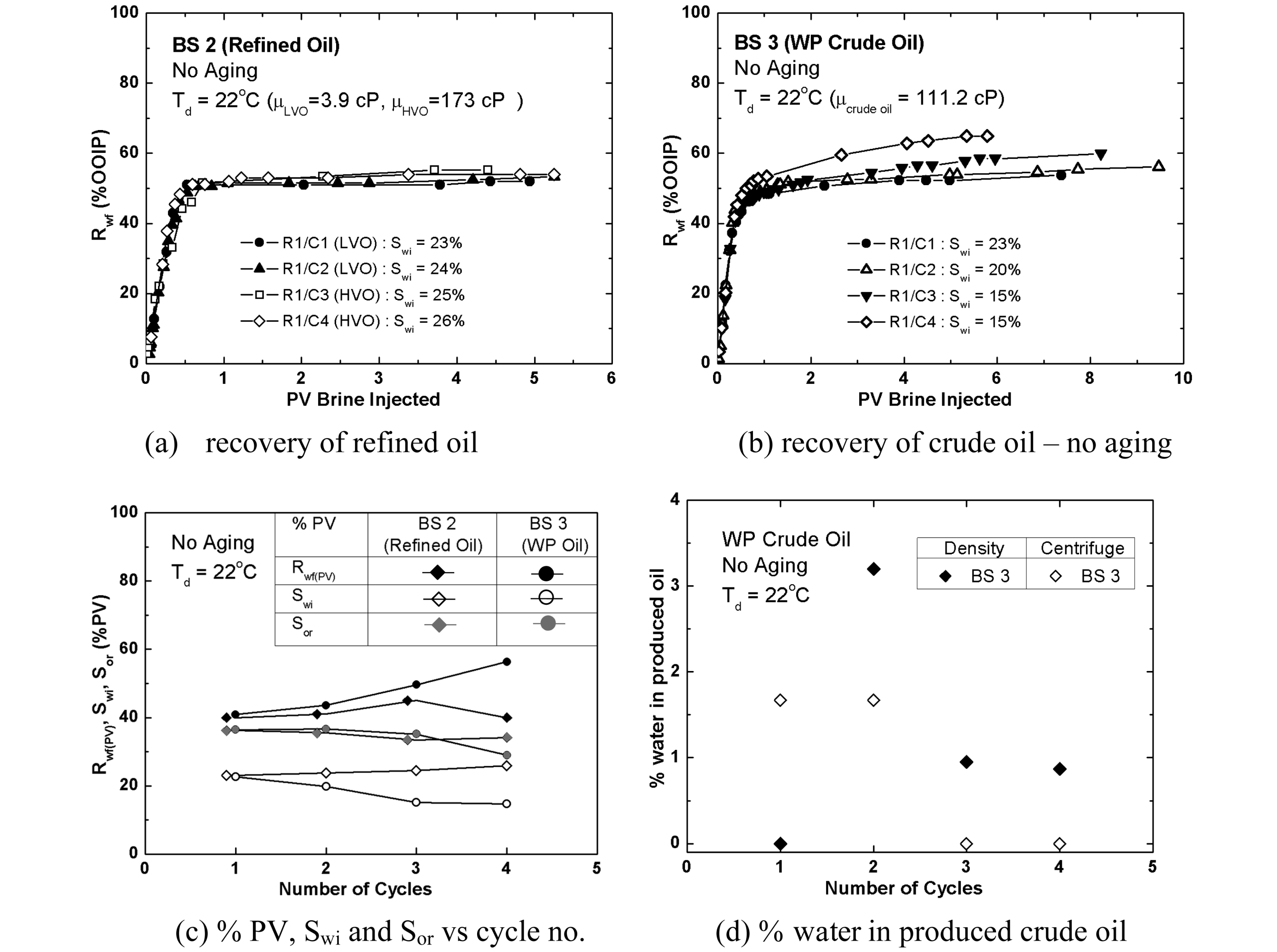


Figure 3. Oil recovery for sequential seawater floods at ambient temperature for low- and high-viscosity mineral oil and crude oil without aging.

fell close to that for the light oil. Cycle 4 (S_{wi} = 25.9%) with HVO gave close reproducibility of the cycle 3 recovery curve.

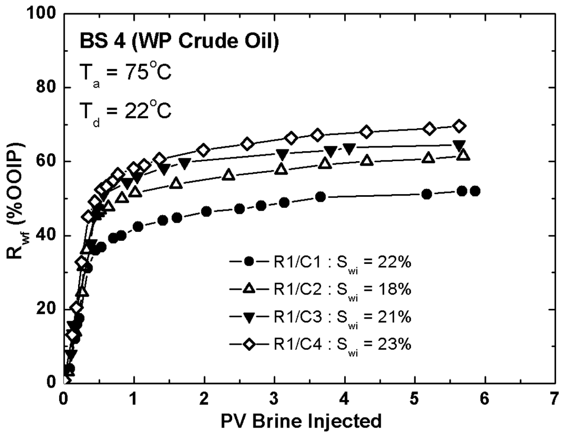
The reproducibility of the results indicates that the basic volumetric material balances used to determine saturation changes were satisfactory. The reproducibility is consistent with results for recovery of mineral oil at elevated temperature reported previously by Tang and Morrow.[16] The values of viscosity of the mineral oil cover the values of viscosity of the WP crude oil for ambient and elevated temperature.

Berea BS 3: No Aging, with All Cycles at Room Temperature. Recovery of crude oil was tested for BS 3. The core was not aged at elevated temperature, and injection of brine was started within 1 h of establishing an initial brine saturation of 23% by flow of crude oil. Recovery for cycle 2 was only slightly higher than for cycle 1. Recovery for cycle 3 showed an increased recovery with extended flooding, and cycle 4 showed a significantly higher increase in recovery (see Figure 3b). This behavior indicates that the contact time with the crude oil, even at ambient temperature, causes significant change in the wettability of the non-aged core. A comparison of the initial water saturation, oil recovery (percentage of PV), and residual oil versus the cycle number is presented in Figure 3c for mineral oil and crude oil recovery at ambient temperature. The amount of brine in the oil was less than 2% of the oil volume, except for one case given by density measurement (Figure 3d).

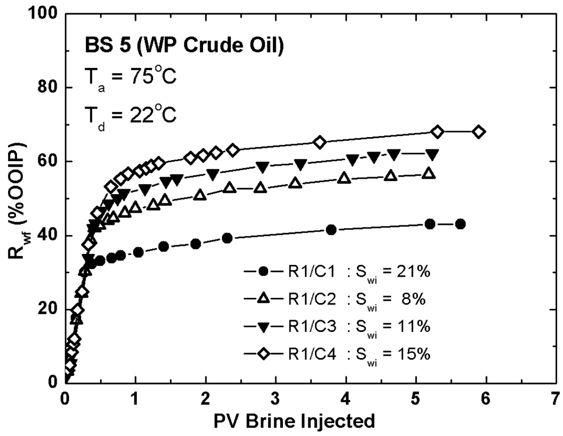
Berea BS 4 and BS 5: Aging at Elevated Temperature, with Waterfloods at Room Temperature. Berea sandstone BS 4 was aged at elevated temperature and tested at ambient temperature. Results are shown in Figure 4a for four sequential waterfloods. A consistent trend of the increase in recovery with each cycle was obtained.

A second set of four sequential waterfloods was run on core BS 5, with most features of the procedure for BS 4 repeated, except that, after cycles 1 and 2, the core was left at residual oil for about 12 h to test the robustness of the residual oil saturation when flooding was continued. Only a very slight amount of additional oil was produced after the waiting period. Results for core BS 5 are presented in Figure 4b. As for BS 4, the results show a consistent trend of increase in recovery, expressed as a percentage of OOIP, with each cycle.

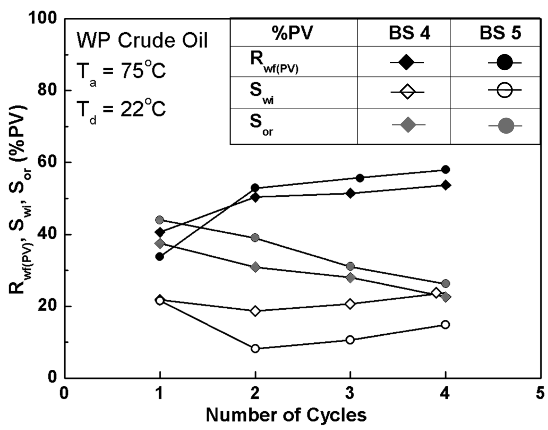
Trends for BS 4 and BS 5 of the initial water saturation, oil recovery (percentage of PV), and residual oil versus the cycle number are compared in Figure 4c. The initial water saturation established for the second cycle was much lower for BS 5 than BS 4. Otherwise, the overall trends for the two tests are in good agreement. Breakthrough recovery showed a marked increase for the second cycle for both cores. The difference between aging at elevated temperature and simply displacing the crude oil without the aging step before displacement at room temperature can be seen from a comparison of results for BS 3 in Figure 3c to those in Figure 4c. An increase in oil recovery for the non-aged core BS 3 for consecutive floods was much less than for BS 4 and BS 5. The amount of brine in the produced oil because of emulsification for BS 3 and BS 4 was always less than 2% (see Figure 4d).



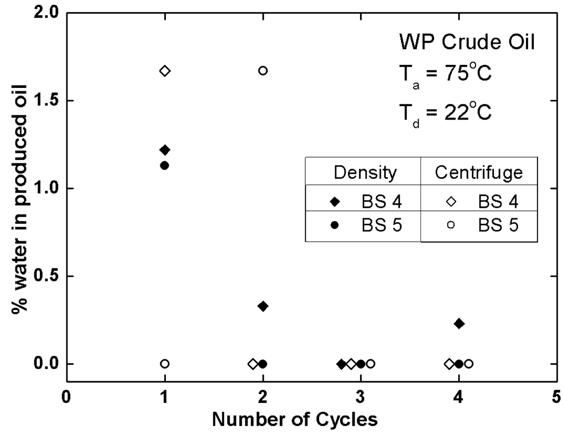
(a) oil recovery - BS 4



(b) oil recovery – BS 5



(c) % PV, S_{wi} and S_{or} vs cycle no.



(d) % water in produced crude oil

Figure 4. Recovery of crude oil (μ = 111.2 cP) for sequential seawater floods of duplicate sandstone cores at ambient temperature after aging at 75 °C for 14 days.

Berea BS 6 and BS 7: Aging and Waterflooding at Elevated Temperature. Results for duplicate tests of recovery of crude oil by sequential flooding at 60 °C for duplicate Berea sandstone cores BS 6 (three cycles) and BS 7 (four cycles) show increased recovery for consecutive cycles (panels a and b of Figure 5).

Both data sets showed trends of an increase in the percentage of PV oil recovery for consecutive cycles (Figure 5c). Trends in initial water saturation and residual oil are also shown in Figure 5c. For BS 6, the initial brine was 27, 21, and 25% for consecutive cycles, whereas for BS 7, S_{wi} fell from 23% by about 3% for each following cycle. The volume of produced oil increased from one cycle to the next for both cores (Figure 5c).

The average volume of brine in the produced crude oil because of emulsification was about 2.5% of the produced oil for BS 7 but was either 0% or very small for BS 6 (see Figure 5d).

Limestone. Oolitic limestone outcrop cores were aged and flooded at elevated temperature. Results for cores identified as EdGc 1, EdGc 2, EdGc 3, and EdGc 4 are shown in panels a, b, c, and d of Figure 6, respectively. A sequential increase in recovery (percentage of OOIP) was observed for three of the four cores. For core EdGc 2, the recovery decreased for the second cycle and the third cycle regained the cycle 1 recovery curve.

Plots of the initial water saturation, oil recovery (percentage of PV), and residual oil versus the cycle number are shown in Figure 7a. Overall trends for the limestone cores are in reasonable agreement, except for EdGc 2. The initial brine saturations for the second cycle decreased relative to the first and third cycles, except for core EdGc 2. The permeability of EdGc 2 was about double that of the other cores, indicating that it may have an atypical pore structure, such as fractures.

Results of tests for the presence of brine in the produced oil for the four limestone cores are shown in Figure 7b. For the second and third cycles, the content of emulsified brine in the produced crude oil for core EdGc 2 (about 6.5%) was much higher than for all of the other tests with limestone and sandstone.

Comparison of Sandstone and Limestone. A comparison of oil recovery (percentage of OOIP) at elevated temperature for two outcrop sandstone cores and the three outcrop limestone cores that gave consistent behavior (EdGc 2 is excluded) are presented in Figure 8a. The corresponding residual oil saturations are shown in Figure 8b. Although the sandstone and limestone cores are very different in mineralogy and pore structure, the overall trends are comparable.

Discussion

Injection of low-salinity brine at the outset of a waterflood has been referred to as secondary-mode low-salinity waterflooding.[17] One motivation for this study was to examine

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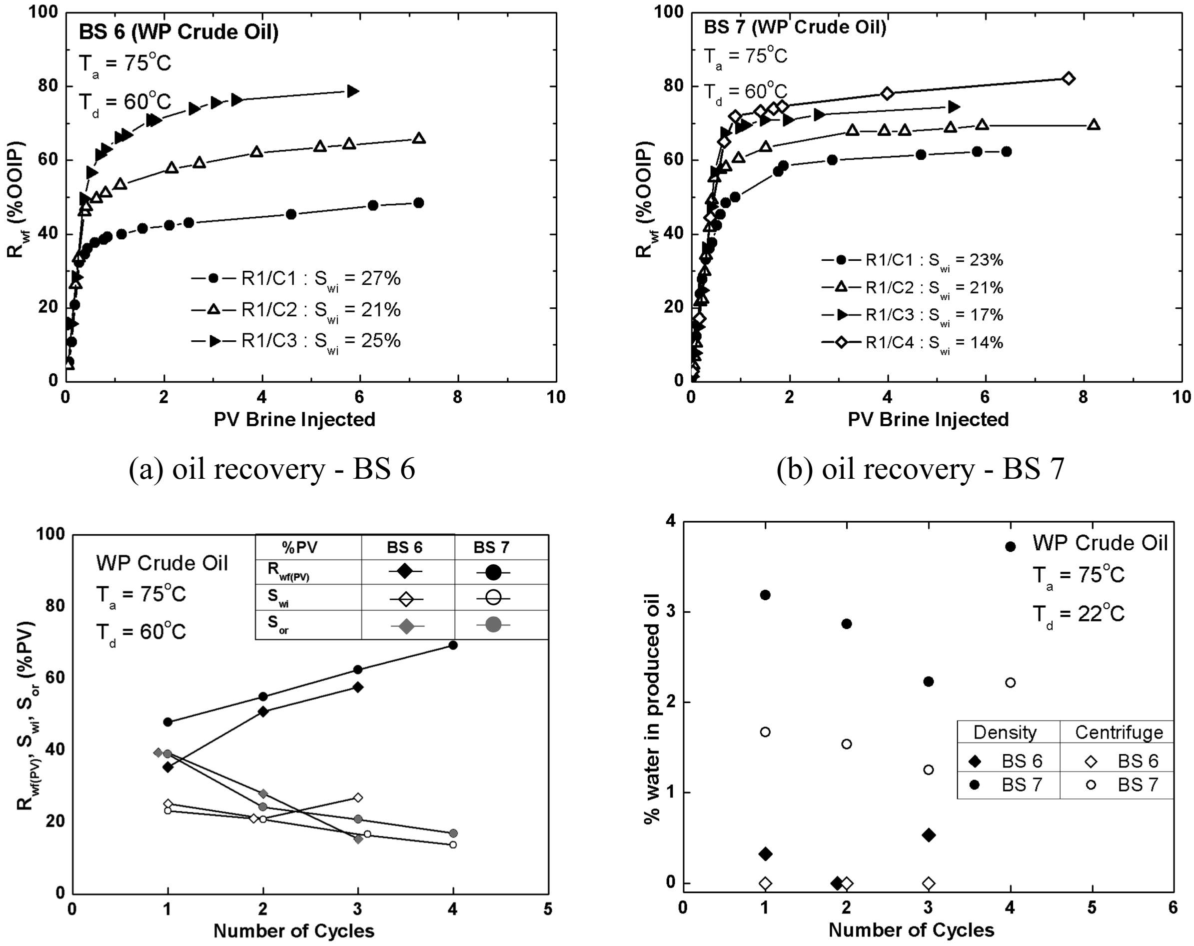

(a) oil recovery - BS 6

(b) oil recovery - BS 7

(c) % PV, S_{wi} and S_{or}

(d) % water in produced crude oil

Figure 5. Recovery of crude oil (μ = 111.2 cP) for sequential seawater floods of duplicate sandstone cores at elevated temperature (60 °C) after aging at 75 °C for 14 days.

baseline results for oil recovery against which the benefits of low-salinity flooding can be assessed. Improved waterflood recovery by injection of dilute brine was demonstrated by core floods on duplicate outcrop sandstone cores using procedures comparable to those of the present work.[18] The results in Figure 1a show the uncertainties that can arise for consecutive flooding of a single core with the change in salinity, even though the core was restored between each test. The results in Figure 1b show changes in displacement behavior that can result from changes in salinity without restoration between floods. For cyclic floods, even without the change in salinity, the results of the present study mostly show increased recovery for consecutive floods. For assessment of low-salinity flooding applied at the outset of waterflooding, comparative tests should, where possible, be made on duplicate core plugs to determine the amount of increased oil recovery that can be safely ascribed to low-salinity flooding.

Previously reported data also indicate that the outcome of a mixed-wet core flood of individual cores is affected by the previous test for a wide range of circumstances.[14] For sequential floods, there is obvious possibility for cumulative uncertainties in the volumetric balances mainly used to determine the initial brine and residual oil saturations. Reproducibility of crude oil recovery for duplicate core floods is usually within ±1.5%. Recovery of mineral oil was shown to be closely reproduced for four cycles of flooding, even after increasing the oil viscosity by well over an order of magnitude after the second cycle. For the presented results, the increases in oil recovery, expressed as a percentage of OOIP or as a percentage of PV, are well above the reproducibility that would be expected if sequential flooding had no effect on recovery. Confirmation of the volumetric balance has been provided by *in situ* measurement of oil saturation by nuclear magnetic resonance imaging and tracer test.[19]

The most readily identifiable change in initial conditions for each sequential flood is in the initial water saturation. Previous studies of spontaneous imbibition behavior show that the initial water saturation and the associated wettability pattern determined by the distribution of oil in contact with the rock surface at the time of aging with crude oil have a dominant effect on wetting properties.[4,6,7] A variation in initial water saturation was obtained in the present work, even though the rate of oil flooding used to establish the initial water saturation was not changed. For the second and subsequent cycles, the initial water is established by injection of oil into cores that contained residual oil. For most of the tests, the initial water saturation decreased after the first cycle but then

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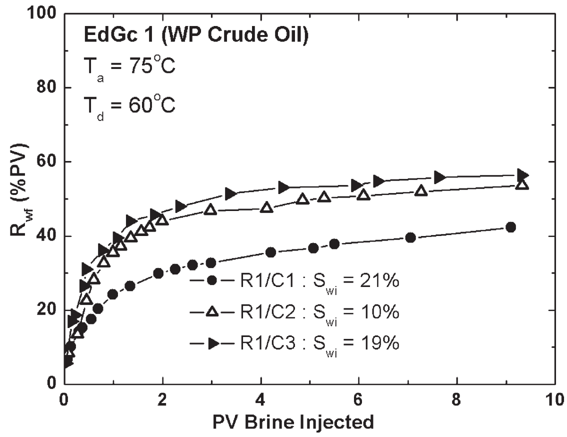
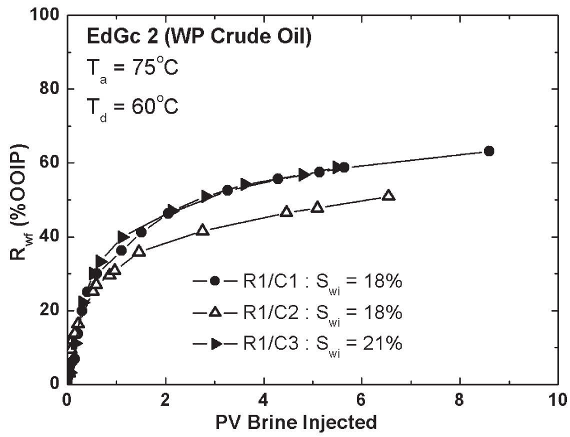
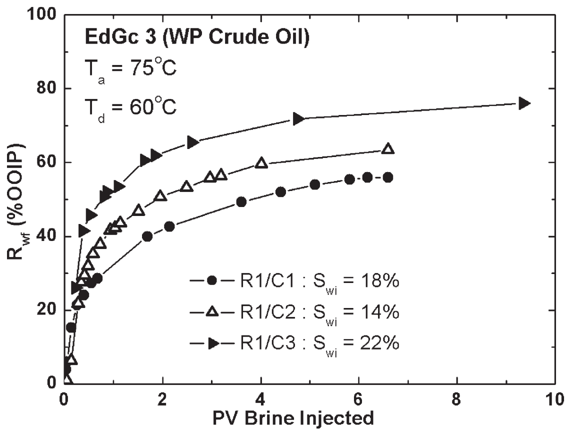


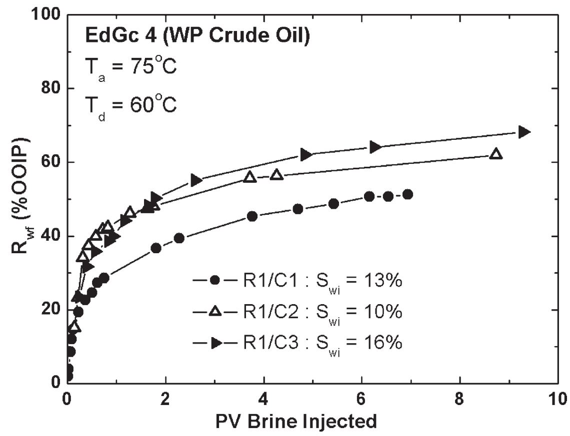
(a) oil recovery - EdGc 1



(b) oil recovery - EdGc 2

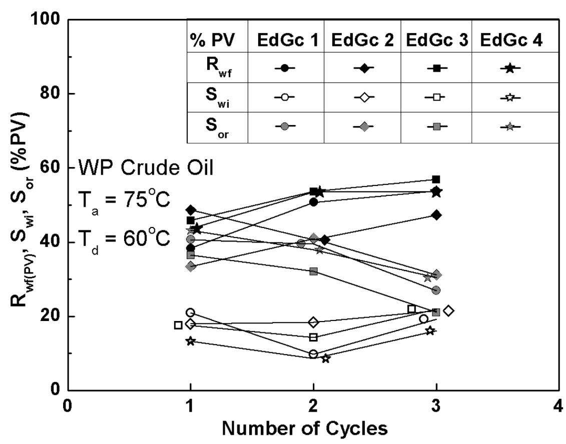


(c) oil recovery - EdGc 3

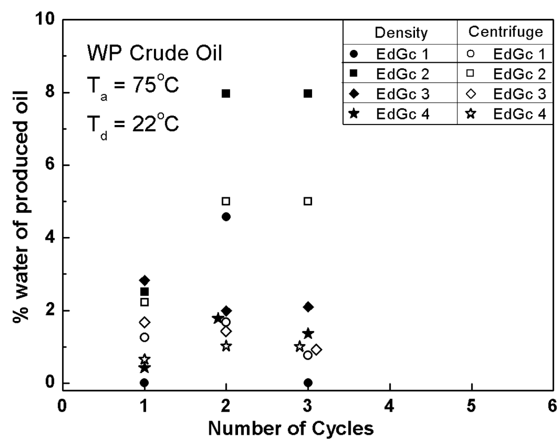


(d) oil recovery - EdGc 4

Figure 6. Recovery of crude oil (μ = 111.2 cP) for sequential seawater floods of four duplicate limestone cores at elevated temperature (60 °C) after aging at 75 °C for 14 days.



(a) % PV, S_{wi}, and S_{or}

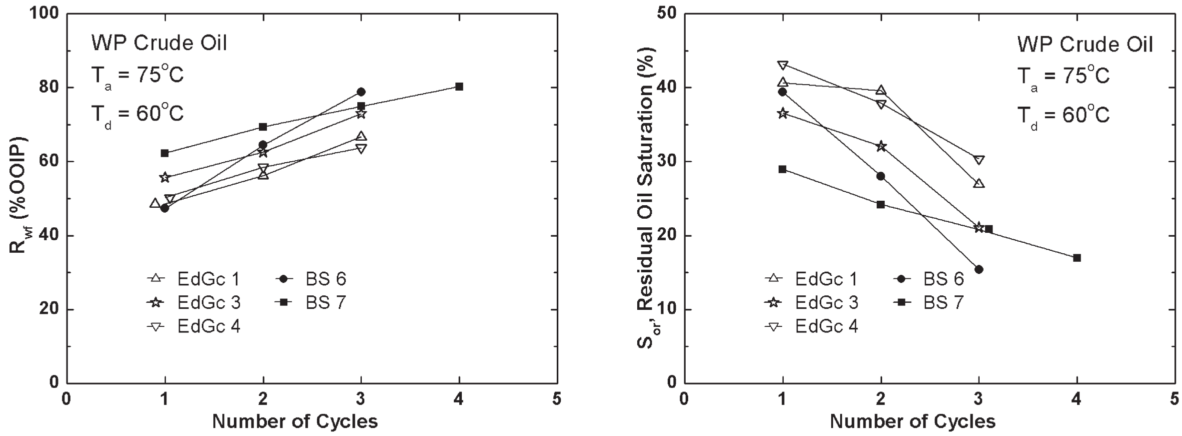


(b) % water in produced crude oil

Figure 7. Comparison of the oil recovery (percentage of PV), S_{wi}, S_{or}, and percentage of water in produced oil for four duplicate limestone cores.

increased for later cycles. The cause and consequences of the variation in initial water saturation and its microscopic distribution are topics that need further investigation.

Checks for the possible contribution of emulsified brine to increased oil-phase production showed that the water content was usually less than about 2% of the oil volume. Although the data on the water content is scattered, the formation of water-in-oil emulsions is symptomatic of the displacement mechanism and points to the complexity of the process by which crude oil is recovered by waterflooding under mixed-wet conditions.



(a) % PV at 6 PV injected (b) % S_{or} at 6 PV injected

Figure 8. Comparison of recovery of crude oil and residual oil saturation for sequential seawater floods of two duplicate sandstone and three duplicate limestone cores at elevated temperature (60 °C) after aging at 75 °C for 14 days.

The potential exists for stabilization of emulsions by natural surfactants in the crude oil and also by fine particles,[20] particularly if they are mixed-wet.[21] Many aspects of the formation of emulsions stabilized by either surfactants or solid particles have been studied in detail. However, it has been pointed out that little is known about emulsions that are stabilized by a combination of particles and surface-active materials,[22] as may be the case for brine-in-crude-oil emulsions. Even though waterflooding has been applied for over 80 years and is by far the most widely used technique for improved oil recovery, much remains to be learned about the interfacial and colloidal phenomena that control the recovery mechanism.

Conclusions

(1) Sequential waterflooding, a term applied to floods run without a change in salinity and without cleaning or re-aging between cycles, gave increased recovery of an asphaltic crude oil from one cycle to the next, for both reservoir and outcrop sandstone and for three of four tested outcrop limestone cores. (2) Increases in recovery for sequential floods of sandstones were observed for recovery of crude oil at ambient temperature for a core that had not been aged and for cores aged at elevated temperature, followed by sequential floods at either ambient or elevated temperature. (3) For limestone cores aged with crude oil, an increase in recovery for sequential floods at elevated temperature was observed for three of four cores. (4) Increases in recovery for sandstone and limestone for the same preparation and flood conditions that included high-temperature aging and displacement were comparable. (5) For consecutive cycles of waterflooding before and after low-salinity water flooding, the original recovery curve for high-salinity flooding was not regained, either with or without cleaning between cycles. (6) Assessment of the benefits of increased waterflood recovery by injection of low-salinity brine at the outset of waterflooding should be made with duplicate core plugs.

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