WETTABILITY EVALUATION OF A CARBONATE RESERVOIR ROCK

Pierre M. Lichaa, Hayrl Alpustun, Jasper H. Abdul, Wasef A. Nofal and Alhasan B. Fuseni
Research Institute
King Fahd University of Petroleum and Minerals
Dhahran, Saudi Arabia

Abstract Recent studies have shown that carbonate reservoir rocks from the Middle East are generally neutral, mixed, or preferentially oil-wet.
Wettability changes during stages of "preserved as received", cleaned, and restored were evaluated by the USBM and Amott methods. Contact angle measurements were also evaluated on calcite and marble surfaces for comparison purposes. Rock/fluid interaction was studied by determining rock composition, brine and oil chemistry, and zeta potential.
The wettability was intermediate in nature regardless of the stage during which it was tested. The results showed that the rocks were neutral to slightly oil-wet in the "preserved as received" state, neutral to very weakly water-wet after cleaning with long and tedious procedures, and remained neutral to slightly oil-wet in the restored state. A technique was developed, and the preliminary results obtained indicate the possible existence of a mixed-wettability system for the reservoir.
A core cleaning technique using steam was utilized which proved to be at least as effective as the currently used solvents, such as methylene chloride, chloroform, pyridine, tetrahydrofuran, and chloroform/methanol azeotrope. Moreover, it is less expensive and much less hazardous to

work with. The results showed that it was impossible to achieve a strongly water-wet condition for these cores. The chemistry of the crude oil, formation and preserving brines, and rock surface properties support the findings of an intermediate wettability state.

The experience gained from this investigation reinforced the need for better understanding of the mechanisms of rock/fluid interactions and wettability at the pore level, or improvement to existing methods especially for carbonate rocks.

INTRODUCTION

It is acknowledged that wettability is among the major factors which affect residual oil saturation, capillary pressures, electrical properties, relative permeabilities, and oil recovery. Although wettability control or its alteration was proposed as a method for improving oil recovery, the subject is still not well developed. Thus, more work is required to better understand the fundamentals and mechanisms which will lead to improved techniques for evaluating wettability.

Extensive review of the literature on carbonate rocks has revealed that the majority of these rocks have a tendency to be preferentially oil-wet (RI/KFUPM, 1990; Cuiec, 1991; Chilingarian et al., 1992). Recent studies have indicated that carbonate reservoir rocks from the Middle East are generally neutral, mixed, or preferentially oil-wet (Cuiec and Yahya, 1991). Several carbonate fields in Saudi Arabia have been submitted to prolonged pressure maintenance or to waterfloods. To be successful, the design of a future, assisted, or (improved) waterflood process must take into account the in situ wettability of the reservoir.

Since it has been reported (Donaldson et al., 1969; Salathiel, 1973; Anderson, 1987) that oil recovery is different for the neutral, mixed, or preferentially oil-wet (whether slightly or strongly oil-wet), wettability must be identified and classified accordingly. Also, a direct measurement of in situ formation wettability is not yet available and therefore the wettability should be measured in a state which represents the reservoir environment in as closely as possible. This is normally done by evaluating the wettability in the "preserved as received" condition

or after restoration to reservoir conditions. The difference between the measured wettabilities at these states will indicate the degree of alteration.

This research was designed to evaluate and compare the wettability of cores from a Saudi Arabian carbonate reservoir in the "preserved as received", cleaned, and restored states. Wettability evaluation was made using the USBM, Amott, and contact angle techniques. The applicability of these methods to the cores studied are discussed.

Methods of analysis along with the results, are presented to explain the possibility of a mixed-wettability state for this reservoir. In addition, a core cleaning technique is discussed which proved to be as effective as the currently used solvents but it is relatively inexpensive and much less hazardous to work with. The paper also presents the procedure utilized to restore the cores to near reservoir conditions.

Rock composition, brine and oil chemistry, and zeta potential measurements are presented. Rock-fluid interaction also is discussed to complement the wettability measurements for explanation of the findings related to the wettability of the carbonate reservoir under study.

Wells Studied

Cores for this study were obtained from the Arab-D reservoir in Uthmaniyah wells UTMN-A and UTMN-B operated by Saudi Aramco in the Kingdom of Saudi Arabia. The reservoir is being waterflooded now. Well UTMN-A, an evaluation/producer well, was drilled to 49 m below the base of Arab-D reservoir with a total depth of about 2418 m. The objective of drilling the well was to dileneate the permeability barrier on the west side of the east injectors and to help define the extent of tar occurrence in a specific Uthmaniyah area.

The UTMN-A well was cored conventionally using a bland water-base coring fluid. The rheology of the bland mud was controlled with water, XC-polymer (xanthan gum biopolymer), dextrid, and carboxymethyl cellulose (CMC). No chemical thinner, soda ash, caustic, diesel, defoamer, or any surfactant was used to minimize any possible alterations of the core wettability. The cores were cut from a depth interval of 2323-2333 m, delivered in plastic tubes and preserved in about 26 000 mg/l deaerated

brine of a composition as shown in Table 1. Table 1 shows also analyses of Arab-D synthetic formation brine and synthetic seawater injection brine.

TABLE 1   Analyses and other data for the brines used.

Analyte	Arab-D synthetic formation brine concentration (mg/l)	Preserving brine concentration (mg/l)	Synthetic seawater injected brine concentration (mg/l)
Sodium	57 040	1220	18 300
Calcium	19 260	7910	650
Magnesium	2284	36.9	2110
Strontium	1008	15.4	0
Potassium	2615	197	0
Lithium	<1.0	0	0
Barium	12.8	0.2	0
Iron	<0.2	<0.1	0
Sulfate	309.4	951	4290
Chloride	131 940	15 460	32 200
Carbonate	<1.0	0	0
Bicarbonate	55.5	145	120
Bromide	21.4	0	0
Total salinity	214 546	26 000	57 670
Density, gm/cm^3			
at 25°C	1.145	1.016	
at 75°C	1.118	Not determined	

Uthmaniyah well UTMN-B was drilled as an evaluation/producer well to 32.8 m below the base of Arab-D reservoir to a total depth of about 2220 m. The well was drilled to help understand a

known area, as a transitional zone between an accelerated flood front to the north, and lagging flood front to the south. The bottom hole temperature is at about 95°C.

The UTMN-B well was cored from a depth interval of 2082-2089 m. The target interval was cored using a water-based fluid with barite, bentonite, caustic, soda ash, dextrid, and XC-polymer as additives. The cores were also delivered in plastic tubes preserved in deaerated brine of ionic composition and strength as shown in Table 1.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

Core Cutting and Core Cleaning

The core samples were delivered preserved in about 26 000 mg/l brine-filled, sealed tubes. In order to minimize the possible wettability alterations, the core plugs were drilled with a brine coolant of a composition identical to that used to preserve the whole cores. Excessive drilling pressures were avoided by hydraulically monitoring the drilling rate and long exposure to the atmosphere was avoided since these might cause mechanical or chemical damage to the cores.

In addition to conventional Dean-Stark, soxhlet, and centrifuge core cleaning methods, a flow-through core cleaning system utilizing solvents also was used. A steam cleaning process also was used: the cores were first extracted in a soxhlet with toluene, dried, and then subjected to leaching by a combination of steam and hot water condensed from the steam (Donaldson *et al.*, 1991).

Rock Description and Fluid Analyses

Thin section and fluorescence microscopy, X-ray diffraction, and scanning electron microscopy techniques, were used to describe the rock mineralogy. The crude oil samples were analyzed for hydrocarbon group types: saturates, aromatics, resins, and *n-hexane* insolubles using high-performance liquid chromatography (HPLC). The resin fractions collected from the HPLC were analyzed by Fourier Transform Nuclear Magnetic Resonance

(FTNMR) and Fourier Transform Infrared (FTIR) techniques to identify the functional groups. Asphaltenes also were separated from the crude using the Institute of Petroleum Standards IP-143/82 method (1983).

Determination of the major elements in crude oil, resin, and asphaltene samples were made using an elemental analyzer. Trace elements in the crude also were determined using calibration curves while those which were below detection limits were estimated. Glass liquid chromatography also was used to separate acids, bases, saturates, aromatics, and polar compounds from the crude oils (ASTM, 1980; Mckay *et al.*, 1981).

Measurement of Contact Angles

Contact angles were measured using two methods. The first included a system which permitted measurements of the angle made by an oil drop pending on the brine-rock interface as a function of temperature and pressure. The system included a stereomicroscope, camera attachment, and a goniometer.

Another device to measure contact angle variation with temperature at atmospheric pressure for different fluid/rock systems was built which consists of an equilibration glass cell, goniometer, and a circulating fluid temperature bath. The equilibration cell has two chambers. One chamber is for the circulation of bath fluid and the other, is for aging an oil drop on a rock substrate. The oil drop is introduced with a hypodermic needle. The chamber was filled with brine while measuring the contact angle at the three-phase line of contact in a brine/oil/rock system.

Wettability Determination

The wettability of the cores were determined using the Amott, USBM and the combined Amott-USBM methods (Amott, 1959; Donaldson *et al.*, 1969; Anderson, 1986a; Sharma and Wunderlich, 1985). Spontaneous imbibition was performed in custom-made Pyrex glass cells. Imbibition varied from days to weeks because of the extremely low permeability of the cores studied. Forced displacement was conducted using a high speed centrifuge fitted with a controlled heating unit and a stroboscope. The volumes of fluids expelled at step increases of centrifuge speed were read.

Because of the low permeability of the cores, these were centrifuged at incrementally increasing speeds from 500 to 10 000 rpm. The speed of the centrifuge was incremented when the fluid displaced from the core attained a constant value.

The capillary pressure at each incremental centrifuge speed at the inlet face of the core and the corresponding inlet face saturations were calculated using the solutions described elsewhere (Rajan, 1986). The generated capillary pressure curves were then fitted with a spline, hyperbolic (Donaldson et al., 1991), or a third order polynomial regression of a log function to provide the best fit for the experimentally observed data.

The USBM wettability index (WI) was calculated by comparing the logarithm of the ratio of the areas under the capillary pressure versus the brine saturation curve. For purpose of discussion, the wettability index range from +1.0 to -1.0 was divided and classified as follows: neutral (-0.1 to +0.1), slightly water-wet (+0.1 to +0.3), water-wet (+0.3 to 1.0), slightly oil-wet (-0.1 to -0.3), and (-0.3 to -1.0) as oil-wet (Cuiec, 1991).

Wettability Restoration

A schematic diagram showing the successive steps utilized in restoring the wettability is shown in Figure 1. After determining the wettability indices in the "preserved as received" state, the wettability was evaluated after cleaning with the most efficient solvents screened. For this, either toluene followed by steam or toluene followed by methylene chloride and a chloroform/methanol (78.2/21.8 vol/vol) azeotrope was used. Depending on the cleaning process utilized, the cores were dried according to either one of the steps shown in Figure 1. The cores were then saturated with synthetic reservoir brine of 214 000 mg/l, followed by brine displacement with reservoir dead crude oil. After establishing the initial reservoir brine and oil saturations, the rock/oil/brine system was aged in reservoir oil at 100°C and 20 685 kPa (3000 psi) for a minimum of six days. This aging period was based on a detailed literature study which demonstrated that an asymptotic value was generally quickly obtained in a matter of few days for the wettability index of carbonate rocks from the Middle East (Cuiec, 1991). Following this aging period, the wettability of the cores was then evaluated at 25 and 75°C

using synthetic formation brine and dead crude oil from the Arab-D reservoir.
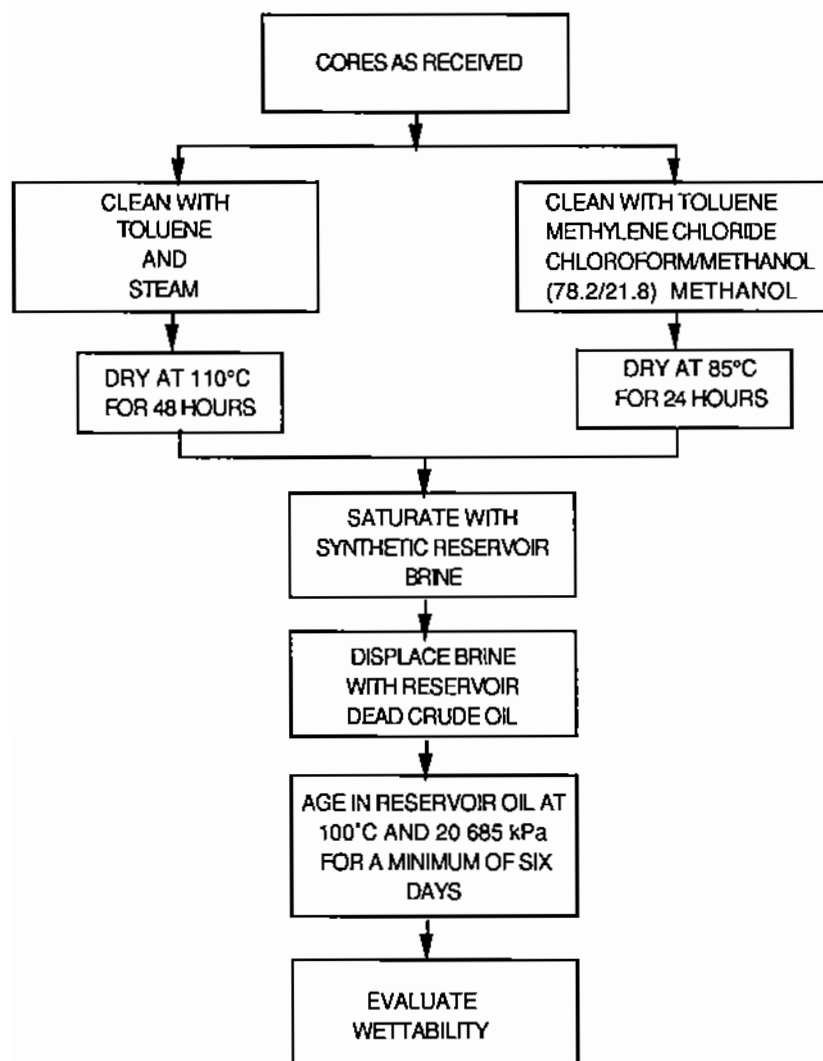

FIGURE 1 A flow diagram of the successive steps used for restoring rock wettability.

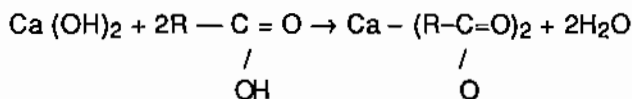## RESULTS AND DISCUSSIONS

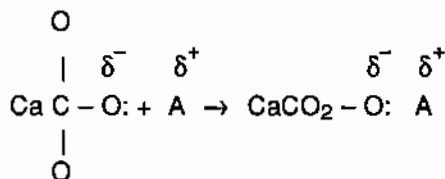## Interaction of Brine-Oil-Uthmaniyah Rock and Wettability Effects

In a carbonate rock, each oxygen must be bonded to its coordinating carbon more strongly than it can possibly be bonded to any other ion in the structure (Dana, 1971). These oxygen atoms are exposed on some faces of the limestone rock and in other faces, calcium atoms are exposed. The surface is characterized as a weak base, having a pair of electrons that are not already being shared in a covalent bond (Iler, 1955; Grim, 1962). Therefore, if polar compounds were present in the crude oil and are of weak acidic nature, these compounds will be attracted to the weak base rock surface. This is in accordance with the proposed generalization which states that weak acids prefer to coordinate with weak bases, and strong acids prefer to react with strong bases (Pearson and Songstad, 1967). In the presence of water alone, the exposed oxygen atom in some faces of the limestone will attach itself to the H ions, while in other faces calcium is exposed attracting OH ions. In both cases, this will produce a preferentially water-wet system. If polar components such as the asphaltenes and resins present in some crude oils can reach the surface, then the acidic and basic radicals will substitute for the H and OH ions and hence, the surface can become preferentially oil-wet (Desbrandes, 1989).

In the case of a carbonate, if the basic characteristic is due to Arrhenius-Ostwald Ca-OH groups, a Brönsted acid may react in the following manner forming a salt on the surface (Cuiec, 1977):

$$Ca\,(OH)_2 + 2R - C = O \rightarrow Ca - (R{-}C{=}O)_2 + 2H_2O$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\;\; OH\qquad\qquad\qquad\;\; O$$

However, if the basicity of the carbonate is due to a Lewis-type basicity because of the electron pairs of the oxygen atoms in

the CO_3 group, then a Lewis acid may adsorb on these surface-oxygen atoms and give rise to the following reaction:

$$
\begin{array}{c}
O \\
| \quad \delta^- \quad \delta^+ \qquad\qquad \delta^- \quad \delta^+ \\
Ca\ C - O: +\ A\ \rightarrow\ CaCO_2 - O:\quad A \\
| \\
O
\end{array}
$$

Therefore, any lipophilic radical whether it is acidic or basic in nature can be attracted to the carbonate rock.
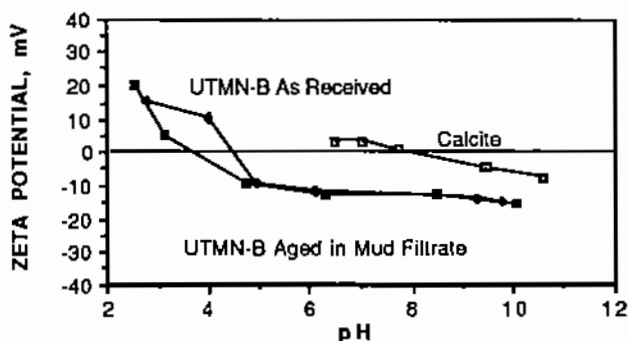
FIGURE 2 Variation of zeta potential with pH of two UTMN-B rocks and calcite tested in deionized water.

The carbonate rocks examined in this study are slightly basic with a pH range of 8.4 to 8.7. Figure 2 shows that in deionized water with a specific conductivity of 32×10^{-7} ohm^{-1} cm^{-1}, the zero point of charge for calcite is about a pH of 8.15 which is in agreement with (Somasundaran and Agar, 1967; Shakeel, 1987). It shows that the surface is positively charged below this value and negatively charged above this pH value. Similarly, Figure 2 shows the variation of zeta potential of two UTMN-B rock samples with pH. One sample was tested "as received" in

deionized water and the other was tested after aging in a mud filtrate representing the coring fluid used in the field. From Figure 2 it is seen that the zero point of charge is located near a pH of 4.6 when tested in the "as received" case and near 3.5 when the rock was aged in the coring-mud filtrate. In Figure 2 the surface charge of the UTMN-B rock is negatively charged above a pH of 4.6 and 3.5 when tested "as received" and aged in mud filtrate respectively. Also, aging the rock in mud filtrate caused the zeta potential to increase negatively, indicating an anionic behavior in the range of pH of 2.5 to about 5, where the zeta potential becomes equal to that of the "as received" state. Above a pH of 5, mud filtrate also caused a slight negative increase in the zeta potential until a pH of about 8.5, where they became identical and remained equal until a pH of 10 was reached.

Figure 3 compares the effect of treating the rock surface in coring-mud filtrate on the zeta potential with pH in 25 000 mg/l preserving-brine solution to results obtained in the "as received" state. This figure indicates that the rock surface becomes highly negative and that the salts present in the preserving brine (Table 1) have pronounced effects on the zeta potential in the whole range of pH tested. In the presence of coring-mud filtrate, the zeta potential became appreciably less negative for the pH range investigated, but in no case it became positive.
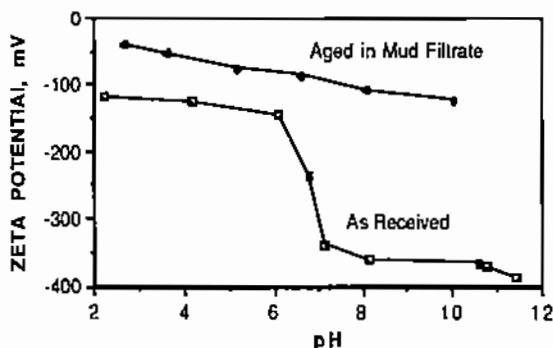

FIGURE 3 Variation of zeta potential with pH of UTMN-B rocks tested in 25 000 mg/l preserving brine.

In a brine/crude oil/rock system the salinity and pH of brine can strongly affect the surface charges on the rock surface and fluid interfaces, which in turn can affect the wettability (Anderson, 1986b). Several researchers studying silica/oil/brine systems, found that multivalent cations in the brine can promote the adsorption of surface active compounds at the rock surface causing a more oil-wet system (Treiber *et al.*, 1972; Somasundaran and Hanna, 1979; Brown and Neustadter, 1980; Morrow *et al.*, 1986). The wettability of these systems were altered by multivalent ions, including Ca^{+2}, Mg^{+2}, Cu^{+2}, Ni^{+2}, and Fe^{+3}. Also a mechanism of promoting oil-wetting was attributed to the multivalent ion acting like a bridge between the rock surface and the surfactant, helping to bind the surfactant to the surface (Leja, 1982). Brown and Neustadter (1980) reported that seawater produced strongly-wetted surface independent of pH, even when the seawater was diluted a hundred-fold by distilled water. The presence of large quantities of multivalent Ca^{+2}, Mg^{+2}, Sr^{+2} ions in the injection seawater and Arab-D brines, and the weak base characteristic of the Arab-D reservoir rock in Uthmaniyah carbonate rocks, suggest that a preferentially oil-wet system should prevail in the presence of polar compounds in the crude oil. The pH of the brine should affect the wetting character, particularly where the zeta potential crosses the zero point of charge (Andersen *et al.*, 1989).

Tables 2 and 3 show that the crude oil sample is acidic and has a relatively high asphaltene and resin content. Therefore, the amount of polar compounds present should play an important role in the wettability behavior. Elemental analyses presented in Table 4 indicate the presence of relatively small amounts of nitrogen. This is also an indication that the crude is acidic since nitrogen contributes to the basicity of the crude oil.

Fractionation of the acidic compounds by infrared spectroscopy and nuclear magnetic resonance techniques indicated the presence of aromatic acids and some aromatic esters. The O-H stretch in the infrared spectrum was quite weak, but an intense C=O stretch was observed. The results were confirmed by NMR spectra. These results indicated that

TABLE 2 Properties of Arab-D, Uthmaniyah crude oil.

Molecular weight	260.69
Refractive index	1.679
Total acid number (mg KOH/g)	0.40
Total base number	Non-measurable
pH	5.40
Asphaltenes (wt %)	4.10
Density, gm/cm^3 at 25°C	0.876
Density, gm/cm^3 at 100°C	0.720
Viscosity, mPa.s at 25°C	15.04
Viscosity, mPa.s at 100°C	3.01

TABLE 3 Hydrocarbon group type analyses of Arab-D crude oil from Uthmaniyah.

Group type	Wt (%)
Saturates	53.77
Aromatics	37.55
Resins	5.76
n-Hexane linsolubles	2.92

TABLE 4 Elemental analyses of Arab-D crude and other fractions from Uthmaniyah oil.

Sample	Element (wt %)				
	C	H	N	O	S
Crude oil	84.50	12.70	0.08	0.42	2.30
Resins*	80.60	9.00	0.21	1.29	8.90
Asphaltenes*	79.80	8.60	0.74	7.16	3.70
Acids*	76.96	8.42	0.99	8.38	4.17
Bases*	63.82	6.82	0.86	12.10	8.17

* Extracted from Arab-D, Uthmaniyah crude oil

carboxylic acids and possibly carboxylic acid esters, both aromatic in nature are present in this crude oil.

The presence of polar compounds in the form of carboxylic acids in the studied Arab-D crude oil should promote preferential oil wetting (Benner and Bartell, 1941; Cuiec, 1977; Donaldson and Crocker, 1980; Anderson, 1986b; Crocker and Marchin, 1986). The Arab-D oil contains 34.8 µg/g vanadium, 4.4 µg/g nickel and 0.39 µg/g iron in addition to the other trace elements. Lowe *et al.* (1973) concluded that a 10 µg/g vanadium was enough to account for wettability changes in the Kirkuk crude oil-rock system investigated. Accordingly, the vanadium content in the crude investigated is enough to provide suitable conditions for a preferentially oil-wet system in this study.

The chemistry of the Arab-D formation brine, seawater injection brine, the Arab-D oil, and the carbonate rocks investigated from the Arab-D reservoir in Uthmaniyah wells UTMN-A and UTMN-B indicate that the fluids would act as a Lewis acid and react with the rock which is weak Lewis base-type favoring an oil-wet system. The results presented should promote preferentially a slightly oil-wet system.

Wettability Evaluation from Contact Angle Measurements

Receding contact angle measurements were made with Arab-D formation brine of a sample of Arab-D dead crude oil as a function of temperature in the range of 25 °C to 90 °C. Test pressure varied from ambient condition to a maximum of 345 kPa (50 psi) to avoid fluid evaporation. Contact angles were measured on a smooth calcite substrate using the pendant drop apparatus. Calcite was chosen since it represented the major component of UTMN-B well, and on the average, 40% of UTMN-A well. Table 5 shows equilibrium time for the interface and equilibrium receding contact angles as a function of temperature.

TABLE 5   Receding contact angles as a function of temperature.

Temperature (°C)	Equilibrium time (hours)	Receding contact angle (θ, degrees)
Arab-D dead oil/brine/calcite sytetm		
25	124	55
50	97	49
70	71	45
90	86	39
Arab-D dead oil/brine/UTMN-A sytetm		
22	105	105
50	80	100
70	80	Drop Vanished
Arab-D dead oil/brine/marble sytetm		
22	45	105
35	96	94
50	48	(distorted) ~ 60

Table 5 shows that the contact angle varied from 55 degrees at 25 °C to 39 degrees at 90 °C. In terms of a coefficient, the change in contact angle with temperature is about -0.12 degree/°C between 25 and 50 °C, -0.2 degree/°C between 50 and 70 °C, and -0.3 degrees/°C between 70 and 90 °C. Based on the receding contact angle measurements alone, it can be deduced that the calcite surface becomes preferentially more water-wet at higher temperatures; however, the tests indicate a weakly water-wet behavior for the Arab-D fluids/calcite system under these conditions.

Receding contact angle measurements were made with Arab-D synthetic formation brine of 214 500 mg/l salinity and Arab-D crude as a function of temperature. Contact angles were measured on 2x1x0.8 cm rock surfaces, cut from UTMN-A core samples plugged from a depth of about 2327 m and from local marble rocks. Table 5 shows equilibrium time for the interface and equilibrium receding contact angles as a function of temperature for the UTMN-A and marble substrate. X-ray diffraction analyses showed a ratio of about 40 (wt %) calcite to 60 (wt %) dolomite for plug samples selected from UTMN-B well. Table 5 shows that the contact angle varied from 105 degrees at 22°C to 100 degrees at 50°C. In terms of a coefficient, the change in contact angle with temperature is about -0.18 degree/°C in this temperature range. Further heating affected the shape of the contact angle drastically, vanishing at 70°C after some 80 hours of testing. It is believed that the oil drop imbibed into the rock pores under these conditions. Based on these measurements alone, it can be deduced that the UTMN-A sample is of intermediate wettability or preferentially, slightly oil-wet at room temperature and becomes preferentially less oil-wet at higher temperatures.

Results in Table 5 show that the change in contact angle with temperature is about -0.62 degree/°C between 22 and 35°C. When the temperature was increased to 50°C the shape of the contact angle started to change until it took a mushroom-like shape. Once this shape was stabilized after about 48 hours, a contact angle of about 60 degrees was read. This contact angle was distorted probably due to formation of rigid films at the oil/brine interface and surface rugosity. This data point should be interpreted qualitatively rather than quantitatively. The contact angle data show that the oil/brine/marble system is slightly oil-wet to having an intermediate wettability, and tends to become weakly water-wet at higher temperatures.

Due to hysterisis in contact angle measurements and because they are influenced by a large number of external conditions, the results obtained should be used with care and no generalizations should be based on contact angle measurements only. Contact angle measurements are never decisive in oil/brine/rock systems due to the complexity of the system and they make a

representative statement of only a very small portion of the system.

When a porous rock is polished and used for the contact angle surface, the fluids interact with the pores of the rock. No matter how carefully the system is polished, the pores still remain and small cavities are present from loss of grains. This interaction of the fluids with the pores will have an unknown and variable influence on the contact angle that develops, thus producing questionable results. In addition, if the viscosities of the fluids are low enough, imbibition of fluids into the pores will occur and will disturb the measurements. Furthermore, when a non-porous substrate is used (calcite, quartz, marble, etc.) for the contact angle measurement, this substrate is not in any way representative of the porous systems of rocks and their interactions with fluids.

Contact angles can thus be used for rapid qualitative screening of trends, but under no circumstances should any generalizations be made with respect to the systems of fluids in rocks (Donaldson, 1992).

Wettability Evaluation by Amott and USBM Methods for Cores in the "Preserved As Received" State

Table 6 shows basic core properties and wettability indices for core plugs drilled from UTMN-A well. The table indicates that all but three cores are of very low permeability. The reference wettability was measured by the Amott and USBM methods. The Amott method was later omitted due to its insensitivity to the cores studied. Preserving brine and dead crude oil were used in determining the wettability indices.

Wettability indices reported in Table 6 indicate generally that the cores tested from two preserving tubes (A1, A6, and A15, A16) are of intermediate wettability or are weakly water-wet while cores investigated from two other tubes (A7, A12, and A13, A14) are of intermediate wettability or are weakly oil-wet. The results indicate that the "as received" state cores have negative as well as positive indices. However, the trend of negative indices is somewhat more dominant, indicating a preferentially more oil-wet than water-wet state. Exceptions to these comments can be made for cores A15 and A6 which show indices higher than +0.3, the cut-off point chosen to indicate for water-wet behavior. Upon

TABLE 6. Basic core properties and wettability indices for Arab-D UTMN-A well.

Core plug (no)	Depth (m)	Porosity (%)	Permeability (md)	W I at 25°C
A1	2322.88	14.0	4.0	+0.17
A2	2322.88	14.0	3.8	-0.04
A4	2322.99	12.0	3.0	+0.30
A6	2323.23	11.0	2.0	+0.40
A7	2323.39	15.5	3.0	-0.13
A8	2323.45	8.8	0.4	-0.14
A9	2323.51	9.5	0.9	+0.13
A10	2323.60	8.8	0.5	-0.15
A11	2323.62	8.4	0.5	-0.12
A12	2323.72	14.2	2.0	-0.11
A13	2324.82	17.0	41.0	-0.29
A14	2324.82	18.0	63.0	-0.09
A15	2325.99	10.0	1.0	+0.46
A16	2325.99	12.0	4.0	+0.18
A17	2326.26	11.0	8.0	+0.20
A18	2326.26	15.0	30.0	+0.32

inspection of the rock properties, type, and composition of these two samples, no significant differences were found, and therefore this wettability behavior cannot be simply explained. This behavior could possibly be due to marked differences in the pore size and pore size distribution, and leaching of oil from the cores while being preserved in the brine before testing. Based upon the indices determined, it can be concluded that the "as received" cores from the interval tested in UTMN-A are of intermediate wettability to very weakly oil-wet.

Basic properties and wettability indices determined by the USBM method for core plugs drilled from UTMN-B well are shown in Table 7. This table indicates a very low to a very high permeability for the core plugs studied. The results indicate a

TABLE 7 Basic core properties and wettability indices for Arab-D UTMN-B well.

Core plug (no)	Depth (m)	Porosity (%)	Permeability (md)	W I at 25°C
B1	2081.78	17.7	2.8	-0.32
B2	2081.90	17.9	64.8	-0.21
B3	2082.31	16.1	2.2	-0.01
B4	2083.11	19.2	2.7	-0.46
B5	2085.38	21.7	509.0	-0.18
B6	2086.26	23.2	139.2	-0.39
B7	2086.32	22.9	485.2	-0.14
B8	2088.67	24.0	201.9	-0.04
B9	2088.75	24.1	1298.0	+0.07
B10	2088.78	22.9	1591.0	+0.04

general trend of intermediate wettability to slightly oil-wet behavior for the "as received" cores investigated. However, samples B9 and B10 demonstrate an intermediate to very slightly water-wet behavior and samples B4 and B6 are preferentially oil-wet. Based upon the indices determined, the interval tested from UTMN-B well in the "as received" state was found to be preferentially weakly oil-wet.

Wettability Evaluation of Cores in the "Cleaned" State

In order to make the cores strongly water-wet, the "flow-through" core-cleaning system and steam-cleaning apparatus discussed earlier were used and various solvents were screened. Strong acidic or basic solvents were not selected so as to avoid any possible chemical reaction between the solvent and the rock. Complex solvent mixtures were also avoided because there is no guarantee of an additive cleaning power. Solvents with high

Hildebrand solvent parameters, including water as steam, were considered. Also considered was the safety in handling these reagents. Preserving brine and dead crude oil were used in determining the wettability indices.

Results shown in Table 8 indicate that core plug B5 was slightly oil-wet (WI = - 0.18) in the "as received" state and remained slightly oil-wet with a small change towards a more preferentially oil-wet (WI = -0.27) state after cleaning with the solvent system shown in the table. This same solvent system was not effective as indicated by plug B9 and no change at all was observed for plug B10.

TABLE 8   Cleaning   efficiency-screening   of   solvents and   USBM   wettability   indices   of   UTMN-A   and   UTMN-B first   cleaning   stage.

Core Plug (no)	Solvent System	W I at 25°C	
		"As received" before solvent treatment	After cleaning with solvent
A13	"Toluene followed by	-0.29	+0.05
A14	methanol"	-0.09	+0.12
B2	"	-0.21	+0.02
A17	"Chloroform followed by	+0.20	Aborted
A18	methanol"	+0.32	+0.20
B4	"	-0.46	+0.05
B6	"Pyridine followed by	-0.39	+0.07
B7	methanol"	-0.14	-0.09
B8	"	-0.04	+0.19
B5	"Tetrahydro-furan followed	-0.18	-0.27
B9	by methanol"	+0.07	+0.13
B10	"	+0.04	+0.04
B1	"Toluene followed by	-0.32	+0.18
B3	steam"	-0.01	+0.24
A1	"	+0.17	Aborted
A16	"	+0.18	+0.11

Except for plugs A18, B7, and A16, where minimal changes are noted in preferential oil- or water-wetness and the observations made on plugs B5, B9, and B10, there is a general tendency for the cores to become slightly water-wet or even water-wet. Although toluene followed by methanol was effective in core A13, pyridine followed by methanol in core B6, and toluene followed by steam in core B1, it is rather difficult, based on these results alone, to select and recommend a single solvent combination system to make the cores water-wet.

The original plan was to screen the solvents in Table 8. When neither system resulted in a distinctive and effective one for making the cores water-wet, additional steps were taken to achieve water wetness. In a recent study it was reported that a 78.7/21.3 vol/vol chloroform/methanol azeotrope was the most effective single solvent, removing 98.9 wt% of the crude oil in a siliceous reservoir core sample (Dubey and Waxman, 1991). The study also concludes that dual-solvent extraction, methylene chloride followed by the chloroform/methanol azeotrope, was marginally more effective. Thus the cores tested were then divided into two groups. One group was submitted to cleaning by methylene chloride followed by the chloroform/methanol azeotrope, and the other group was cleaned by toluene followed by steam. Because of the relatively slightly-better results achieved with toluene and steam, it was felt necessary to do a second cleaning using this system to ascertain its effectiveness. If proven to be more effective, toluene and steam would also result in the easiest, least hazardous, and least expensive system to be used as an intermediate step for restoring wettability of this type of carbonate rocks.

The results of this second cleaning are shown in Table 9. Once again, it is noted that plug B5, which was slightly oil-wet (WI = -0.18) in the "as received" state, remained slightly oil-wet with a small change towards a more preferentially oil-wet (WI = -0.25) state after cleaning with the azeotrope solvent system. When plug B4 was cleaned with toluene followed by steam, the wettability index changed relatively in a significant manner, going from -0.46 to -0.10, however the plug remained slightly oil-wet. Similarly, the second stage of cleaning using the azeotrope or toluene followed by steam was ineffective when used on plugs B10

TABLE 9 Cleaning efficiency-screening of solvents and USBM wettability indices of UTMN-A and UTMN-B second cleaning stage.

Core plug (no.)	Solvent system	W I at 25°C	
		"As received" before solvent treatment	After cleaning with solvent
B1	"Methylene chloride	-0.32	+0.10
B2	followed by	-0.21	+0.13
B5	chloroform/methanol	-0.18	-0.25
B6	azeotrope	-0.39	+0.15
B7	(78.7/21.3 vol/vol)"	-0.14	+0.11
B10	"	+0.04	+0.02
B3	"Toluene followed by	-0.01	+0.12
B4	steam"	-0.46	-0.10
B9	"	+0.07	+0.16
B8	"	-0.04	+0.13
A13	"	-0.29	+0.11
A14	"	-0.09	+0.10

and B9. The wettability of the two plugs remained nearly unchanged from the "as received" state after treatment with the solvents. In order to explain the persistent slightly oil-wet or neutral wettability behavior even after solvent treatment for these plugs discussed above, the wettability would have to be examined at the pore-size scale, taking mineralogy, fluid interaction, pore geometry, and pore distribution into consideration.

Although the change in wettability index was relatively appreciable for the rest of the plugs tested, none of the solvent systems was effective in bringing the rock to a definite water-wet state. The rock wettability remained in the intermediate state or

changed from a slightly oil-wet state to a slightly water-wet state. This is in agreement with the findings of a recent study investigating the wettability of the Asab Thamama Zone B carbonate reservoir in Abu Dhabi (Cuiec and Yahya, 1991). The study concluded that it was impossible to bring the rock from some facies to strong water wetness.

Wettability Evaluation in the Restored State

After determining the wettability indices in the "as received" and cleaned states at an ambient temperature of $25°C$, the wettability of the cores was determined in the restoration mode at this same ambient temperature. The wettability was also determined in the restored state at $75°C$, approximating the reservoir temperature of $95°C$. Restoration of the core wettability was done as described in Figure 1 using synthetic formation brine and dead crude oil.

Results shown in Table 10 indicate that the restored wettability of the system at $25°C$ generally remained in the slightly oil-wet state (WI = -0.1 to -0.3). More specifically, cores B1 and B2 were slightly oil-wet in the "as received" state, changed to slightly water-wet in the cleaned state, and returned to slightly oil-wet in the restored state at $25°C$. In both cases however, the wettability index in the restored case was slightly less than the "as received" case. Similarly, core B3 extracted from the same tube as the other two plugs showed a neutral wettability index (WI = -0.1 to +0.1) in the "as received" case and became slightly water-wet (WI = +0.1 to +0.3) in the cleaned case and slightly oil-wet in the restored case. This plug however indicated an orientation towards more oil wetness in the restored as compared to the "as received" state.

The plug tested and denominated B4 was oil-wet (WI = -0.3 to -1) in the "as received" state, changed to neutral in the cleaned state and behaved as slightly oil-wet when restored. However, B6 plug was oil-wet in the "as received" state, changed to slightly water-wet after cleaning, and returned to slightly more oil-wet condition after restoration. Also B8 plug which was neutral when tested "as received" changed to slightly water-wet when cleaned and became oil-wet when restored. The other two plugs extracted from same tube, B9 and B10 were neutral in the

**TABLE 10 USBM indices of UTMN-A and UTMN-B core
samples evaluated during three different states.**

Core plug (no)	Solvent system	W I at 25˚C			W I at 75˚C
		"As received"	Cleaned with solvent	Restored	Restored
B1	"Methylene	-0.32	+0.10	-0.14	
B2	chloride followed	-0.21	+0.13	-0.18	-0.03
B5	by chloroform/	-0.18	-0.25	-0.05	0.00
B6	metha-nol	-0.39	+0.15	-0.44	-0.22
B7	azeotrope	-0.14	+0.11	-0.19	-0.03
B10	(78.7/21.3 vol/vol)"	+0.04	+0.02	+0.20	
B3	"Toluene followed	-0.01	+0.12	-0.26	
B4	by steam"	-0.46	-0.10	-0.16	
B9	"	+0.07	+0.16	+0.10	
B8	"	-0.04	+0.13	-0.44	-0.26
A13	"	-0.29	+0.11	aborted	
A14	"	-0.09	+0.10	-0.20	

"as received" case, remained neutral or changed to slightly water-wet when cleaned and remained neutral to slightly water-wet when restored.

For the plugs tested from the UTMN-A well, one was aborted during the restoration experiment and the other one, A14, was neutral when tested "as received", remained neutral or was slightly water-wet when cleaned, and became slightly oil-wet when restored. Except for B6 and B8, which were oil-wet when restored, the general tendency of the wettability behavior of the cores was to be in the intermediate to the slightly oil-wet condition when restored. Also, seven of the cores tested showed

higher values of the same preferential wettability tendencies in the restored case than those in the "as received" case while four plugs demonstrated the opposite behavior.

These conclusions also indicate that the wettability in the restored state was generally the same as in the "as received" state. These results are in agreement with results obtained on similar rocks (Cuiec, 1991; Cuiec and Yahya, 1991). This could indicate that the cores as preserved by Saudi Aramco did not undergo major wettability alteration due to the coring-mud fluid used, evaporation, oxidation, and or contamination. Figure 3, however demonstrated that the coring-mud filtrate had a marked effect on the zeta potential; but it was not enough to reverse the sign of the zeta potential and make it positive under the conditions tested of pH and ionic composition and strength of the system. This would lead to the assumption that there was little or no invasion of the cores by the mud filtrate, or the effect on wettability by the coring-mud alone was masked since it was of the same magnitude and in the same direction as the native reservoir crude oil as reported in a separate study (RI/KFUPM, 1992a).

Table 10 shows results of wettability of five plugs tested in the restored state at $75°C$, approximating the reservoir temperature of about $95°C$. The results indicate a tendency towards water-wetness but the wettability of the cores remained either slightly oil-wet or approached a neutral or intermediate wettability as the test temperature approached the reservoir temperature.

Mixed Wettability Study

A study was initiated to examine the possible existence of a mixed-wettability system in the Arab-D reservoir. Three cores were extracted from UTMN-B well and denominated as B20, B21, and B22. For comparison purposes, two Berea sandstone samples were also tested. For the five cores, the wettability was evaluated at ambient conditions in the "as received" and restored states using Arab-D dead crude oil and synthetic preserving brine. In other tests, the polar fraction of the dead crude oil was extracted, dissolved in benzene, and injected to saturate the cleaned cores. This was followed by saturating the cores with synthetic preserving brine and displacement with dead crude oil.

The cores were then aged in dead crude oil at 100°C and 20 685 kPa (300 psi) for six days before beginning the USBM test with dead crude oil and synthetic preserving brine. The wettability of the cores was measured also by first saturating the cores with synthetic preserving brine, followed by displacement with the non-polar fraction of the crude oil, aging in the non-polar fraction, and completing the USBM tests using the non-polar fraction of the oil and synthetic preserving brine.

The wettability indices of the three UTMN-B cores show that the cores are slightly oil-wet in the "as received" state and became more oil-wet in the restored state as seen in Table 11. The wettability changed to slightly water-wet when tested with the non-polar fraction of the crude and became definitely oil-wet when the polar components were allowed to contact the plugs before effecting the wettability test. The polar components extracted from the crude were dissolved in benzene before contacting the plugs. The difference between this case and the restored case indicates the possible existence of a mixed wettability for the Uthmaniyah rock under the conditions of the study.

TABLE 11 Mixed wettability study for well UTMN-B.

Core plug (no)	Depth (m)	"As received"	"Restored"	Non-polar fraction of crude oil	Polar fraction of crude oil
		USBM wettability index at 25°C			
B20	2085.61	-0.15	-0.21	+0.08	-0.42
B21	2087.76	-0.32	-0.41	+0.11	-0.53
B22	2087.77	-0.23	-0.34	+0.15	-0.43
Berea *	N.A.**	+0.30	+0.30	+0.76	+0.07
Berea	N.A.**	+0.26	+0.27	+0.73	+0.02

*   Fired at 400°C for 24 hours
**   Not available

Detailed pore size distribution data indicate that about 10-15 % of the pores in UTMN-A and UTMN-B rock have an average diameter under about 0.1 microns (RI/KFUPM, 1992a). Preliminary studies indicate that the asphaltene particles in Uthmaniyah crude have an average diameter of about 0.6 microns (RI/KFUPM, 1992b). Depending on the crude type, Lichaa (1977) found that asphaltenes derived from several Venezuelan crudes had a major diameter ranging from about 0.2 to 0.98 microns. From these data it is apparent that the asphaltene particles are larger than some of the pores and thus can not flow through. Because of this, it is believed that even if these pores can still be contacted by the oil, the oil will be deprived of the polar components and therefore these pores will be preferentially water-wet. The larger pores which permit the entrance of the oil with its polar components tend to be preferentially oil-wet. A similar situation can exist in the Arab-D reservoir creating a mixed-wettability system.

Table 11 also indicates that preferential oil wetness is due to rock interaction with the polar compounds. The rock type is also important as seen from the wettability indices of the Berea sandstone. Berea sandstone was slightly water-wet as received, remained the same when restored, became strongly water-wet when tested with the non-polar fraction of the crude, and finally became neutral when tested after contacting with the polar compounds.

CONCLUSIONS

1. The wettability of Arab-D reservoir rock in UTMN-A and UTMN-B wells is generally slightly oil-wet when tested "preserved as received", becomes weakly water-wet when cleaned with powerful solvents, and behaves as slightly oil-wet when restored and tested at ambient conditions. Furthermore, the wettability of the Arab-D reservoir decreases slightly with temperature and tends to become neutral or intermediate at 75°C.

2. It was impossible to achieve a water-wet state for this reservoir rock with any of the cleaning methods that were used.
3. The slightly oil-wet to intermediate system of this rock is due mainly to the slightly acidic nature of the crude interacting with a slightly basic carbonate surface.
4. Detailed characterization and elemental analysis of the crude oil confirmed the presence of carboxylic acids, nitrogen and sulfur compounds; vanadium; and nickel compounds that play an important role in wettability.
5. Preliminary results indicate that Arab-D reservoir rock in UTMN-A and UTMN-B wells has a mixed wettability state.
6. The experience gained from this investigation reinforced the need for a better understanding of the mechanisms of rock-fluid interaction and wettability at the pore level. There is also a need to improve existing methods or find alternate techniques for the determination of the wettability of this type of carbonate rock.

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