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WETTING BEHAVIOR OF SELECTED CRUDE OIL/BRINE/ROCK SYSTEMS

Final Report

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DISCLAIMER

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	iv
INTRODUCTION	1
EXPERIMENTAL	1
Crude Oil	1
Brines	2
Cores	3
Establishing S_{wi}	3
Imbibition and Waterflood Tests	3
RESULTS AND DISCUSSION	3
Aging Time	4
Salinity of Connate and Invading Brine	4
Change in Invading Brine Salinity	6
Change in Connate Brine Salinity	7
Temperature	7
Aging at Residual Oil Saturation	8
Crude Oil Composition	9
Crude Oil/Brine/Rock Interactions	10
Relationship Between Oil Recovery and Wettability	12
CONCLUSIONS	14
NOMENCLATURE	15
SUBSCRIPTS	15
REFERENCES	16

LIST OF TABLES AND FIGURES

Table		Page
1.	Properties of the Crude Oil Samples	2
2.	Composition (ppm) of Synthetic Reservoir Brines	2
3.	Interfacial Tensions and Viscosity Ratios	2
4.	Conditions for Imbibition and Waterflood Tests	4
5.	Observed Effect of Variables on Wettability and Oil Recovery	13

Figure		Page
1.	Change With Aging Time of Oil Recovery for Dagang Crude Oil and Dagang Brine	18
2.	Change in Oil Recovery of Dagang Crude Oil With Brine Concentration	19
3.	Effect of Invading Brine Concentration on Recovery of Dagang Crude Oil	20
4.	Effect of Connate Brine Concentration on Recovery of Dagang Crude Oil	21
5.	Effect of Change in T_d on Oil Recovery by Imbibition and Waterflooding	22
6.	Change Toward Water Wetness Resulting From the Core Aged at High Water Saturation	23
7.	Change in Viscosity vs Temperature Removal of Light Ends From A-95 Crude Oil	23
8.	Effect of Light Components on Recovery of A-95 Crude Oil by Spontaneous Imbibition	24
9.	Effect of Oil Composition on Oil Recovery by Spontaneous Imbibition and Waterflooding	25

EXECUTIVE SUMMARY

The effect of aging and displacement temperatures, and brine and oil composition on wettability and the recovery of crude oil by spontaneous imbibition and waterflooding has been investigated. This study is based on displacement tests in Berea Sandstone using three distinctly different crude oils and three reservoir brines. Brine concentration was varied by changing the concentration of total dissolved solids of the synthetic brine in proportion to give brine of twice, one tenth, and one hundredth of the reservoir brine concentration. Aging and displacement temperatures were varied independently. For all crude oils, water-wetness and oil recovery increased with increase in displacement temperature.

Tests on the effect of brine concentration showed that salinity of the connate and invading brines can have a major influence on wettability and oil recovery at reservoir temperature. Oil recovery increased over that for the reservoir brine with dilution of both the initial (connate) and invading brine or dilution of either.

Removal of light components from the crude oil resulted in increased water-wetness. Addition of alkanes to the crude oil reduced the water-wetness, and increased oil recovery. Relationships between waterflood recovery and wettability are summarized.

INTRODUCTION

Reservoir wettability has a direct influence on recovery factors for the displacement of oil by water. Laboratory studies have demonstrated the complexity of crude oil/brine/rock (COBR) interactions and point to the uncertainty in assessments of wetting behavior in reservoirs. Reservoir conditions displacement tests are most likely to be valid if results for preserved and restored state cores coincide (Cuiec 1991). Even greater confidence follows if there is consistency between laboratory tests and in-situ measurements of reservoir residual oil saturation and between forecasted and actual production.

The expense and time involved in obtaining core analysis data must always be weighed against their reliability and significance. Laboratory tests designed to duplicate reservoir conditions always include compromises. For example, in laboratory displacements, the connate brine and the injected brine usually have the same composition, but in practice they are different. Laboratory tests are run at isothermal conditions with very small pressure differences across the core. In the reservoir, the injected water is often colder than the reservoir fluids, as evidenced by thermal fracturing, and there are large differences in pressure between injection and production wells.

Dependency of oil recovery on brine composition has been demonstrated (Jadhunandan and Morrow 1995, Yildiz and Morrow 1996, Yildiz et al. 1996). The objective of this work is to show how differences in brine composition and temperature can affect wettability and oil recovery by waterflooding. Exploratory results on crude oil composition suggest that wettability will be sensitive to reservoir pressure. There is potential for improved recovery through factors that are not usually considered in reservoir management.

EXPERIMENTAL

Crude Oil

Three crude oils were used in this study. They are designated as Dagang, A-95 (Prudhoe Bay), and CS. Their properties are listed in Table 1. Change in wettability with crude oil composition was investigated by removing light ends by vacuum, or by addition of alkanes (pentane, hexane, and decane).

Table 1. Properties of the Crude Oil Samples

Oil Samples	Temp. (°C)	Viscosity (cP)	Density (g/cm^3)	C_7-asphaltenes (%)	Wax content (%)
DG	22	solid	solid	6.31*	19.2*
	50	337.0	0.872		
	75	55.1	0.864		
A-95	22	40.3	0.906	6.55	NM
	50	19.2	0.890		
	75	11.3	0.860		
CS	22	70.5	0.891	0.78	12.0*
	55	23.6	0.860		
	75	11.6	0.835		

*Provided by Oil Companies. NM: Not Measured

Brines

Three kinds of synthetic reservoir brines (RB) were prepared. They are designated as DG (Dagang), PB (Prudhoe Bay), and CS. Compositions are listed in Table 2. Viscosities ranged from 1.0512 to 0.5172 cP according to composition and temperature. Variations in brine density were minor. Salinity was varied by changing the concentration of the synthetic reservoir brines listed in Table 2 by factors of 0.01, 0.1, and 2. Brine/oil interfacial tensions (IFT) were measured by the du Noüy ring method. Values are listed in Table 3.

Table 2. Composition (ppm) of Synthetic Reservoir Brines

Brines	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO^-	SO_4^{2-}	pH	TDS
DG*	4,267	7,237	218	32	13,414	-	-	6.9	24,168
PB	8,374	52	110	24	13,100	-	-	7.0	21,660
CS	5,626	56	58	24	8,249	1,119	18	7.3	15,150

*Produced Reservoir Brine 2 Years Ago.

Table 3. Interfacial Tensions and Viscosity Ratios

Temp.	DG crude oil*/ DG brine		A-95 crude oil/ PB brine		CS crude oil/ • CS brine	
(°C)	IFT (mN/m)	μ_o/μ_w	IFT (mN/m)	μ_o/μ_w	IFT (mN/m)	μ_o/μ_w
22	-	-	31.6	38.2	22.3	68.2
50	-	-	32.0	25.3	23.4	31.6
75	28.7	106.4	32.9	21.9	23.9	21.1

*Solid at ambient temperature

Cores

All of the cores were cut from the same batch of Berea Sandstone. The cores were 3.8 cm in diameter and 7.6-7.8 cm in length. Permeability to nitrogen ranged from 787 to 1001 md and to brine from 487 to 614 md. Porosities were close to 23% (Table 4).

Establishing S_{wi}

The core samples were first saturated with brine, equilibrated at room temperature for at least 10 days, then flooded with crude oil at 1.5 ml/min for 5-8 PV. The established initial water saturations, S_{wi}, were nearly all in the range 21 to 25% (Table 4).

Aging

After establishing the initial water saturation by displacement with crude oil, the cores were removed from the core holder and submerged in the same oil, then aged at temperature, T_a, for time, t_a. The initial water in the core will be referred to as connate water.

Imbibition and Waterflood Tests

After aging, the cores were set in the coreholder and flushed with fresh crude oil. The cores were then placed in glass imbibition cells initially filled with brine. The oil expelled from the cores was collected in a graduated tube at the top of the cell. Oil recovery by imbibition, R_{im}, was recorded vs time. Waterflood tests were either run on duplicate core plugs or the same plug after imbibition measurement. In the latter case, restored connate water saturations were all close to the original values. The flood rate was 24.6 ft/d for Dagang (A-95) crude oil/Dagang or Prudhoe brine/Berea Sandstone ensembles and 10 ft/d for CS crude oil/CS brine/ Berea Sandstone ensembles. The relatively high rate of 24.6 ft/d was based on the frontal advance measured by tracer test in a well-swept zone of the Dagang formation. Oil recovery vs injected brine volume was recorded for a total injection of 10-12 PV.

RESULTS AND DISCUSSION

Characterization of wettability. The following scaling group has been shown to correlate imbibition data for very strongly water-wet conditions (Ma et al. 1995).

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

Table 4. Conditions for Imbibition and Waterflood Tests

core	ϕ %	k_g md	k_b md	S_{wi} %	oil[2]	ini.brine/ inv.brine	t_a day	T_a °C	T_d °C	test	R_{im} %	R_{wf} %
Change in t_a												
DG-9	23.1	850.1	611.7	23.6	DG	DG/DG	0	75	75	I/W	45.2	53.2
DG-10	23.1	835.2	540.2	19.6			3.5				39.6	55.7
DG-8	23.2	859.0	597.6	21.3			8.5				33.5	58.0
DG-4	22.9	812.8	487.9	22.9			18				29.1	62.6
Change in Salinity												
DG-27	23.3	838.2	536.7	23.7	DG	0.01 DG	3.0	75	75	I/W	71.1	76.9
DG-26	23.4	853.3	613.8	23.6		0.1 DG				I/W	58.1	69.7
DG-14	23.3	877.1	560.4	23.1		2 DG				I/W	37.3	53.7
DG-2	23.1	881.4	578.1	23.2		DG				I/W	38.3	55.2
DG-60	23.1	827.8	529.5	23.9		0.01DG/DG				I	47.5	-
DG-61	23.2	839.2	566.2	23.3		0.01DG/DG				W	-	78.1
DG-62	23.0	893.9	590.6	24.5		0.1 DG/DG				I	43.5	-
DG-63	23.3	856.2	531.6	22.7		0.1DG/DG				W	-	63.1
DG-50	23.1	845.5	511.2	21.0		DG/0.01DG				I	56.7	-
DG-51	23.1	867.0	541.8	22.3		DG/0.01DG				W	-	58.2
DG-67	23.1	886.6	579.5	20.8		DG/0.1DG				I	46.6	-
DG-68	23.2	841.6	569.8	19.9		DG/0.1DG				W	-	56.3
Change in Temperature (T_a=T_d)												
DG-19	23.3	870.2	604.1	25.0	A-95	DG /DG	3.0	22	22	I	31.3	-
DG-20	23.2	847.0	611.4	23.5				22	22	W	-	47.3
DG-23	23.3	869.4	525.7	20.3				50	50	I	39.7	-
DG-21	23.0	835.5	532.0	22.0				50	50	W	-	52.7
DG-24	23.1	847.0	582.3	21.1				75	75	I	44.7	-
DG-25	23.4	811.6	553.4	22.5				75	75	W	-	55.0
Change in T_d during Displacement											R_{im}(%)	
DG-30	23.2	786.9	542.2	24.9	A-95	PB/PB	3.0	22	22/50	I	33.1 /56.7	
DG-28	22.8	859.1	539.6	24.3	A-95	PB/PB	3.0	22	22/75	I	32.9 /60.7	
CS-20	23.0	1001	612.5	23.3	CS	CS/CS	30	75	22/75	W	51.2 /65.8	
DG-65	23.1	995.4	577.0	24.0	A-95	PB/PB	12	75	22/75	W	50.2 /64.0	
Aging with Brine at High Temperature												
DG-66	22.8	913.0	555.6	22.5	A-95	PB/PB	65	75	75	I	23.8	-
DG-66[1]	22.8	913.0	555.6	24.7			1				42.5	
Change in Composition of A-95 by Vacuum or Addition of Light Ends[2]												
V-0	23.0	801.0	524.6	22.4	0	PB/PB	3.0	75	75	I	25.6	-
V-9.86	23.3	911.1	582.3	21.1	-9.86		3.0	75			49.7	
V-8.26	22.8	862.0	522.6	25.6	-8.26		3.0	75			49.3	
V-4.38	23.3	850.0	520.9	23.3	-4.38		3.0	75			52.3	
A-0	23.0	814.6	529.2	25.1	-3.2		14	80			50.2	
A-C10	23.1	855.3	593.4	24.4	+10		14	80			48.3	
A-C6	22.8	922.7	522.9	24.9	+10		14	80			43.5	
A-C5	23.2	871.2	593.2	26.7	+10		14	80			36.7	
A-C6'	23.1	901.7	529.8	25.5	+10		14	80			36.0	

(1) DG-66: the core was aged with brine at S_{or} at 80°C for 12 days. (2) a negative number in the oil column indicates removal of light components (%), and a positive number indicates addition of light components (%).

where t_D is dimensionless time, t is real time, $\sqrt{\frac{k}{\phi}}$ is proportional to a microscopic pore radius, L_c^2 is determined by the sample size, shape and boundary conditions, σ is the interfacial tension, and μ_o and μ_w are the viscosities of oil and water.

Imbibition data are presented as oil recovery, R_{im} (% OOIP), vs t_D; the correlation given by Equation 1 for very strongly water-wet (VSWW) displacement is included as a reference. Decrease in rate and amount of oil recovered by spontaneous imbibition relative to the VSWW curve is principally ascribed to the effect of wettability. In assessing trends in relationships between wettability and oil recovery, the general form and relative positions of imbibition curves are examined rather than characterizing wettability by a single parameter, such as the Amott Index to water (Amott, 1959).

Aging Time

The effect of aging time on oil recovery by spontaneous imbibition and waterflooding for DG crude oil/DG brine for aging and displacement at reservoir temperature is shown in Figure 1. Oil recovery by spontaneous imbibition decreases with increase in aging time, whereas oil recovery by waterflooding increases with aging time. This trend is consistent with previous results obtained for cores aged at reservoir temperature, T_{res}, and displacements run at T_{amb}, for a Prudhoe Bay (A-93) crude oil (Zhou et al. 1996). Comparison with results for displacement temperature, T_d=T_{amb}, was not possible for the Dagang crude oil because it was solid at T_{amb}. The variation with aging time in oil recovery by imbibition and waterflooding for DG crude oil (T_d=T_a= T_{res}) is much less than for A-93 (T_a= T_{res} and T_d=T_{amb}) (Zhou et al. 1996).

Salinity of Connate and Invading Brine

Imbibition

The imbibition data shown in Figure 2 were obtained by changing the concentration of Dagang reservoir brine. The same salinities were used for the connate and invading brines. They are indicated as 2RB, RB, 0.1RB, and 0.01RB; related tests will be referred to by these concentrations. Final oil recovery at t_D>10,000 (t>2 days) increases with decrease in salinity. The increase in recovery with decrease in salinity is well developed above t_D=1000 (t≈5 h). Early time imbibition data show instances of crossover. The most notable is that the most dilute brine gave slow initial recovery but gave the highest final recovery. Crossover points for 0.01RB, RB and 2RB were all close to t_D=150 (t ≈ 0.4 h).

A possible explanation of the high recovery after slow initial imbibition is that wettability, particularly at high T_d, is sensitive to some combination of the effect of the advancing oil-water interface, increase in water saturation, and decrease in capillary pressure within the core. This situation is beneficial if the high displacement efficiency of weakly water-wet conditions is aided by an increase in the capillary driving force. The hypothesized transition toward increased water-wetness with increase in water saturation becomes significant within about 0.5 to 5 h, depending on the COBR ensemble.

Waterflooding

Initial water saturation was re-established by oilflooding after measurement of spontaneous imbibition. Cores were then waterflooded for the conditions listed in Figure 2b. From comparison of the waterflood data with the imbibition results shown in Figure 2a, it can be seen that waterflood recoveries, R_{wf} (%OOIP), increase systematically with increase in imbibition rate, at least for $t_D>1,000$.

The increase in oil recovery with increase in water-wetness was surprising because it is opposite of previously observed trends (Jadhunandan et al. 1995 and Zhou et al. 1996). Because of the aforementioned possibility of change in wetting during imbibition, the initial wetting states for the subsequent waterflood tests may be somewhat more water-wet than at the beginning of the imbibition tests. However, a comparable set of imbibition and waterflood data with respect to dilution of both connate and invading brine was obtained for a CS crude oil/CS brine combination (Morrow et al. 1996). For this set, the imbibition and waterflood tests were made with duplicate plugs, rather than performing both tests in sequence on a single plug. The relationship between imbibition for $t_D>120$ and waterflood recovery was qualitatively the same as that shown in Figure 2.

Change in Invading Brine Salinity

Imbibition

Scaled imbibition data with Dagang RB as the initial brine and imbibed brine compositions of RB, 0.1RB, and 0.01RB are presented in Figure 3a. Initial recovery curves are close. This is to be expected, because all of these cores were prepared with the same initial brine composition. For $t_D>150$, the effect of invading brine composition is evident because the imbibition curves diverge. The imbibition rate and amount of oil recovery increases with decrease in concentration of the imbibed brine.

Waterflooding

Waterflood results are shown in Figure 3b for duplicate cores prepared in parallel with cores used to obtain the imbibition data shown in Figure 3a. Oil recovery increased with decrease in salinity of the injected brine, but there was little difference in breakthrough recoveries. The difference in final recovery given by the injection of reservoir brine and the most dilute brine was less than 10%. Because of the significant change in oil recovery by spontaneous imbibition (Figure 3a) and previously observed dependency of breakthrough recoveries on the composition of the injected brine (Yildiz and Morrow 1996), further waterflood tests at lower flooding rates are justified.

Change in Connate Brine Salinity

Imbibition

Oil recoveries by spontaneous imbibition of Dagang RB with connate brine of composition RB, 0.1RB, and 0.01RB are shown in Figure 4a. In contrast to the results shown in Figure 3a, for which the salinity of the connate brine was unchanged, initial imbibition rate with RB as the invading brine is sensitive to the initial brine composition. This reflects the effect on wettability of aging the core with connate brines of different salinities. The final recoveries by imbibition increase with decrease in salinity, but the differences are much smaller than those shown in Figure 2a and Figure 3a.

Waterflooding

Oil recovery by waterflooding is highly sensitive to the salinity of the connate brine (Figure 4b). Oil recovery at breakthrough and subsequent recovery increased by up to 50% with decrease in salinity of the connate brine. Final recovery for connate brine of salinity 0.01 RB was comparable to that for 0.01 RB connate and injected brine (Figures 4b and 2b).

Temperature

For the crude oils and brines used in the present work, imbibition results are scaled to compensate for differences in IFT and viscosity (Table 3).

In considering effects of temperature, it is necessary to distinguish between the aging temperature, T_a, and the displacement temperature, T_d. Previous studies show that if T_a is increased, for displacements run at ambient temperature, water-wetness decreases (Jadhunandan 1995). However, if T_d=T_a, the rate and amount of spontaneous imbibition increased with temperature for all values of dimensionless time (Morrow et al 1996).

From previous experience (Jadhunandan 1995), for T_a = 75 °C, and T_d=T_{amb}, the imbibition curve would be expected to fall below the imbibition curve for T_a=T_d=T_{amb} (22°C). The corresponding waterflood recovery would be higher for T_a=75°C, T_d=T_{amb} than for T_d =T_a=T_{amb}, provided the induced wettability states are on the water-wet side of neutral.

As a test of the sensitivity of wettability to temperature, the imbibition temperature was changed from T_{amb} to high temperature during the course of an imbibition experiment. When T_d was increased from 22°C to 75°C, the rate of spontaneous imbibition increased dramatically. In a comparable experiment, T_d was raised to 50°C. A lesser, but still distinct, increase in imbibition rate was observed. Increase in imbibition rate with increase in T_d from T_{amb} to T_{res} was also measured for CS crude oil and brine (Figure 5a).

Results for imbibition tests run at temperatures of 22°C and 75°C are shown in Figure 5b. The result for A-95 crude oil/PB brine shows that change in temperature corresponded closely to transition from the imbibition curve measured at 22°C to that at 75°C.

An imbibition curve was also measured for a refined oil (Soltrol 220). In contrast to the large change in imbibition recovery for crude oil, increase in temperature during the course of imbibition had essentially no effect for the refined oil. Crude oil/brine/rock interactions are therefore responsible for the dramatic increase in oil recovery with temperature rather than some change related to the rock properties alone.

All of the results reported in the present work are for Berea Sandstones. It is not known to what extent these results are specific to the selected Berea Sandstone samples. However, comparable behavior has been reported for chalk core samples (Dangerfield and Brown, 1985).

Waterflood tests for two different crude oil/brine combinations, A-95 crude oil/PB brine and CS crude oil/CS brine, are shown in Figure 5c. After flood-out, T_d was raised from 22°C to 75°C. There was an unexpectedly large response; increase in oil recovery ranged from 10-17% OOIP.

Aging at Residual Oil Saturation

Cores aged in crude oil decrease in water-wetness with increase in aging time. The possibility of an opposite change toward water-wetness at high water saturation was investigated for the conditions given in Figure 6. The core was aged with A-95 crude oil for 65 days at 75°C at an S_{wi} of 22.5%. Spontaneous imbibition at 75°C began after 100 mins and thereafter was very slow. After about 5 days, produced oil recovery reached 23% OOIP. The core was then flooded with brine to a residual oil saturation of 34.7% and aged at 80°C for 12 days, then flooded with fresh A-95 crude oil to an S_{wi} of 24.7%. After aging for only 1 day, oil recovery by spontaneous imbibition was remeasured. The induction time for commencement of imbibition was greatly reduced, and the rate and extent of spontaneous imbibition were much higher than for the imbibition tests run after 65 days of aging.

This indicates that the wettability of the rock achieved during aging depends upon the saturation and distribution of the oil and brine phases and the contact time. It also implies that adsorption of crude oil components on rock surfaces and related wettability change are at least partly reversible and that the wettability of a sandstone reservoir will change toward increased water-wetness during the course of waterflooding.

Crude Oil Composition

Dead crude oils differ from live crude oils through the loss of low molecular weight components. In the present work, the crude oil was usually further degassed under vacuum to avoid formation of gas bubbles during the course of an experiment.

The effect of loss of light ends was investigated by evacuation of the A-95 crude oil. The reduction in weight of the dead crude oil as supplied ranged from 1.2 to 9.9 wt.%. Viscosities of the modified A-95 crude oils are presented in Figure 7. Spontaneous imbibition measurements were then made for the conditions listed in Figure 8a. Reduction in weight of the oil sample by 1.2 and 4.38% caused change in imbibition rate towards greater water-wetness. Further reductions in weight caused only minor change in the imbibition behavior. These results suggest that a live crude oil will tend to be less water-wet than a dead crude oil.

After removing 3.2% of light ends by evacuation of A-95 crude oil, the effect of addition of hexane on imbibition was measured. The results presented in Figure 8b show that water-wetness is decreased by addition of hexane and further decreased by doubling the amount of added hexane.

The effect of addition of 10% by weight of hexane, heptane or decane to the crude oil was also tested. The imbibition data presented in Figure 9a show that water-wetness decreased with decrease in molecular weight of the added alkane.

Preliminary waterflood results show that addition of alkanes cause waterflood recovery to increase over that for the A-95 crude oil. The increase was approximately the same for addition of either pentane or decane (Figure 9b).

Crude Oil/Brine/Rock Interactions

There are a variety of possible mechanisms by which COBR interactions control wettability and the efficiency of oil recovery. The chemistry of all three components of the defined COBR ensembles used in the present work are complex in themselves. Development of a working knowledge of COBR interactions and their effect on oil recovery requires that dominant factors be identified for a broad range of situations.

Buckley (1996) recently categorized crude oil/brine/solid interactions as polar, surface precipitation, acid/base, and ion binding. Direct adsorption from crude oil onto a dry solid surface is ascribed to polar interactions. Acid-base interactions determine oil-brine and brine-solid surface charges. Changes in wettability resulting from instability of a water film occur almost instantaneously. A contact time of 2 minutes has been adopted for adhesion tests (Buckley et al. 1989 and Buckley and Morrow 1991). Adhesion within 5 seconds after contact has been reported (Valat and Bertin 1996). Adsorption by ion binding occurs through attachment of polar components of the crude oil to specific surface sites on the solid via multivalent ions. This is a relatively slow process, which may account for the long aging times involved in wettability alteration by crude oil. Surface precipitation is identified with conditions of poor solvency of asphaltenes in the oil phase. Atomic force microscopy and surface force measurements indicate that adsorption can give thick adsorbed films (~30-40 nm) (Buckley et al. 1996 and Christenson and Israelachvili 1987)

It is quite possible that the wetting states achieved by adsorption from crude oil can involve a combination of mechanisms. For example, water films may be penetrated at various locations by specific adsorption. Adsorption sites can then serve as a nucleus for surface aggregation of polar components from the oil phase. Molecular association (including ion binding) of crude oil components at the oil-water interface will promote lateral aggregation and the formation of an organic mat that may still be largely separated from the solid surface by a thin water film. The stability of this mat with respect to an invading oil-water interface would be strongly dependent on the relative strength of attachment via specific adsorption at the solid surface versus the lateral interactions that determine the integrity of the organic mat. Results reported in this work will be examined with respect to this one of many possible scenarios by which crude oil can alter wettability in presence of brine.

Crude Oil Solvency

The light components that are removed under vacuum prior to obtaining the results shown in Figure 8a are not, in themselves, likely to cause significant changes in wettability. Their removal increases the concentration of the components that do cause wettability alteration. However, removal of alkanes increases the solvency of the crude oil (Buckley et al. 1996) and so reduces the tendency for aggregation at the rock surface.

The observed suppression of imbibition rate by addition of alkanes (Figure 8b and Figure 9a) also supports the conclusion that wettability by adsorption is dependent on the solvency of the crude oil. The amount of added solvent is small, and the oil solvency is probably still well removed from that for the onset of asphaltene precipitation. Nevertheless, the ability of heavy components of crude oil to adsorb appears to be strongly dependent on the crude oil solvency. The suppression of imbibition rate with decrease in alkane molecular weight (Figure 9a) is also expected from considerations of crude oil solvency (Buckley and Liu 1996 and Buckley et al. 1996).

In the reservoir, the solvency of the oil is dependent on reservoir pressure, temperature, and oil composition. For reservoirs above the bubble point, decrease in reservoir pressure will decrease the solvency of the oil. The results shown in Figure 8a suggest that the reservoir would tend to become less water-wet with decrease in solvency. The most likely condition for asphaltene precipitation is at the bubble point. Below the bubble point, the solvency of crude oil increases with evolution of gas and the reservoir will tend to become more water-wet. For reservoirs on the water-wet side of neutral, the preliminary results on waterflood recovery shown in Figure 9b suggest that if wettability is controlled by crude oil solvency, wettability conditions close to the bubble point will be optimum for oil recovery.

Temperature

In the process of inducing wettability change, the use of high aging temperature, T_a, favors organization of crude oil surface aggregates into thermodynamically favorable configurations. The thickness of these structures at the rock surface may be very great compared to monolayer adsorption, but the intermolecular associations are only marginally stronger than in the bulk crude oil. If water invades the core, it appears that the condition of the rock surface with respect to adsorbed components is not necessarily stable. Wettability changes towards increased water-wetness with increase in temperature for T_d=T_a (Morrow et al. 1996). If cores are cooled after aging, the structures developed at high temperature are quenched and become relatively robust. Imbibition rate at ambient temperature for cores prepared in this way can feature an induction time, and imbibition is extremely slow. This type of imbibition behavior is ascribed to slow desorption (Zhou et al. 1996).

From the results shown in Figure 5a, oil recovery by spontaneous imbibition responds rapidly to increase in displacement temperature, T_d. The thickness of the surface aggregates probably decreases with increase in thermal energy. Increase in temperature also results in increased solvency of asphaltenes in the crude oil, and the tendency for surface aggregation probably decreases. Desorption of asphaltenes as evidenced by decrease in contact angle at high temperature has been reported (Hjelmeland and Larrondo 1986 and Liu and Buckley 1996).

The increase in imbibition rate with temperature shown by the results in Figure 5a and also reported for chalk (Dangerfield and Brown 1985) show that COBR interactions can be highly temperature sensitive, as would be expected if wettability is mainly determined by surface aggregation.

Brine Saturation and Salinity

Results reported for this task add to the evidence that brine composition can affect wettability and oil recovery without causing extremes of pH or significant lowering of interfacial tension. Only incomplete and tentative explanations can be offered for some of the observed effects. For example, change in wettability with salinity (Figure 2a) may result from decrease in ion binding with decrease in concentration of divalent ions. Wettability transitions toward increased water-wetness may be related to the ease with which adsorbed material, perhaps surface aggregates, can be removed from the rock surface during the course of displacement. However, many other factors may contribute to COBR interactions and their consequences.

Increase in water saturation will be associated with decrease in capillary pressure. This could affect adsorbed brine films as oil/brine interfaces advance through pore spaces and across rock surfaces. Difference in injected and connate brine composition and in capillary pressure vs disjoining pressure of adsorbed films will give rise to osmotic and solution effects.

Relationship Between Oil Recovery and Wettability

Observed trends, some of which are based on very limited data, between wettability and oil recovery for water-wet conditions are summarized in Table 5. The difference between situations that give improved waterflood recovery with a decrease in water-wetness and those that show an opposite trend appears to depend on the relative robustness of the initial wettability condition. Wettability conditions achieved by increase in t_a, decrease in S_{wi}, or increase in T_a (with T_d=T_{amb}) are relatively stable. Change in cation valency and addition of light ends also appear to provide conditionally robust behavior (Morrow et al. 1996).

In contrast, decrease in salinity and increase in T_d, either from the outset or during the course of the displacement, result in transition toward water-wetness. These transitions, as opposed to strongly water-wet conditions, are highly favorable to recovery by both imbibition and waterflooding. The microscopic displacement efficiency is high, and the increase in capillary forces that accompanies change toward water-wetness is favorable to oil recovery.

Table 5. Observed Effect of Variables on Wettability and Oil Recovery

Variable	Water Imbibition Rate	Waterflood Recovery
Increase in aging time, t_a	↘	↗
Decrease in initial water saturation, S_{wi} (Jadhunandan and Morrow, 1995; Zhou et al., 1996)	↘	↗
Increase in aging temperature, T_a (Jadhunandan and Morrow, 1995)	↘	↗
Increase in valency of cation, Na^+, Ca^{2+}, Al^{3+}(Morrow et al., 1996)	↘	↗
Decrease in radius of hydration, Li^+, Na^+, Cs^+(Morrow et al., 1996)	↘	?
Decrease in brine concentration (invading and initial)	↗*	↗
Decrease in initial brine concentration	↗*	↗
Decrease in invading brine concentration	↗*	↗
Increase in run temperature, T_d	↗*	↗
Increase in T_d during run	↗	↗
Removal of light ends	↗	?
Addition of light ends	↘	↗

*: Early time imbibition data sometimes show crossover

↘:decreases ↗: increases

Reservoir wettability is usually treated as an essentially fixed property. However, the agreement often observed between fresh and restored state cores implies that reservoir wettability is at equilibrium, which can be re-established if all of the important variables are respected (Cuiec1991). This suggests that reservoir wettability will change if the significant variables in the reservoir are changed. From consideration of the trends presented in Table 5, there appears to be opportunity to improve reservoir management through advantageous manipulation of wettability.

CONCLUSIONS

1. Water-wetness and oil recovery by waterflooding increased with decrease in salinity.

2. Transitions towards water-wetness occur when the temperature is raised during the course of displacement.

3. Changes in wettability induced by crude oil are related to changes in solvency of the crude oil with respect to its heavy polar components.

NOMENCLATURE

L_c = characteristic length, L, cm

k = permeability, L^2, md

R = oil recovery, % OOIP

S = saturation, %

T = temperature, °C

t = time, t, min

VSWW = very strongly water wet

μ = viscosity, cP

Φ = porosity, %

σ = interfacial tension, dynes/cm

SUBSCRIPTS

a = aging

amb = ambient

b = brine

D = dimensionless

d = displacement

g = gas

im = imbibition

o = oil

or = residual oil

res = reservoir

w = water

wf = waterflood

wi = initial water

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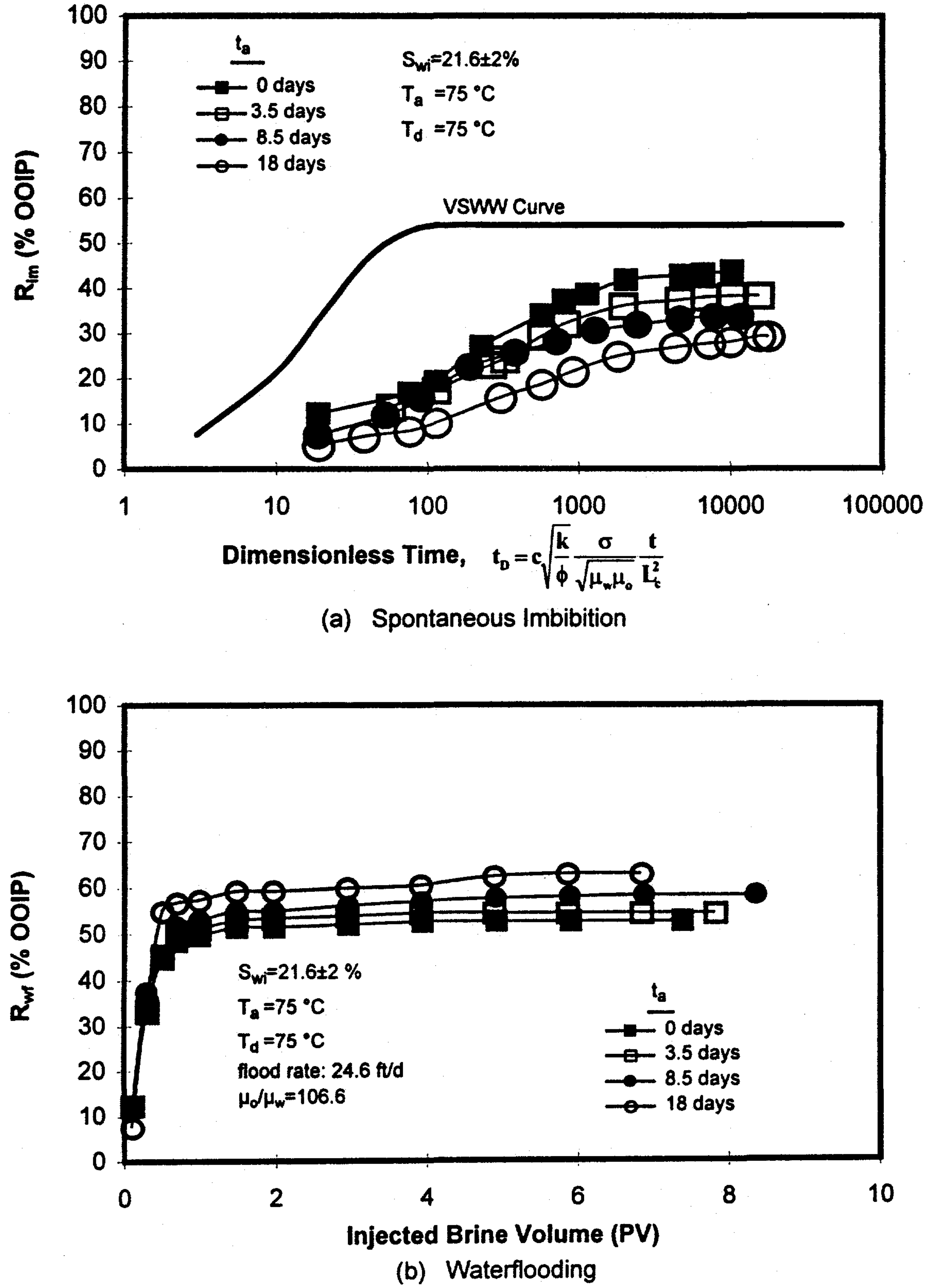
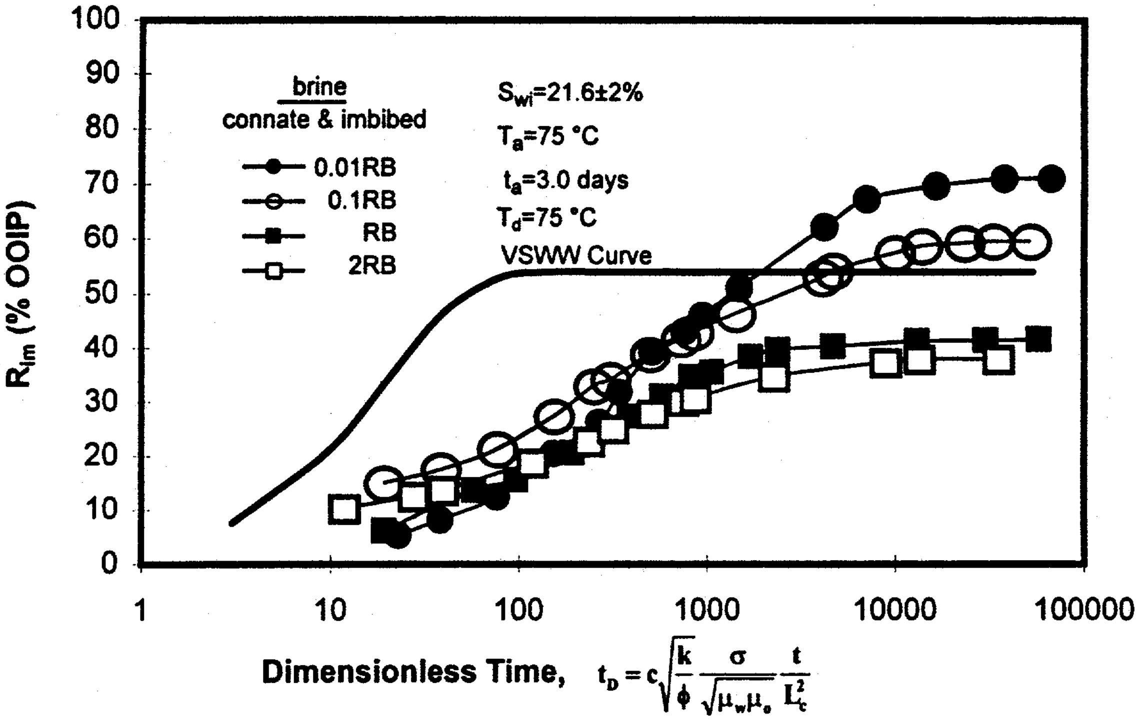


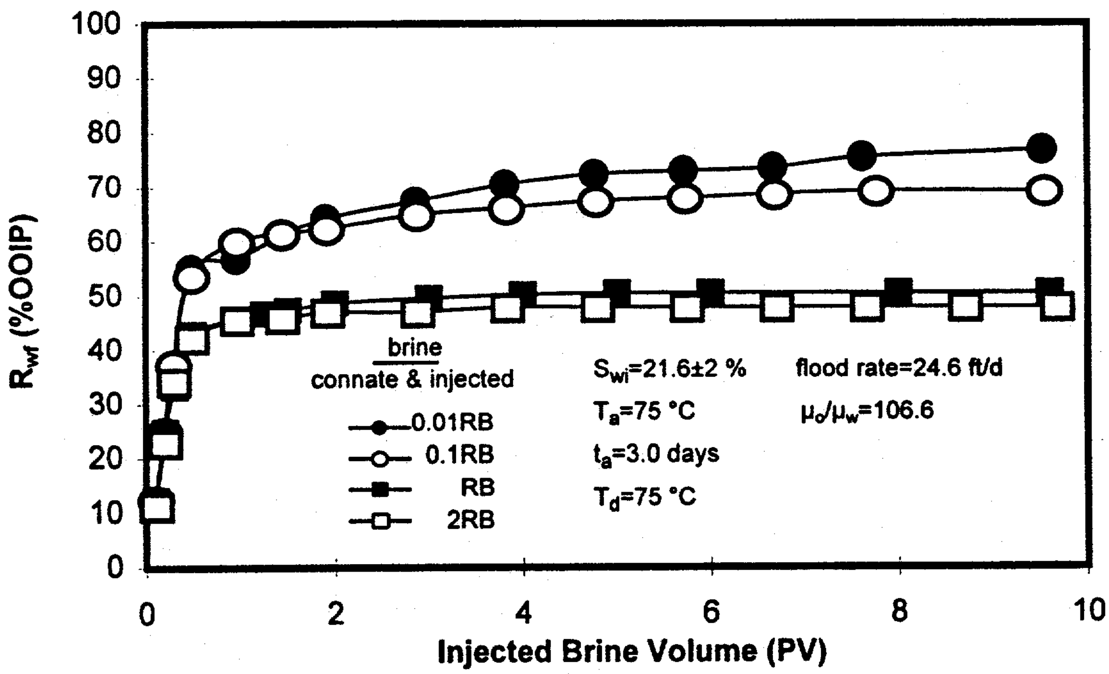
(a) Spontaneous Imbibition

(b) Waterflooding

Figure 1. Change With Aging Time of Oil Recovery for Dagang Crude Oil and Dagang Brine

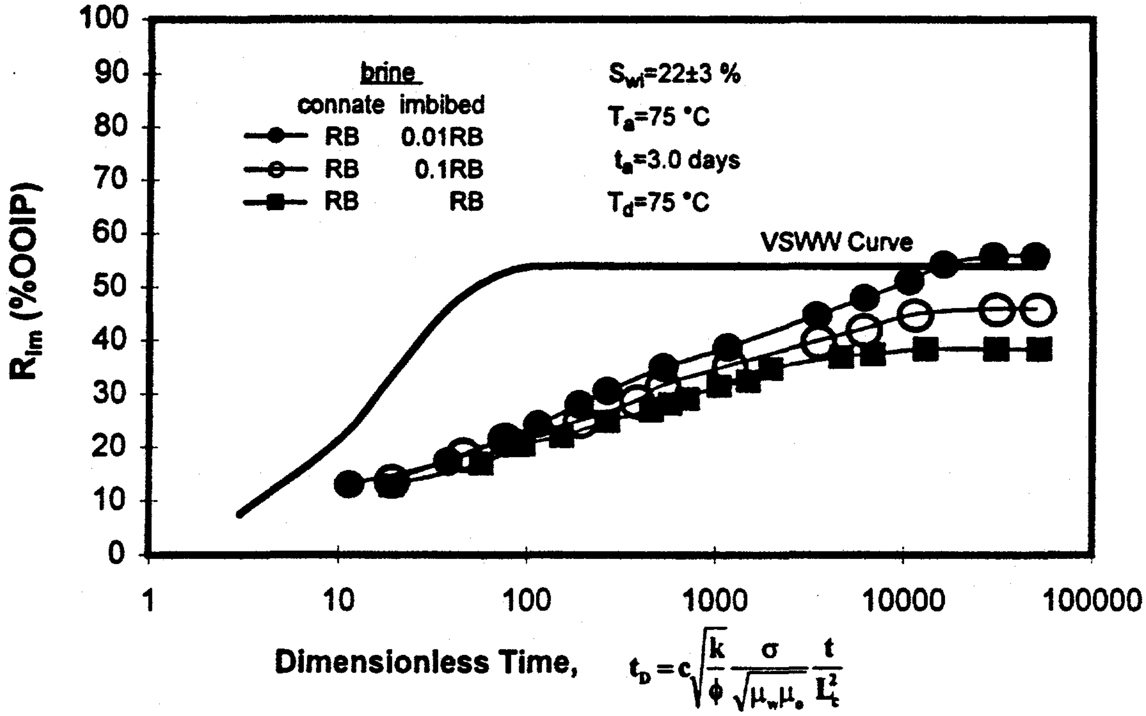


(a) Spontaneous Imbibition

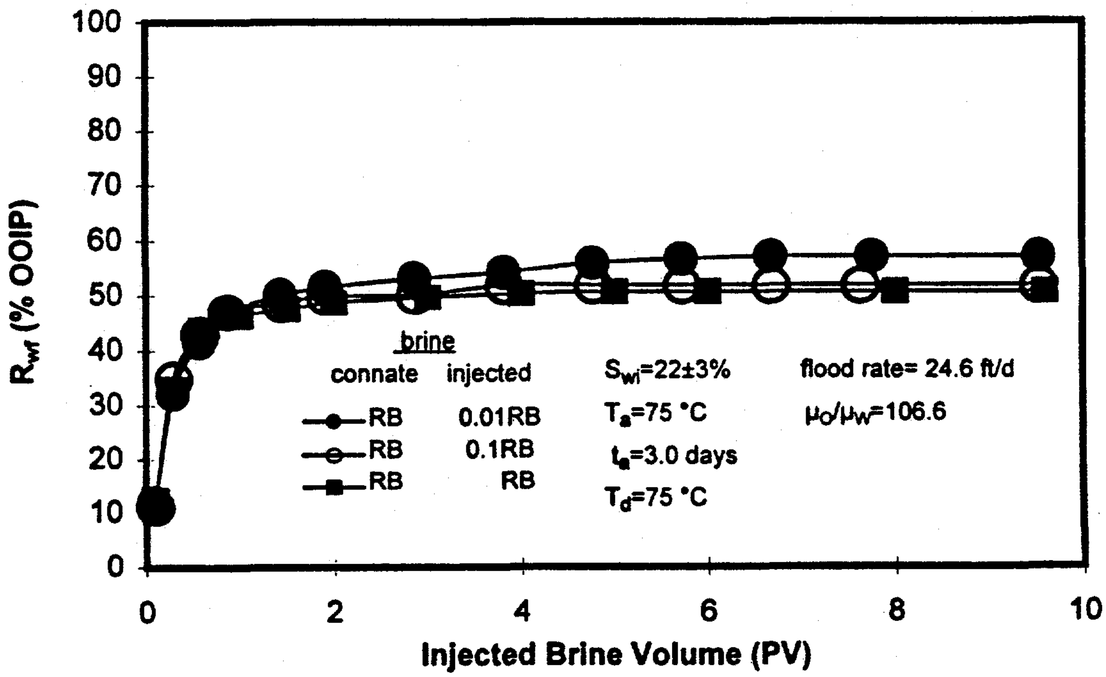


(b) Waterflooding

Figure 2. Change in Oil Recovery of Dagang Crude Oil With Brine Concentration (RB=DG Brine)

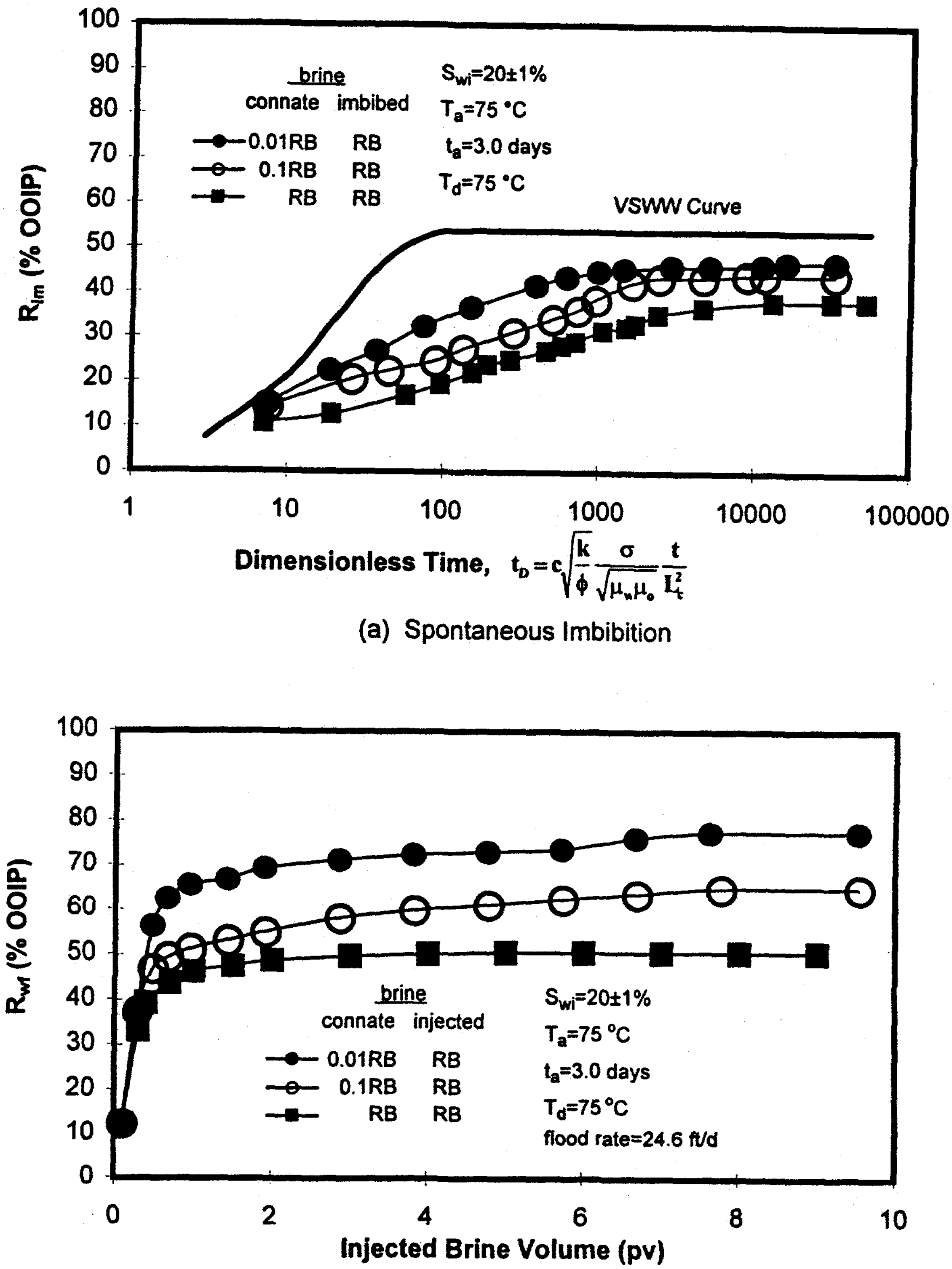


(a) Spontaneous Imbibition



(b) Waterflooding

Figure 3. Effect of Invading Brine Concentration on Recovery of Dagang Crude Oil (RB=DG Brine)



(a) Spontaneous Imbibition

(b) Waterflooding

Figure 4. Effect of Connate Brine Concentration on Recovery of Dagang Crude Oil (RB=DG Brine)

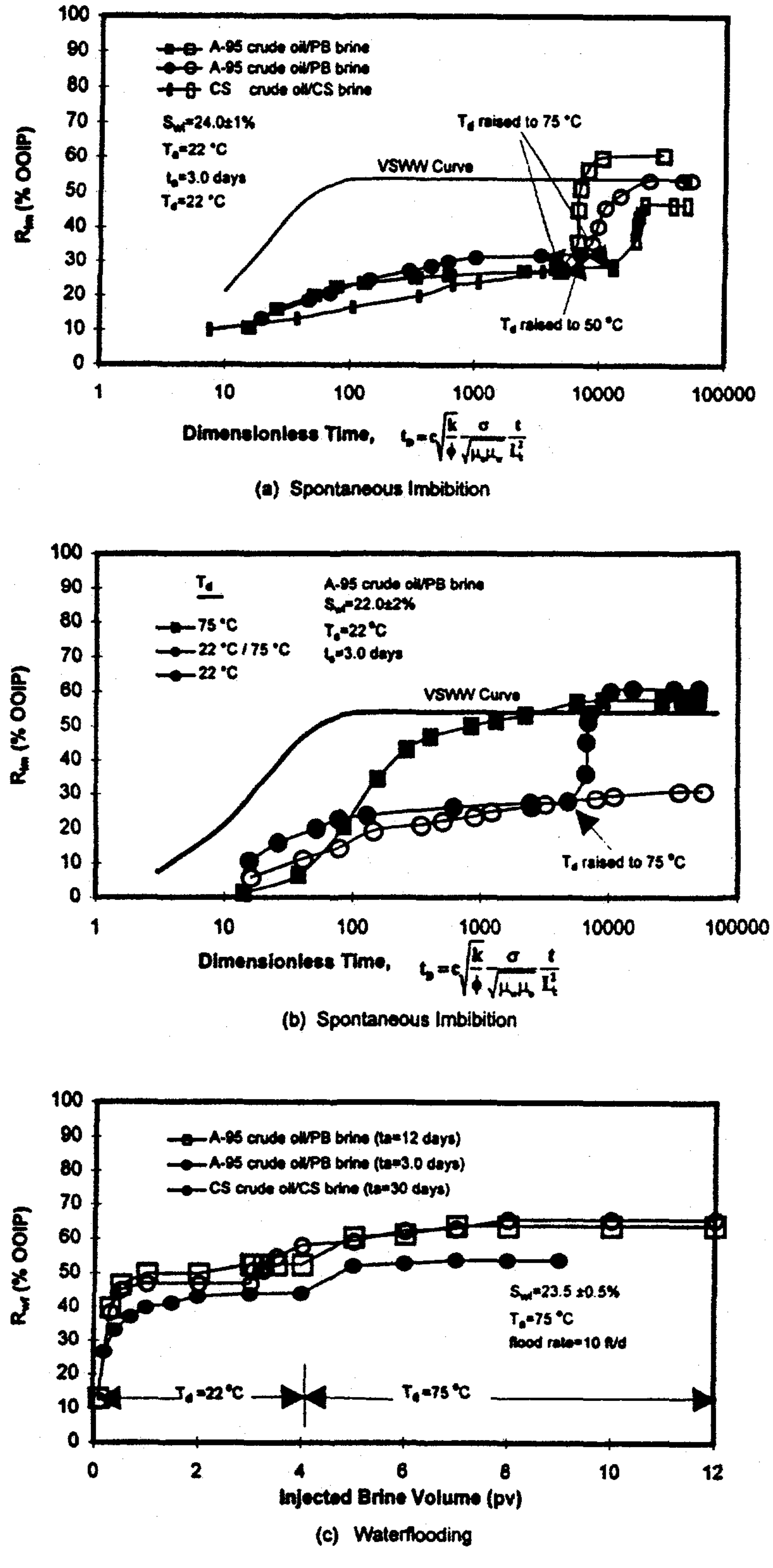


Figure 5. Effect of Change in T_d on Oil Recovery by Imbibition and Waterflooding

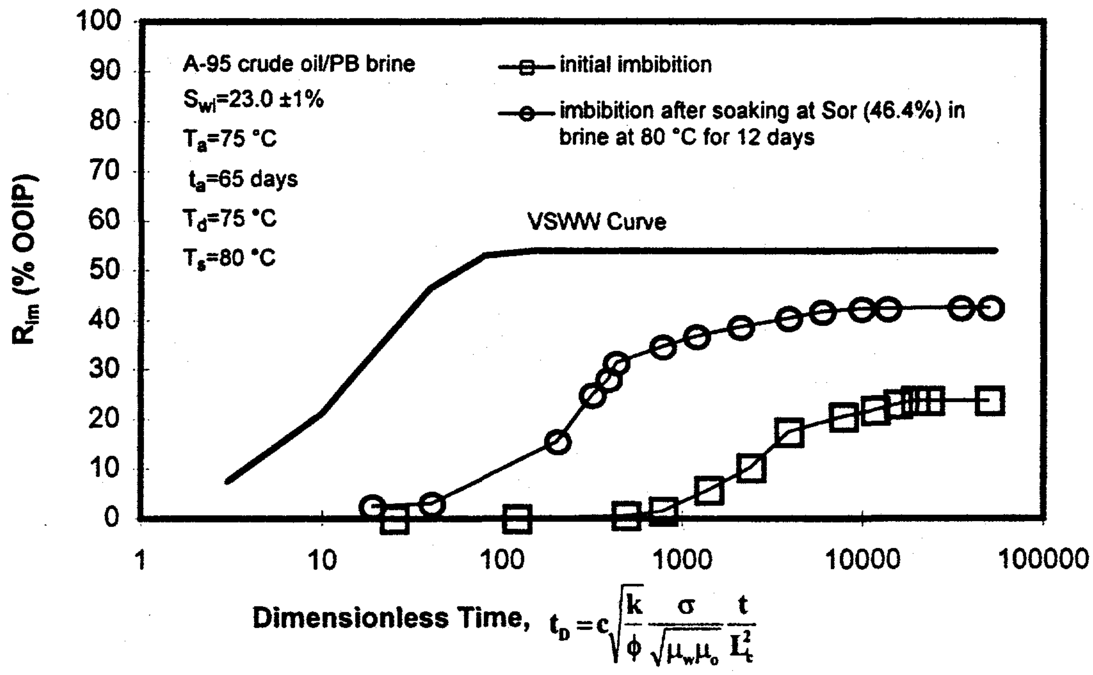


Figure 6. Change Toward Water Wetness Resulting From the Core Aged at High Water Saturation

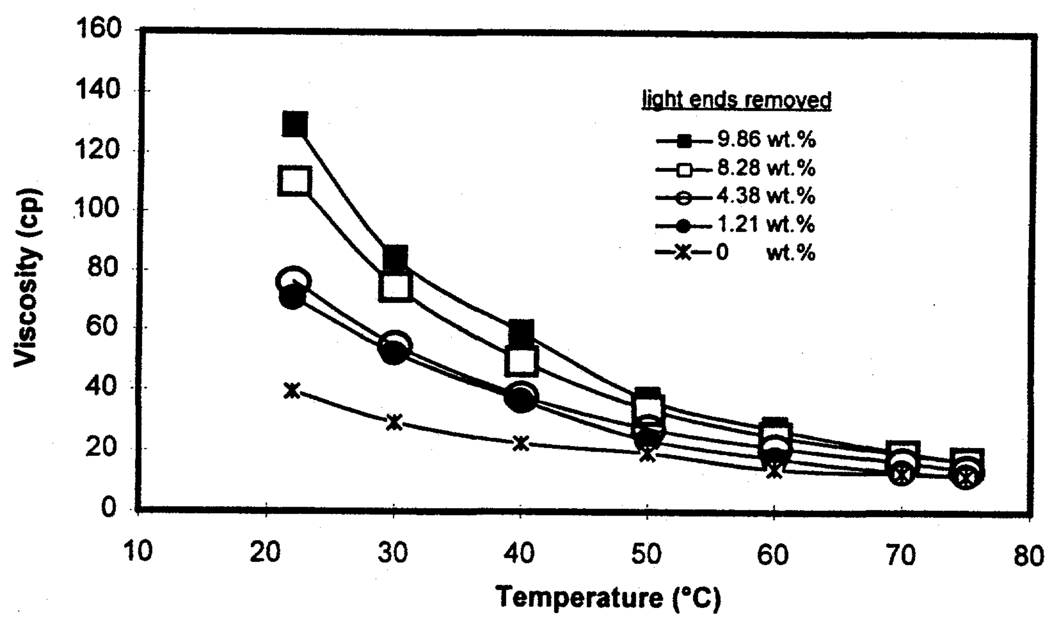
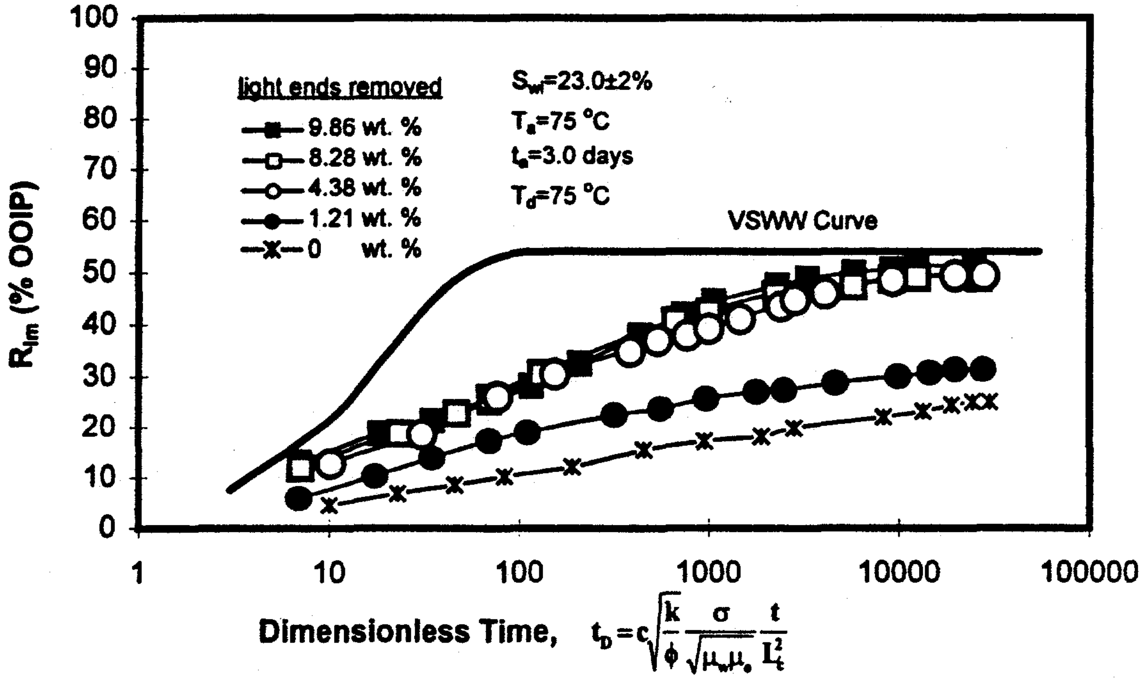
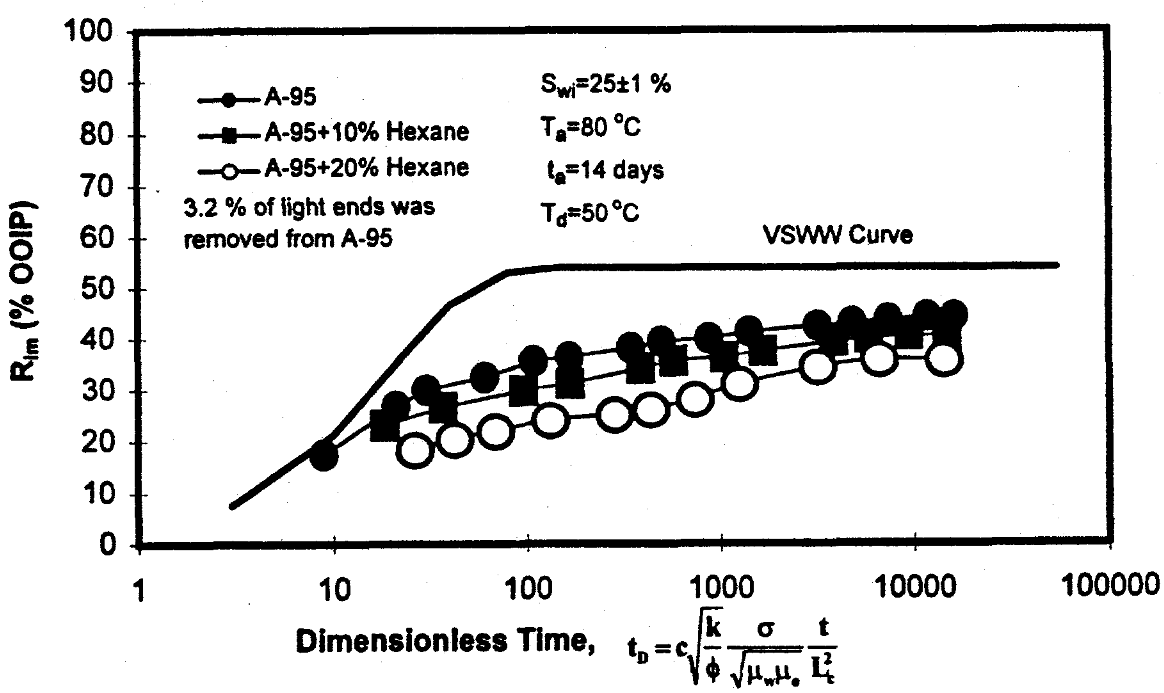


Figure 7. Change in Viscosity vs Temperature With Removal of Light Ends From A-95 Crude Oil

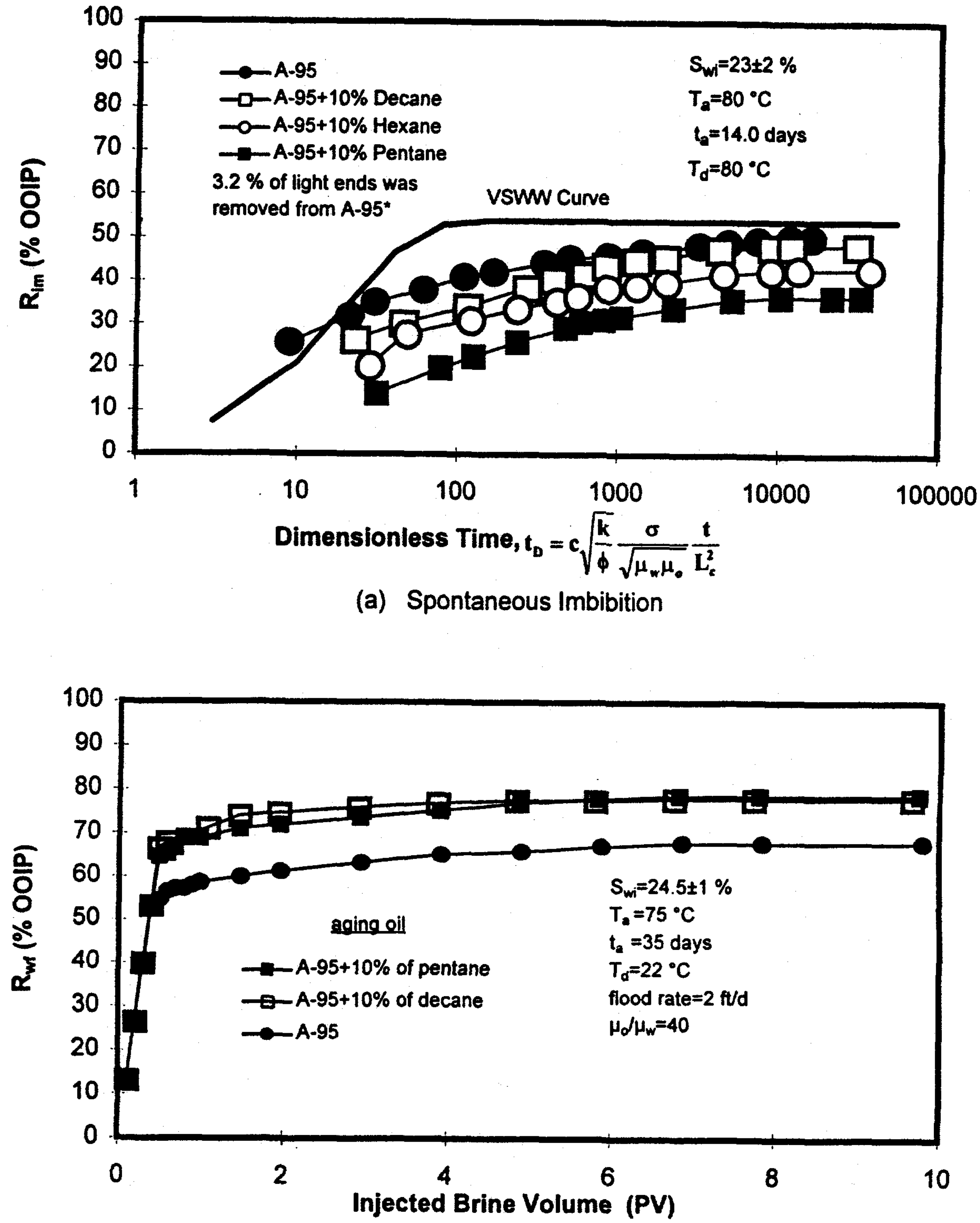


(a) Removal of Light Ends



(b) Addition of Hexane

Figure 8. Effect of Light Components on Oil Recovery of A-95 Crude Oil by Spontaneous Imbibition



(a) Spontaneous Imbibition

(b) Waterflooding

Figure 9. Effect of Oil Composition on Oil Recovery by Spontaneous Imbibition and Waterflooding