OIL RECOVERY BY WATERFLOODING AND IMBITION - INVADING BRINE CATION VALENCY AND SALINITY

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Abstract

Laboratory studies show that numerous variables are involved in the crude oil/brine/rock interactions that determine wetting behavior and oil recovery. Among these, it has been shown that brine composition can have a large effect on the microscopic displacement efficiency of oil recovery by waterflooding and spontaneous imbibition; further observations are presented in this paper. Recovery of crude oil from Berea sandstone is reported for brines prepared from chloride salts of different cation valencies. Waterflood recovery increased and imbibition rate decreased with increase in cation valency for 1% solutions of NaCl, $CaCl_2$ and $AlCl_3$. In general, oil recovery increased with decrease in salinity. An exception was found in the present work for $AlCl_3$, which is ascribed to the effect of pH. With reservoir crude oil and synthetic reservoir brine as connate water, injection of dilute brines (0.0085M) of five different types all gave comparable increases in recovery (8 to 13% of original oil in place) over that given by injection of the reservoir brine. Reduction in injection brine salinity during the course of waterflooding also gave increased oil recovery for brines containing either monovalent or divalent cations. However, injection of dilute brine at the outset rather than at a later stage of waterflooding has the advantages of increased recovery at breakthrough and higher final oil recovery.

Introduction

Brine has been shown to mediate adsorption from crude oil onto mineral surfaces (Buckley and Morrow, 1991). The brine properties which affect crude oil/brine/rock interactions and hence wetting properties include pH, ionic species, and salinity (Buckley et al., 1998, Tang and Morrow, 1998). Evidence that brine composition can affect oil recovery is now sufficient to justify systematic study of a new approach to improved waterflood efficiency.

Exploratory studies have been made of the effect of cation valence and salinity on wetting and oil recovery for selected crude oil/brine/rock systems. It is shown that injection of low salinity brine, no matter whether monovalent or multivalent, can increase oil recovery by waterflooding.

2. Experimental

2.1 Crude oil/brine/rock systems

Crude oil. A-95 (Prudhoe Bay) and CS crude oil samples were used as the oil phase. The A-95 crude oil was rich in asphaltenes and the CS sample had a high wax content (Table 1).

Brine. Five single cation brines, NaCl, KCl, $CaCl_2$, $MgCl_2$ and $AlCl_3$ and two synthetic reservoir brines, PB (Prudhoe Bay) and CS of the compositions given in Table 2, were used as initial and invading brines. Salinities are commonly expressed as wt % (g dry salt per 100 ml of water), molarity, ppm, and ionic strength. According to context, the term salinity refers to both amount and type of salt that makes up the ionic composition of the brine.

Rock. All of the core samples were Berea sandstone of 3.8 cm diameter and 7.7-7.8 cm length. Permeability to nitrogen ranged from 799 to 971 md and to brine from 507 to 653 md. Porosities were close to 23% (Table 3).

2.2 Procedures

Establishing initial water saturation, S_{wi}. Cores were saturated with brine for 10 days at room temperature and then flooded with 5PV of crude oil and a further 5PV in the reverse direction. The established S_{wi} ranged from 20.1 to 26.0% (Table 3).

Aging. Cores at S_{wi} were immersed in crude oil in sealed vessels and aged for 10 days at reservoir temperature (55 °C for CS crude oil and 75 °C for A-95 crude oil).

Imbibition and waterflood tests. After aging, each core plug was set in a Hassler core holder and flushed with 3-5 PV of fresh crude oil. The core was then ready for waterflood tests. Oil recovery, R_{wf}, expressed as percent original oil in place (%OOIP), was recorded vs. injected brine volume (PV). A summary of test conditions and results is given in Table 3. For imbibition tests, each core was placed in an imbibition cell containing the test brine. All displacement tests were run in ovens set at reservoir temperature. Thus the aging temperature, T_a, and the temperature of measurement, T_m, were equal for all tests. For spontaneous imbibition tests, oil recovery (%OOIP) by imbibition, R_{im}, was recorded vs. time, t.

Assessment of wettability. Use of the Amott Index to characterize the wetting behavior is of limited value for differentiating between the different types of water wetness observed in the present work. The Amott index depends mainly upon final recovery but not on rate. Consideration of imbibition rate and extent provides an alternative method of evaluating wettability. The features of each imbibition curve are examined after scaling results by a semi-empirically determined dimensionless time, t_D, to adjust for differences in test conditions other than wettability (Ma et al., 1997). These included core properties (air permeability, k, and porosity, ϕ), fluid properties (viscosity of oil and water, μ_o and μ_w, and interfacial tension between oil and water, σ), and core geometry (by a characteristic length, L_c). The dimensionless time t_D is defined by,

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

The decrease in t_D relative to correlated data for very strongly water wet conditions provides a qualitative assessment of wettability. A quantitative method of assessing wettability from imbibition rate has also been proposed (Ma et al., 1994).

In examining imbibition data, features of interest include how and when spontaneous imbibition starts, the rate at which it progresses, and the final recovery. If imbibition does not occur immediately, the delay in commencement is referred to as an induction time.

3. Results

3.1 Cation Valence

CS crude oil was used as the oil phase. Three kinds of brines, NaCl, $CaCl_2$, and $AlCl_3$ (all 1% by weight solutions), were used as aqueous phase. Values of molarity and ionic strength are included in Table 3. The measured pH values were 7.0 for NaCl, 6.8 for $CaCl_2$, and 3.5 for $AlCl_3$.

Imbibition. The test results for spontaneous imbibition with NaCl, $CaCl_2$, and $AlCl_3$ are shown in Figure 1. Rate and extent of imbibition were all significantly less than the reference curve VSWW included in Fig. 1 given by correlation of data for very strongly water wet conditions and zero initial water saturation (Ma et al., 1997). The rate and/or extent of oil recovery by spontaneous imbibition were in the order of NaCl>$CaCl_2$>$AlCl_3$. This sequence also holds if the salinity is expressed as molarity or ionic

strength. From the differences in rate of imbibition it is concluded that water wetness decreases with increase in cation valence.

For $AlCl_3$ brine there was an induction time of about one hour followed by long-term continuous production of oil. The induction time indicates transition in wettability with time towards water wetness. Transitions towards water wetness for wettability states induced by crude oil have also been observed with increase in temperature and after aging a core at high water saturation achieved by waterflooding (Tang and Morrow, 1997, Morrow et al., 1998).

Decrease in water-wetness with increase in cation valence for the same salinity is partly ascribed to ion binding by multivalent cations between the negatively charged polar groups at the oil-brine interface with negatively charged minerals at the rock surface. Adsorption of polar organic compounds onto the rock surface by ion binding will tend to increase with cation valence. Interactions between clay particles and between these particles and the pore walls at which they reside has also been suggested as playing a significant role in the mechanism by which salinity affects oil recovery (Tang & Morrow, 1998).

Waterflooding. The results for waterflood tests with different cation brines are presented in Figure 1b. Waterflood recoveries, both breakthrough and final, increased with increase in cation valence.

From the imbibition results (Figure 1a), it can be concluded that waterflood recovery increased with decrease in water-wetness. This trend of increase in waterflood recovery with decrease in water-wetness is consistent with correlations obtained between Amott index and waterflood recovery (Jadhunandan and Morrow, 1995) and with results obtained for the effect of aging time, aging temperature, increase in the fraction of light components in crude oil, and initial water saturation on wetting and oil recovery for A-93, A-95, and Dagang crude oils (Zhou et al., 1996, Tang and Morrow, 1997, Tang, 1998).

3.2 Salinity

3.2.1 NaCl brine

The effect of change in salinity for 0.17, 0.85, and 1.71 molar NaCl brines was reported previously (Morrow et al., 1998). In these tests, the cores were aged at reservoir temperature and displacement tests were at room temperature; also, there were some differences between the conditions for the imbibition tests versus those for drainage. Waterflood recovery increased with decrease in salinity but in contrast to the trends already mentioned extent and rate of imbibition also increased with decrease in salinity. The effect of salinity for brines containing divalent and trivalent cations is also of interest and data are reported here for calcium and aluminum chloride brines.

3.2.2 $CaCl_2$ brine

Five $CaCl_2$ brines (0.01%, 0.05%, 0.1%, 1.0%, and 2.0%) were used for imbibition tests on recovery of A-95 crude oil. The pH for these brines ranged from 6.3 to 6.7. Waterflood recoveries of CS crude oil were measured for two $CaCl_2$ brines (0.1% and 1%).

Imbibition. There was a general tendency for rate of imbibition to decrease with increase in the $CaCl_2$ concentration. However, the final oil recoveries were all close (64.7% for 2%, 65.0% for 1% l, 63.3% for 0.1%, 68% for 0.05%, 66.7% for 0.01%) compared to 54% for the VSWW correlation (Fig. 2a). From these results and inspection of the imbibition curves, water wetness increased with decrease in $CaCl_2$ concentration.

Waterflooding. Waterflood test results for two kinds of $CaCl_2$ brine, 1% and 0.1% are shown in Figure 2b. Waterflood recoveries were about equal at breakthrough (52.5% for 0.1% $CaCl_2$, and 51.0% for

1% CaCl$_2$). At 2 PV injection, the recovery for the more dilute brine was 10% OOIP higher than for the 1% brine, and 6% OOIP higher after 10 PV injection. The trend in waterflood recovery with salinity is qualitatively the same as observed for NaCl brines (Morrow et al., 1998) and for dilutions of DG and CS reservoir brines (Tang and Morrow, 1997 and 1998).

3.2.3 AlCl$_3$ brine

Two kinds of AlCl$_3$ brines, 1% and 0.1%, were used for these tests. Because of hydrolysis, the pH of this brine was 3.5 for 1% AlCl$_3$ and 4.5 for 0.1% AlCl$_3$. CS crude oil was used as the oil phase.

Imbibition. The imbibition curves for the AlCl$_3$ brines are presented in Figure 3a. The results show that decrease in salinity results in increased rate of oil recovery by spontaneous imbibition, but the influence of salinity was small compared to that observed for NaCl and CaCl$_2$ brines.

Waterflooding: Waterflood data are presented in Figure 3b. Breakthrough and final recoveries for 1.0% AlCl$_3$ brine were higher than for 0.1% AlCl$_3$ brine. This is the only observed example to date for which oil recovery decreased with decrease in salinity. However, the recovery of CS crude oil for 0.1% AlCl$_3$ gradually increased after 6 PV of 0.1% AlCl$_3$ had been injected and equaled that for the 1% brine at 10 PV injection.

Values of effluent brine pH are included in Figure 3b. The effluent pH for 1% AlCl$_3$ was almost constant (4.2) shortly after breakthrough and oil recovery showed little change after 4PV injection. For the 0.1% AlCl$_3$ brine, the effluent pH at breakthrough was 6.8 and decreased to 4.5 after injection of 6 PV with the largest drop being between 5 and 6 PV. This fall in pH coincided with start of a steady increase in oil recovery. For AlCl$_3$ brine it is concluded that the effect of pH on crude oil/brine/rock interactions and oil recovery dominates over that of ionic strength.

3.3 Invasion of dilute single cation brines

A reservoir brine, PB RB, was used as connate brine and the invading brine for the reference condition of no change in the invading brine. Recovery of A-95 crude oil was measured for injection of five kinds of single cation 0.0085 M brines: NaCl, KCl, CaCl$_2$, MgCl$_2$, and AlCl$_3$. Thus for all tests, the salinity of the connate brine (PB=21,660 ppm) was much higher than for the invading brines. The ionic strength of PB RB was 0.371, (43.6 times that of NaCl and KCl, 17.5 times that of CaCl$_2$ and MgCl$_2$, and 8.7 times that of AlCl$_3$).

Imbibition. The test results are presented in Figure 4a. There was no systematic overall effect of cation valence on imbibition rate, such as shown in Figure 1. For all brines except AlCl$_3$, initial recovery behavior was similar. As observed previously (Tang and Morrow, 1998), connate water has a dominant effect on early time imbibition, but the imbibition recovery curves for invading brines of different salinity diverge as imbibition progresses. The difference between imbibition rates for the single cation brines, NaCl and KCl, are probably related to differences in interactions with clay, in particular kaolinite in the Berea sandstone.

Waterflooding. Oil recovery by waterflooding for different dilute single-cation brines are presented in Figure 4b together with oil recovery for injection of PB RB. The results show that injection of dilute single-cation brines, no matter what the cation valence, gives increase in both breakthrough and final recoveries. Final recoveries increased by 9-15% OOIP compared to PB RB, with CaCl$_2$ giving the highest recovery.   Recovery curves for the other four brines fell close together. The separation in recovery by spontaneous imbibition for NaCl and KCl brines is not reflected by the waterflood behavior.

3.4 Change in injection brine at high water cut

PB RB as the initial brine: The tests were run at the same conditions as above, except that the core was first flooded with PB RB for 1 PV. Waterflood recovery up to this stage duplicated that measured previously for injection of PB RB brine (Fig. 5); the produced water-cut was over 90%. The injection brine was then changed to 0.0085 M $MgCl_2$ brine. The response in oil recovery is shown in Fig. 5. Final recovery increased by 7% (OOIP) over that obtained for PB RB. Fines production and increase in effluent brine pH were observed for dilute brine displacement.

NaCl as initial brine: For this test, 1% NaCl was the initial brine and CS crude oil was the oil phase. The core was first flooded with 5 PV of 1% NaCl to establish the baseline recovery for no change in injection brine. The core was then flooded with 12 PV of 0.05% NaCl, 12 PV of 0.01% NaCl, and 12 PV of 0.01% $CaCl_2$ as indicted in Fig.6. When the 0.05% NaCl was replaced with 0.01% NaCl as injection brine, fines production was observed for the first 2 PV.

A reference waterflood given by injection of 40 PV of 1% NaCl is included in Fig. 6. Oil recovery attained a plateau for 2- 5 PV of 1% NaCl injected and the water cut was 100%. With injection of 12 PV of 0.05% NaCl, there was a gradual increase in oil recovery of about 3%. When the injection brine salinity was decreased to 0.01%, there was an immediate response in oil recovery. The oil recovery increased from 64% to 68% after the first 2 PV of 0.01% NaCl injected. The total increase in oil recovery for 0.01% NaCl after injection of 28 PV was about 6% with oil recovery still increasing slowly. The effect of cation valence on oil recovery was tested by switching the injection brine to 0.01% $CaCl_2$. The oil production ceased for about 4 PV injection but then resumed at very low rate to give a further increase in recovery of about 4% (Fig.6).

Compared with the oil recovery for the core flooded throughout with 1% NaCl (Fig. 6) the increase in oil recovery resulting from change in the injection brine was 12% greater than the plateau at 2 to 5 PV injected. The reference curve for 1% NaCl showed a very slow increase in recovery of 3% of OOIP over about 30 PV injection.

$CaCl_2$ as initial brine: 0.1% $CaCl_2$ was the initial brine and CS crude was the oil phase. The core was first flooded with 5 PV of 0.1% $CaCl_2$, followed by 13 PV of 0.01 $CaCl_2$ and 22 PV of 0.01 NaCl as indicated in FIG. 7.

A reference waterflood with 0.1% $CaCl_2$ was also performed. The recovery for 5 PV 0.1% $CaCl_2$ was 56% compared to 59% for 0.1% NaCl. This is opposite to the trend observed for 1% solutions of these brines. (Fig. 1b). However, after 40 PV injection, the recoveries for the two 0.1% brines were almost equal (Figs. 6 and 7).

When the injection brine salinity was decreased by 10 times, oil recovery increased from 56% to 63% after 13 PV of 0.01 $CaCl_2$ had been injected. After injection of a further 4PV without increase in recovery, the injection brine was switched to 0.01% NaCl. Oil recovery increased by 3% OOIP with injection of 12 PV and then ceased (Fig. 7). The final recovery was 68.5%, which was 12.5 % OOIP higher than the initial plateau for injection of 0.1% $CaCl_2$, and 6% higher than given by the reference curve after 40 PV injection.

As for injection of 0.01% NaCl, production of fines was observed when 0.01% $CaCl_2$ was injected, but the amount was very slight and there was no obvious permeability damage.

4. Discussion

The factors which control crude oil/brine/rock interactions and their effect on wettability and oil recovery involve complex and sometimes competing mechanisms. There is a considerable body of data, including that of the present work, which shows that oil recovery can be dependent on brine composition. It has also been demonstrated for sandstone that adsorption of polar components from crude oil, and the presence of clays and connate water are necessary conditions for this dependency (Tang & Morrow, 1998).

According to DLVO theory (Israelachvili, 1991), as the ion valence and/or salinity increase, the Debye length decreases and the electrical double layer between surfaces of opposite charge becomes compressed. The results shown in Figures 1 and 2 suggest that cation valency can play an important role when the salinity is comparatively high. Compression of the electrical double layer will tend to promote adsorption from the crude oil and decrease the water wetness of the rock. Multivalent cations can also promote adsorption from crude oil by binding negatively charged surface active groups in crude oil with negatively charged solid surfaces. However, an opposite effect is possible; they can also tie up pairs of charged sites on surfaces which could reduce adsorption of positively charged groups from the crude oil (Buckley et al., 1998).

When the salinity was decreased, no matter what the cation valence, oil recovery increased except for the special case of $AlCl_3$. The results shown in Figures 5, 6, and 7 support previous observations that injection of dilute brine can improve oil recovery (Tang and Morrow, 1997 and 1998, and Morrow et al., 1998). They also show that improvement in recovery is observed no matter whether at an early or later stage of injection. The increased recovery was accompanied by modest production of fines and increase in effluent brine pH. However, the production of fines did not cause obvious permeability damage. A detailed study of permeability and brine composition will be reported. It has been hypothesized that the improved recovery is related to transfer of a fraction of fine particles from the rock walls to the oil-water interface during the course of displacement (Tang and Morrow, 1998). Future work on brine composition and oil recovery will include experiments designed to test this hypothesis.

5. Conclusions

1. Cation valence is of specific importance to crude oil/brine/rock interactions. When the salinity is high, increase in cation valence tends to decrease water-wetness, but the corresponding oil recovery by waterflooding tends to increase. The effect of cation valence on wetting and oil recovery was much less when the salinity was low.

2. Decrease in NaCl and $CaCl_2$ brine concentration can result in wettability transitions towards increased water-wetness and increase in waterflood recovery. These results are consistent with trends obtained previously for dilution of two synthetic reservoir brines. However, for $AlCl_3$ brine, decrease in salinity can result in increased water-wetness and decreased oil recovery.

3. For a given connate brine composition (both reservoir brine or single cation brine), injection of dilute single cation brine (no matter what the cation valence) always resulted in increased oil recovery.

4. Switching the injection brine from a high salinity brine to a dilute brine at high water-cut can also result in increased oil recovery by waterflooding. However, earlier injection of dilute brine is of benefit with respect to both increased breakthrough and final oil recovery.

(China), ELF (France), Exxon, JNOC (Japan), Marathon, Norsk Hydro (Norway), Phillips, Shell (The Netherlands), Statoil (Norway), and the Enhanced Oil Recovery Institute of the University of Wyoming.

Nomenclature

k = permeability, md	b = brine
L_C = characteristic length, cm	D = dimensionless
R = oil recovery, %OOIP	g = gas
S = saturation, %	im = imbibition
t = time, minutes	m = measurement
T = temperature	o = oil
μ = viscosity, cP	or = residual oil
ϕ = porosity, %	res = reservoir
σ = IFT, dyne/cm	w = water

Subscripts
	wf = waterflood
a = aging	wi = initial water
amb = ambient	

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Table 1   Viscosity and Density of Oils

Oil samples	Temp (^{o}C)	Viscosity (cP)	Density (g/cm^3)	Asphaltene content (%)	Wax content (%)	Acid[1] Number (KOH/g oil)	Base[1] Number (KOH/g oil)
CS	22	70.5	0.891	0.78	12.6	0.33±0.03	1.16±0.18
	50	23.6	0.860				
	75	11.6	0.835				
A-95	22	40.3	0.906	6.55	Very low	0.24±0.05	2.2±0.01
	50	19.2	0.890				
	75	11.3	0.860				

1.   Buckley et al, 1998

Table 2 Synthetic Reservoir Brine Compositions (ppm)

Brine	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	HCO$_3^-$	SO$_4^{2-}$	pH	TDS
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

Table 3 Core Properties and Experimental Data

core	ϕ (%)	k_g (md)	k_b (md)	S_{wi} (%)	oil	initial brine & ionic strength (I)	injection brine & ionic strength (I)	V (ft/d)	R_{im} (%)	R_{wf} (%)
change in cation valence										
*I97-1	23.3	892	567	24.7	CS	NaCl (0.171 M)	NaCl (0.171 M)	-	37.3	-
I97-2	23.2	901	569	24.5	CS	CaCl$_2$ (0.225 M)	CaCl$_2$ (0.225 M)	-	33.1	-
I97-3	23.3	879	551	24.8	CS	AlCl$_3$ (0.3775 M)	AlCl$_3$ (0.3775 M)	-	32.7	-
*W97-1	23.3	925	583	25.1	CS	NaCl (0.171 M)	NaCl (0.171 M)	3.0	-	56.7
W97-2	23.3	909	598	25.5	CS	CaCl$_2$ (0.225 M)	CaCl$_2$ (0.225 M)	3.0	-	60.9
W97-3	23.3	931	628	25.4	CS	AlCl$_3$ (0.3775 M)	AlCl$_3$ (0.3775 M)	3.0	-	71.6
change in brine salinity (initial=injection)										
I96-4	23.3	862	579	25.7	A95	CaCl$_2$ (0.00225 M)	CaCl$_2$ (0.00225 M)	-	66.7	-
I96-5	23.3	899	544	24.8	A95	CaCl$_2$ (0.01125 M)	CaCl$_2$ (0.01125 M)	-	68.0	-
I96-6	23.2	903	608	24.5	A95	CaCl$_2$ (0.0225 M)	CaCl$_2$ (0.0225 M)	-	63.3	-
I96-7	23.3	922	633	25.4	A95	CaCl$_2$ (0.225 M)	CaCl$_2$ (0.225 M)	-	65.0	-
I96-8	23.4	877	580	25.8	A95	CaCl$_2$ (0.45 M)	CaCl$_2$ (0.45 M)	-	64.7	-
W97-4	23.3	971	638	25.6	CS	CaCl$_2$ (0.0225 M)	CaCl$_2$ (0.0225 M)	3.0	-	65.1
W97-5	23.3	938	615	25.9	CS	CaCl$_2$ (0.225 M)	CaCl$_2$ (0.225 M)	3.0	-	60.9
I98-1	23.3	872	594	25.2	CS	AlCl$_3$ (0.03775 M)	AlCl$_3$ (0.03775 M)	-	34.3	-
I98-2	23.2	857	585	25.4	CS	AlCl$_3$ (0.3775 M)	AlCl$_3$ (0.3775 M)	-	32.7	-
W98-1	23.3	867	617	25.7	CS	AlCl$_3$ (0.03775 M)	AlCl$_3$ (0.03775 M)	3.0	-	71.6
W98-2	23.4	925	644	25.9	CS	AlCl$_3$ (0.3775 M)	AlCl$_3$ (0.3775 M)	3.0	-	71.6
change in injection brine salinity										
I96-4	23.3	969	653	24.4	A95	PB RB (0.375 M)	NaCl (0.0085 M)	-	62.0	-
I96-5	23.3	936	634	24.6	A95	PB RB (0.375 M)	KCl (0.0085 M)	-	48.0	-
I96-6	23.3	961	652	24.3	A95	PB RB (0.375 M)	CaCl$_2$ (0.02125 M)	-	55.3	-
I96-7	23.2	869	524	25.2	A95	PB RB (0.375 M)	MgCl$_2$ (0.0213 M)	-	53.3	-
I96-8	23.3	866	579	25.0	A95	PB RB (0.375 M)	AlCl$_3$ (0.0425 M)	-	60.0	-
W96-4	23.3	883	567	25.2	A95	PB RB (0.375 M)	PB RB (0.375)	1.2	-	66.7
W96-5	23.3	861	538	24.9	A95	PB RB (0.375 M)	NaCl (0.0085 M)	1.2	-	76.7
W96-6	23.1	801	507	25.2	A95	PB RB (0.375 M)	KCl (0.0085 M)	1.2	-	76.0
W96-7	23.2	843	544	24.7	A95	PB RB (0.375 M)	CaCl$_2$ (0.02125 M)	1.2	-	81.3
W96-8	23.3	862	576	25.1	A95	PB RB (0.375 M)	MgCl$_2$ (0.0214 M)	1.2	-	77.3
W96-9	23.3	895	621	25.4	A95	PB RB (0.375 M)	AlCl$_3$ (0.0425 M)	1.2	-	79.4
W96-10	23.3	862	540	25.6	A95	PB RB (0.375 M)	PB RB (0.375 M)/ MgCl$_2$ (0.0213 M)	1.2	-	74.4
W98-3	23.3	909	622	22.7	CS	NaCl (0.171 M)	NaCl (0.171 M)/ NaCl (0.0086 M)/ NaCl (0.00171 M)/ CaCl$_2$ (0.00225 M)	6.0	-	72.5
W98-4	23.3	917	601	22.9	CS	NaCl (0.171 M)	NaCl (0.171 M)	6.0	-	63.8
W98-5	23.3	893	618	20.1	CS	CaCl$_2$ (0.0225 M)	CaCl$_2$ (0.0225 M)/ CaCl$_2$ (0.0023 M)/ NaCl (0.00171 M)	6.0	-	68.5
W98-6	23.4	945	655	20.3	CS	CaCL$_2$ (0.0225 M)	CaCl$_2$ (0.0225 M)	6.0	-	62.5

t_a=10 days, T_d=T_a=55°C (CS), and 75°C (A95);

*I=imbibition, W=waterflooding
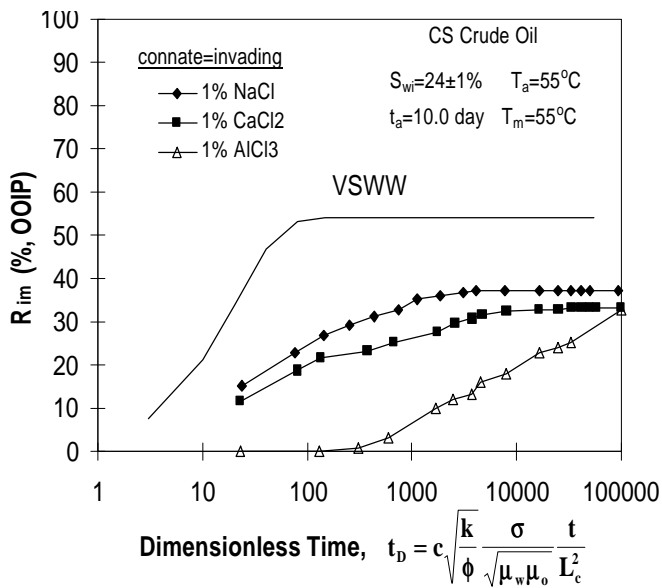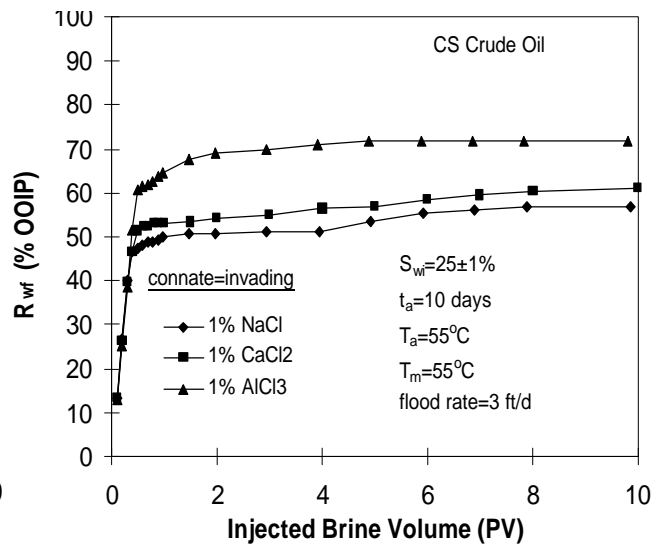
Fig. 1 Cation Valence and Oil Recovery

Fig. 2 CaCl$_2$ Concentration and Oil Recovery
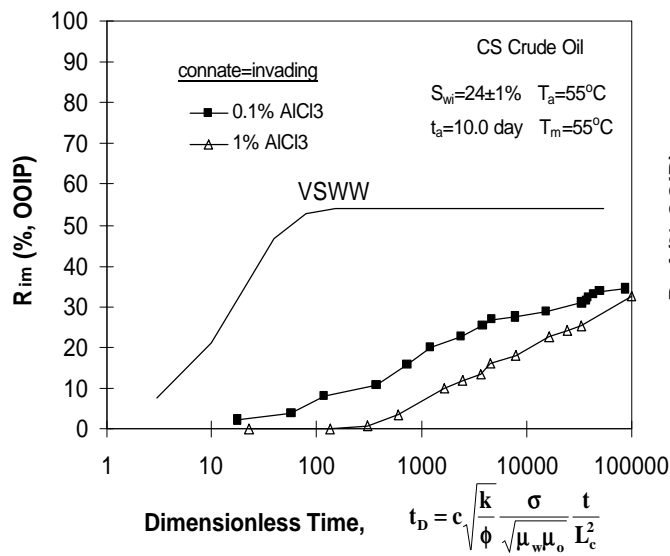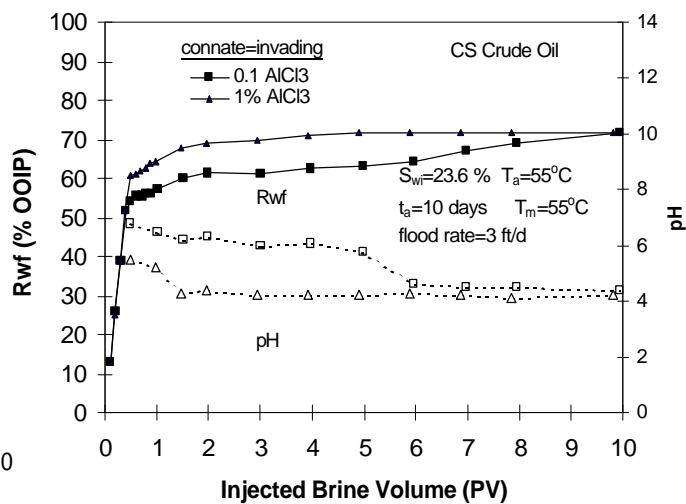
Fig. 3 AlCl₃ Concentration and Oil Recovery
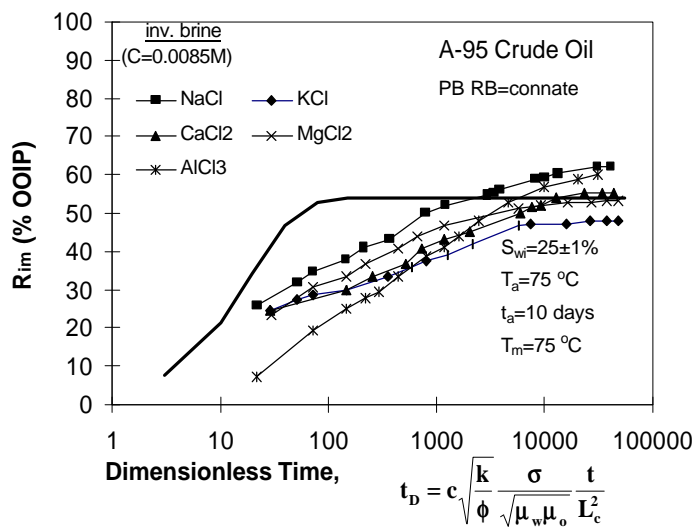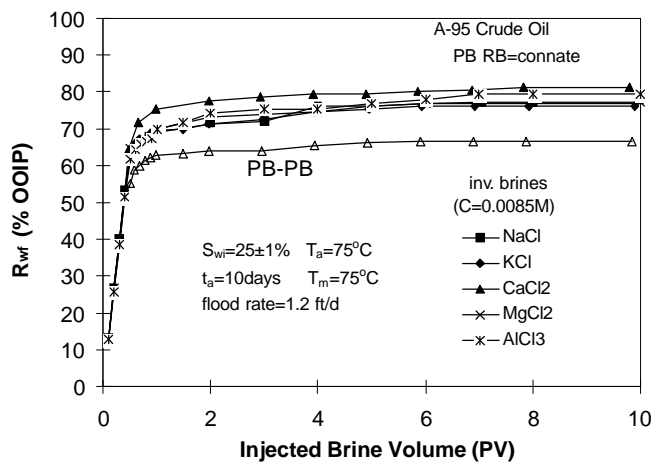
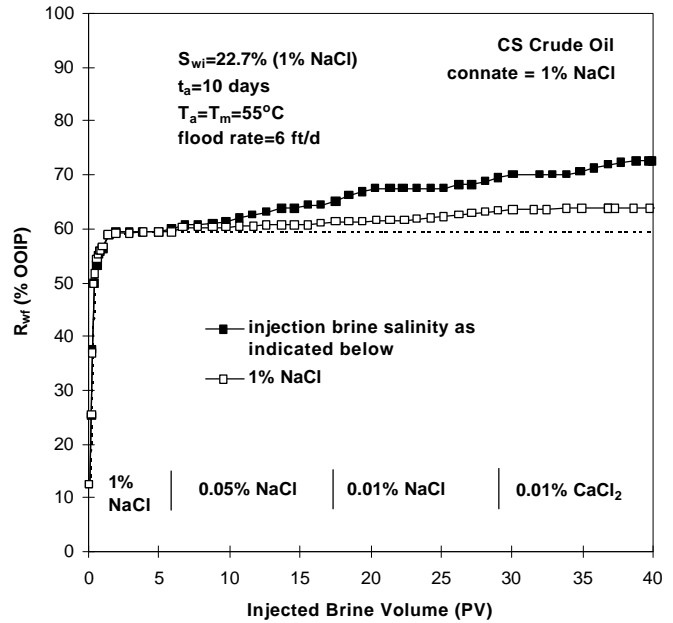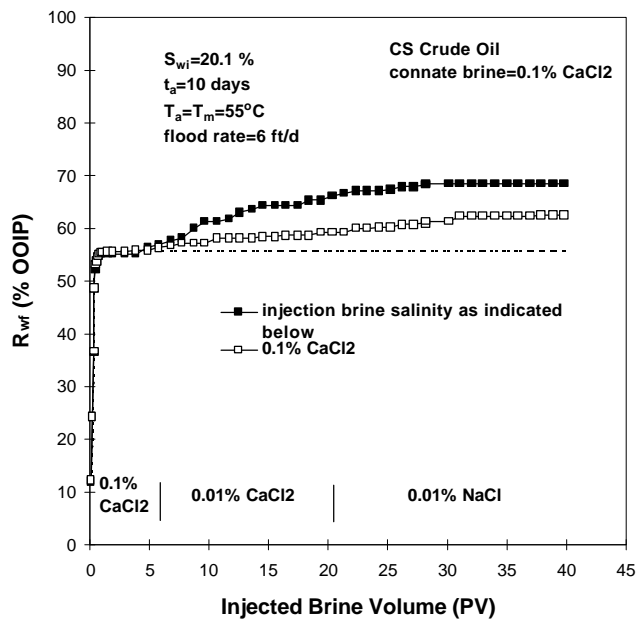**Fig. 4 Invasion of Dilute Single Cation Brines and Oil Recovery**
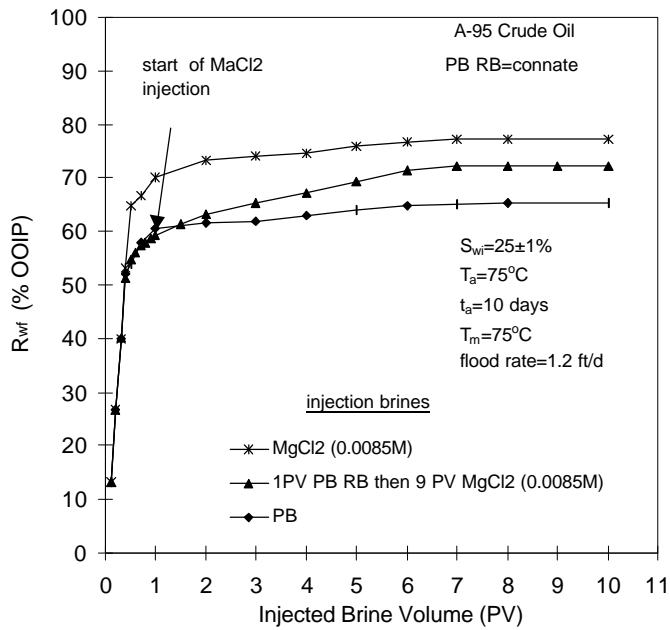
Fig. 5 Increase in Oil Recovery with Injection of Dilute MgCl₂ at High Water Cut

Fig. 6 Change in Oil Recovery at High Water Cut with Decrease in Concentration of NaCl

Fig. 7 Change in Oil Recovery at High Water Cut with Decrease in Concentration of CaCl₂