WETTABILITY CONTROL BY ADSORPTION FROM CRUDE OIL – ASPECTS OF TEMPERATURE AND INCREASED WATER SATURATION

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ABSTRACT

The adsorption of polar compounds from crude oil onto rock surfaces largely determines the wetting properties of hydrocarbon reservoirs. It is now widely accepted that the distribution of adsorbed organic compounds is controlled by the location of connate water at rock surfaces to give a condition described as mixed wettability. Methods designed to simulate reservoir wetting conditions in laboratory core analysis studies mostly fall into two categories. In both, reservoir connate water saturation is established and the core is aged at reservoir temperature with crude oil. Oil recovery measurements (in cores identified as MXW) can then be made on the recovery of crude oil. The alternative approach is to replace the crude oil with a mineral oil. The refined oil/brine/rock interactions that determine displacement behavior are then dependent on the nature and distribution of the adsorbed organic film retained at the rock surface; this mixed wettability condition is referred to as MXW-F. Numerous technical and economic considerations enter into the choice of a particular procedure.

In the present work, study of wettability change is focused on the effect of temperature and the consequence of change in mobile water saturation. The MXW sandstone cores were prepared by crude oil marination in the presence of initial water saturation at elevated temperature. MXW-F cores were prepared by displacement of crude oil with an intermediate solvent (decalin) followed by mineral oil. The mineral oil served as the probe oil in subsequent displacement experiments. Increase in temperature increased the rate and extent of spontaneous imbibition for both MXW and MXW-F cores. Imbibition behavior indicates that wettability tends to change towards water wetness as water saturation increases during the course of spontaneous imbibition at elevated temperature. Aging at waterflood residual oil saturation always resulted in change towards water wetness whereas re-aging at connate water saturation usually made MXW cores less water wet.

INTRODUCTION

Dependence of wettability and oil recovery on temperature and aging conditions has been reported previously [1-4]. For a reservoir, wettability alteration occurred because crude oil migrated into a reservoir trap and lowered the water content down to the reservoir connate water saturation. In laboratory studies, the water wetness of rocks decreases with increase in time of aging with crude oil [2]. Elevation of temperature is needed to promote reduced water wetness by adsorption from crude oil within a few days to weeks [1, 2, 5]. Wettability restoration procedures are designed to duplicate the wettability state achieved over geologic time [6]. However, elevation of temperature has also been related to increase in water wetness of rocks under a variety of scenarios [1, 7-12]. Counter examples of decrease in water wetness with increase of temperature have also been reported [13, 14].

In the present work, study of wettability alteration is focused on the effect of temperature and change in water saturation. Mixed wettability states (MXW) were induced by adsorption from crude oil onto Berea sandstones in the presence of low initial water saturation. MXW-F wetting states were prepared by displacement of the crude oil with decalin which was in turn displaced by mineral oil to leave a film of adsorbed organic polar components at the rock surfaces [15, 16]. Use of the MXW-F wetting control method is particularly suited to study of the wetting properties and stability of adsorbed organic films without the complication of further adsorption from the bulk oil phase. Tong *et al.* [17, 18] observed that the wetting states were stable at ambient conditions for MXW-F Berea sandstone samples. In the present work, the effect of temperature and increase in water saturation is evaluated through changes in rate and extent of oil recovery by spontaneous imbibition. The effect of aging at residual oil saturation after either spontaneous imbibition or further reduction in oil saturation by forced displacement for MXW and MXW-F cores was also investigated. Overall, the results indicate that at elevated temperature, the encroachment or presence of increased water content in mixed wet rocks tends to shift the wettability towards water wetness.

EXPERIMENTAL MATERIALS AND PROCEDURES

Materials

The properties of tested Berea sandstones, Minnelusa crude oil, and brines are summarized in Tables 1, 2, and 3. Mineral oils of different viscosity were prepared by mixing Soltrol 220® (S220) mineral oil (3.8 cP) and a viscous mineral oil (VMO) (175 cP). Both mineral oils were initially purified by exposure to silica gel and alumina. Interfacial tensions of oil/brine, obtained by Krüss DVT-10 drop volume tensiometer, are presented in Table 4.

Initial Water Saturations and Core Aging

The core samples were first saturated with and soaked in brine for at least 10 days to obtain ionic equilibrium. Initial water saturation, S_{wi}, was then established in the cores. For cores from B block, target values of S_{wi} of about 24% were attained by direct displacement of brine with M'98 crude oil at 45°C. For Ev8 block cores, S_{wi} was obtained by displacing brine with VMO which was in turn displaced by decalin. The decalin was then displaced by M'02 crude oil. The cores were then submerged in the selected crude oil and aged at 75°C (T_a) in sealed pressure vessels for 10 days. Cores so prepared are referred to as MXW. MXW-F cores were prepared by displacing crude oil with decalin followed by mineral oil. Any further treatment of cores is given with the results.

Imbibition Tests

The initial imbibition tests were conducted at either ambient temperature or 75ºC (T_m). Initial water saturation was then re-established by crude oil displacement for MXW cores and VMO displacement followed by the selected mineral oil for MXW-F cores. In some tests, cores were re-aged at S_{wi} or residual oil saturation, S_{or}, (imb.) for spontaneous imbibition or S_{or} (forced) for viscous displacement, at 75ºC, for periods as specified. Spontaneous imbibition to brine starting from restored S_{wi} was then re-measured.

For imbibition tests at elevated temperature, the prepared core, imbibition cell, and brine were pre-heated to the test temperature of 75ºC. In order to test for possible evolution of gas from the crude oil during MXW imbibition tests at elevated temperature, a series of eight cores were immersed in brine in pressure vessels. Hydrostatic pressure of 200 psi was set with an ISCO piston pump. In these experiments, after a specific imbibition time, a core was recovered from the vessel and oil recovery was evaluated volumetrically and gravimetrically.

For strongly water wet conditions, spontaneous imbibition behavior was scaled by a semi-empirical scaling group [19].

$$t_D = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_o \mu_w}}\frac{1}{L_c^2} \tag{1}$$

where t_D is dimensionless time, t is time, k is permeability, ϕ is porosity, σ is the interfacial tension, and μ_o and μ_w are the oil and brine viscosities. L_c is a characteristic length that compensates for sample size, shape and boundary conditions.

This correlation has been used to assess the wetting behavior of a variety of MXW conditions [2, 20]. The viscosity term was found to correlate results for MXW-F cores for a wide range of oil/water viscosity ratios [16]. The correlation has also been shown to hold at very strongly water wet conditions for variation of aqueous phase viscosities for aqueous/oil viscosity ratios of up to about 4 [21]. In the present work, imbibition data is presented as percent of original oil in place (OOIP) recovered versus dimensionless time, t_D. Rates of recovery are discussed in terms of scaled time.

RESULTS AND DISCUSSION

Oil Recovery from MXW Cores

Effect of Temperature on Spontaneous Imbibition Measurement for MXW Cores

For comparison, reference curves obtained for spontaneous imbibition at very strongly water wetting (VSWW) conditions with zero initial water saturation are shown in Fig. 1a. Berea 500 [22] gave a consistent correlation for a wide range of oil viscosity and boundary conditions. However, VSWW results for the currently available low permeability Berea sandstones (60-120 md) do not fit the correlation and show differences from one block to another [16]. For low permeability sandstones tested in the present work, all Berea 90 [16] cores were cut from B block. Cores from Berea Ev8 block are referred to as Ev8 cores. Each of the three categories of VSWW imbibition results was reasonably self-consistent.

MXW imbibition at ambient temperature for Ev8 cores are included in Fig. 1a. Use of crude oil to establish an initial water saturation can require large volumes of oil. In order to conserve the laboratory stock of Minnelusa crude oil and for ease of control of initial water saturation, S_{wi} for Ev8 block cores was established by flow of VMO. The VMO was then displaced by decalin which was in turn flushed by M'02 crude oil. The results exhibited close reproducibility (see Fig. 1a), including a consistent induction time before the start of imbibition. An average curve for MXW M'98/B block cores [23] is also included in Fig. 1a. In contrast to the Ev8 cores, these cores did not exhibit induction times.

Shown in Fig. 1b is the imbibition result for MXW Core Ev8h27a at 75ºC. The test was run at elevated temperature in a glass cell at close-to-ambient pressure. The imbibition rate and oil recovery were significantly higher than for the MXW (ambient temperature) average curve over most of the imbibition period. At elevated temperature, an almost flat oil recovery plateau was reached. The final recovery of Ev8h27a was slightly lower than for the VSWW reference curve with S_{wi} of 24.4%.

As a test for the possibility that evolution of gas contributed to the early time recovery at elevated temperature, a set of imbibition tests were run in stainless steel pressure vessels at elevated temperature (75ºC) and pressure (200 psi). The individual points shown in Fig. 1b for the eight cores (Ev8h 23a, 24a, 26b, 25b, 25a, 24b, and 23b) defined the overall imbibition behavior. Agreement with the results for Ev8h27a confirmed the validity of the imbibition results obtained at elevated temperature and ambient pressure for a single core.

The effect of temperature on MXW imbibition behavior of B block samples is shown in Fig. 1c. Average results (see Fig. 1a) for MXW B block cores 5B2, 5B8 and 2BV6b [23] are also presented for comparison. Initial water saturation of 25% was established for Core 5B12 by M'98 crude oil flooding. Imbibition was then measured for Core 5B12 at 75ºC. In terms of dimensionless time (results are compensated for differences in viscosity and interfacial tension), Core 5B12 imbibed water about five times faster than for MXW cores tested at 22ºC. As for the elevated temperature results for Ev8 cores (Fig. 1b), the oil recovery of 5B12 reached a well-defined plateau. The trend of wetting behavior change for both B and Ev8 MXW cores is in agreement with previous work which showed that imbibition rate increased with temperature [1]. Change of the IFT of Minnelusa crude/brine with temperature is only slight (see Table 4) and is scaled by Equation (1). The increase in imbibition rate and oil recovery is mainly ascribed to some form of change in wettability towards increased water wetness, a change that possibly occurred during the course of imbibition at elevated temperature.

As a test for wettability change, after the initial imbibition of Core Ev8h27a at 75ºC (Fig. 1b), S_{wi} was re-established by flow of M'02 crude oil. The second cycle of imbibition was then performed at ambient conditions without re-aging. Results are shown in Fig. 1d together with the average curve for the initial imbibition tests on Ev8h cores at ambient temperature. At early time, the imbibition rate was slightly faster than for the imbibition at 75ºC but up to 10 times faster than for the MXW cores at ambient temperature; the imbibition curve then crossed the average curve for M'02 MXW Ev8 cores. In terms of imbibition behavior at early time, the results indicate that, after imbibition at elevated temperature, permanent wettability alteration towards increased water wetness occurred for Ev8h27a.

Re-Aging MXW Cores in Crude Oil at Initial Water Saturation

After the first cycle of imbibition, the initial water saturation of 5B2 and 5B8 was re-established by displacement with M'98 crude oil. The cores were then re-aged at 75ºC in the parent crude oil for 10 days and then retested. Aging was repeated to give four sequential imbibition tests. Results for four cycles of imbibition are given in Figs. 2a and 2b. For both cores, the imbibition rate and oil recovery of the second cycle were significantly decreased compared to the first cycle. (Tong *et al.* [18] previously reported that 10 days of additional aging of M'98 MXW-F cores in crude oil at initial water saturation showed significant and reproducible decrease in water-wetness when re-tested as MXW-F cores.) Subsequent aging of Core 5B8 resulted in a decrease in imbibition rate from one cycle to the next whereas the change for 5B2 was only slight. Extended aging of MXW cores at elevated temperature and S_{wi} was never observed to cause increase in imbibition rate.

Re-Aging MXW Cores in Brine at Residual Oil Saturation (S_{or})

In Fig. 3a, results are presented for the fifth cycle of imbibition of the MXW Core 5B8. At the end of the fourth cycle of imbibition, the core at S_{or} (imb.) (S_w = 43.2%) was left immersed in brine for about 25 days at 75ºC. During that time, water saturation increased to 68.3% which corresponds to additional oil recovery of 33.1% (OOIP). S_{wi} was then re-established by crude oil displacement, and the fifth cycle of imbibition was started. The oil recovery and imbibition rate increased towards the first cycle, indicating that, during re-aging, temperature and the aqueous phase saturation are significant factors in shifting wettability towards increased water wetness. (The agreement between cycle 1 and 5 for Core 5B8 is probably coincidence.) Similar shifts were measured for a duplicate sample (Core 5B2). Comparable behavior was reported by Tang and Morrow for A95 crude oil and Berea sandstone [1].

Core 2BV6b (Fig. 3b), after the initial imbibition test, was water flooded to S_{or} (forced) (S_w = 53.6%) and soaked in brine at 75ºC for 30 days. Then the initial water saturation was re-established (23.7%) and imbibition was run at ambient temperature. The second cycle imbibition ran significantly faster than the first cycle but later crossed the first cycle. This behavior is comparable to that shown in Fig. 1d.

Effect of Temperature and Re-Aging at S_{or} (imb) - MXW-F

Use of the MXW-F wetting control method in which mineral oil serves as the probe oil is particularly suited to study of the wetting properties and stability of adsorbed organic films without the complication of further adsorption from the bulk oil. In all cases, after aging, the crude oil was displaced by decalin which was in turn replaced by mineral oil.

MXW-F Imbibition at 75ºC

Tong *et al.* [17, 18] observed that MXW-F wetting was stable for several cycles of imbibition and drainage at ambient conditions. Extended aging of MXW-F cores at elevated temperature in mineral oil at low water saturation had minor effect on wetting behavior as indicated by imbibition at ambient conditions [24]. In Fig. 4a imbibition results are shown for M'98 MXW-F Cores (5B1, 5B4, 5B10, and 5B27) at 75ºC. The recovery for the four MXW-F cores (5B10, 5B27, 5B1 (4th cycle), and 5B4 (4th cycle)) increased significantly over the ambient temperature MXW-F average curve. This indicated that elevation of temperature caused change in wettability of the MXW-F cores towards increased water wetness.

At ambient temperature, MXW-F imbibition is consistently lower than for the parent MXW cores for both sandstones and carbonates [18, 25] (see also Fig. 4a.). At 75ºC, MXW-F imbibition increased but recovery and imbibition rate were still lower than for the B block MXW average results at ambient temperature (see Fig. 4a.). The marked difference in imbibition behavior between MXW and MXW-F cores shows that the properties of the probe oil such as its solvency for asphaltenes has significant effect.

Sequential Imbibition of MXW-F Cores Before and After Re-Aging in Brine at S_{or} (imb)

After imbibition measurements at elevated temperature, the fifth cycle imbibition for the 5B1 and 5B4 Cores was conducted at ambient conditions as a check on wettability after imbibition measurement at elevated temperature. Results for the two cores were in very close agreement (see Fig. 4b). Imbibition was clearly faster and higher at early time than the results originally measured for both elevated and ambient temperature (see Fig. 4b). At late time, there was cross-over with the 75ºC imbibition curve. The change in ambient temperature imbibition signified permanent change in wetting of MXW-F cores after imbibition at elevated temperature.

At the end of the fifth cycle of imbibition, 5B1 and 5B4 were soaked in brine at S_{or} (imb.) (S_w = 39.7% for 5B1 and 36.9% for 5B4). S_{wi} was then re-established by VMO flooding. For the sixth cycle imbibition at ambient temperature, the oil recovery and imbibition rate of both cores (see Fig. 4c) were very close to that for the fifth cycle except for being lower at early time.

Fig. 4d shows the sequential imbibition results for MXW-F Core 5B10. After the initial imbibition test at 75ºC (see Fig. 4a), the core was re-flooded with mineral oil to restore the initial water saturation. The second cycle imbibition was then started again at 75ºC. At early time, the imbibition rate was higher than that for the first cycle, but at late time, it crossed and fell below the first cycle curve. This result implied permanent wettability shift. The second cycle of imbibition was also close to the fifth cycle average curve for 5B1 and 5B4 cores (Fig. 4b) obtained at ambient conditions. This indicated that the wetting state of 5B10 did not change greatly during the second period of imbibition at elevated temperature. Initial water saturation was re-established for Core 5B10 and a third cycle of imbibition was run at ambient temperature. At early time, the core tracked the first cycle results and then showed a slight relative increase in rate of recovery.

Discussion

For imbibition at elevated temperature and/or aging at higher water saturation corresponding to S_{or} (imb) or S_{or} (forced), both MXW (Figs. 1 and 3) and MXW-F (Fig. 4) cores became more water wet. Change towards increased water wetness of a sandstone reservoir after waterflooding for about 20 years has been reported [26]. In the present work, the imbibition test temperature was either 22ºC or 75ºC. The brine composition and salinity were constant, so surface charge or potential of the core samples should also be constant, and a clay mobilization mechanism of wettability alteration [1, 3] is not likely to come into play. For MXW-F cores (see Fig. 4), it is unlikely that any change towards increased water wetness is caused by solubilization of adsorbed asphaltenes at elevated temperature.

At elevated temperature, the bonding between an adsorbed organic film and the rock surface mineral may be weakened, and encroachment of water between the rock surface and the adsorbed organic film may then occur. Buckley and Lord [27] reported from AFM that adsorbed organic films on weakly water-wet mica surface could blister and detach after immersion in water. Moreover, Buckley *et al.* [28] reported that adsorbed asphaltenes sometimes desorbed from tested flat quartz surfaces on contact with bulk water and formed rigid films at the water-oil interface accompanied by drastic decrease in contact angle. In a rock, if the adsorbed film peels off or peels and doubles over, the underlying water-wet mineral surface will be exposed.

Wetting behavior is usually dominated by the outermost moiety of an adsorbed organic film. For example, during imbibition, the outermost asphaltenes may change the orientation of polar groups to adjust to the properties of the overlying bulk liquid or at the three-phase line of contact so that imbibition is enhanced. For both MXW and MXW-F cores, a persistent pattern in which subsequent imbibition curves crossed those for the initial imbibition was observed (see Figs. 1d and 3b, and Figs. 4b, 4c, and 4d). Identification of the pore level/molecular mechanisms that cause the observed change would provide significant advance in the working knowledge of crude oil/brine/rock wetting behavior at elevated temperature.

CONCLUSIONS

1. Additional aging in crude oil at initial water saturation caused either no change or a decrease in water wetness.

2. Aging cores at elevated temperature and residual oil saturation to either spontaneous imbibition or forced displacement causes change towards water wetness.

3. Use of crude oil as the probe oil in imbibition tests gives consistently more water wet behavior than use of a mineral oil at both ambient and elevated temperature.

4. Increase in temperature of measurement increased the scaled rate and recovery of oil by spontaneous imbibition for both MXW and MXW-F cores through increased water wetness.

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REFERENCES

1. Tang, G.Q. and N.R. Morrow, “Salinity, temperature, oil composition, and oil recovery by water-flooding,” *SPE Reservoir Engineering*, (Nov. 1997) 269-276.
2. Zhou, X., N.R. Morrow, and S. Ma, “Interrelationship of wettability, initial water saturation, aging time and oil recovery by spontaneous imbibition and water flooding,” *SPE J*, (June 2000) Vol. **5**, No.2, 199-207.
3. Tang, G.Q. and A.R. Kovscek, “Experimental study of heavy oil production from diatomite by water imbibition at elevated temperature,” SPE 75132, the 13th SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, 13-17 April 2002.
4. Schembre, J.M., G.Q. Tang, and A.R. Kovscek, “Wettability alteration and oil recovery by water imbibition at elevated temperatures,” Proceedings of the 8th International Symposium on Reservoir Wettability, Houston, TX, USA, 16-18 May 2004.
5. Graue, A., E. Tonheim, and B. Baldwin, “Control and alteration in low permeability chalk,” Proceedings of the 3rd International Symposium on Evaluation of Reservoir Wettability and its Effect on Oil Recovery, Laramie, WY, USA, 21-23 Sept. 1994, 123-128.
6. Wendel, D.J., W.G. Anderson, and J.D. Meyers, “Restored-state core analysis for the Hutton reservoir,” *SPERE*, (Dec. 1987) 509-17.
7. Kyte, J.R., and C.C. Mattax, “Effect of reservoir environment on water-oil displacement,” *JPT*, (June 1961) 579-582.
8. Poston, S. W., S. Ysrael, A.K.M.S. Hossain, E.F. Montgomery, III, and H.J. Ramey, Jr., “The effect of temperature on irreducible water saturation and relative permeability of unconsolidated sand,” *Soc. Pet. Eng. J.*, (June 1970) 170-180.

9. Sinnokrot, A.A., H.J. Ramey, and S.S. Marsden, "Effect of temperature level upon capillary pressure curves," *SPEJ*, (March 1971) 13-22.
10. Wang, W. and A. Gupta, "Investigation of the effect of temperature and pressure on wettability using modified pendant drop method," SPE 30544, presented at the SPE Annual Technical Conference & Exhibition, Dallas, TX, USA, 22-25 Oct. 1995.
11. Chimienti, M.E., S.N. Illiano, and H.L. Najurieta, "Influence of temperature and interfacial tension on spontaneous imbibition process," SPE 52668, the SPE Latin American and Caribbean Petroleum Engineering Conference, Caracas, Venezuela, 21-23 April 1999.
12. Al-Hadhrami, H.S. and M.J. Blunt, "Thermally induced wettability alteration to improve oil recovery in fractured reservoirs," *SPEREE,* (June 2001) 179-186.
13. Bennion, D.B., F.B. Thomas, and D.A. Sheppard, "Formation damage due to mineral alteration and wettability changes during hot water and steam injection in clay-bearing sandstone reservoirs," SPE 23783 presented at the SPE International Symposium on Formation Damage Control, Lafayette, LA, USA, 26-27 Feb. 1992.
14. Rao, D.N., "Wettability effects in thermal recovery operations," *SPE Reservoir Eval. & Eng.,* (Oct. 1999) Vol. **2**, No. 5, 420-430.
15. Graue, A., B.G. Viksund, and B.A. Baldwin, "Reproducible wettability alteration of low-permeable outcrop chalk," The SPE/DOE improved Oil Recovery Symposium, Tulsa, OK, 19-22 April 1998.
16. Tong, Z., X. Xie, and N.R. Morrow, "Scaling of viscosity ratio for oil recovery by imbibition from mixed wet rocks," *Petrophysics,* (2002) Vol. **43**, No.4, 338-346.
17. Tong, Z., N.R. Morrow, and X. Xie, "Spontaneous imbibition for mixed-wettability states in sandstones induced by adsorption from crude oil," *J. Petrol. Sci. & Eng.,*(2003) Vol. **39**, No. 3 - 4, 351-361
18. Tong, Z., X. Xie, and N.R. Morrow, "Crude oil composition and the stability of mixed wettability in sandstones," *Petrophysics*, (July-August 2003) Vol. **44**, No. 4, 233-242.
19. Ma, S., N.R. Morrow, and X. Zhang, "Generalized scaling of spontaneous imbibition data for strongly water-wet systems," *J. Pet. Sci. & Eng.,* (1997) **18**, 165-178.
20. Xie, X. and N.R. Morrow, "Oil recovery by spontaneous imbibition from weakly water-wet rocks," *Petrophysics*, (July-August 2001) Vol. **42**, No. 4, 313-322.
21. Fischer, H. and N.R. Morrow, "Scaling of oil recovery by spontaneous imbibition for wide variation in aqueous phase viscosity with glycerol as the viscosifying agent," presented at the 8th International Symposium on Reservoir Wettability, Houston, TX, 16-18 May 2004.
22. Zhang, X., N.R. Morrow, and S. Ma, "Experimental verification of a modified scaling group for spontaneous imbibition," *SPE Reservoir Evaluation, (*Nov. 1996) Vol. **11,** No. 4, 280-285.
23. Tong, Z. and N.R. Morrow, "Variation in wettability behavior of mixed-wet cores resulting from probe oil solvency and exposure to synthetic oil-based mud emulsifiers," presented at the 8th International Symposium on Reservoir Wettability, Houston, TX, 16-18 May 2004. *JPSE,* in press.

24. Tong, Z., Oil Recovery by spontaneous imbibition from mixed-wet rocks, PhD Dissertation, University of Wyoming, Laramie, WY, USA, 2005, 115.
25. Tie, H., Z. Tong, and N.R. Morrow, “The effect of different crude oil/brine/rock combinations on wettability through spontaneous imbibition,” Proceedings of the SCA International Symposium, Pau, France, 22-25 September 2003.
26. Zhang, H., Q. Liu, F. Li, and Y. Lu, “Variation of petrophysical parameters after sandstones reservoir watered out in Daqing Oil Field,” *SPE Advanced Technology Series*, (1995) Vol. **5**, No.1, 128-139.
27. Buckley, J.S. and D. Lord, “Wettability and morphology of mica surfaces after exposure to crude oil,” *JPSE*, Vol. 39, No. 3-4, 261-273.
28. Buckley, J.S., Y. Liu, X. Xie, and N.R. Morrow, “Asphaltenes and crude oil wetting-The effect of oil composition,” *SPEJ*, (June 1997) 107-119.

Table 1.Core properties

Core #	L, cm	D, cm	K_g, md	ϕ	S_{wi},%	μ_o, cp (22 ºC)	Wetness
Minnelusa 98 crude oil							
2BV6b	7.632	3.780	125.0	0.1824	26.3	59.0	MXW
5B2	7.745	3.784	92.5	0.1790	24.6	77.2	MXW
5B8	7.394	3.785	103.7	0.1847	24.6	59.0	MXW
5B12	7.482	3.785	99.3	0.1854	24.9	11.5 at 75ºC	MXW
5B1	7.693	3.785	87.0	0.1769	24.9	83.8	MXW-F
5B4	7.758	3.785	102.6	0.1844	24.9	172.6	MXW-F
5B10	7.765	3.785	100.5	0.1874	25.0	9.7 at 75ºC	MXW-F
5B27	7.532	3.786	77.3	0.1778	25.0	9.7 at 75ºC	MXW-F
Minnelusa 2002 crude oil							
Ev8h1a	7.864	3.786	101.5	0.1760	23.9	68.0	MXW
Ev8h2b	7.538	3.765	71.7	0.1652	23.7	68.0	MXW
Ev8h6b	7.736	3.764	67.6	0.1605	22.0	68.0	MXW
Ev8h16a	8.280	3.759	114.0	0.1778	22.1	68.0	MXW
Ev8h23a	8.011	3.753	64.5	0.1671	24.3	15.5 at 75ºC	MXW
Ev8h23b	7.822	3.754	69.3	0.1674	25.3	15.5 at 75ºC	MXW
Ev8h24a	7.180	3.748	100.0	0.1711	24.5	15.5 at 75ºC	MXW
Ev8h24b	8.107	3.748	97.5	0.1716	24.8	15.5 at 75ºC	MXW
Ev8h25a	7.813	3.728	83.7	0.1718	24.0	15.5 at 75ºC	MXW
Ev8h25b	7.989	3.720	79.5	0.1730	24.0	15.5 at 75ºC	MXW
Ev8h26a	7.697	3.790	117.1	0.1739	23.6	15.5 at 75ºC	MXW
Ev8h26b	7.606	3.789	117.0	0.1734	22.6	15.5 at 75ºC	MXW
Ev8h27a	8.148	3.754	121.0	0.1740	23.0	15.5 at 75ºC	MXW

Table 2. Selected properties of crude oil samples

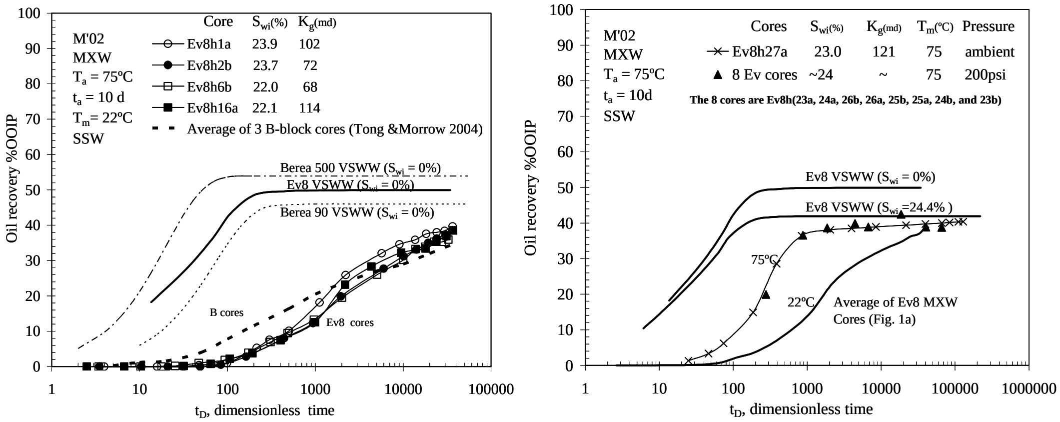
Crude oil	ρ_o, g/ml	μ_o at 22°C, cp	n-C7 asphalt., wt%
Minnelusa 98	0.9062	77.2	9.0
Minnelusa 02	0.9076	68.0	9.5

Table 3. Synthetic brine composition

Brine	NaCl (g/L)	KCl (g/L)	$CaCl_2$ (g/L)	$MgCl_2$ (g/L)	$MgSO_4$ (g/L)	Na_2SO_4 (g/L)	NaN_3 (g/L)	pH	TDS (mg/L)
Minnelusa	29.8	-	2.1	-	0.394	5.903	0.1	6.8	38297
Sea water	28	0.935	2.379	5.365	-	-	0.1	6.6	36779

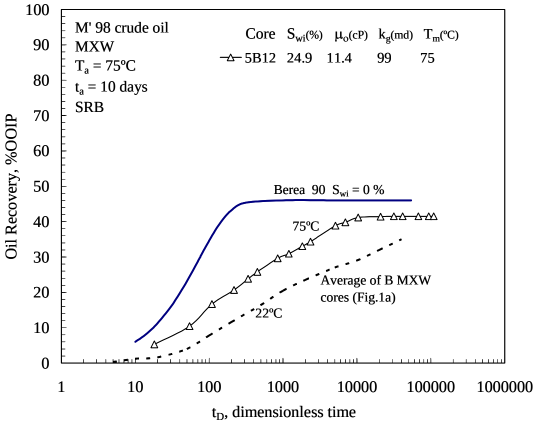
Table 4. Interfacial tensions between oleic phase and aqueous phase

	Samples	Temperature, ºC			
		20.0	30.0	45.0	75.0
IFT, mN/m	S220/SSW	53.3			46.9
	M’02/SSW	23.1	23.5	23.9	24.5
	M’98/SRB	28.8			29.7



1a. Reproducibility at 22ºC

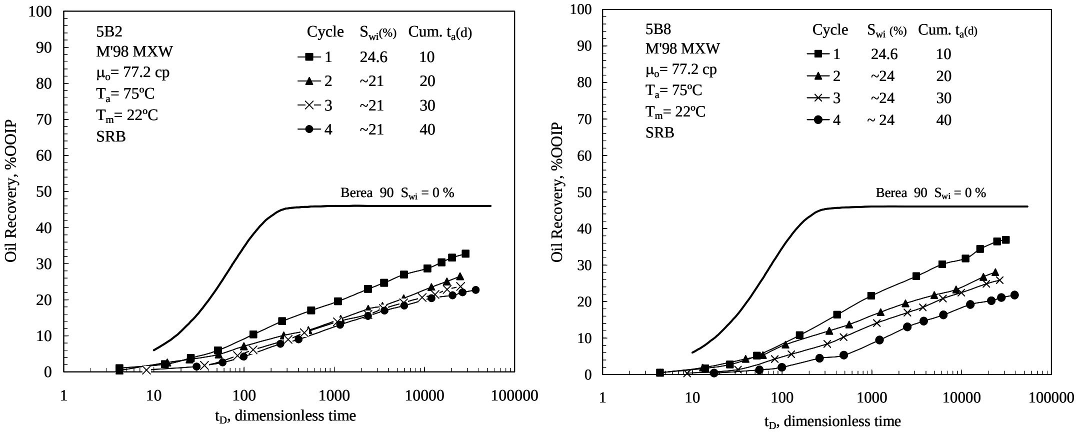
1b. Reproducibility at 75ºC (ambient vs. elevated pressure) and comparison with 22ºC



1c. Effect of temperature on Core 5B12

1d. Subsequent imbibition at 22ºC after imbibition at 75ºC

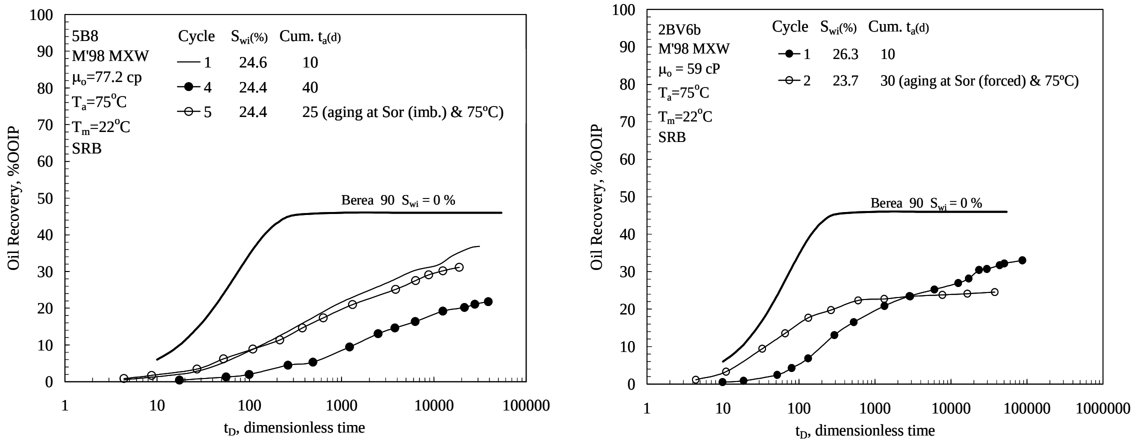
Figure 1. Effect of temperature on oil recovery by spontaneous imbibition for MXW cores.



2a. 5B2 core

2b. 5B8 core

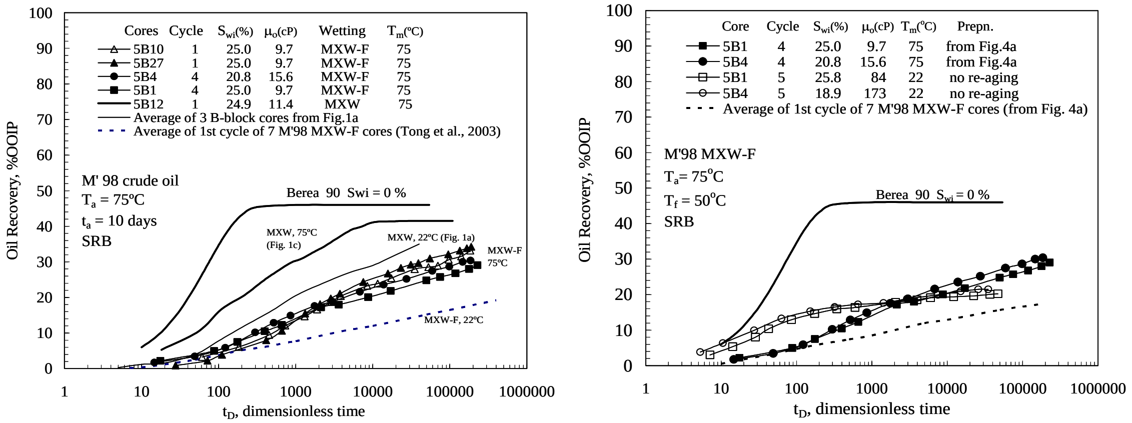
Figure 2. The effect of cumulative aging at S_{wi} and 75ºC on sequential oil recovery by spontaneous imbibition at ambient temperature (MXW B cores).



3a. Aged at S_{wi} vs. S_{or} (imb.) at 75°C

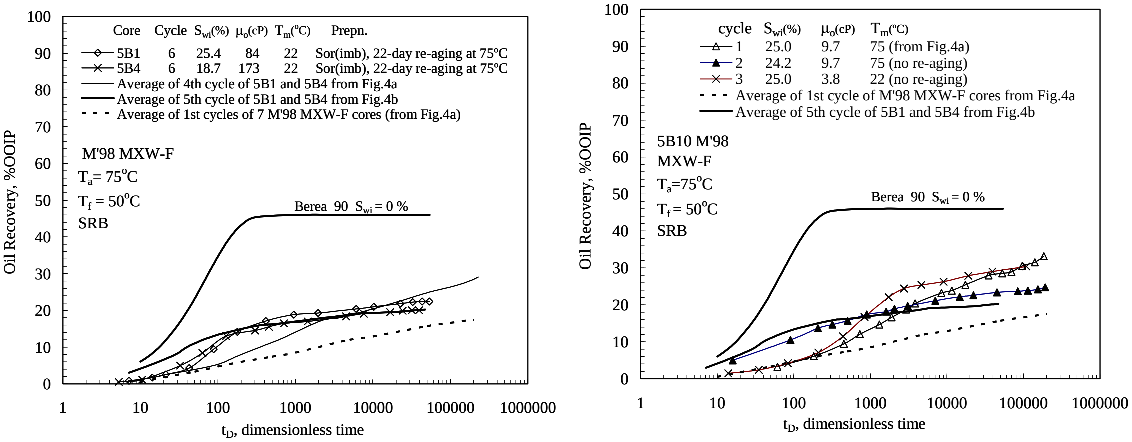
3b. Aged at S_{wi} vs. S_{or} (forced) at 75°C

Figure 3. Sequential imbibition at 22°C after re-aging at S_{or} (imb. or forced) at 75°C (MXW B cores) (Agreement of Core 5B8 between cycle1 and 5 is probably coincidence).



4a. MXW-F imbibition at 75°C

4b. Change in imbibition at 22°C after 4th cycle imbibition at 75°C



4c. Re-aged at S_{or} (imb) and 75°C for MXW-F cores

4d. Sequential imbibition of MXW-F Core 5B10

Figure 4. Imbibition at 75°C and re-aging at S_{or} and 75°C for MXW-F cores.