TITLE: EVALUATION OF RESERVOIR WETTABILITY AND ITS EFFECT ON OIL RECOVERY

Cooperative Agreement No.: DE-FC22-96ID13421
Contractor Name and Address: Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, Socorro, NM 87801

Date of Report: October 1, 1997

Award Date: July 1, 1996

Anticipated Completion Date: June 30, 2001

Government Award for Current Fiscal Year: $100,000

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Reporting Period: July 1, 1997 - September 30, 1997

Objectives

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

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

Summary of Technical Progress

1. Crude Oil/Brine/Solid Interactions

The interactions between crude oils, brines, and solid surfaces have been studied using a variety of core materials as well as in two-dimensional micromodels of interconnecting pores and throats. In the work reported this quarter, these same interactions have been applied to create mixed-wet conditions in a very simple model porous material, namely square glass tubes which have the advantage of permitting dual occupancy by both wetting and nonwetting phases simultaneously.[1,2]

The interactions between crude oil samples from Prudhoe Bay have been studied on a variety of surfaces. **Figure 1** outlines the regions of stable and unstable brine compositions with A-93, a sample from Prudhoe Bay, and glass surfaces. A brine with pH 8 and 1 *M* concentration of NaCl produces a stable water film between glass and A-93 crude oil. If the brine has pH 4 and 0.01 *M* NaCl, thin films of water are unstable and oil contacts the glass. Between these extremes is a wide band of brine compositions for which film stability is conditional.

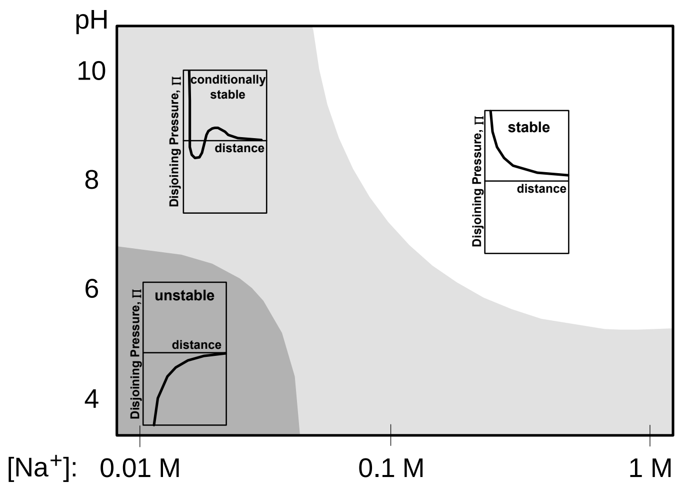

Figure 1. A-93/NaCl brine/glass stability regions (from reference 3).

Making use of the influence of brine composition on wetting alteration by A-93 crude oil allows the creation of a range of wetting conditions in the square tubes. These can be used to demonstrate the effects of wetting on imbibition.

2. Wetting Evaluation

The extent of spontaneous imbibition is often used to quantify the wetting of cores. Comparison of the amount of water or oil that imbibes spontaneously to that produced by viscous displacement, as proposed by Amott,[4] gives two indices, one for water (I_w) and another for oil (I_o). A great deal more information about the details of wetting might be obtained, however, from the rates at which these fluids imbibe if the mechanisms of imbibition were better understood. **Figure 2** shows the rate of imbibition of water into artificial cores that have been treated with varying pH brines and A-93 crude oil. These results demonstrated that varying the brine pH in order to influence water film stability can affect wetting alteration by adsorption from a crude oil in this model system. They also demonstrate that, as pointed out by Morrow,[5] I_w fails to distinguish between differences in wetting of very strongly water-wet and less strongly water-wet conditions (illustrated here by the pH 8 brine case), both of which have $I_w = 1$. In addition, there is an induction time[6] before significant amounts of oil began to be produced from either of the crude oil-treated cores. For the pH 8 case, this time was only a few minutes, but for pH 4, it was more than two days. Imbibition rates are affected by many factors including fluid viscosities, interfacial tensions, core dimensions, porosity, and permeability. Scaling to account for all of these factors has been proposed,[7] but in the cases shown here the differences persist, leaving wettability as the most likely explanation.

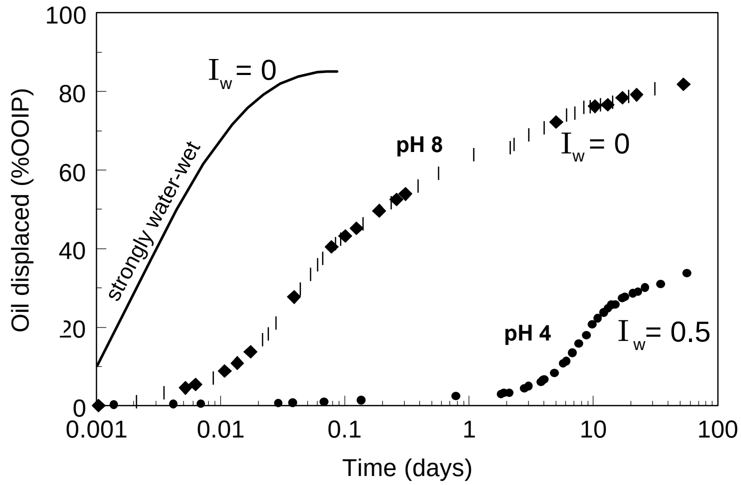

Figure 2. Water imbibition rate into Aerolith cores treated with brine and A-93 crude oil (from Ref. 8). Untreated, strongly water-wet core is shown for comparison (from Ref. 9).

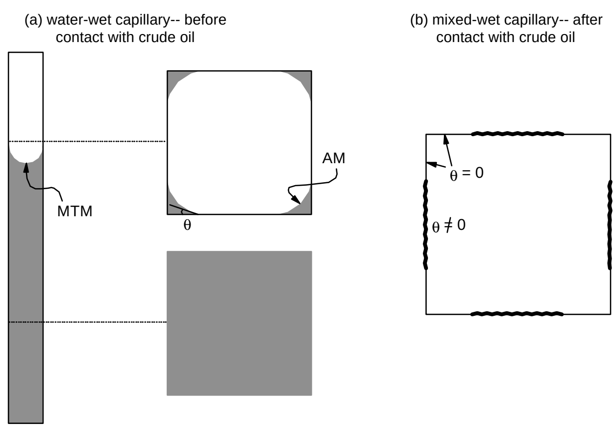

Figure 3. Square capillary tube: (a) Distribution of fluids in a water-wet capillary, partially filled with a nonwetting fluid. Note presence of water wedges in drained portion of the tube. (b) Wetting is altered on portions of the glass surface that were not covered by water during aging in crude oil.

A preliminary study of wetting alteration by crude oil in square capillary tubes has been completed.[10] Excerpts from that study are presented here to illustrate some of the similarities between imbibition into the tubes and that reported in previous studies with cores. Distribution of water and oil in a strongly water-wet square capillary partially filled with oil, are shown in **Fig.**

3a. When the capillary is drained, water is left as wedges in the corners. Subsequent filling with and aging in crude oil can alter the wetting of the pore walls without changing the wetting in the water-filled corners, as suggested by the drawing in **Fig. 3b**. Tubes were aged at 25°C.

Water/air imbibition and drainage

Mixed-wet conditions in the treated tubes were demonstrated by measurements of capillary rise of water against air, before and after treatment with brines of varying pH and A-93 crude oil. Meniscus height is related to capillary pressure, which is the product of interfacial tension and curvature. From the value of curvature, contact angles can be calculated using MS-P analysis (see for example Ref. 2 and references cited therein). In **Table 1** results are summarized for 1 mm^2 tubes aged first in brine (for 24 hours), then in A-93 crude oil (for 24-48 hours). Crude oil was removed by rinsing with toluene and decane after which the tubes were dried. Imbibition tests started with dry tubes; other tubes were refilled with water to observe drainage. Distilled water containing 3 vol % of red food color was the test fluid. In the columns headed $\theta_{uniform}$, contact angles were calculated assuming that the whole tube changed in wetting uniformly. θ_{mixed} indicates that wetting was assumed to correspond to **Fig. 3b** above. These numbers provide upper and lower limits on contact angles (with water as the reference phase).

Table 1. Results of water/air imbibition and drainage experiments in mixed-wet capillaries

Brine	Aged in oil	Drainage		Imbibition	
pH / [NaCl]	(hours)	$\theta_{uniform}$	θ_{mixed}	$\theta_{uniform}$	θ_{mixed}
4, 0.01	24	35°	42°	78°	115°
	48	25°	29°	80°	119°
4, 1	24	25°	29°	73°	105°
	46			77°	113°
6, 0.01	24			75°	109°
	46	18°	19°	75°	109°
6, 1	24			65°	90°
	46			57°	78°
8, 0.01	24			60°	81°
	48			65°	90°
8, 1	24			65°	90°
	48			66°	93°

Several observations can be made from the data in **Table 1**.

1. Contact angles decrease with increasing pH.

2. Hysteresis between advancing and receding contact angles is marked, as reported previously for contact angles measured on flat glass surfaces.[11]

3. An important observation is that wedges often form above the interfaces reported for imbibition in **Table 1**. Since wedges only form in a 90° corner if θ_A is less than 45°, and since all calculated values (with either the uniform or mixed-wet assumption) are greater than 45°, the formation of wedges is evidence for more water-wet surfaces remaining in the corners and thus for the mixed-wet model.

4. Note that imbibition in the case of a mixed-wet tube can occur even if the contact angle on the altered surfaces is greater than 90°.

Water/oil imbibition

Oil-filled tubes were submerged horizontally in brine and imbibition was observed with the aid of a microscope. The volume of oil remaining, estimated by measuring lengths of water-filled and oil-filled regions, was recorded as a function of time. Selected results are shown in **Fig. 4**. Also noted were the mechanisms by which water displaced oil. The two main mechanisms were piston-like motion of a main terminal meniscus (as defined in **Fig. 3**) and swelling of the water in the tube corners which can lead to snap-off and trapping of oil.

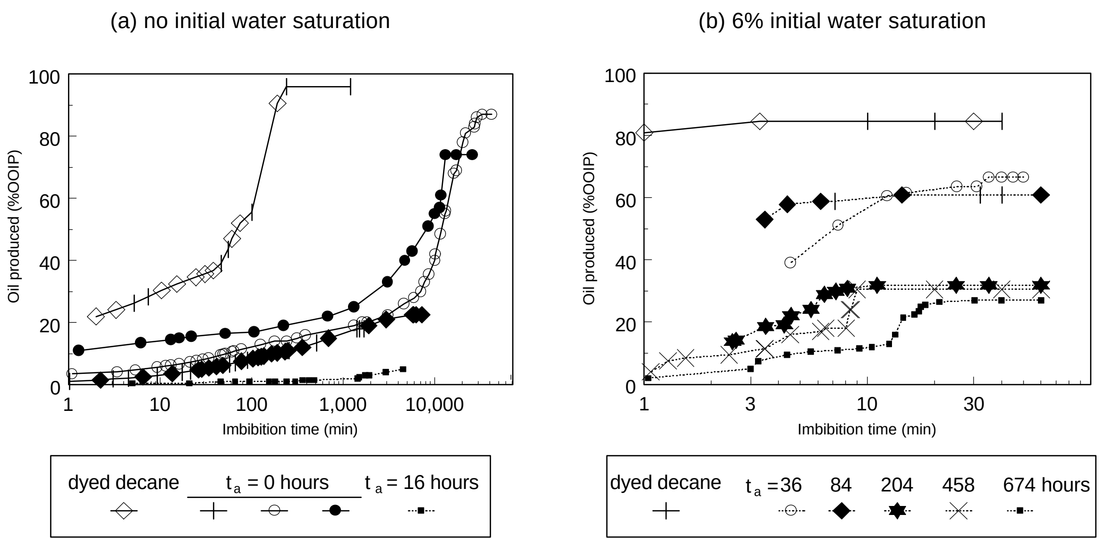

Figure 4. Rates of imbibition of 1 *M* NaCl brine (pH 8) into capillaries filled with dyed decane or A-93 crude oil and aged as indicated. (a) S_{wi} = 0, and (b) S_{wi} = 6%.

The rates shown in **Fig. 4a** are for capillaries with no initial water saturation. All interface movement was piston-like; little or no water could be seen in the tube corners. For dyed decane (θ_A = 20°), nearly all of the oil was removed by the spontaneously imbibing brine. When the oil was A-93, imbibition began slowly and the amount of oil imbibed varied widely in replicate tests. Imbibition continued, in some cases, for a week or more. Aging in oil for as little as 16 hours before submerging the capillary in brine almost eliminated imbibition.

Rates of brine imbibition into capillaries that had an initial brine saturation are shown in **Fig. 4b**. Note that the imbibition times in **Fig. 4b** are considerably shorter than those in **Fig. 4a**. When an initial water saturation was present, imbibition ceased within an hour. Displacement efficiency of dyed decane was 84% with the remainder trapped by snap-off of brine from the corners. For the crude oil, capillaries aged for as long as 28 days continued to imbibe, although the amount and rate of imbibition both generally decreased with aging time. In this the square tubes are reminiscent of similarly treated sandstone cores.[8] The lag or induction time at the start of imbibition also is similar to rates of imbibition for weakly water-wet cores (**see Fig. 2**). In square tubes, the induction period is associated with movement of water in the corner wedges, whereas most of the oil production occurs when the main terminal meniscus moves along the tube.

Details of these and many other experimental conditions including different brine compositions and combinations of aging and imbibing brines, as well as capillaries that were cleaned after aging so that imbibition began with no initial water saturation are covered in Ref. 10 and an accompanying videotape.

This preliminary study has demonstrated that

- noncircular capillaries can be rendered mixed-wet by treatments with selected brines and crude oils,
- the rate, extent, and mechanisms of imbibition can be observed, and
- imbibition rate curves have many similarities to measurements in cores.

The methods developed show great promise for relating contact angles to the spontaneous displacement of oil by water and improving wettability assessment in porous media.

References

1. Mason, G. and Morrow, N.R.: “Capillary Behavior of a Perfectly Wetting Liquid in Irregular Triangular Tubes,” *J. Colloid Interface Sci.* (1991) **141**, No. 1, 262-274.
2. Ma, S., Mason, G., and Morrow, N.R.: "Effect of Contact Angle on Drainage and Imbibition in Regular Polygonal Tubes," *Colloids and Surfaces A* (1996) **117**, 273-291.
3. Buckley, J.S., Liu, Y., Xie, X., and Morrow, N.R.: "Asphaltenes and Crude Oil Wetting—The Effect of Oil Composition," *SPEJ* (June, 1997) 107-119.
4. Amott, E.: "Observations Relating to the Wettability of Porous Rock," *Trans.*, AIME (1959) **216**, 156-162.
5. Morrow, N.R.: "Wettability and Its Effect on Oil Recovery," *JPT* (Dec. 1990) 1476-1484.
6. Zhou, X., Morrow, N.R., and Ma, S: "Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding," paper SPE 35436 presented at the 1996 SPE/DOE IOR Symposium, Tulsa, 21-24 April.
7. Ma, S., Morrow, N.R., and Zhang, X.: "Generalized Scaling of Spontaneous Imbibition Data for Strongly Water-Wet Systems," presented at the 1995 Saskatchewan Petroleum Conf., Regina, 16-18 Oct.
8. Buckley, J.S., Bousseau, C., and Liu, Y.: "Wetting Alteration by Brine and Crude Oil: From Contact Angles to Cores," *SPEJ* (Sept. 1996) **1**, No. 3, 341-350.

9. Hamon, G. and Vidal, J.: "Scaling-Up the Capillary Imbibition Process from Laboratory Experiments on Homogeneous and Heterogeneous Samples," paper SPE 15852 presented at the 1986 European Pet. Conf., London, Oct. 20-22.
10. Spildo, K. and Buckley, J.S.: “Mixed Wetting in Square Glass Capillaries,” PRRC 97-30 (October, 1997).
11. Liu, Y. and Buckley, J.S.: "Evolution of Wetting Alteration by Adsorption from Crude Oil," *SPEFE* (Mar. 1997) 5-11.