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EVALUATION OF RESERVOIR WETTABILITY AND ITS EFFECT ON OIL RECOVERY

Quarterly Technical Progress Report
October 1, 1998-December 31, 1998

By
Jill S. Buckley

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New Mexico Institute of Mining & Technology
Socorro, New Mexico

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Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Purna Halder, Project Manager
National Petroleum Technology Office
P.O. Box 3628
Tulsa, OK 74101

Prepared by
New Mexico Institute of Mining & Technology
Petroleum Recovery Research Center
Kelly Building
801 Leroy Place
Socorro, NM 87801

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Objectives

This project has three main goals. The first is to achieve improved understanding of the surface and interfacial properties of crude oils and their interactions with mineral surfaces. The second goal is to apply the results of surface studies to improved predictions of oil production in laboratory experiments. Finally, we aim to use the results of this research to recommend ways to improve oil recovery by waterflooding.

In order to achieve these goals, the mechanisms of wetting alteration must be explained. We propose a methodology for studying those mechanisms on mineral surfaces, then applying the results to prediction and observation of wetting alteration in porous media. Improved understanding of the underlying mechanisms will show when and how wettability in the reservoir can be altered and under what circumstances that alteration would be beneficial in terms of increased production of oil.

Summary of Technical Progress

1. Crude Oil/Brine/Solid Interactions

The standard suite of wettability tests is being applied to an expanding number of crude oils. Studies of asphaltenes are also progressing. Ongoing work in this area will be summarized in future quarterly reports.

2. Wetting Evaluation: Crude Oil-Brine-Mica Interactions: Drainage of Initial Brine

Introduction

A test for evaluating interactions between crude oils and solid surfaces—with or without brine—was first described in 1992.[1] Since then, the test protocol has evolved as experience has accumulated with a wide range of crude oils[2-5] and with different mineral surfaces.[6]

The adsorption test protocol was designed to capture key elements of crude oil interactions with mineral surfaces in an oil reservoir. Reservoir wetting is now considered to be the result of adsorption of materials from crude oil onto portions of the solid surface. The important roles played by connate brine—which can enhance some adsorption interactions while it shields other parts of the porous medium from contact with the oil—dictate that water, oil, and mineral must all three be considered as important variables in these tests.

There is as yet no one, irrefutable method for evaluating crude oil/brine/ rock (COBR) interactions. Instead, we have developed a consistent protocol that permits comparison of different oils, brines, and minerals under similar test conditions. The details of the procedure are somewhat arbitrary. Nevertheless, for comparative purposes it has been useful to have a standard evaluation procedure. The most important features of the standard protocol are outlined in **Fig. 1.**

(1) Cleave mica sheets to produce clean surfaces
(2) Equilibrate with brine
(3) Drain by one of several methods
(4) Age in crude oil
(5) Rinse with toluene
(6) Measure decane/water contact angles

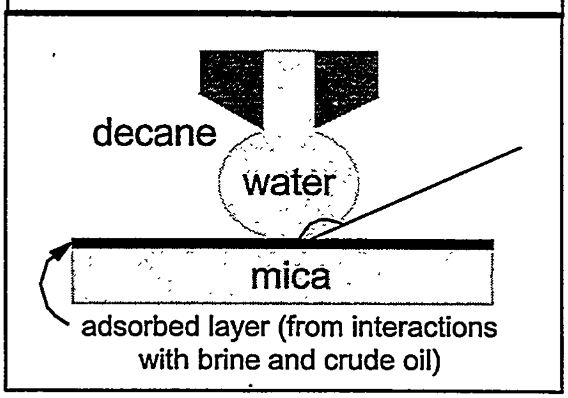

Figure 1. Outline of the standard adsorption test protocol and illustration of water-advancing contact angle measurement on brine and oil-treated surface.

The effects of variations in many of the steps in this protocol have been examined previously. Little difference was found between quartz glass and soft glass.[7] Different minerals, with varying surface charge and surface chemistry, are important variables in COBR interactions.

Differences between glass and mica were shown by Liu and Buckley.[6] The effects of pretreatment with brine, oil composition, and aging conditions of time and temperature are also variables that have been extensively studied (e.g. ref. 4). Removal of bulk oil is a crucial step. Rinsing with a poor solvent that precipitates asphaltenes from the oil can make surfaces more oil-wet.[3] Details of the contact angle measurements with probe fluids, after removal of bulk oil, show smaller effects of the order of measurement (water advancing or receding measured first) or measuring technique. Dynamic measurements using a Wilhelmy plate compare reasonably with static captive drop observations.[7]

One step that has not yet received sufficient attention is the treatment of the surface after equilibration in brine and before exposure to oil. In a recent paper,[8] Yang *et al.* adopted a protocol similar to that described above, but with one potentially important difference. To accelerate drainage of brine from the surface, they imposed a centrifugal field. Whether variations in the extent of water drainage prior to exposure of a surface to crude oil affect the adsorption processes and thus the subsequently measured contact angles is explored in this report.

Experimental Methods

Materials

Two crude oils were selected for comparison: Mars-97 crude oil, which produces fairly water-wet mica surfaces,[5] and C-98 crude oil, which can produce more oil-wet conditions. **Table 1** lists physical properties of these two crude oils.

Table 1. Crude oil properties.

Property	C-98	Mars-97
Density @ 25°C (g / mL)	0.8706	0.8811
API Gravity	29.9	30.3°
Acid # (mg KOH/g oil)		0.368
Base # (mg KOH/g oil)	1.00	1.79
RI @ 20°C	1.4952	1.4950
P_{RI} with n-C_7	1.442	1.432
Asphaltene ppt with n-C_5 (wt%)	2.37	3.25
Asphaltene ppt with n-C_7 (wt%)	2.00	1.86

Brine compositions based on seawater were used in these tests. The composition of synthetic seawater (SSW) is given in **Table 2**. A dilution to 10% of these concentrations was made by adding distilled water to the 100% brine. The pH values of the 100% and 10% SSW brines were 6.71 and 5.84 respectively.

Table 2. 100% Synthetic Sea Water (SSW) Composition

Salt	Amount (g/L)
$NaHCO_3$	0.0382
Na_2SO_4	3.9163
$CaCl_2 \bullet 2H_2O$	1.4673
$MgCl_2 \bullet 6H_2O$	10.6395
$NaCl$	24.0047

HPLC grade toluene and *n*-decane were further purified chromatographically in a column of silica gel and alumina.

Procedures

Muscovite mica samples were cut into 1"x 0.3" strips. Clean surfaces were obtained by cleaving the mica strips between two pieces of adhesive tape. The freshly cleaved mica strips were equilibrated with brine for 24 hours, drained, then transferred to a crude oil and aged for 24 hours (t_a=24 hrs) at an aging temperature of 25°C (T_a=25°C). After aging in oil, the mica samples were removed from the crude oil, rinsed with toluene, and immersed in decane. Contact angles were measured by the captive drop technique using a contact angle goniometer (Gaertner Scientific Corp.) to observe the water/oil contact line for water advancing and receding on mica.

Three methods of drainage were compared: (1) drainage of bulk water in air, (2) centrifuging in air, and (3) centrifuging in oil. The first method has been the standard procedure. After equilibration with brine, some bulk water is allowed to drain in air while the mica sample is held with forceps. Drops of water are removed by the wicking action of a clean laboratory paper towel. Using this procedure, an unknown amount of bulk water remains on the surface when it is immersed in oil. Some time is required for that water to redistribute in accordance with the surface properties of solid and oil. Remaining bulk water is indicated by portions of the surface on which a water drop spreads. After several days, the effects of the bulk water are usually less evident than they are initially.[9]

Removing bulk water by centrifugation may provide a more uniform, thinner film of water as the initial condition of the surface when first exposed to oil. If water can redistribute, however, the results should eventually converge, regardless of the amount of water present initially, although less time might be required to redistribute water if some of it is removed by centrifugation. In the second series of tests, mica samples were centrifuged in air for approximately one minute at 1000 RPM, followed by immersion in crude oil. Finally, a third series of mica samples were removed from brine, immersed in crude oil and centrifuged in that oil for 15 minutes at 1000 RPM, after which they were allowed to age for the remainder of the 24-hour aging period.

After 24 hours in oil, samples were removed, rinsed first with toluene, then with *n*-decane, and placed in a quartz optical cell containing purified *n*-decane. Contact angles were measured with distilled water and *n*-decane as probe fluids. The test conditions and average water-advancing angles on treated surfaces are summarized in **Table 3.**

Table 3. Summary of drainage tests
(t_a=24hrs, T_a=25°C)

Crude Oil	Brine	Drainage Process	θ_A
Mars-97	100% SSW	(1) Drain in air*	34.0 ± 7.0
Mars-97	100% SSW	(2) Centrifuge in air	31.3 ± 6.1
Mars-97	100% SSW	(3) Centrifuge in oil	22.4 ± 4.7
C-98	10% SSW	(1) Drain in air	95.3 ± 23.8
C-98	10% SSW	(2) Centrifuge in air	129.6 ± 12.0
C-98	10% SSW	(3) Centrifuge in oil	121.5 ± 8.4

*data from ref. 5

Results and Discussion

There is typically considerable scatter in the contact angles measured with water and decane on surfaces that have been exposed to crude oil. Scatter is particularly apparent when aging times are short (less than a few days at room temperature or a few hours at elevated temperature). In the results reported in Table 3, standard deviations range from 7 to 25% of the average water advancing contact angles.

In **Fig. 2**, results from the standard drainage method are compared to samples from which 10% SSW was removed by centrifuging under C-98 oil. Two identically treated mica surfaces were tested using each drainage method. Six to eight drops were tested on as many different positions on each piece of treated mica and measurements were made on either side of the two-dimensional projection of each water drop. Figure 2a shows that significant scatter is associated with the standard drainage method. Discrepancies are smaller for sample 2 than for sample 1, but the average water-advancing contact angles on the two samples are comparable (93° and 98°, respectively). Centrifuging under oil produced more uniformly wetted surfaces and higher values of water-advancing contact angles, as shown in Fig. 2b (averages are 117° and 127°).

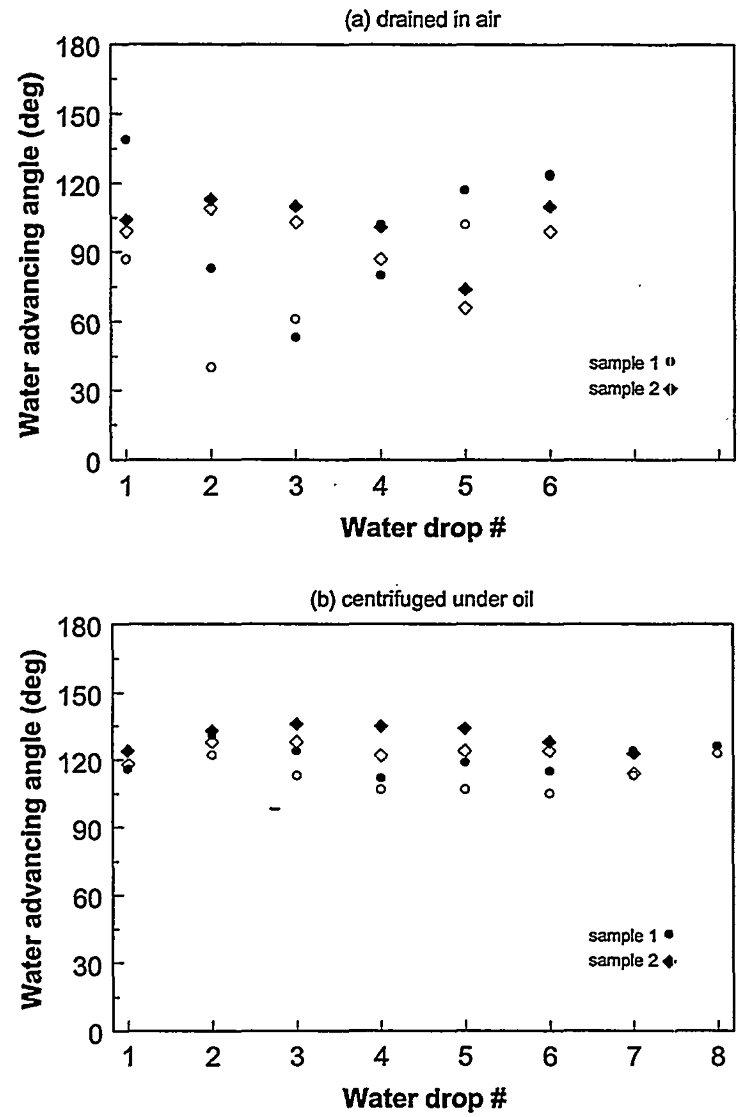

Figure 2. Contact angles measured on mica treated with 10% SSW and C-98 crude oil (t_a=24hrs; T_a=25°C). (a) Drained in air and (b) Drained under oil in centrifuge. Closed symbols are measured on the left side of the drop image, open symbols are from the right side.

A comparison of the average water-advancing angles for all the tests is shown in **Fig. 3**. All three methods lead to similar results for both the water-wet Mars-97-treated mica and the more oil-wet C-98-treated samples. In all cases, standard deviations are lowest for the samples centrifuged under oil (Table 3). Previous experience suggests that with extended aging time in oil, wetting of samples prepared with the standard drainage method would become more uniform, but centrifuging under oil appears to accelerate the redistribution of water without biasing the results toward more oil-wet behavior. Centrifuging in air, included here for comparison, is not recommended because it provides an opportunity for evaporation that changes the brine composition and might even result in deposition of solid salt crystals on the surface.

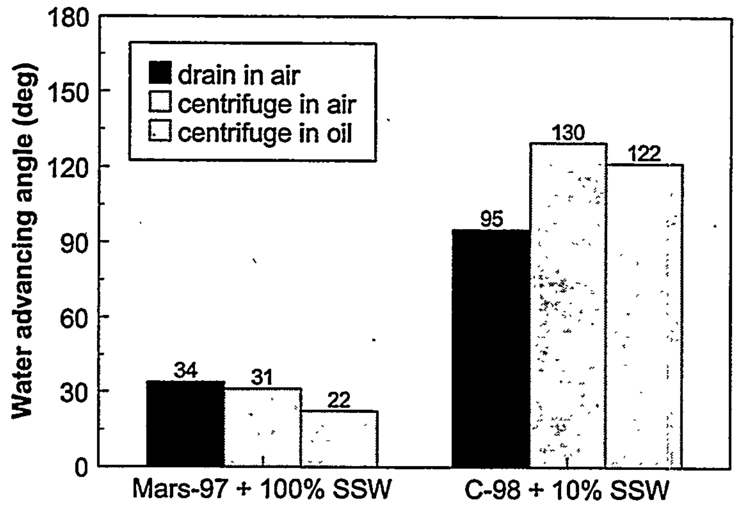

Figure 3. Comparison of average contact angles measured for two combinations of brine and oil using three different methods of draining the brine prior to oil exposure.

Conclusions and Recommendations

The amount of water remaining on a wet surface when it is immersed in oil can influence the COBR interactions to some extent, especially if aging time in oil is brief and the aging temperature is low. Removal of the brine by centrifuging under oil, as suggested by Yang *et al.*,[8] accelerates the redistribution of water and leads to less ambiguity in the wetting conditions resulting from COBR interactions. For the conditions tested, centrifuging under oil did not appear to bias the resulting surface properties toward more oil-wet conditions. It is therefore recommended that removal of brine by centrifuging samples under oil be adopted as the standard procedure for adsorption tests of COBR interactions.

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