

# **Wetting Behavior of Selected Crude Oil/Brine/Rock Systems**

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## EXECUTIVE SUMMARY

Previous studies of crude oil/brine/rock (COBR) and related ensembles showed that wettability and its effect on oil recovery depend on numerous complex interactions. In the present work, the wettability of COBR ensembles prepared using Prudhoe Bay crude oil, a synthetic formation brine, and Berea Sandstone was varied by systematic change in initial water saturation and length of aging time at reservoir temperature (88°C). All displacement tests were run at ambient temperature. Various degrees of water wetness were achieved and quantified by a modified Amott wettability index to water, the relative pseudo work of imbibition, and a newly defined apparent advancing dynamic contact angle.

Pairs of spontaneous imbibition (oil recovery by spontaneous imbibition of water) and waterflood (oil recovery vs pore volumes of water injected) curves were measured for each of the induced wetting states. Several trends were observed. Imbibition rate, and hence water wetness, decreased with increase in aging time and with decrease in initial water saturation. Breakthrough recoveries and final oil recovery by waterflooding increased with decrease in water wetness. Correlations between water wetness and oil recovery by waterflooding and spontaneous imbibition are presented.

## INTRODUCTION

Wettability is an important factor in the performance of waterfloods.<sup>1</sup> Final recovery of oil by waterflood is expressed in this paper as  $R_{wf}$ , the fraction of the original oil in place (OOIP) recovered. Review of literature showed variations in  $R_{wf}$  could be very large and were strongly dependent on how wettability was established.<sup>2,3</sup> The wettability state induced by adsorption in the presence of an initial water saturation,  $S_{wi}$ , is referred to as mixed. The main characteristic of mixed wettability is that only the areas of rock surface exposed to crude oil undergo changes in wetting that are significant to the displacement process. The term mixed wettability was adopted by Salathiel<sup>4</sup> to describe this form of wettability distribution with strongly water-wet and strongly oil-wet surfaces. However, a wide range of wetting states can be induced by contact with crude oil, and adsorption of oil components does not necessarily result in a strongly oil-wet surface. Nevertheless, the geometric description of mixed wettability envisaged by Salathiel is still appropriate and in this paper is applied to all possible types of mixed wetting that depend on the location of bulk water in the rock at the time of adsorption. The term bulk water is used here to identify water retained by capillary forces as distinct from water retained by adsorption at solid surfaces as thin films. The fraction of  $S_{wi}$  existing as surface films is very small except at extremely low water saturations.

Jadhunandan and Morrow<sup>5</sup> showed that wettability can be varied in Berea Sandstone by changing the conditions for adsorption from crude oil. Variations in the crude oil/brine/rock (COBR) ensembles that were studied included the crude oil, brine, initial water saturation,  $S_{wi}$ , aging temperature of the rock in crude oil,  $T_a$ , and rate of flooding. The aging time,  $t_a$ , was standardized at 10 days. From the results for over 50 waterfloods, a correlation was obtained between oil recovery and wettability defined by the Amott-Harvey wettability index,<sup>6,7</sup>  $I_{w-o}$ , with the oil recovery peaking at close to neutral wettability (see Figure 1). For all wettability conditions below  $I_{w-o}=0.9$ , with two exceptions, produced water was accompanied by a small and decreasing fraction of oil. This mode of production was postulated by Salathiel<sup>4</sup> to result from a bi-continuous distribution of oil and water within the rock.

Jadhunandan and Morrow<sup>8</sup> also investigated factors influencing the rate of oil recovery by spontaneous imbibition. Two sets of imbibition and waterflood data measured under comparable conditions showed that the systems with the lower, but still finite, imbibition rates gave higher waterflood oil recoveries. Determination of the circumstances under which there are systematic relationships between oil recovery by spontaneous imbibition and by forced displacement (waterflooding) would be of special value in evaluating possible methods of improved oil recovery.

The objective of the present work was to obtain data for a COBR ensemble in which wettability was varied systematically. The selected system was Prudhoe Bay crude oil/synthetic formation brine/Berea Sandstone. In laboratory studies related to prediction of reservoir performance, choice of  $t_a$  is mainly governed by the need to provide sufficient time to achieve



adsorption equilibrium. This condition is assumed to match the reservoir wettability. Values of  $t_a$  on the order of two to six weeks are commonly adopted.<sup>9,10</sup> For investigation of relationships between wettability and oil recovery, variation of  $t_a$  provides a convenient method of obtaining systems with graded wettability,<sup>11</sup> while holding other variables constant. This approach was used in the present work to obtain 23 sets of spontaneous imbibition and waterflood data for different  $t_a$  at three levels of  $S_{wi}$  (nominally 15, 20, and 25%).

Special attention is given to using spontaneous imbibition curves (oil recovery vs imbibition time) to quantify wettability. This requires that the effect of wettability on imbibition rate be separated from the effect of interfacial tension, liquid viscosities, differences in permeability and porosity, and the size, shape, and boundary conditions of the core samples. A definition of dimensionless time has shown that these effects can be correlated for very strongly water-wet conditions.<sup>12</sup> Reduction in imbibition rate relative to the correlation for very strongly water-wet conditions can be ascribed to wettability. In the present work, relationships are presented between wettability and oil recovery by spontaneous imbibition and waterflooding.

## EXPERIMENTS

### Fluids

A Prudhoe Bay, Alaska, crude oil (A'93) was used as the oil phase. The crude oil was evacuated before use to reduce the possibility of gas evolution during the course of an experiment. The evacuated crude oil had a viscosity,  $\mu_o$ , of 39.25 cP and density,  $\rho_o$ , of 0.895 g/cc at 25°C. A refined oil, Soltrol 220,  $\mu_o$ =3.98 cP, was used to obtain a set of imbibition and waterflood data for very strongly water-wet conditions. A synthetic formation (SF) brine was prepared: 21.3g/l NaCl, 0.6g/l  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.1g/l KCl, 0.2g/l  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The brine, with viscosity,  $\mu_w$ , of 0.967 cP and density,  $\rho_w$ , of 1.012 g/cc at 25°C, was evacuated for about four hours before use. The interfacial tension between the brine and the evacuated crude oil was  $\sigma$ =24.2 dynes/cm measured by du Nouy ring tensiometer. The ring was flamed and immersed in brine. Crude oil was poured on the brine and the tension was measured for the ring passing from the brine to the oil phase.

### Preparation and Properties of Core Samples

A total of 41 core plugs were cut from several blocks of Berea Sandstone. Diameters and lengths of the cores were in the range of 3.80-3.82 cm and 6.4-7.8 cm, respectively. After cutting the plugs, the core samples were washed and dried at ambient temperature for two days. The cores were then dried in an oven at 105°C for at least two days and cooled in a vacuum chamber. Nitrogen gas permeability,  $k_g$ , of the cores was measured using a Hassler-type core holder at a confining pressure of 300 psi.

The dry core samples were vacuumed and saturated with the SF brine. Porosity,  $\phi$ , was determined from change in weight. The saturated cores were left immersed in brine for about 10 days to establish ionic equilibrium between the rock constituents and the brine. The original brine was then displaced with about 10 pore volumes (PV) of fresh brine during the course of measuring brine permeability,  $k_b$ . Values of porosity, gas permeability, and brine permeability are listed in Table 1.

### **Initial Water Saturation**

The brine was displaced by 3-5 PV of the A'93 crude oil at 25-30 psi pressure drop to give nominal initial water saturations,  $S_{wi}$ , of 25%. With the oil injection pressure reduced to 20-25 psi and the amount of oil injected increased to 5-10 PV, it was found that  $S_{wi}$  values of close to 20% could be obtained consistently. Initial water saturations of about 15% were established by oilflooding at 5 psi initially. The pressure drop was then gradually increased to 55 psi. Oil flow was continued for up to 15 pore volumes until the required water content was established. Initial water saturations for each experiment are listed in Table 1. During oilflooding, the direction of oil flow was reversed to alleviate possible end effects.

### **Core Sample Aging**

After establishing an initial water saturation, the core samples were removed from the core holder, immersed in the crude oil, and aged at 88°C for 1 to 240 h (Table 1). The beakers were covered with aluminum foil and sealed with a high-temperature glue to minimize loss of water and light ends from the crude oil during the aging period. After aging, cores were allowed to cool for at least 6 hrs. Comparison of core weight before and after aging showed essentially no change in initial water saturation. The oil that was in the core during aging was displaced with 8-10 PV of evaporated stock crude oil at 10-15 psi injection pressure prior to making the spontaneous imbibition and waterflood measurements. Tests were also run on cores for which there was no aging at elevated temperature and contact time with the crude oil before initiation of the test was minimal (nominal aging time of 0 h).

### **Spontaneous Imbibition**

The rates of spontaneous imbibition into the aged cores were measured at ambient temperature. A core was suspended in degassed brine by monofilament line attached to an electronic balance (accuracy to 0.0001 g). The change in weight of the core suspended under brine was recorded vs time. The amount of oil expelled was determined gravimetrically. Before weighing, expelled oil that was still attached to the core was removed with a polytetrafluorethylene (Teflon) rod.

**Table 1 Experimental Conditions, Oil Recovery and Wettability**

Core No.	$\phi$ (%)	$k_g$ (md)	$k_b$ (md)	$S_{wi}$ (%)	$t_a$ (h)	Test	R (%OOIP)	$I'_w$	$W_R$	$\cos \theta_{Ad}$
1	21.3	639	358	15.5	0	WF	41.6	0.73	0.35	0.25
2	22.2	666	359	16.0	1	WF	43.3	-	-	-
3	21.8	640	365	15.8	4	WF	47.4	0.70	0.16	0.027
4	21.3	661	366	16.3	6	WF	50.8	-	-	-
5	21.1	625	353	16.8	12	WF	52.2	-	-	-
6	21.3	625	354	15.0	24	WF	55.2	-	-	-
7	21.3	649	353	16.2	48	WF	58.0	0.50	0.051	0.0047
8	21.6	627	343	15.2	72	WF	60.2	0.42	0.021	0.0012
9	21.1	641	361	15.7	240	WF	63.1	0.19	0.0066	0.00074
10	21.7	667	360	15.4	0	SI	30.7	0.73	0.35	0.25
11	21.5	625	355	15.1	4	SI	33.3	0.70	0.16	0.027
12	21.4	614	365	15.9	48	SI	29.0	0.50	0.051	0.0047
13	22.5	585	300	16.9	72	SI	25.4	0.42	0.021	0.0012
14	21.7	617	364	15.4	240	SI	11.8	0.19	0.0066	0.00074
15	21.8	536	351	20.2	0	WF	38.2	0.84	0.37	0.3
16	22.5	540	373	19.7	1	WF	39.1	0.80	0.28	0.17
17	22.4	510	388	20.2	4	WF	41.1	0.92	0.19	0.036
18	22.4	601	372	21.5	6	WF	48.2	0.76	0.17	0.029
19	21.8	454	202	20.0	12	WF	50.7	0.70	0.12	0.012
20	21.9	467	194	20.3	24	WF	51.7	0.68	0.073	0.0053
21	21.4	467	216	20.0	48	WF	54.8	0.59	0.048	0.0046
22	21.6	525	216	19.8	72	WF	57.8	0.47	0.03	0.0018
23	21.8	566	355	21.2	240	WF	59.2	0.23	0.0093	0.00079
24	22.3	562	365	19.6	0	SI	32.1	0.84	0.37	0.3
25	22.0	500	363	19.0	1	SI	31.4	0.80	0.28	0.17
26	22.6	542	360	19.9	4	SI	37.7	0.92	0.19	0.036
27	22.0	532	336	20.5	6	SI	36.7	0.76	0.17	0.029
28	22.5	565	343	19.5	12	SI	35.3	0.70	0.12	0.012
29	22.6	594	374	19.5	24	SI	35.1	0.68	0.073	0.0053
30	22.0	522	357	20.4	48	SI	32.8	0.59	0.048	0.0046
31	22.3	581	367	20.1	72	SI	27.2	0.47	0.03	0.0018
32	21.8	566	355	20.6	240	SI	13.7	0.23	0.0093	0.00079
33	22.1	509	343	25.4	0	WF & SI	36.3	0.95	0.41	0.36
34	22.2	523	381	24.7	1	WF & SI	37.3	0.98	0.37	0.63
35	22.1	469	308	25.2	4	WF & SI	41.8	0.96	0.24	0.057
36	21.8	534	359	25.0	6	WF & SI	40.3	0.88	0.18	0.040
37	22.2	521	394	26.0	12	WF & SI	39.4	0.81	0.16	0.034
38	22.1	501	354	25.9	24	WF & SI	36.1	0.73	0.13	0.025
39	20.5	525	315	25.1	48	WF & SI	35.1	0.71	0.15	0.021
40	22.0	521	352	26.1	72	WF & SI	32.3	0.66	0.058	0.0080
41	20.8	552	347	25.1	240	WF & SI	24.2	0.45	0.031	0.00072

## Waterfloods

The waterflood apparatus used in this study was designed for either constant rate or constant pressure waterfloods at ambient temperature. All of the waterflood tests were performed at slow rates using a constant pressure of 5 psi. Oil production vs time was determined from volumetric measurements. The waterflood was stopped after 4-15 PV of brine injection when the water-oil ratio was greater than 99 to 1. This criterion provided an operational definition for final waterflood recovery,  $R_{wf}$ .

## Duplicate and Reused Core Plugs

For core samples with  $S_{wi} \approx 25\%$ , after completion of the spontaneous imbibition tests, the core samples were flushed with about 5-10 PV of the crude oil at 30 psi to re-establish the initial water saturation. The duration of oilflooding and the magnitude of the displacement pressure depended on the amount of water production. First and second initial water saturations agreed within 1%, and so for initial water saturations of 25%, core plugs were reused for the waterflood measurements. Difficulty was encountered in re-establishing initial water saturations of 20% and 15%. Duplicate cores, one for spontaneous imbibition and the other for waterflood tests, were therefore used.

# RESULTS AND DISCUSSION

## Imbibition and Waterflood Recovery Curves

Waterflood and imbibition results are presented for nominal values of initial water saturation,  $S_{wi}$ , of 15%, 20%, and 25% in Figures 2, 3, and 4, respectively. Test conditions for 23 spontaneous imbibition tests and 27 waterfloods are summarized in Table 1. Aging times ranged from 1 to 240 hrs.

Figures 2a, 3a, and 4a show the effect of aging time on the relationships between oil recovery by imbibition,  $R_{im}$ , and imbibition time,  $t$ . Imbibition rate decreases systematically with increase in aging time. Oil recovery by imbibition exhibited a maximum at 4 hrs aging time for all three data sets. Increase in recovery by imbibition over that for very strongly water-wet conditions has been attributed to increased microscopic displacement efficiency.<sup>13, 14</sup>

The effect of aging time on the relationships between oil recovery by waterflooding,  $R_{wf}$ , and pore volumes of brine injected at initial water saturations of 15, 20, and 25% is shown in Figures 2b, 3b, and 4b, respectively. Oil recovery by waterflooding increases with increase in aging time. Comparison of recovery curves by imbibition (Figures 2a, 3a, and 4a) with recovery curves by waterflooding (Figures 2b, 3b, and 4b) shows that as imbibition rate decreases, oil recovery by

waterflooding increases. The results for recovery of Soltrol 220 by waterflooding and A'93 crude oil for a nominal aging time of zero shows water breakthrough to be earlier for the crude oil. The crude oil was more viscous than Soltrol 220 by a factor of ten. Final recoveries were almost identical.

The effect of initial water saturation,  $S_{wi}$ , on oil recovery by imbibition and waterflooding is shown in Figures 5a and 5b for an aging time of 240 h. Both imbibition rate and final recovery by imbibition decrease with decrease in initial water saturation, whereas oil recovery by waterflooding increases.

Oil recovery by waterflooding,  $R_{wf}$ , vs oil recovery by imbibition,  $R_{im}$ , is shown in Figure 6. At each initial water saturation,  $R_{im}$  passed through a maximum in recovery that corresponds to about 4 hrs of aging. At longer aging times, waterflood recovery increases with decrease in  $R_{im}$ .

Oil recovery by waterflooding at breakthrough,  $R_{bt}$ , is a key parameter in economic evaluation of waterfloods.  $R_{wf}$  may not be achievable in practice because the required volume of injected water is unrealistic. Effects of aging time,  $t_a$ , and initial water saturation,  $S_{wi}$ , on oil recovery by waterflooding at breakthrough,  $R_{bt}$ , and final waterflood oil recovery,  $R_{wf}$ , are summarized in Figure 7. From this figure, it can be seen that both  $R_{bt}$  and  $R_{wf}$  increase with aging time. The final oil recoveries by waterflooding, shown in Figure 7, are compared in Figure 8 with oil recovery by imbibition as a function of aging time.

Figure 8 shows that, for any aging time,  $R_{im}$  decreases with decrease in initial water saturation. This decrease in  $R_{im}$  is consistent with reduced water wetness; as  $S_{wi}$  decreases, more of the rock surface is exposed to wettability alteration by adsorption from the crude oil. Quantitative analysis of the effect of exposed solid surface and contact angle on imbibition pressures has recently been presented for pores of polygonal cross sections.<sup>15</sup>

### **Scaling of Spontaneous Imbibition**

Imbibition data for very strongly water-wet conditions can be scaled through use of a dimensionless time,  $t_D$ , defined by,<sup>16</sup>

$$t_D = t \sqrt{\frac{k}{\phi} \frac{\sigma}{\sqrt{\mu_w \mu_o}} \frac{1}{L_C^2}} \quad (1)$$

where

$L_C$  is a characteristic length determined by the size, shape and boundary conditions of a sample.

$$L_c = \sqrt{\frac{V}{\sum_{i=1}^n \frac{A_i}{X_{Ai}}}} \quad (2)$$

$V$  is the bulk volume of the core sample,  $A_i$  the area perpendicular to the  $i$ th imbibition direction, and  $X_{Ai}$  the distance from  $A_i$  to the no-flow boundary.

The driving force for imbibition is proportional to the interfacial tension,  $\sigma$ . Applicability of the geometric mean of the water and oil viscosities,  $\mu_{gm}$ , for scaling of imbibition data was determined by experiment.<sup>16</sup>

The term  $\sqrt{k/\phi}$  is proportional to a microscopic radius, usually known from the parallel bundle of equal cylindrical tubes model as the Leverett radius,<sup>17</sup>

$$r_L = \sqrt{\frac{8k}{\phi}} \quad (3)$$

Use of  $\sqrt{k/\phi}$  in Equation 1 provided close correlation of results for a limited number of types of strongly water-wet porous media.<sup>12</sup> Further investigation of this aspect of the correlation is needed for a wider variety of rock types.

Imbibition data from Figures 2 through 4 are presented as plots of oil recovery, normalized with respect to final recovery, vs  $t_D$  (Figure 9). A reference curve of  $R_m$  vs  $t_D$  for very strongly water-wet (VSWW) Berea Sandstone cores of different sizes and boundary conditions<sup>18</sup> is included in Figure 9. Differences between this curve and the data identified by various aging times are ascribed to wettability.

## **Characterization of Wettability**

### **Amott Wettability Index**

The Amott wettability index is defined as the ratio of saturation change by spontaneous imbibition,  $\Delta S_m$ , to the saturation change by both spontaneous imbibition and forced displacement,  $\Delta S_{wf}$ . The Amott wettability index to water,  $I_w$ , can then be expressed as

$$I_w = \frac{\Delta S_{im,w}}{\Delta S_{im,w} + \Delta S_{wf}} \quad (4)$$

Similarly, the Amott wettability index to oil,  $I_o$ , is defined by

$$I_o = \frac{\Delta S_{im,o}}{\Delta S_{im,o} + \Delta S_{of}} \quad (5)$$

The difference between  $I_w$  and  $I_o$  gives the Amott-Harvey wettability index.<sup>6,7</sup>

$$I_{w-o} = I_w - I_o \quad (6)$$

In the original method proposed by Amott,<sup>6</sup>  $\Delta S_{wf}$  was measured by centrifuging the core after allowing spontaneous imbibition for 20 hours. Jadhunandan and Morrow<sup>5</sup> substituted waterflooding for the centrifuge step as proposed by Cuiec.<sup>10,19</sup> Small variations in measured wettability that depend on the sequence of displacements have been discussed by Jadhunandan.<sup>20</sup> In the present work, recovery by imbibition and waterflooding were determined separately. A modified Amott index to water,  $I'_w$ , can be defined as:

$$I'_w = \frac{R_{im,w}}{R_{wf}} \quad (7)$$

$I_w$  and  $I'_w$  are equivalent if the recovery obtained by waterflooding is equal to the recovery obtained by imbibition followed by forced displacement.

In this study, only the value of  $I'_w$  was measured.  $I'_o$  and  $I'_{w-o}$  can be defined by analogy with the definitions of  $I_o$  and  $I_{w-o}$ . Displacement of water by spontaneous imbibition of oil, if observed at all, is very small except for very weakly water-wet systems.<sup>5</sup> Thus, except when  $I'_w$  is low, comparisons between  $I'_w$  and  $I'_{w-o}$  should be equivalent.

### Pseudo Work of Imbibition

The application of spontaneous imbibition data to characterization of wettability has been summarized by Cuiec.<sup>10</sup> Recently, Ma *et al.*<sup>13</sup> proposed a wettability index described as the relative pseudo work of imbibition,  $W_R$ . Figure 9 shows that increase in aging time results in decrease in the rate of spontaneous imbibition. The first step in determining  $W_R$  for such data is to derive pseudo capillary pressure curves,  $P_{c,s}$  vs  $S_w$ , where

$$P_{c,s} = t_D^{-\frac{1}{2}} \quad (8)$$

The  $P_{c,s}$  vs  $S_w$  curves, for systems with initial water saturation of 15, 20, and 25% are shown in Figure 10. The curves are based on changes in saturation under dynamic conditions and are obviously not directly related to standard capillary pressure imbibition curves. The pseudo capillary pressure curves for very strongly water-wet systems are also included in Figure 10.

The area under each  $P_{c,s}$  vs  $S_w$  curve gives the pseudo work of imbibition,  $W$ .

$$W = \int_{S_{wi}}^{1-S_{or,in}} P_{c,s} dS_w \quad (9)$$

The ratio of  $W$  to the value of  $W$  for VSWW conditions, described as the relative pseudo work of imbibition, defines the wettability index,  $W_R$ .

The relative pseudo work of imbibition,  $W_R$ , represents primarily the rate and also the extent of spontaneous imbibition. The value of  $W_R$  is strongly influenced by early time behavior (Equations 8 and 9).

A plot of  $W_R$  vs  $I'_w$ , presented in Figure 11, shows there is a close correlation between  $I'_w$  and  $W_R$  for  $I'_w < 0.8$ . Amott wettability indices are determined by endpoint values for spontaneous imbibition without direct regard to imbibition rate. Use of a wettability index based on imbibition rate is especially advantageous for distinguishing degrees of water wetness for systems that are commonly given the single classification of very strongly water-wet when  $I_w > 0.8$ .



### Apparent Dynamic Advancing Contact Angle

A more direct approach to wettability characterization is to assume that imbibition rate is proportional to the cosine of an effective dynamic advancing contact angle,  $\Theta_{Ad}$ . This angle can be defined by analogy with the cylindrical tube model. Various approaches can be taken to determining  $\Theta_{Ad}$  through comparison with recovery for very strongly water-wet conditions. If  $\cos \Theta_{Ad}$  is defined by the ratio of the dimensionless time for half the total recovery by spontaneous imbibition for very strongly water-wet conditions to the corresponding  $t_D$ , then

$$\Theta_{Ad} = \cos^{-1} \frac{t_{D,vsww}(0.5)}{t_D(0.5)} \quad (10)$$

Imbibition data is then automatically correlated at the  $0.5 R_{im}$  point by defining  $t_{D\theta}$  as

$$t_{D\theta} = t_D \cos \Theta_{Ad} \quad (11)$$

or

$$t_{D\theta} = t_D \sqrt{\frac{k}{\phi} \frac{\sigma \cos \Theta_{Ad}}{\sqrt{\mu_w \mu_o}} \frac{1}{L_C^2}} \quad (12)$$

Differences in shapes of imbibition curves can be compared by use of  $t_{D\theta}$ .

The relationship between  $\Theta_{Ad}$  and contact angles operative within the rock is complex. Surface roughness, pore geometry, the minerals lining the relevant pore surfaces and the location of the initial and invading brine will all contribute to determining local values of contact angle that result from interactions with the crude oil.

If curvatures and dynamic capillary pressure are defined respectively as

$$C_{im} \propto \frac{\cos \Theta_{Ad}}{r_L} \quad (13)$$

and

$$P_{cd} \propto \frac{\sigma \cos \Theta_{Ad}}{r_L} \quad (14)$$

$t_{D\theta}$  can be expressed as,

$$t_{D\theta} \propto t \frac{k}{\phi} \frac{P_{cd}}{\sqrt{\mu_w \mu_o}} \frac{1}{L_C^2} \quad (15)$$

The correlation shown in Figure 12 between  $\Theta_{Ad}$ , based on a single point, and  $W_R$ , based on the complete imbibition curve, shows that either of these related quantities can be used to characterize wettability for this data set.

For  $W_R$  below 0.20, all of the values of  $\Theta_{Ad}$  are between  $87^\circ$  and  $90^\circ$ . This does not mean that the distribution of advancing contact angles at pore surfaces within the cores are necessarily close to these values. (This would obviously be a great coincidence.) Imbibition can occur even for angles well in excess of  $90^\circ$  provided water occupies the corners of the pores.<sup>15</sup> The combined effect of the oil/water interfaces and the contact angle at the COBR three-phase line of contact determines the interface curvature and, hence, the capillary pressure that drives the imbibition process.

As  $\Theta_{Ad}$  approaches  $90^\circ$ , it appears that imbibition depends on slow changes in wettability that accompany encroachment of the three-phase line of contact on surfaces that are overlain by crude oil. Decrease in oil/brine contact angles with time and complex phenomena related to adsorption/desorption of crude oil components have been reported.<sup>21-23</sup> As the interface advances, the interface curvature remains very close to zero, but the capillary pressure is still slightly positive. This explains why COBR imbibition capillary pressures determined by conventional methods are often observed to remain very close to zero over a wide range of increase in water saturation. It may also explain why the COBR imbibition process sometimes exhibits an induction period before oil recovery begins, as shown in Figures 9a and b.

### **Aging Time, Initial Water Saturation, and Wettability**

#### **Aging Time**

Figure 13 shows how the relative pseudo work of imbibition,  $W_R$ , and the wettability index to water,  $I'_w$ , decrease with aging time,  $t_a$ . For aging times of less than about 4 hrs,  $I'_w$  is not sensitive to  $t_a$ , whereas  $W_R$  decreases sharply. At long aging times,  $I'_w$  is more sensitive than  $W_R$ .

### Initial Water Saturation

Figure 14 shows that  $W_R$  decreases with decrease in  $S_{wi}$ . It has been shown that relationships between wettability and initial water saturation can be strongly dependent on crude oil properties.<sup>5</sup> Correlations between  $I_w$  and  $S_{wi}$  for Moutray and ST-86 crude oils are shown in Figure 15. Results from the present study for 48-, 72-, and 240-hr aging times are also included in this figure. As aging time increases, the data for A'93 crude oil approach the correlation obtained for Moutray crude oil (see Figure 15).

### Wettability and Oil Recovery

Oil recovery at breakthrough,  $R_{bt}$ , vs relative pseudo work of imbibition,  $W_R$ , and final oil recovery by waterflooding,  $R_{wf}$ , vs  $W_R$  are shown in Figure 16. Both  $R_{bt}$  and  $R_{wf}$  are fairly constant for systems with  $W_R > 0.20$ . For  $W_R < 0.20$ , there is close correlation between  $R_{bt}$  vs  $W_R$  and  $R_{wf}$  vs  $W_R$ , especially for initial water saturations of 15% and 20%; results for 25% initial water saturation are relatively more scattered. This may be related to employing reused, rather than duplicate, core plugs. For mixed wettability systems, the water saturation retained after secondary drainage is generally higher than for primary drainage.<sup>24</sup> Even though measures can be taken to achieve the same magnitude of initial water saturation as for primary drainage, the distribution may not be the same. Furthermore, possible desorption and/or adsorption of crude oil components onto rock surfaces related to the distribution of water and the reuse of cores may also affect the waterfloods.

Figure 17 shows the relationship between oil recovery by imbibition,  $R_{im}$ , and the relative pseudo work of imbibition,  $W_R$ . The correlation between  $R_{wf}$  and  $W_R$  is also included in this figure for comparison. For  $W_R < 0.20$ , there is close correlation of results for all levels of initial water saturation.

The relationships between oil recovery by waterflooding at breakthrough,  $R_{bt}$ , and final oil recovery by waterflooding,  $R_{wf}$ , and Amott wettability index to water,  $I'_w$ , are shown in Figure 18. Figure 19 shows the relationship between oil recovery by imbibition,  $R_{im}$ , and  $I'_w$ . The correlation between  $R_{wf}$  and  $I'_w$  is also included in this figure. Both the relative pseudo work of imbibition and the Amott wettability index to water correlate with oil recovery.

The results of this study further demonstrate the highly significant effect of wettability on the waterflood recoveries both at and after breakthrough. The trend of increase in waterflood recovery with decrease in imbibition rate agrees with previous results for which wettability was varied by differences in aging temperature.<sup>8</sup> However, both imbibition rate and waterflood recovery were observed to increase for a synthetic core material with increase in brine pH from 4 to 8.<sup>25</sup> Thus, while

change in imbibition rate usually signifies a change in waterflood recovery, the direction of change can be highly dependent on the circumstances. Additional imbibition and waterflood data sets for variation in all three components of COBR ensembles and testing protocol are needed to establish a satisfactory working knowledge of the relationships between wettability and oil recovery.

## CONCLUSIONS

Based on results for which cores were aged with crude oil at elevated temperature and imbibition and waterflood tests were run at room temperature to provide varying degrees of water wetness, the following conclusions can be drawn:

1. Rate of spontaneous imbibition is highly sensitive to wettability. Correlated spontaneous imbibition data can be used to characterize wettability either through the relative pseudo work of imbibition, which involves the whole imbibition curve, or by an apparent dynamic advancing contact angle based on the time required for 50% recovery by imbibition.
2. Increase in aging time resulted in decrease in water wetness as indicated by the Amott wettability index to water, the apparent dynamic advancing contact angle, or the relative pseudo work of imbibition.
3. Decrease in initial water saturation in the range of 25-15% resulted in decrease in water wetness.
4. Oil recovery by spontaneous imbibition passes through a maximum in recovery with decrease in water wetness from very strongly water-wet conditions.
5. Oil recovery by waterflooding increased with decrease in water wetness for crude oil/brine/rock ensembles in which aging time and initial water saturation were varied and other factors were held essentially constant.

## NOMENCLATURE

A = area, $L^2$ , $cm^2$	V = bulk volume, $L^3$ , $cm^3$
I = Amott wettability index	W = pseudo work of imbibition
k = permeability, $L^2$ , md	X = distance from imbibition surface to no-flow boundary, L, cm
L = length, L, cm	$\Theta$ = apparent dynamic advancing contact angle
N = dimensionless number	$\mu$ = viscosity, m/Lt, cP
P = pressure, m/Lt <sup>2</sup> , psi	$\phi$ = porosity
r = radius, L, cm	$\rho$ = density, m/L <sup>3</sup> , g/cm <sup>3</sup>
R = oil recovery	$\sigma$ = interfacial tension, m/t <sup>2</sup> , dynes/cm
S = saturation	
t = time, t, min	
T = temperature, °C	

## SUBSCRIPTS

a = aging	im = imbibition
A = advancing	L = Leverett or length
b = brine	o = oil
bt = breakthrough	of = oilflood
C = characteristic	oi = initial oil
cd = dynamic capillary	or = residual oil
c,s = pseudo capillary	R = relative
C,S = characteristic for simulation	VSWW = very strongly water wet
D = dimensionless	w = water
d = dynamic	wf = waterflood
g = gas	wi = initial water
gm = geometric mean	w-o = Amott-Harvey water-oil
i = ith imbibition direction	

## SUPERSCRIPTS

' = modified Amott index

## **DISCLAIMER**

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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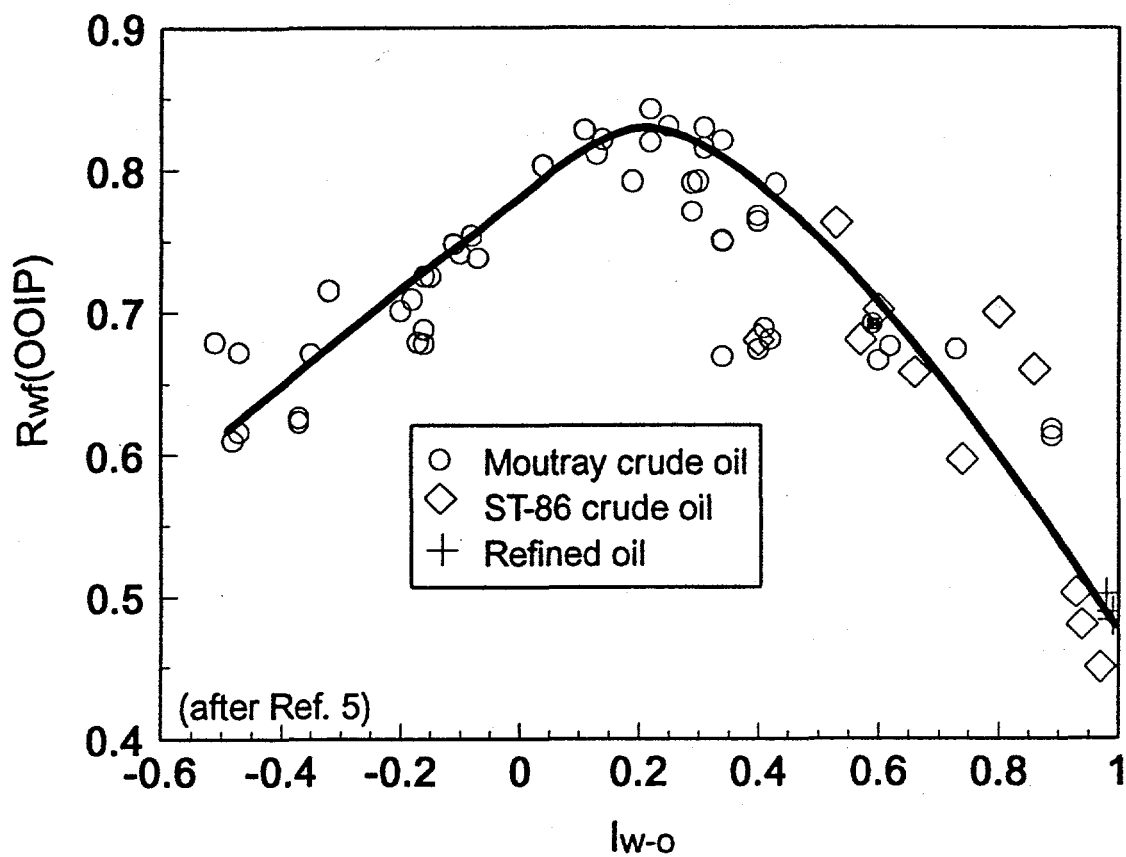


Figure 1. Waterflooding recovery at 20 pore volumes (pv) of brine injection vs Amott-Harvey wettability index for different oils.

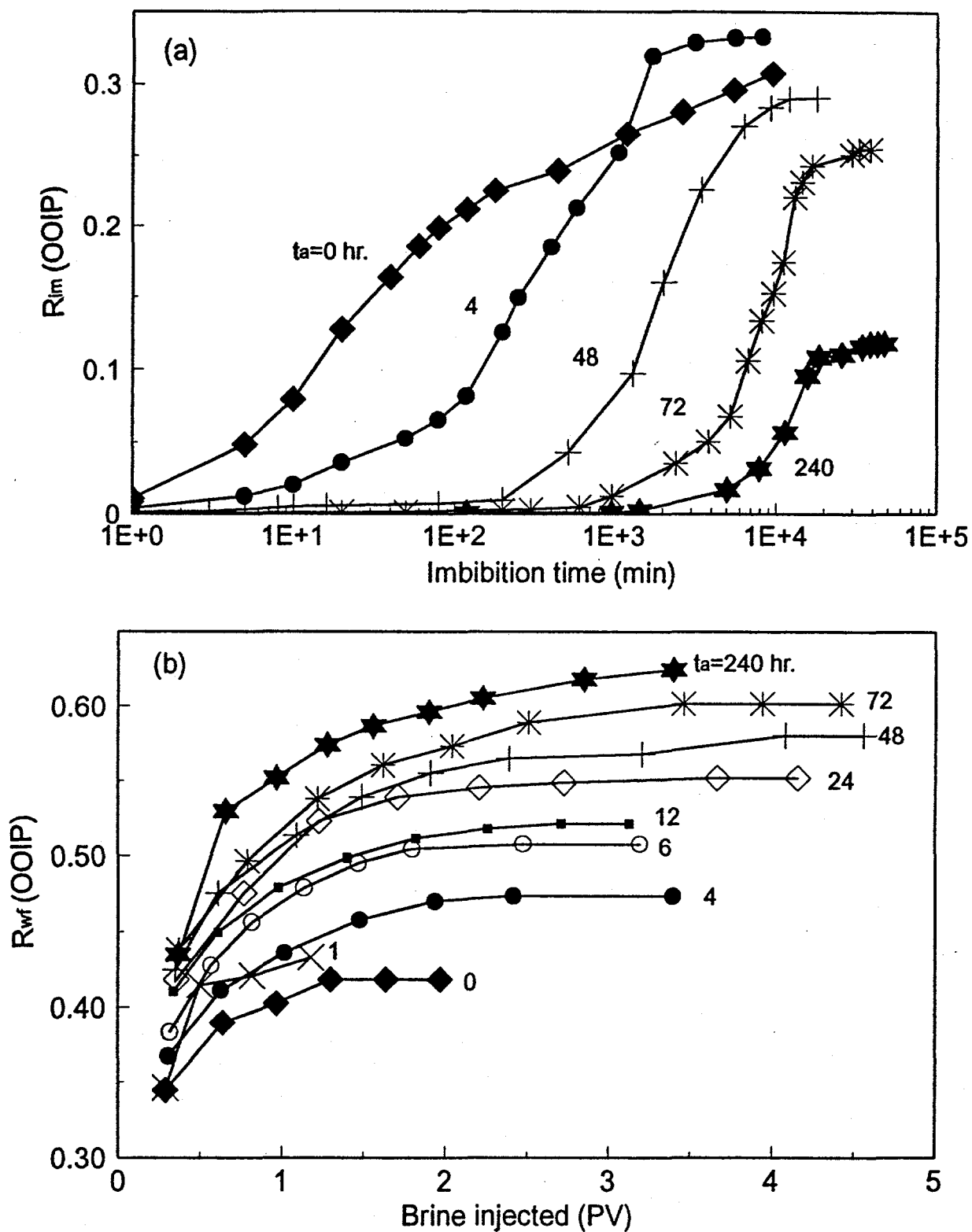


Figure 2. (a) Oil recovery by imbibition vs. imbibition time and (b) oil recovery by waterflooding vs. pore volumes of brine injected for crude oil/brine/rock (COBR) systems at different aging times ( $S_{wi}=15\%$ ).

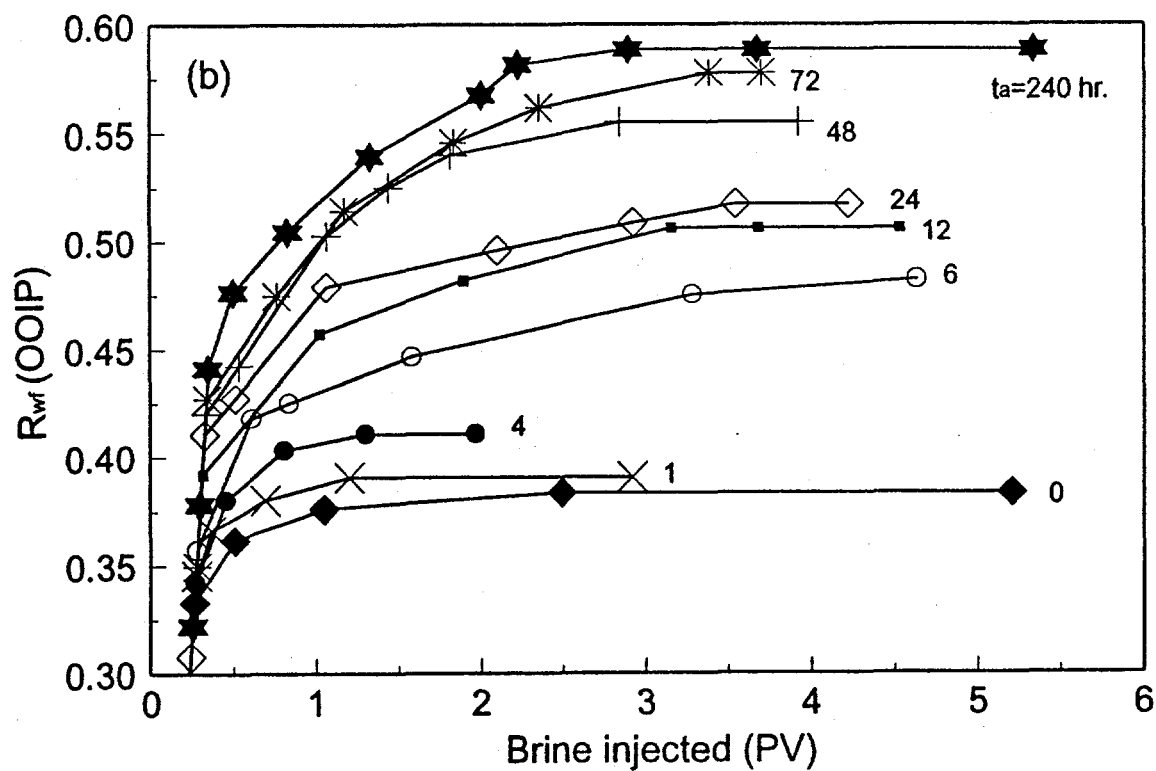
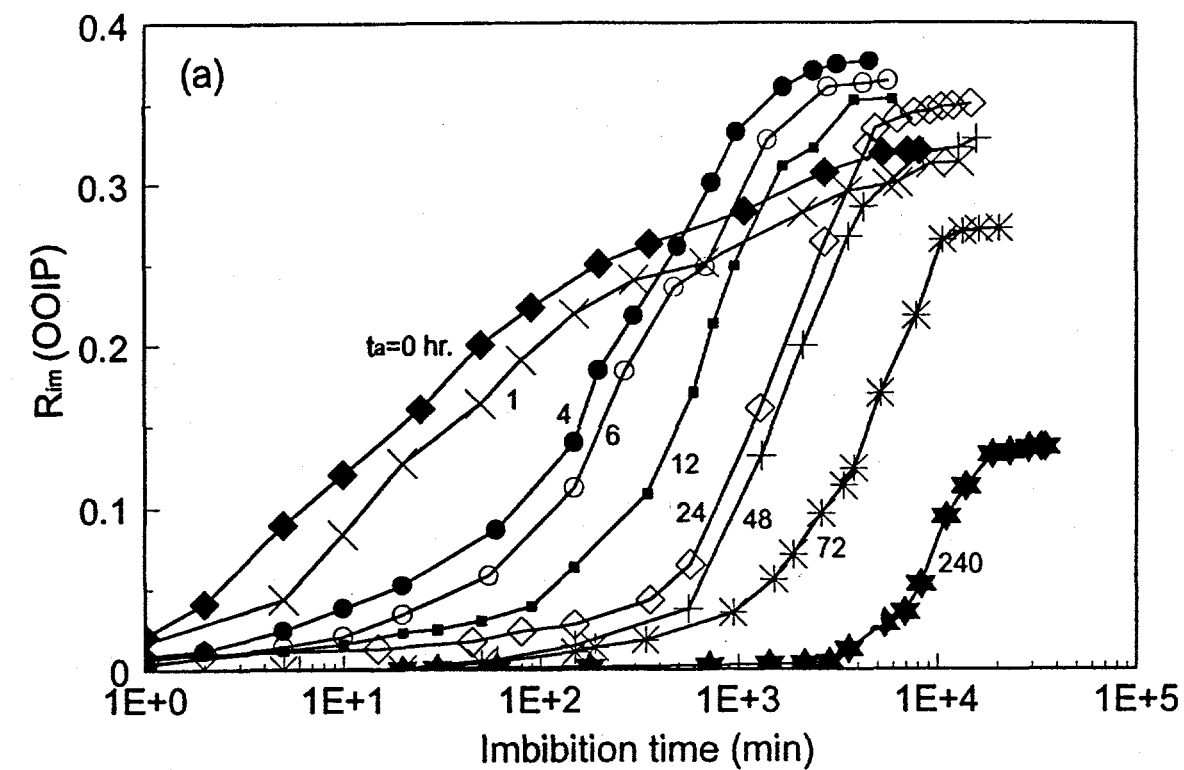


Figure 3. (a) Oil recovery by imbibition vs. imbibition time and (b) oil recovery by waterflooding vs. pore volumes of brine injected for COBR systems at different aging times ( $S_{wi}=20\%$ ).

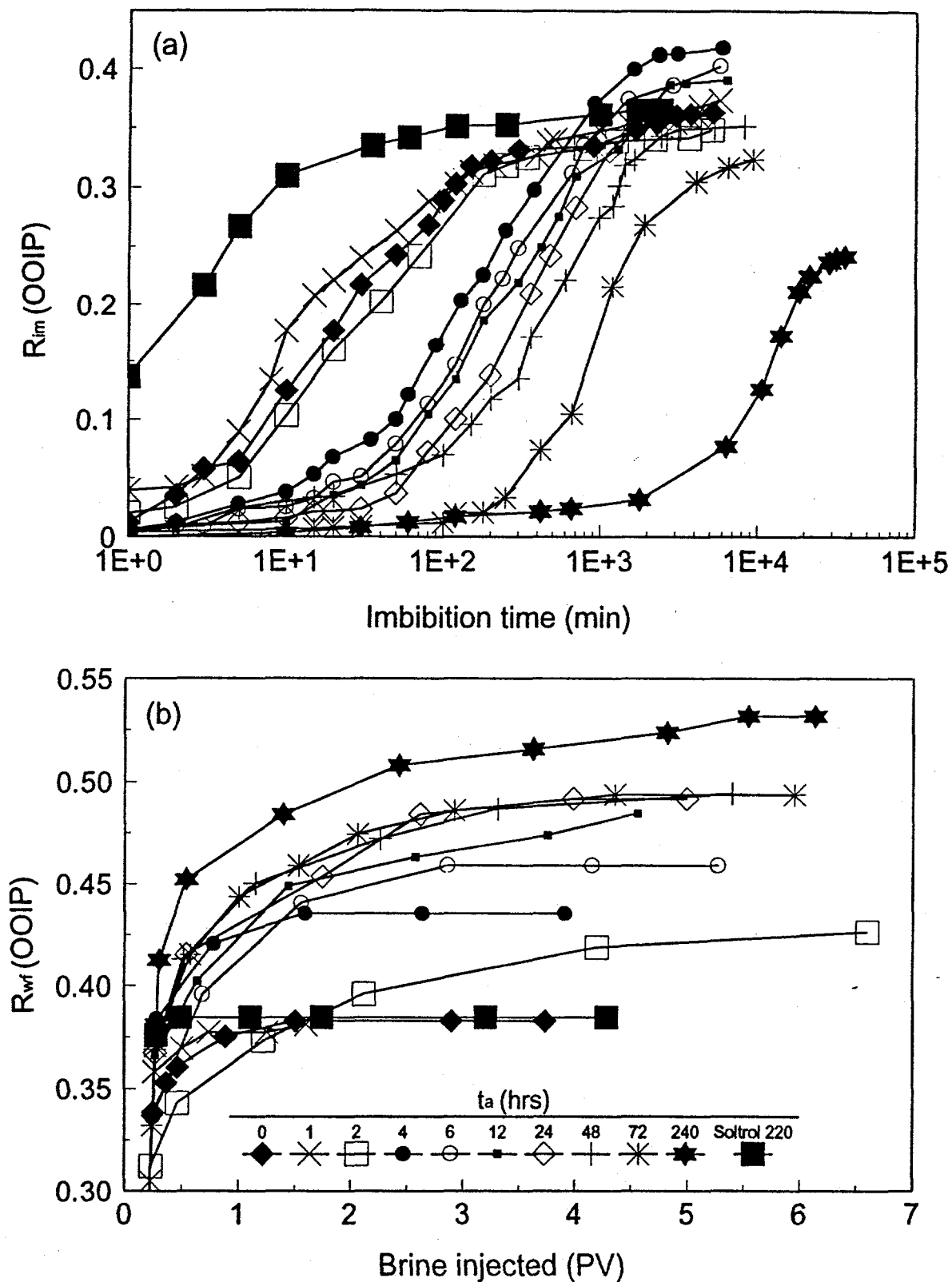


Figure 4. (a) Oil recovery by imbibition vs. imbibition time and (b) oil recovery by waterflooding vs. pore volumes of brine injected for COBR systems at different aging times ( $S_{wi}=25\%$ ).

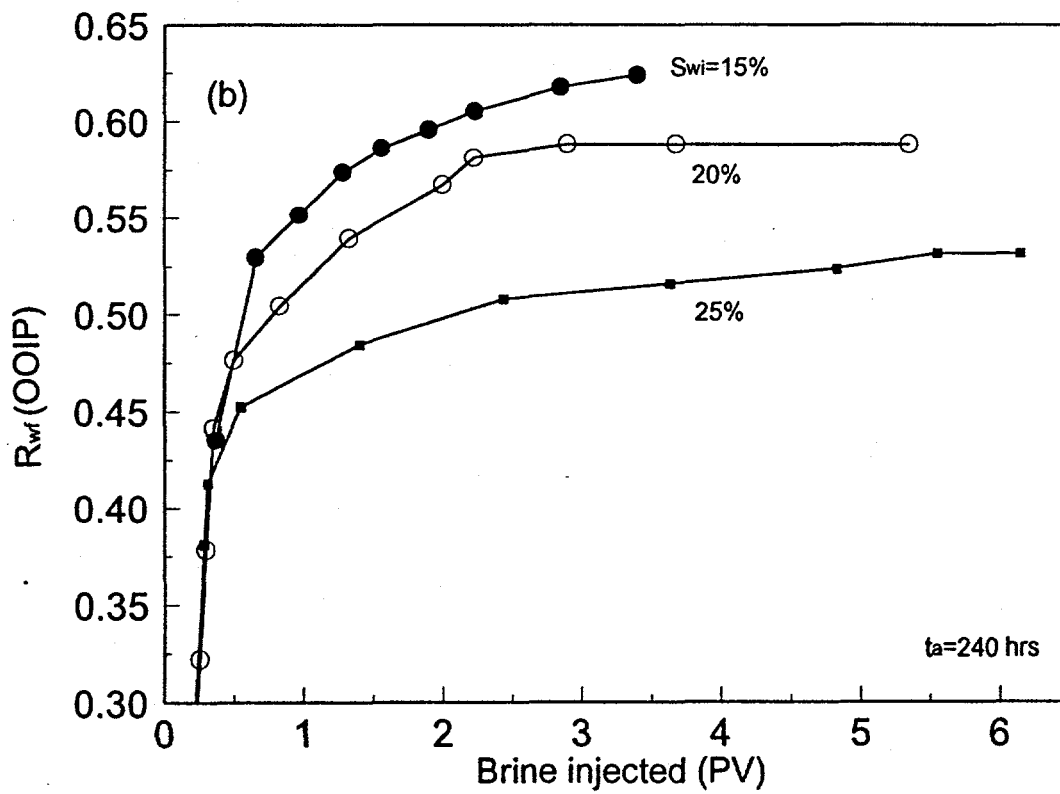
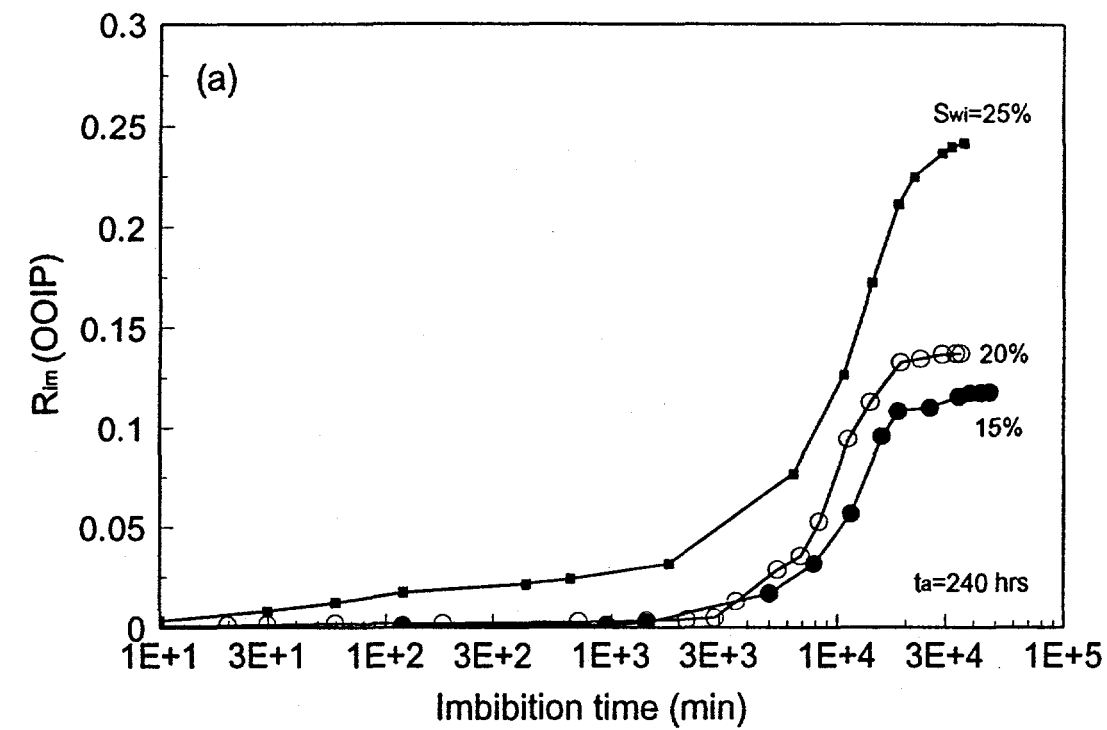


Figure 5. Example of the effect of initial water saturation on relationships between (a) oil recovery by imbibition vs. imbibition time and (b) oil recovery by waterflooding vs. pore volumes of brine injected.

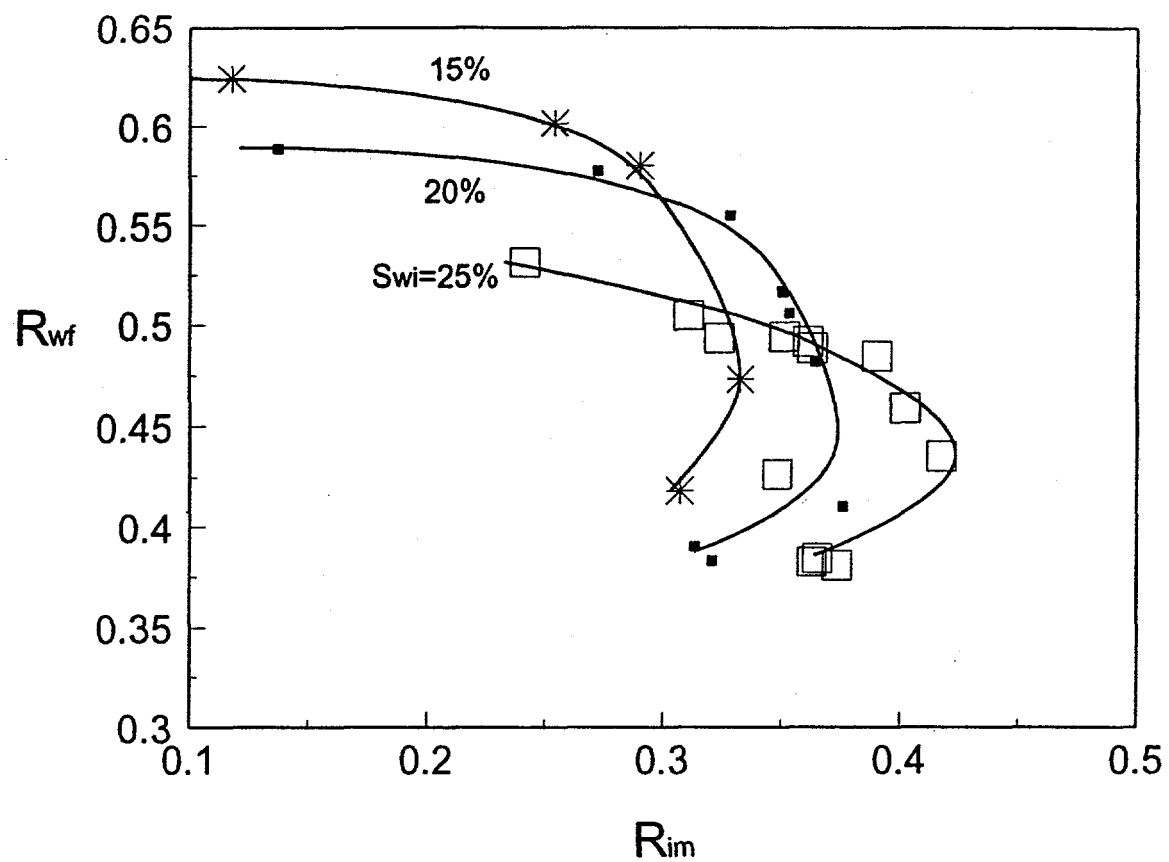


Figure 6. Final waterflood oil recovery,  $R_{wf}$ , vs final oil recovery,  $R_{im}$ , for different water saturations.

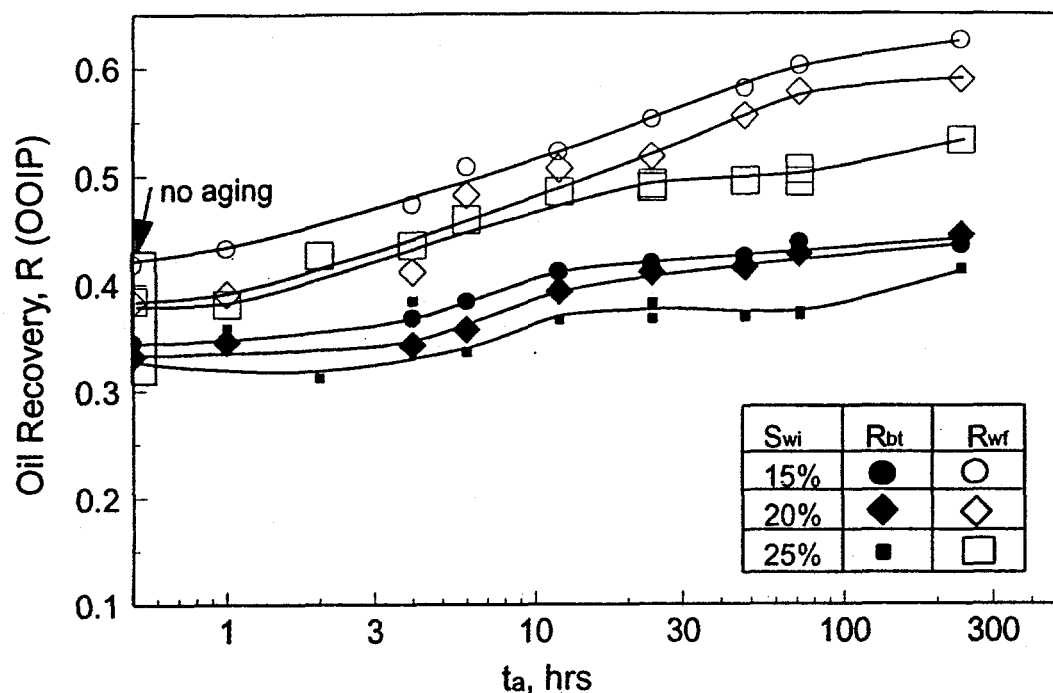


Figure 7. Oil recovery by waterflooding at breakthrough,  $R_{bt}$ , and final waterflood oil recovery,  $R_{wf}$ , vs aging time at initial water saturations of 15, 20 and 25%.

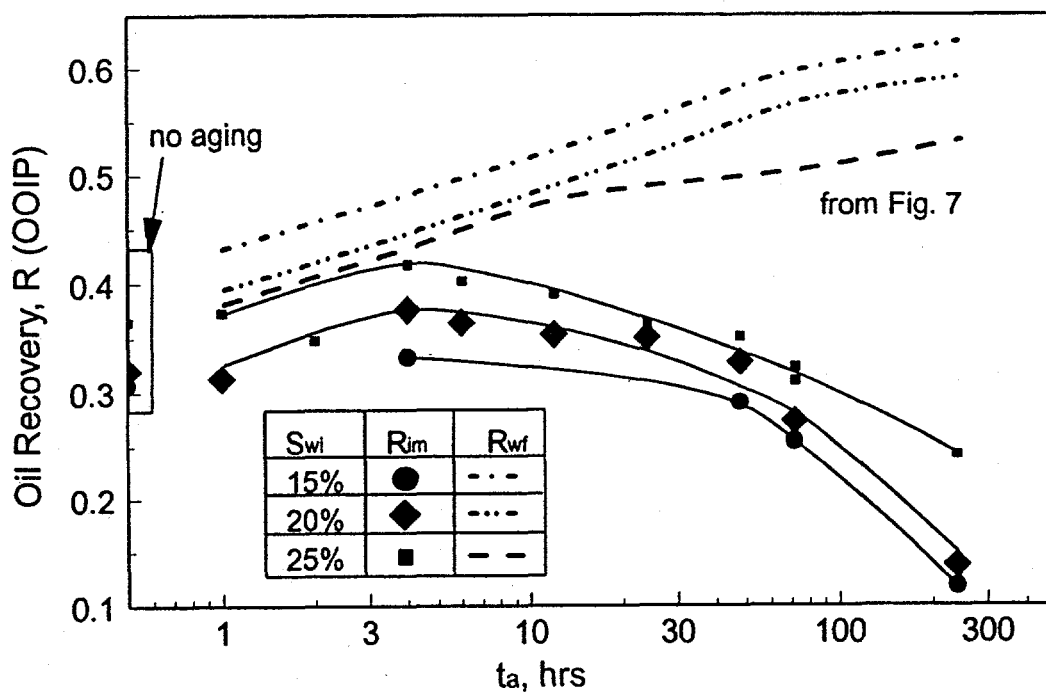


Figure 8. Oil recovery by imbibition,  $R_{im}$ , and final waterflood oil recovery,  $R_{wf}$ , vs aging time at different initial water saturations.



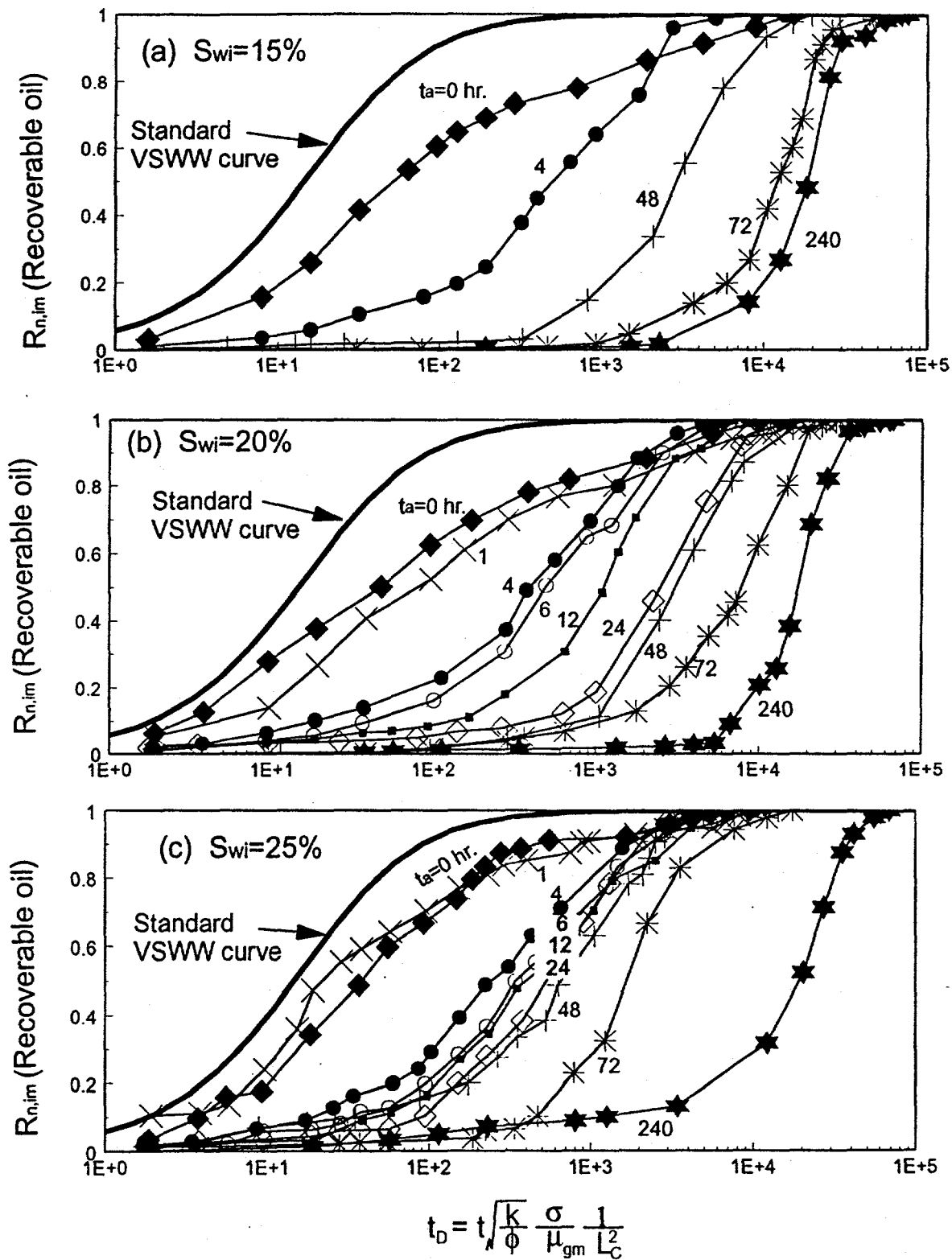


Figure 9. Effect of aging time on relationships between normalized oil recovery by imbibition and dimensionless time for systems with nominal initial water saturations of (a) 15%, (b) 20%, and (c) 25%.

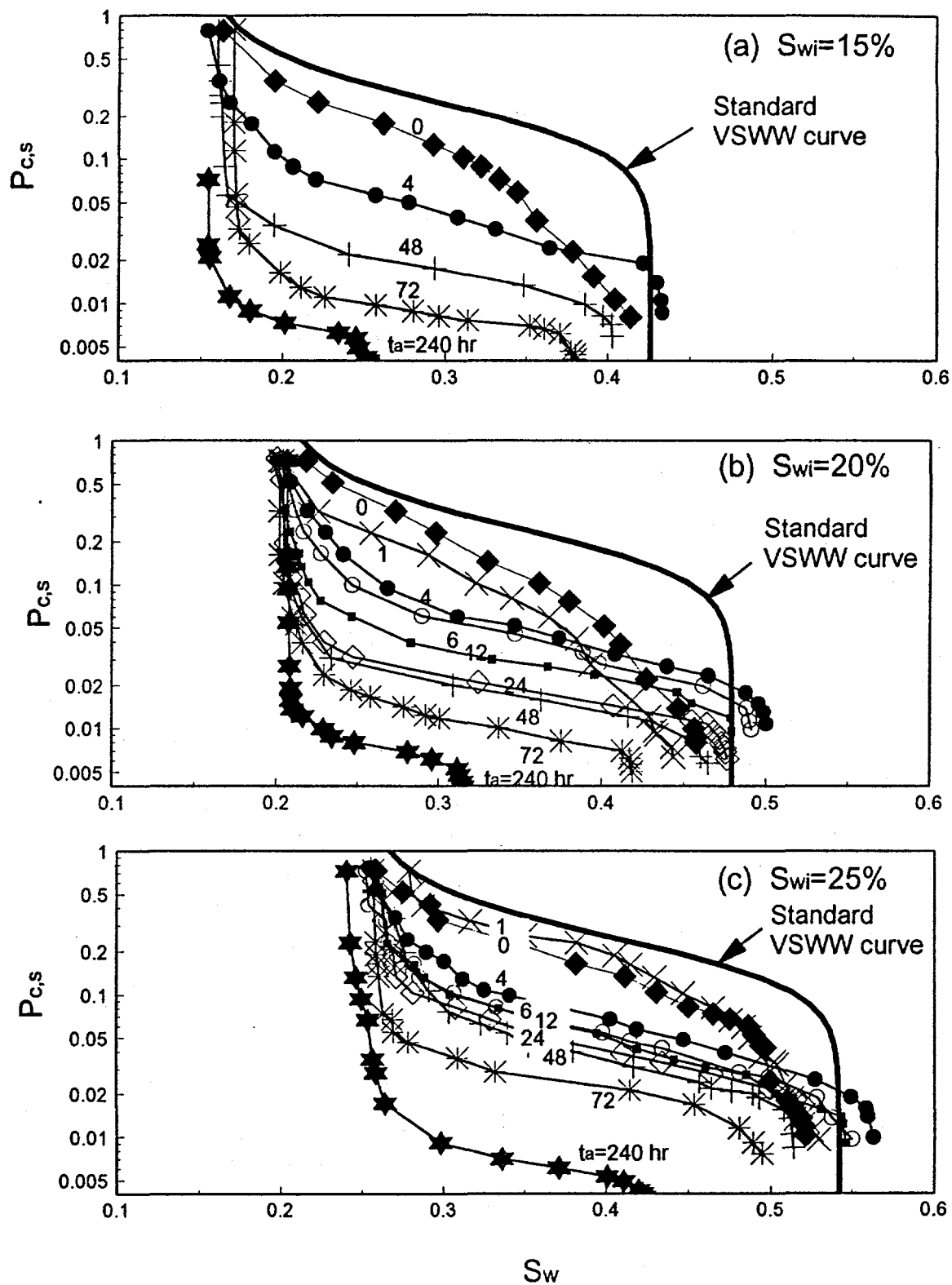


Figure 10. Effect of aging time on psuedo capillary pressure curves for systems with nominal initial water saturations of (a) 15%, (b) 20%, and (c) 25%.

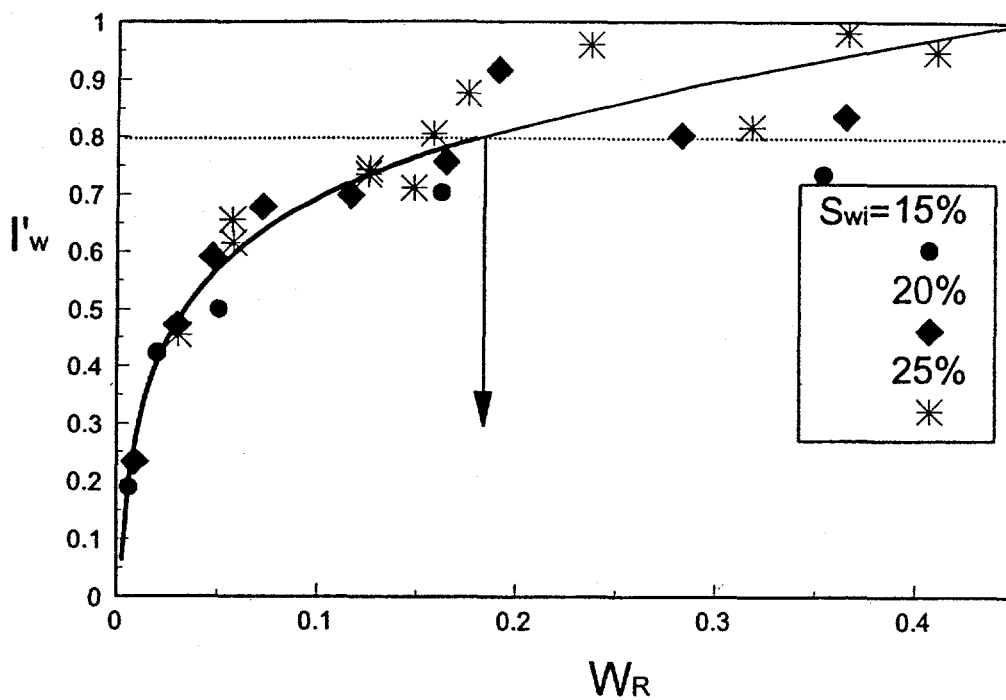


Figure 11. Amott wettability index to water,  $I_w$ , vs relative psuedo work of imbibition,  $W_R$ .

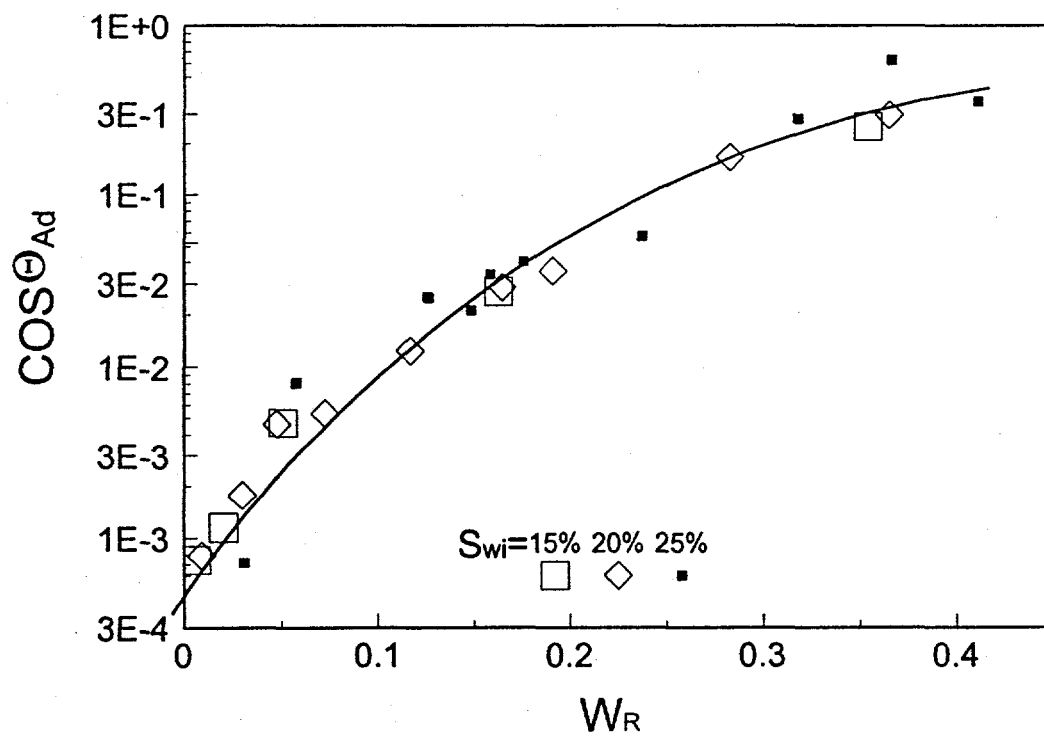


Figure 12. Apparent dynamic advancing contact angle vs relative psuedo work of imbibition.

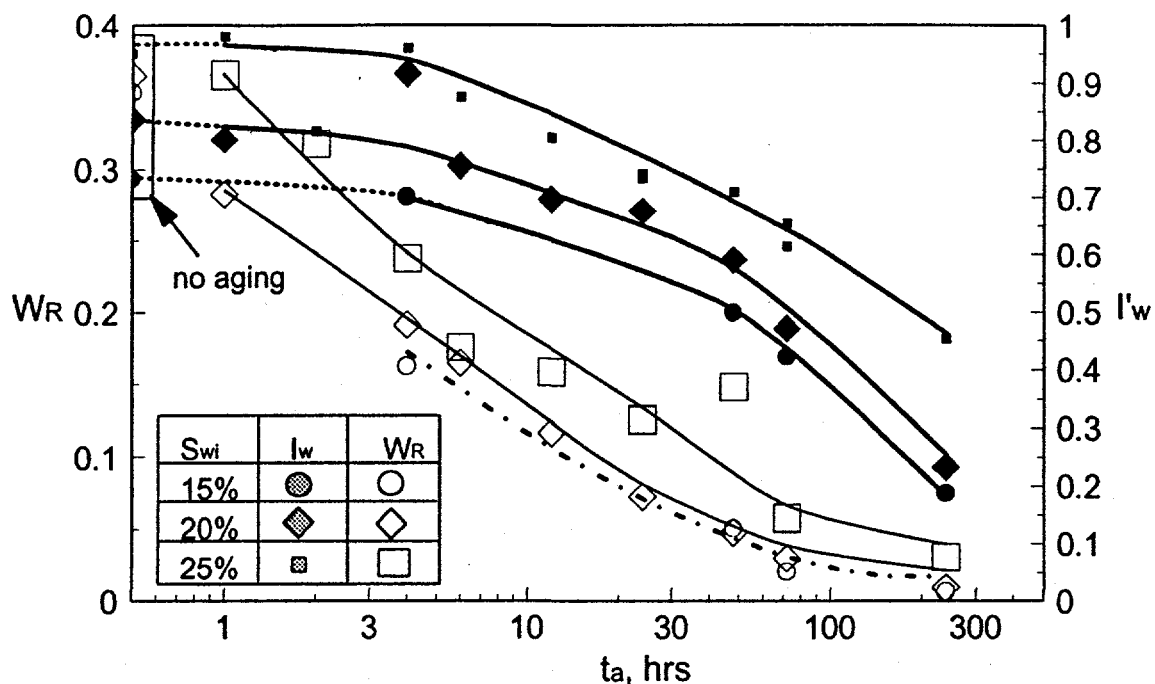


Figure 13. Effect of initial water saturation on relationships between aging time and Amott wettability index to water and relative psuedo work of imbibition.

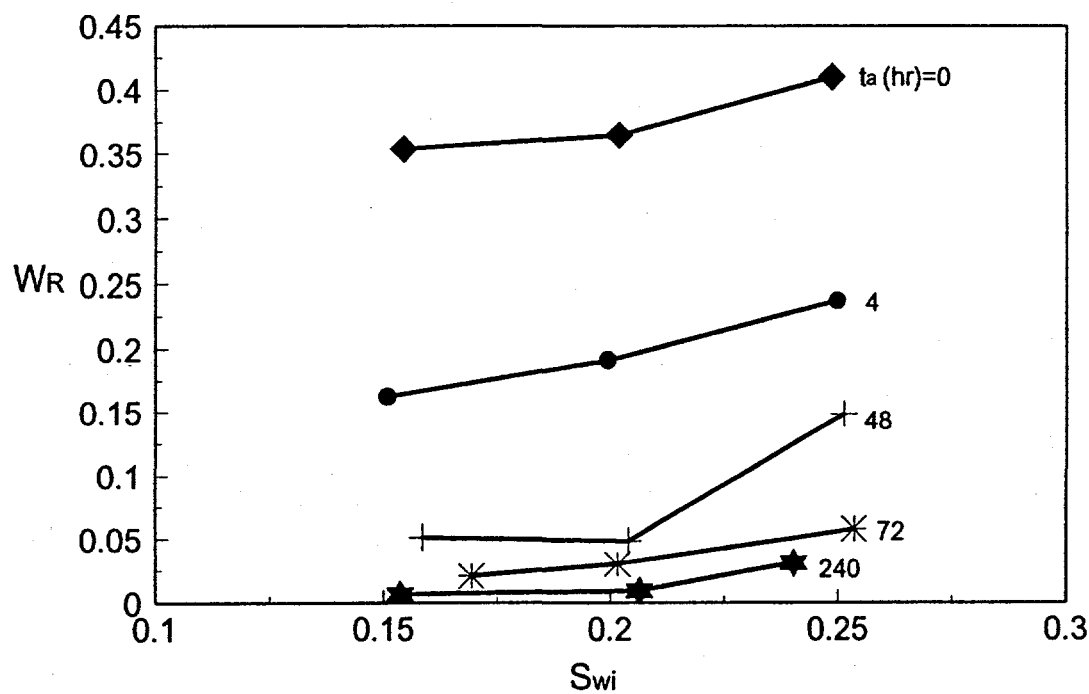


Figure 14. Effect of aging time on relationships between initial water saturation and relative psuedo work of imbibition.

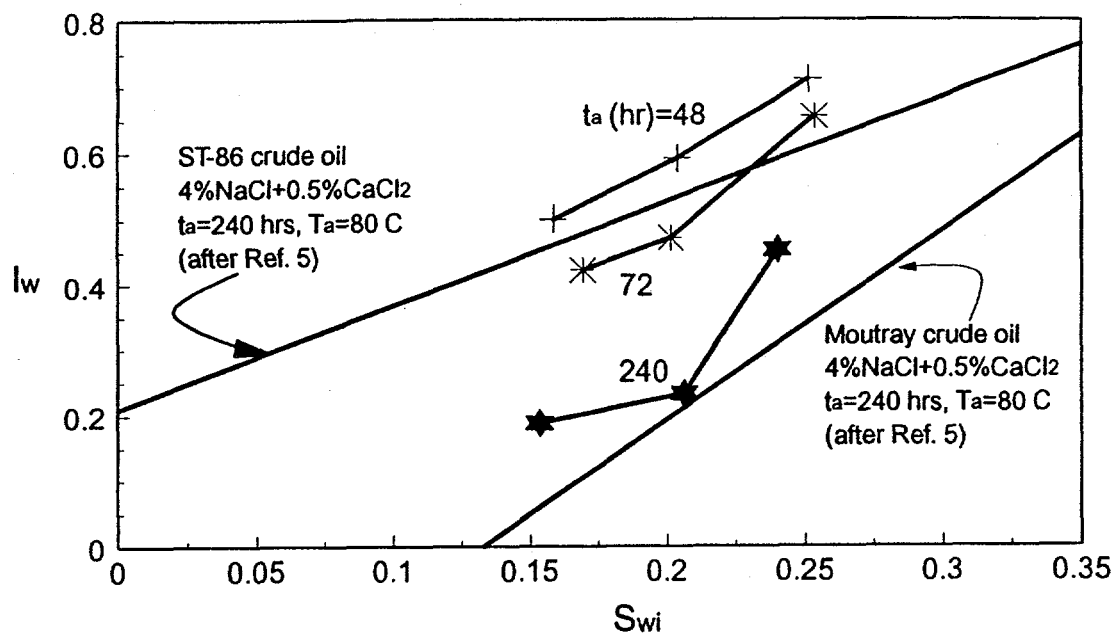


Figure 15. Comparison of relationships between  $S_{wi}$  and  $I_w$  with different COBR systems.

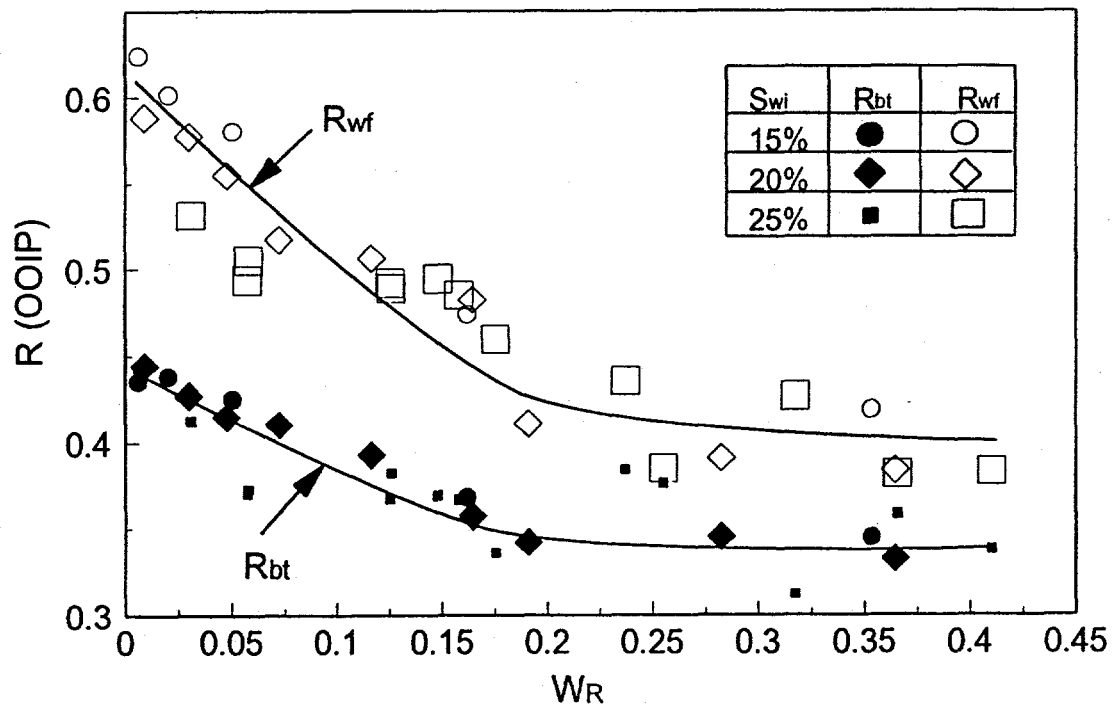


Figure 16. Oil recovery by waterflooding at breakthrough,  $R_{bt}$ , and by final recovery,  $R_{wf}$ , vs relative pseudo work of imbibition.

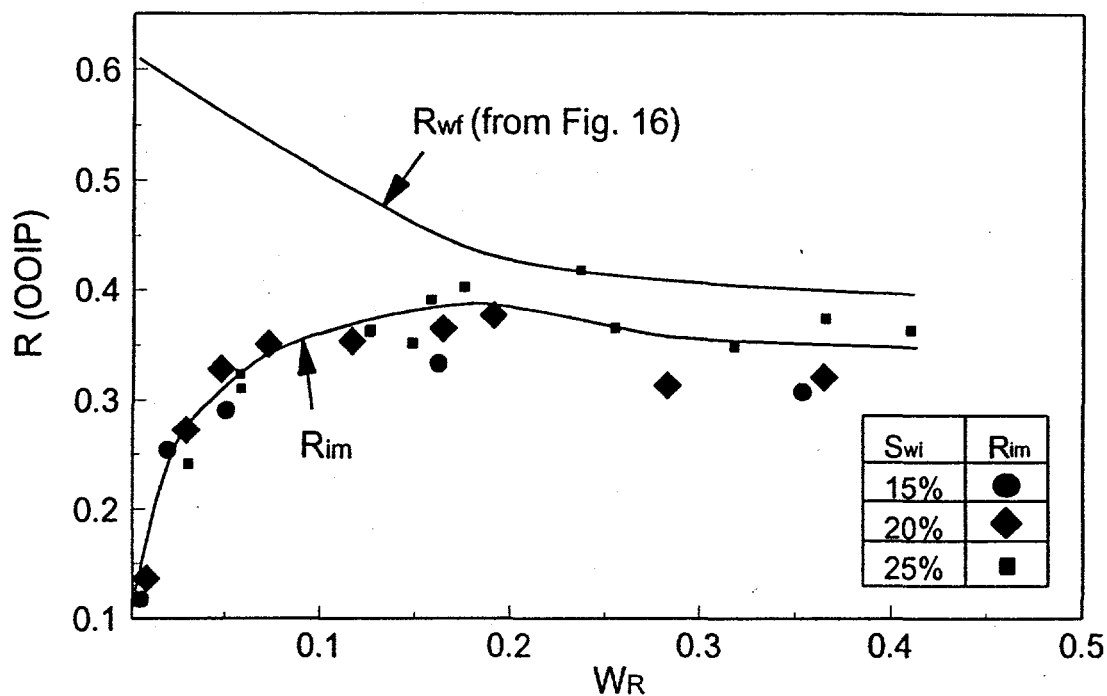


Figure 17. Oil recovery by imbibition,  $R_{im}$ , and by final recovery,  $R_{wf}$ , vs relative pseudo work of imbibition.

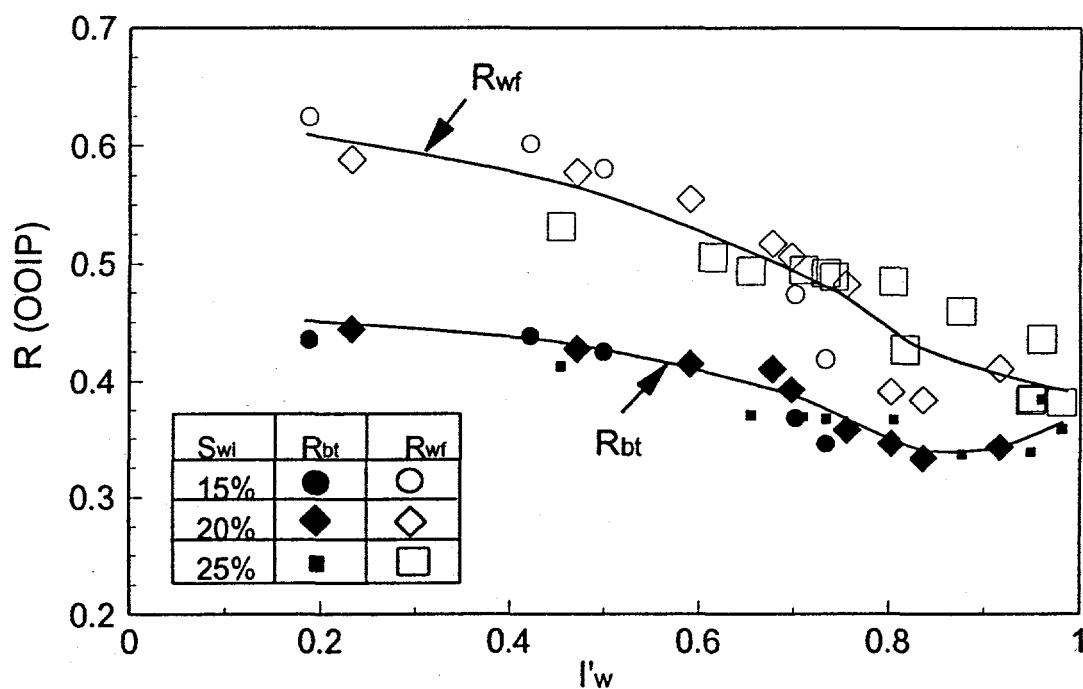


Figure 18. Oil recovery by waterflooding at breakthrough,  $R_{bt}$ , and by final recovery,  $R_{wf}$ , vs Amott wettability index to water.

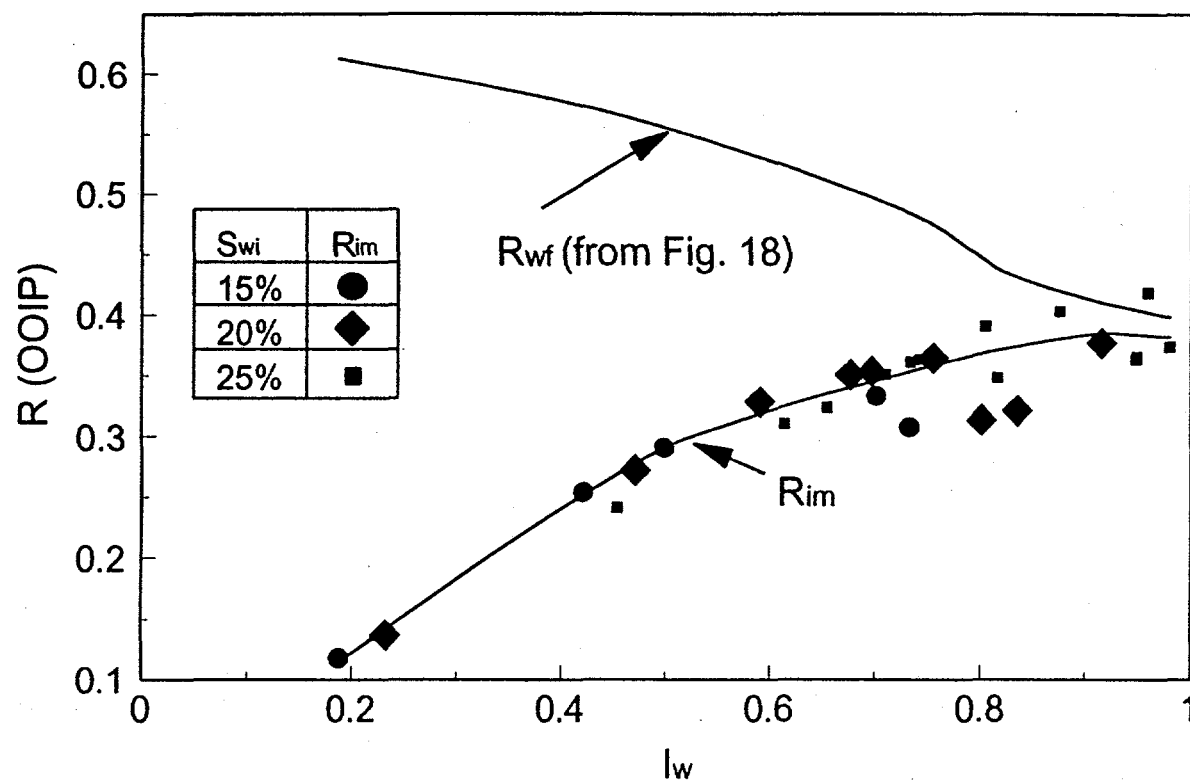


Figure 19. Oil recovery by imbitition,  $R_{im}$ , and by waterflooding,  $R_{wf}$ , vs Amott wettability index to water.