# WETTABILITY AND WATER-OIL DISPLACEMENT INVESTIGATIONS FOR SOME HIGH PERMEABILITY TURBIDITE RESERVOIRS

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## ABSTRACT

Investigations have been conducted to evaluate water-oil wetting properties and associated water-oil displacement characteristics of three deepwater oil reservoirs. Two contain light oil and one has medium gravity crude. The channel deposit pay zones are essentially clay-free, consisting of more than 95% quartz.

Wettability studies involved fundamental geochemical and contact angle measurements in addition to direct evaluations of core samples. The task was complicated by widespread contamination of the high permeability (typically 1-4 darcy), poorly consolidated core by synthetic oil based mud used for drilling. This caused the wettability and displacement properties measured on core material preserved in its retrieved state to be erroneous, a well-known problem.

The engineering requirement was to define realistic water-oil flow properties, particularly displacement efficiency and terminal relative permeability information, for timely reservoir predictions impacting waterflood project design and overall development decisions. Obtaining reliable SCAL results required us to develop effective core cleaning and test approaches for these deepwater channel sands.

Different core cleaning methods were tested. A relatively simple procedure involving sequential extractions with two low boiling point solvents proved to be effective. It was found that wettability determinations on core plugs by Amott/USBM methods were sometimes inconclusive, due to the high permeability of the rock and the need to encase samples with sleeves and screens. Mechanistic wettability evaluations were helpful in providing complementary information on likely reservoir wetting properties. These studies also gave useful support on mud contamination, core cleaning, and wettability restoration issues.

From the mechanistic studies, the reservoirs are expected to be preferentially water-wet. Ambient condition tests with cores cleaned with a series of solvents most closely approached weakly water-wet conditions. Oil recovery (microscopic displacement efficiency) in these cores was in the range of 65% to 70% OOIP (residual oil saturations of 25% to 30% PV) and water relative permeability endpoints were about 0.3 (relative to Koil at Swi). Continuing core studies focus on additional evaluations with restored-state samples.

## INTRODUCTION

This paper reports results of investigations to define realistic water-oil displacement properties in high permeability, often unconsolidated, deepwater sands from three reservoirs in a block under development by ChevronTexaco and Partners. The reservoirs are principally massive sands that, although structureless, usually have poorly-sorted grain content. There is evidence of extensive contamination by invasion of synthetic oil-based mud filtrate, including the occurrence of high "oil" saturations (over 65%PV) in core from below oil-water contacts and extensive suppression of UV fluorescence over cored oil zones in the massive sands (for which the permeability generally exceeds one darcy).

It is well recognized that synthetic oil-based muds, now in common use because of their reliability for drilling and environmental attractiveness,[1] are deliberately formulated with oil-wetting and emulsifying agents. The surfactants obviously deviate from the core analyst's ideal of using bland mud coring formulations. Even low invasion coring technology might not completely eliminate contamination problems for these high-permeability sands. It should be noted, however, that the cores available for this study were obtained with conventional synthetic oil-based muds, not with specially-designed low invasion muds. Initial displacement tests raised questions about the wetting condition of the cores available for this study. Subsequent core tests were conducted to evaluate the wettability of cores as received and after cleaning and restoration.

A mechanistic study of wetting alteration was designed to test crude oil samples obtained from the three deepwater reservoirs for their tendency to alter wetting of silicate surfaces. For a given mineral surface, the extent of wetting alteration is a complex function of the polar components in the crude oil, asphaltene stability, and the composition of the aqueous phase with which both mineral and oil are in contact. Although no direct relationship between contact angles measured on smooth surfaces and wetting conditions in cores has been established, such tests can be used to compare crude oils from different sources and to examine the magnitude of potential wetting alteration by oil, mud filtrate, and various cleaning techniques.

## EXPERIMENTAL MATERIALS AND METHODS

### Oil Samples

Five samples of dead oil from the three reservoirs were used in the mechanistic wettability study; chemical and physical properties are summarized in Table 1. Refractive index (RI) was measured at 20°C using an automatic refractometer (Index Instruments GPR11-37). RI at the onset of asphaltene flocculation ($P_{RI}$) was measured with n-heptane. Together RI of the oil and $P_{RI}$ provide a measure of asphaltene stability. None of the oils in this study falls into the unstable range. The amount of asphaltene is measured by addition of 40 ml of n-heptane to 1 g oil. Acid number is measured according to the ASTM-recommended method;[2] base number measurements use the method described by Dubey and Doe.[3] Oils from these three reservoirs are fairly typical in terms both of their asphaltene stabilities and acidic and basic characters. Oil samples 2b, 3b, Klearol (a 12cp refined oil), Isopar L (~1.5 cp refined oil), and decalin, were used in the core tests.

**Table 1.** Oil Properties

| | Oil 1 | Oil 2a | Oil 2b | Oil 3a | Oil 3b |
|---|---|---|---|---|---|
| **API gravity (°API)** | 37.1 | 18.9 | 19.1 | 34.0 | 31.6 |
| **Average MW (Daltons)** | 196 | 319 | | 216 | 241 |
| **RI at 20°C** | 1.4739 | 1.5287 | | 1.4779 | 1.4858 |
| **n-$C_7$ $P_{RI}$ (20°C)** | 1.426 | 1.432 | | 1.426 | |
| **n-$C_7$ asphaltenes (wt%)** | 1.33 | 3.52 | | 1.39 | 1.42 |
| **density at 20° C (g/cm$^3$)** | 0.8361 | 0.9374 | 0.9365 | 0.8515 | 0.8644 |
| **Acid #, $N_A$ (mg KOH/g oil)** | 0.50 | 2.44 | 2.55 | 0.21 | 0.05 |
| **Base #, $N_B$ (mg KOH/g oil)** | 2.67 | 5.19 | 5.66 | 2.30 | 2.50 |

## Mud Samples

Two samples, obtained from synthetic oil-base drilling muds (SBMs) used in the wells that produced Oils 2 and 3, were used in this study. One was a filtered "end of run" sample. The other was the supernatant from a centrifuged sample. They will be referred to as filtrate and centrifugate, respectively, although it is worthwhile to note that they are also from different sources originally, not simply from different separation processes.

## Brines

Test brines included two buffered NaCl solutions (pH 4, 0.01*M* NaCl and pH 8, 1*M* NaCl) and synthetic reservoir brines.

## Contact Angle Measurements

Based on previous studies,[4] mica was selected as the test surface, oils were tested with buffered solutions of NaCl designed to control stability of thin water films between solid and crude oil[5] as well as with synthetic reservoir brines. Tests proceeded through an established sequence of steps in which mica was exposed first to the buffer or brine, then to oil. Additional steps showed the effects of exposure to the drilling mud samples and the efficacy of several cleaning techniques. Contact angles were measured after removal of bulk crude oil using decane and water as probe fluids.

## Core Samples

Plug samples were stored in kerosene. Because the rock is poorly consolidated, test plugs were carefully drilled with nitrogen from the preserved whole core usually in a cooled or frozen state. Test plugs were subsequently packaged in tin sleeves and 120 mesh stainless steel end screens.

**Displacement and Imbibition Tests**

Displacement tests were carried out with selected 1½" diameter by 3" long horizontal plugs at the net effective stress representative of the specific reservoir, which varied from 1500psi to 2100psi. These tests included both unsteady-state relative permeability and floods to obtain terminal saturation and displacing phase permeability information without continuous monitoring of recovery and pressure history. Water (synthetic reservoir brine) injection rate usually approximated an initial gradient of 1psi/ft, similar to an average gradient in a reservoir flood. Upon flood-out (99.5% water cut), two or three "bump" (increasing displacement rate) steps were tested, at up to at least 3 times the original rate. The observed changes in remaining oil saturation and water relative permeability find use in defining sensitivity cases for reservoir simulation, as well as providing qualitative indicators of rock wetting preference. Relative permeabilities were derived using the standard JBN/Jones-Roszelle approach.

Core wettability was assessed by the USBM and Amott methods. Experimental details, which depended on whether or not the cores were consolidated, are discussed in more detail in the section on Core Wettability.

## RESULTS AND DISCUSSION

### Initial Tests of Core Samples As-Received

Cores were first flooded with dead crude oil at elevated temperature to define an effective permeability at initial conditions. A high-temperature constant rate waterflood was then performed, with a backpressure applied to avoid free gas in the system. Figure 1 shows relative permeability results obtained from an early test with core and crude oil from Reservoir 1, with high gravity oil. The effective oil permeability is only 35% of absolute permeability, suggesting contamination by invaded mud filtrate—likely including some relocation of initial water due to oil wetting of the rock. The relative permeability results show poor oil displacement efficiency. Furthermore, the large changes in saturation and water relative permeability seen to occur with bump tests are characteristic of end effects in an oil-wet system. Although the JBN analysis used is not strictly valid with large end-effects, poor overall waterflood efficiency is evident. Similar behavior was found in tests for Reservoir 2 (not shown), which has a medium gravity oil.

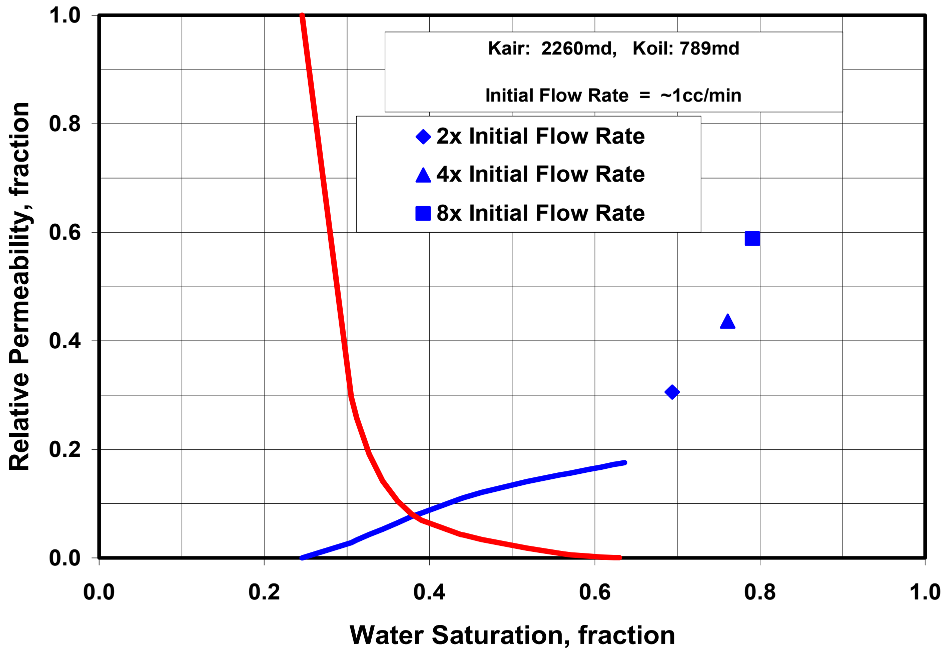



**Figure 1.** Water-oil Kr results for as-received samples measured with Reservoir 1 stock tank oil at elevated temperature.

## Baseline Tests of Crude Oil/Brine/Mica Interactions

Average advancing and receding contact angles, measured with a drop of water in at least 6 positions on samples exposed to brine for one day and to oil for 3 weeks, rinsed with toluene, and immersed in decane, are summarized in Fig. 2. Note that contact angles were measured through the water phase and that advancing and receding conditions are defined with respect to the water phase. Standard deviations were 1 - 6°, consistent with previous experience. Contact angles with all test brines were in the preferentially water-wet region ($\theta_A \leq 60°$). Previous experience (with angles measured for 78 different crude oils) has shown that water/decane values of $\theta_A$ measured on mica surfaces treated with pH 4 buffer range from a high of 155° to a low of 31° with a median value of 70° and a mean of 81° ± 35°. All of the oils in this study are at the lower end of the scale in terms of their wettability-altering tendency on negatively charged silicate surfaces. These results suggest that the oil-wet conditions in the cores as received may not accurately represent the wetting conditions of these reservoirs.

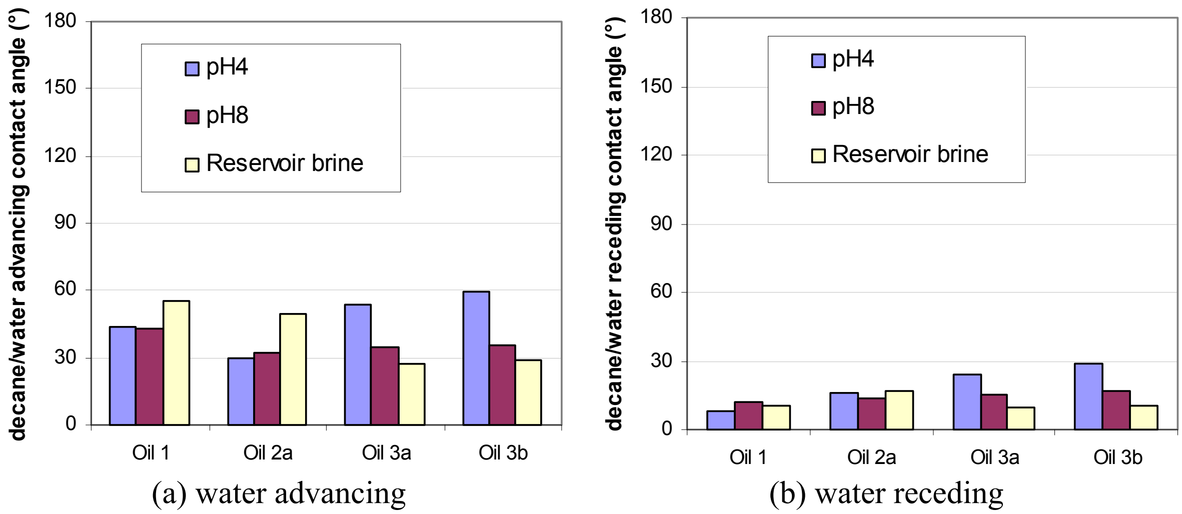
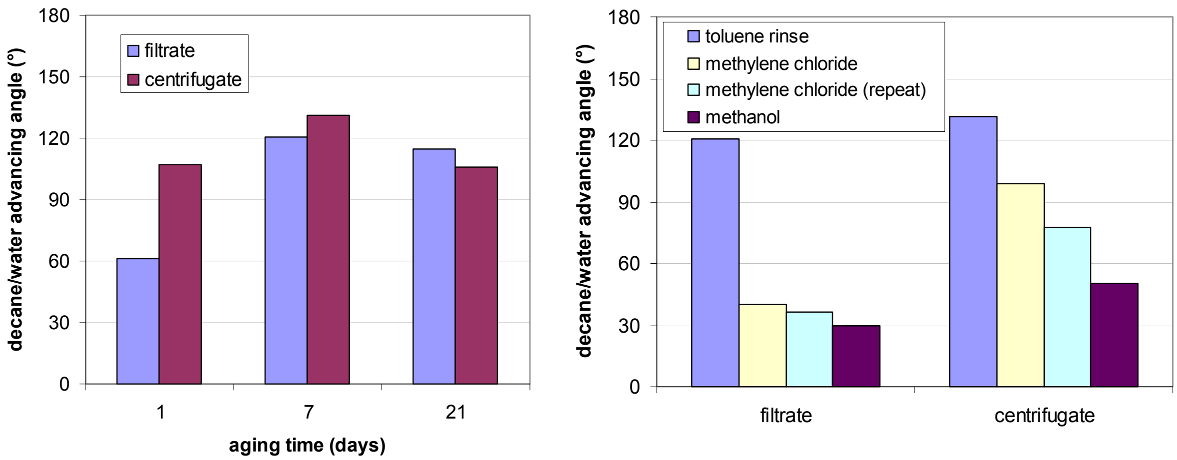



**Figure 2.** Contact angles between probe liquids (decane and water) on mica surfaces aged for 21 days in Oils 1, 2a, 3a, and 3b.

**Wetting of Mica Exposed to SBM Drilling Mud Fractions**

The highest water-advancing angles measured in this study were produced by aging clean, dry mica surfaces in SBM filtrate or centrifugate. Figure 3a shows that 7 days of aging in these mud fractions is sufficient to produce maximum interactions. These surfaces, like those aged in crude oil, were rinsed with toluene and submerged in decane for decane/water contact angle measurements. Surfaces treated with one of the SBM fractions for 7 days were subsequently cleaned by soaking in solvents for approximately 45 min; results are shown in Fig. 3b. Advancing contact angles were reduced below the values obtained for samples that were only rinsed with toluene in all cases, although none were returned to strongly water-wet conditions ($\theta = 0°$). Results of these cleaning experiments were encouraging, especially in the case of the filtrate.

A somewhat more realistic test of the effect of drilling fluids involved exposure of clean mica both to crude oils and to filtrate or centrifugate. Mica surfaces that were pre-equilibrated with reservoir brines for one day, then aged in with Oils 1, 2a, or 3a for 21 days, and finally exposed for 7 days to one of the SBM fractions, were cleaned with organic solvents. The results are summarized in Table 2. The highest advancing angles were measured when no cleaning, other than the standard toluene rinse, was attempted. Cleaning efficiency was generally greatest for combinations of methylene chloride, chloroform, and methanol.




(a) wetting alteration due to aging in SBM filtrate or centrifugate

(b) cleaning of surfaces aged for 7 days in SBM filtrate or centrifugate

**Figure 3.** Decane-water advancing angles on mica surfaces exposed to SBM filtrate or centrifuge (a) as a function of aging time and (b) after cleaning with solvents.

**Table 2.** Cleaning of mica surfaces exposed to reservoir brine, oil, and mud fraction.

| **Washing solvent(s)** | **water advancing contact angle, $\theta_A$ (°)** | | |
|---|---|---|---|
| | **Oil 1 filtrate** | **Oil 2a filtrate** | **Oil 3a centrifugate** |
| toluene rinse only | 65 ± 6 | 60 ± 5 | 66 ± 5 |
| methylene chloride ($CH_2Cl_2$) | 50 ± 7 | 48 ± 4 | 52 ± 3 |
| hot $CH_2Cl_2$ (37°C) | 63 ± 5 | | |
| methanol ($CH_3OH$) | 42 ± 4 | | |
| chloroform ($CHCl_3$), $CH_2Cl_2$ | 36 ± 2 | | |
| $CHCl_3$, $CH_3OH$ | | 39 ± 3 | 39 ± 3 |
| $CH_2Cl_2$, $CH_3OH$ | | 50 ± 9 | 39 ± 3 |
| $CH_3OH$, $CH_2Cl_2$ | 44 ± 2 | 50 ± 3 | |
| $CH_2Cl_2$, $CHCl_3$, $CH_3OH$ | | 37 ± 2 | 35 ± 3 |
| hot $CH_2Cl_2$, $CHCl_3$, $CH_3OH$ | | 57 ± 5 | 57 ± 3 |

## Core Cleaning

Flow-through of Standard Solvents

A common cleaning approach is to flow toluene followed by methanol through the core, cycling the solvents until no discoloration of effluent is observed. Figure 4 shows relative permeabilities measured on four samples from Reservoir 2 cleaned in this way at ambient temperature, without prior drying. Initial conditions were established using an overburden centrifuge to a capillary pressure representing the average oil column. The oil phase was Klearol, a 12cp laboratory mineral oil. The results still show less efficient displacement characteristics than expected for this type of open pore structured channel sand.

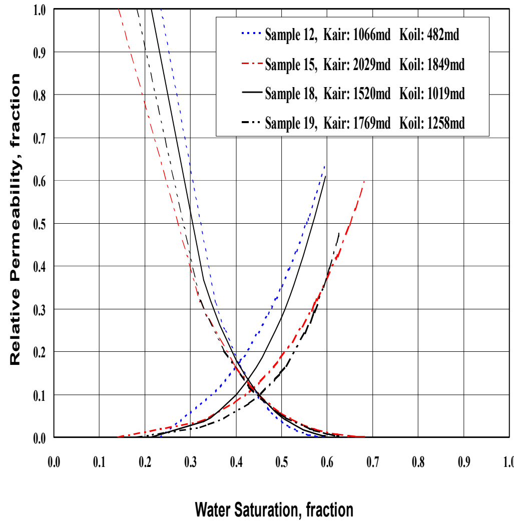



**Figure 4.** Water-oil Kr results after standard flow-through cleaning. (Ambient conditions, Reservoir 2)

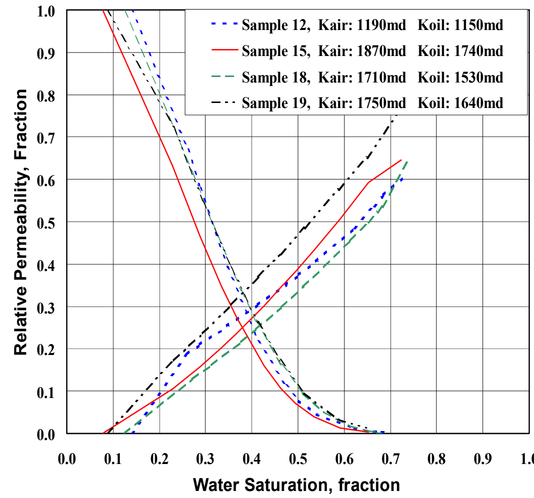



**Figure 5.** Water-oil Kr results after additional cleaning. (Ambient conditions, Reservoir 2)

<u>Flow-through with Additional Solvents</u>

Figure 5 summarizes results obtained after additional flow-through cleaning of the four samples shown in Fig. 4. Bleach was used in one case, and toluene-methanol with 1% ammonium hydroxide in another. The results for the four samples were surprisingly similar, showing only minor variation among different cleaning treatments. Initial oil permeabilities were substantially higher for three of the four samples following this additional cleaning—more than double in one case—appearing to confirm that further cleaning had occurred. The overall displacement efficiency is also improved although the unusual linear shapes of the curves and high end-point water relative permeabilities were a concern.

<u>Cleaning by Soxhlet Extraction with Methylene Chloride and Methanol</u>

Since none of the flow-through cleaning methods produced water-wet cores, Soxhlet extraction with methylene chloride and methanol was tested. The solvents selected have boiling points below that of water: methylene chloride has a boiling point of only 40°C. It can selectively remove crude oil without evaporating off the water remaining on rock surfaces (in contrast to what occurs with toluene Dean-Stark extraction). It is also an excellent solvent for organics that is often used for removing heavy oil from cores and as a carrier fluid in oil chromatography studies. Methanol (boiling point of 65°C) is an effective polar solvent, and should be effective after oil removal with the water phase still present. Figures 6 and 7 show relative permeabilities obtained at ambient conditions after extraction for samples from Reservoirs 2 and 3, respectively.

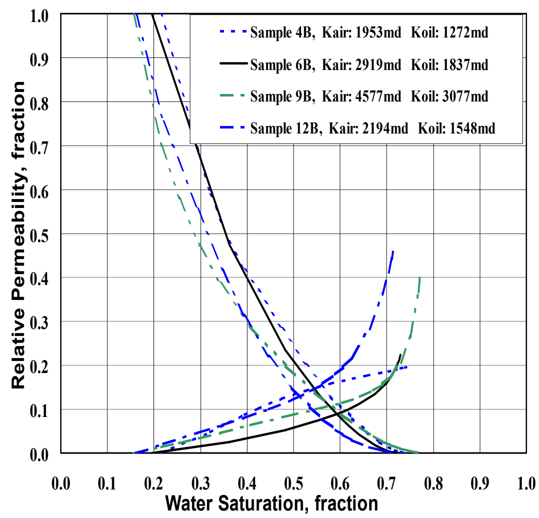



**Figure 6.** Water-oil Kr results after extraction with methylene chloride and methanol. (Reservoir 2)

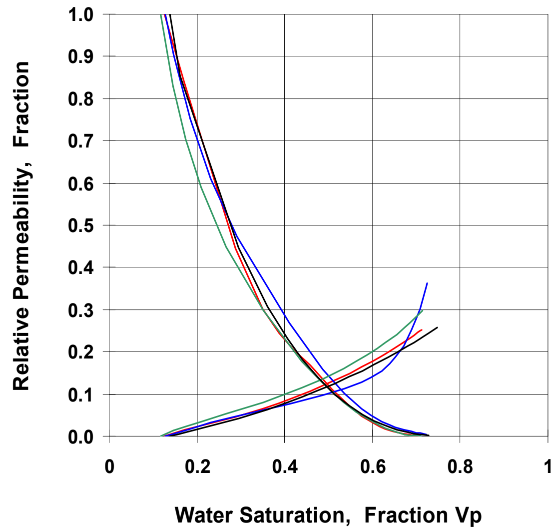



**Figure 7.** Water-oil Kr results of four closely spaced, weakly consolidated samples (Kor: 781 – 1164 md, Reservoir 3)

The four samples from Reservoir 2, which is essentially unconsolidated, cover a wide range of permeabilities and the results show some scatter. On the other hand, the four closely-spaced core plugs from a weakly consolidated zone of Reservoir 3 exhibit very similar water-oil relative permeabilities. In all cases, efficient displacement characteristics—in terms of the curve shapes, end point saturations, and terminal water relative permeability—were obtained. Increasing the water injection rate by a factor of three or more at the end of the flood typically caused only 2%PV of additional oil to be produced, accompanied by a 20% increase in the terminal water relative permeability. The wettability in core plugs cleaned by the extraction technique is addressed in the following section.

## Core Wettability

A wettability investigation was conducted with core samples from Reservoir 3 using plugs from weakly-consolidated zones

### Screened Samples

Five core plugs were tested by the combined USBM and Amott methods[6] using an overburden centrifuge. The purpose was to compare wetting characteristics of 1) as-received, 2) cleaned, and 3) cleaned and restored samples. Restored samples were aged in crude oil with a representative initial water saturation at elevated temperature for 1 - 2 weeks. Crude oil used in the restoration process was miscibly displaced with decalin, on the assumption that the established wetting conditions are preserved.[7,8] It should be noted that the centrifuge method does not allow strictly spontaneous imbibition. Instead, spontaneous imbibition is simulated by limiting the centrifuge speed to very low values, equivalent to 0.1 - 0.2 psi applied capillary pressure. This pressure is similar to the impedence to water imbibition estimated for the oil-wet stainless steel end screens of 120 mesh size used to contain the test plugs.

Table 3 summarizes results from the USBM and Amott evaluations. Some discrepancies can be seen between wettability designations from USBM information (based on capillary pressure curves) and the Amott, or free imbibition, tests. The cleaned Sample 1 is classified as water-wet by USBM and intermediate by Amott (with no free imbibition of water or oil), perhaps due to interference from the screen. The cleaned and re-aged test of Sample 2 was oil-wet by the USBM test and intermediate according to the Amott test. The three as-received tests (Samples 3-5) appeared to be oil-wet in both tests in all but one case.

Table 3. Summary of initial wettability analyses (Reservoir 3) – screened samples.

| Sample and preparation | Depth Feet | Permeability to Air, md | Permeability to Oil at Swi, md | Wetting Preference | | |
|---|---|---|---|---|---|---|
| | | | | USBM | Amott Oil Index | Amott Water Index |
| 1 - Cleaned | 8974.90 | 1179 | 672 | **0.278 Water Wet** | **0.002** | **0.035 Intermediate** |
| 2 - Cleaned, Aged | 8975.05 | 1371 | 875 | **-0.788 Oil Wet** | **0.000** | **0.019 Intermediate** |
| 3 - As-Received | 8975.20 | 1148 * | 252 ** | **-0.486 Oil Wet** | **0.425** | **0.002 Oil Wet** |
| 4 - As-Received | 8989.55 | 907 * | 273 ** | **-0.250 Oil Wet** | **0.000** | **0.019 Intermediate** |
| 5 - As-Received | 9023.30 | 2187 * | 470 ** | **-0.723 Oil Wet** | **0.735** | **0.021 Oil Wet** |

* Permeability to air measured at the end of the wettability analysis, after cleaning the sample.

** Permeability to oil measured at the start of the wettability analysis.

Unscreened Samples

Two additional core samples from Reservoir 3 (#6 and #7) were sufficiently well-consolidated to permit spontaneous imbibition measurements of wettability after removal of end screens. These samples were evaluated sequentially under the three conditions of as-received, cleaned, and restored. They were found to be moderately oil-wet in the as-received state, and weakly water-wet after cleaning. Spontaneous imbibition results, after removing one end screen from the sample to allow monitoring of countercurrent imbibition are given in Figure 8. Results for restored samples (cleaned and crude-oil aged) indicate an intermediate system, with very minor amounts of oil and water imbibing into the samples in the presence of residual oil and initial water, respectively.

Two cycles of restored condition tests were conducted. At the end of the second oil-resaturation step, both end screens and the sleeve were removed to assess free water imbibition with the entire surface of the samples exposed. Very little water imbibition was again seen to occur. Then, after remounting the cores in holders, water displacement tests were performed. Finally, Dean Stark extraction of the samples determined that residual oil saturations of the two samples were 29% and 31% PV. This is within the range of displacement efficiency observed with cleaned core samples. In addition, end-point water relative permeabilities averaged 0.35, which is similar to that exhibited with cleaned plugs.

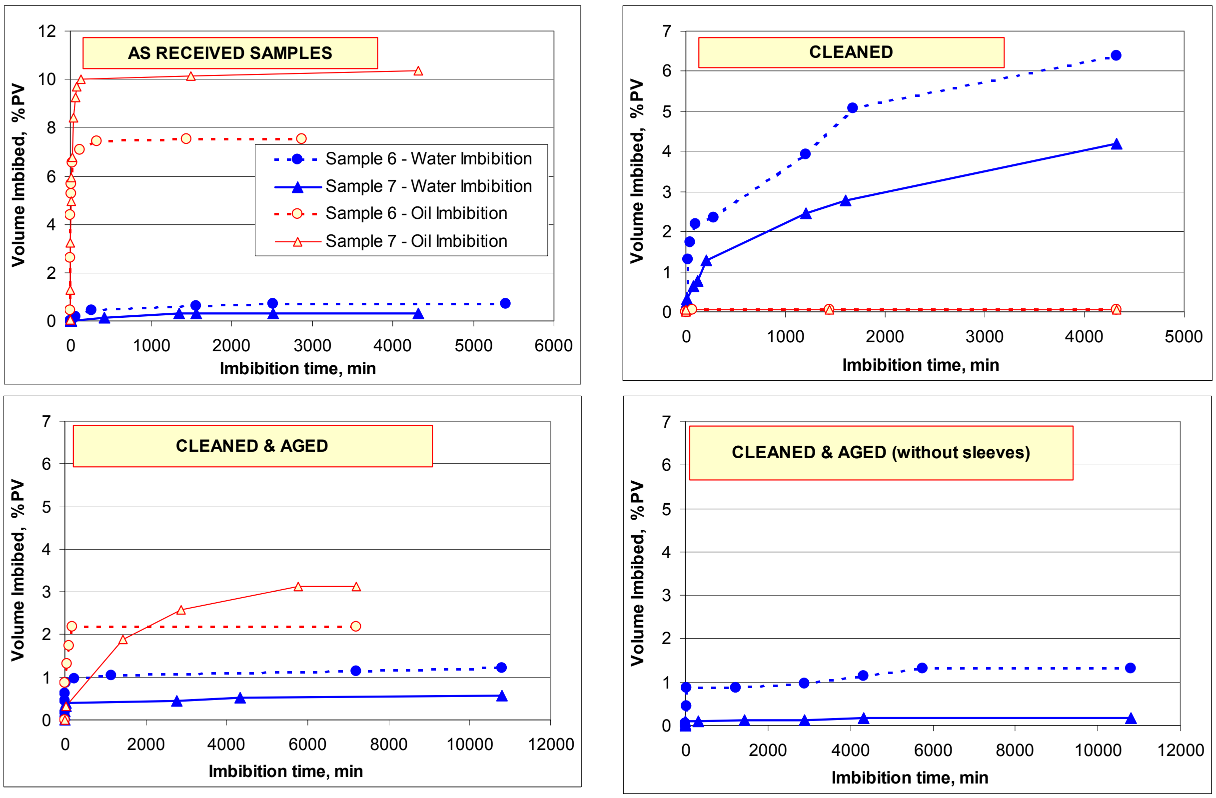



**Figure 8.** Spontaneous countercurrent imbibition, Reservoir 3.

## RECOMMENDATIONS AND SUMMARY OF RESULTS

A principal recommendation for follow-up from our findings to date is to pursue more core displacement evaluations under crude-restored conditions, for further comparison with results obtained on cleaned samples. Some higher end relative permeability measurement and interpretation approaches, with in situ saturation monitoring, may be warranted in this work. Additional mechanistic wettability studies could also be pursued, such as contact angle determinations on quartz.

Results of the present study are summarized as follows:

1. Mechanistic wettability studies, involving oil geochemistry and contact angle measurements, provide qualitative indication that the three reservoirs studied are likely to be preferentially water-wet. These studies also support other evidence that as-received core samples are oil-wet, caused by mud-filtrate contamination.

2. Relatively mild cleaning of core samples by sequential extractions with two low boiling point solvents, methylene chloride and methanol, produces a weakly water-wet condition, in general agreement with contact angle results.
3. Ambient condition water-oil displacement tests on cleaned core plugs exhibit efficient characteristics, consistent with their being weakly water-wet. In particular, residual oil saturations are typically 25% to 30% PV, and water relative permeability endpoints are about 0.3.
4. Limited tests on cleaned core samples re-aged with crude oil from one reservoir show a shift to an intermediate wettability, without a large change in water-oil displacement efficiency or the terminal water relative permeability.
5. High permeability, poorly consolidated, sandstone rocks are found to pose unique wettability measurements and interpretation challenges, due to the need to package samples and the generally low capillary forces involved.

## ACKNOWLEDGMENTS

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