

LOW SALINITY WATERFLOODING OF A RESERVOIR ROCK

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This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Calgary, Canada, 10-12 September, 2007

ABSTRACT

Numerous laboratory and field tests indicate that waterflood oil recovery is dependent on the composition and salinity of the injected water, and that low salinity water injection can improve oil recovery. However, the extent of increase in oil recovery by low salinity brine flooding is highly specific to crude oil-brine-rock (COBR) combinations and cannot be predicted. This paper presents laboratory results and analysis for recovery from four cores taken from a sandstone reservoir. The sandstone contained chert, lithic fragments, and kaolinite and was poorly sorted and friable. Recovery was tested in both secondary and tertiary mode for two crude oils, characterized by their physical properties, asphaltene content, and acid and base numbers, using brines with salinities ranging from 350 ppm to 35,000 ppm. Large increase in oil recovery was observed in both modes. Secondary oil recovery increased by 16% OOIP for 10 times diluted seawater, and 29% for 100 times dilution. Tertiary mode recoveries given by injection of seawater followed by low salinity brine gave additional recovery up to 17% OOIP depending on core history. The pH of the effluent brine usually stayed close to neutral. Substantially increased secondary recovery for injection of seawater, subsequent to low salinity waterflooding, provided added evidence that low salinity brine injection can cause complex changes in pore surfaces and related patterns of mixed wettability. Changes in rock properties with low salinity waterflooding were also evidenced by increase in absolute permeability to brine (accompanied by modest production of fines) and increase in gas permeability. Pressure response indicated that formation of temporary crude oil/brine emulsions also contributed to the recovery performance.

INTRODUCTION

Laboratory and field tests indicate that injection of low salinity brine, ranging up to 4000 ppm, can extend the economic life of fields that are in a mature stage of waterflooding through tertiary mode recovery. Laboratory tests also show that injection of low salinity brine can give marked increase in secondary mode recovery compared to high salinity brine (Tang and Morrow, 1997, 1999; Webb et al., 2004, 2005; McGuire et al., 2005; Zhang and Morrow, 2006; Lager et al., 2006, 2007). Investigation of the mechanisms by which recovery is increased presents a considerable challenge because they depend on complex crude oil/brine/rock interactions. At present, no readily available outcrop sandstone has been identified that can serve as a model rock for systematic investigation of low salinity flooding.

Responses of reservoir cores to low salinity flooding have, in general, been distinctly more encouraging than results for all types of outcrop sandstone. Lager et al. (2006) reported tertiary mode response to low salinity flooding with increase in recovery ranging from 2 to 18% for 18 reservoir sandstones. Investigation of the mechanism that gives rise to improved recovery is now focused on the use of reservoir cores. This approach raises problems of availability and heterogeneity. Interpretation of sequential tests of low salinity flooding on individual cores and comparisons between cores must be treated with caution because the COBR interactions, particularly after low salinity flooding, result in identifiable changes in response from one flood to the next.

EXPERIMENTAL

Four core samples from a sandstone reservoir were tested (Table 1). Thin section analysis indicated that the sandstone contains quartz, chert, lithic (rock) fragments and clays (mainly kaolinite) and is poorly sorted and poorly cemented (Figure 1). X-ray analysis also showed the presence of abundant kaolinite, a small amount of smectite, and trace illite.

Most of the tests were run with a crude oil designated as LC. Recovery of a second crude oil (designated as WP) was also tested. Crude oil asphaltene content, acid and base numbers, density, and viscosity are listed in Table 2. Synthetic seawater based on North Sea water composition, dilute seawater and/or sodium chloride solutions with different concentrations were used as the brine phase. Seawater diluted 10 times with distilled water was designated as 0.1 seawater, and a hundred times diluted as 0.01 seawater. The seawater composition is listed in Table 3.

In the restoration process, the core was cleaned by flooding with 8 PV of toluene to remove organic components, followed by 8 PV of methanol to remove soluble salts. A further 8 PV of toluene was used to remove any newly exposed organic components. After cleaning, the core was dried at room temperature and then at 105°C. The air permeability of the dry core was measured. For each restoration, the core was first saturated with seawater by vacuum and allowed to equilibrate for about 10 days. The core was then, in most cases, flooded with 5PV of crude oil at about 15 to 20 psi pressure difference followed by 1.5 PV in the reverse direction. The core was aged in the crude oil for 2 to 3 weeks at 60°C before waterflooding. A cycle (C) was defined as flooding with brine followed by re-establishment of initial water saturation by flow of crude oil. Restoration (R) refers to re-cleaning and re-aging the core. Tests on each core are identified according to the sequence of restoration and the sequence with respect to the total number of flooding cycles. Cores were flooded with low salinity brine either in secondary or tertiary mode. Injection rate, q , ranged from 0.2 to 0.25 ml/min (about 1 ft/day). The volume of oil produced and the pressure change along with the effluent brine pH were recorded. All the waterflood tests were performed at 60°C. Detailed test information for each core is listed in Table 4 according to restoration and cycle numbers.

RESULTS AND DISCUSSION

Core 2065/1

After R1 ($S_{wi} = 33.0\%$), the wettability of the core was assessed by measurement of spontaneous imbibition at 60°C. The core was initially immersed in seawater. The imbibition rate was very slow and after 7 days only 2.9% OOIP was produced. The core was next immersed in 0.1 seawater for 7 days and a further 2% was produced. Finally the core was immersed in 0.01 seawater and an additional 3% was produced after 7 days. This behavior indicated that the core was very weakly water wet with respect to all three brines. No special significance can be deduced with respect to the effect of brine composition on wettability because there was no clear cessation of oil production after any of the 7 day periods. Comparable total recovery might have been achieved if the core had remained in seawater for 21 days. Total oil recovery after 21 days of imbibition was 8.9% OOIP. Previous observations on other crude oils for both outcrop sandstone and carbonate rocks showed much greater extent of imbibition (Tie and Morrow, 2005).

After the imbibition test, the water saturation had increased to 38.9% through imbibition as described above. The test R1/C1 shown in Figure 2a began with direct flooding with seawater. Substantial breakthrough occurred after recovery of 48% OOIP. After injection of 4.5 PV seawater, recovery reached 63.2% OOIP at a water/oil ratio of 16. Injection was then switched to 0.1 seawater and the pressure drop, ΔP , rose rapidly from 2 psi to about 11 psi and then stabilized at 13.5 psi for over 3 PV injection. Response in recovery was observed after 0.42 PV injection; the tertiary recovery was 8.4% OOIP and the water/oil ratio had risen to 18.3 after injection of 3.6 PV of 0.1 seawater. Total oil recovery was 71.6% OOIP. Effluent brine pH fluctuated slightly at around 7.5 and then showed small linear increase up to 8.3 with injection of 0.1 seawater (Figure 2a). No clay particles were observed in the effluent brine or at the oil/brine interface in the collector.

The core was cleaned and saturated with seawater and allowed to equilibrate for 10 days and then flooded with 65 PV of 35,000 ppm NaCl solution. The objective was to test low salinity flooding after divalent ions had been removed from the rock by ion exchange. The pH rose from 7 to 9 over the course of about 10 PV injection. After about 30 PV injection, the permeability to NaCl increased from 227 to 297 md (Figure 2b) and the effluent pH decreased to about 8.5. Production of fine particles was observed in the effluent brine. When the core was removed from the holder it was fractured laterally.

Secondary Recovery by Seawater Flooding – Cores 2060/4, 2060/1 and 2065/3B

Oil recovery given by injection of seawater is compared in Figure 3a for Core 2060/4 R1/C1 and Core 2060/1 R1/C1. There were differences in the character of the breakthrough recoveries for the two cores but the final recoveries after 4PV injection were only 3.7% OOIP apart even though the cores had large difference in initial water saturation. The recovery curves for Core 2060/4 R1/C1 and Core 2060/1 R1/C1 provide a reasonably consistent baseline for secondary recovery by injection of seawater.

Core 2065/3B was restored with the WP crude oil and seawater with $S_{wi} = 10.5\%$. This core was about double the permeability of the other tested cores but of lower porosity (see Table 1). The oil recovery was 64.5% OOIP by secondary flooding with seawater. The core was re-flooded with WP crude oil and a connate water saturation of 11.2% was established. Flooding with seawater resulted in 69.1% OOIP oil recovery compared to 64.5% OOIP for R1/C1 (Figure 3b). Examples of increase in oil recovery by cyclic waterfloods have been reported previously (Tang and Morrow, 1999). Such behavior may impact the benefits ascribed to low salinity flooding.

Core 2060/4

In total, seven restorations were performed on this core. The air permeability of the core was measured before the first, sixth and seventh restoration; no significant change was detected. For the first five restorations, initial brine saturation, S_{wi} , was established by flooding the core with LC crude oil. For the 6th and 7th restoration, S_{wi} was established by flooding with WP crude oil. The test details along with final oil recovery R_f as % OOIP are listed in Table 4.

The effect of dilute brine injection on improved oil recovery in secondary mode was tested for Core 2060/4. The core was restored between each test to give the sequence R1/C1 (seawater), R2/C2 (0.1 seawater), and R3/C3 (0.01 seawater). As shown in Figure 4a, at 12 PV injected, the final oil recovery given by injection of seawater was 50.9% OOIP. Recovery after injection of 0.1 seawater was 66.7% OOIP, an increase of 16% OOIP over that given by seawater. The recovery for injection of 0.01 seawater was 80%, an increase of nearly 30% OOIP over that given by seawater. Exposure of the core to low salinity brine in the prior test R2/C2 may be a factor in this high recovery. The effluent brine pH for all three tests was close to neutral.

The pressure drop across the core and effluent pH versus injected PV are shown in Figure 4b. The pH basically stayed constant during the flooding. No clays were observed in the effluent brine and the oil-water interface in the separator was clearly defined. Before brine breakthrough, the pressure increased sharply. The seawater flood showed the earliest and greatest decline from the peak pressure drop. The maximum pressure and the pressure decay for R2/C2 was comparable to those for R1/C1. R3/C3 had lower maximum ΔP and much less decay in ΔP .

For R4/C4, tertiary mode was tested by flooding with seawater, 0.1 seawater and 0.01 seawater sequentially (Figure 5a). The final oil recovery of 75.3% OOIP for injection of 12 PV seawater was 24% OOIP higher than for R1/C1. This test is a clear example of how results can change because of change in core properties as a result of exposure of the core to low salinity brine even though the core was restored after each test. Injection of 12 PV seawater was followed by injection of 13.64 PV 0.1 seawater. The pressure drop doubled but there was no response in recovery. When injection was switched to 0.01 seawater the rate of oil recovery decreased slightly. From the form of the data, injection

of low salinity brine did not appear to give any increase in recovery over that given by continued injection of seawater. The effluent brine pH remained close to neutral.

For R5/C5 (Figure 5b), the initial seawater saturation was 33.5% and could not be reduced by further oil flooding. The core was flooded sequentially with NaCl solutions of 35,000, 3,500 and 350 ppm. Oil recovery after flooding with 5 PV 35,000 ppm NaCl solution was 62.1%. This recovery was 12% OOIP higher at 5.6 PV injection than that of seawater flooding for R1/C1 but 13.2% OOIP lower at 5.4 PV injection of seawater given by R4/C4. Flooding with 5.4 PV 3,500 ppm NaCl caused an increase in ΔP and recovery rate. After 5 PV injection, recovery had increased to 67.9%. Flooding with 350 ppm NaCl solution gave an additional 10% OOIP recovery. Although the oil recovery by flooding with 35,000 ppm NaCl solution was initially much lower than that by injecting seawater (test R4/C4, Figure 5a), after injection of low concentration NaCl, the overall oil recovery for R5/C5 was similar to that for R4/C4 (see Figure 5b).

Each time the NaCl salinity was reduced, increase in oil recovery was accompanied by increased and sustained pressure drop. Examination by microscope of the produced oil showed that there were small water droplets in the produced oil, indicating the formation of a brine-in-oil emulsion. The effluent brine pH increased slowly from 6.5 to 9.3 (Figure 5b). Unlike the effect of NaCl flooding on Core 2065/1, there was no obvious catastrophic core damage, probably because of the lower volume throughput and the presence of crude oil. Before R6, the air permeability of the dry core was 510.08 md, as compared to 478.96 md prior to R1.

For comparative study of different crude oils, WP crude oil was selected for R6/C6. Because of the changes in core properties that result from low salinity flooding, the comparisons will have obvious limitations and uncertainties. Compared to LC crude oil, WP crude oil does not have detectable wax content at room conditions. The WP oil has higher viscosity at room temperature which is particularly advantageous with respect to obtaining low S_{wi} by displacement with crude oil.

The core was flooded first with seawater and then with 1,500 ppm dilute seawater. There was no significant response to low salinity injection. The effluent brine pH was close to neutral. ΔP across the core was less than 2 psi during the course of the seawater flooding and only increased slightly with injection of the 1,500 ppm brine (Figure 6a).

Prior to R7/C8, at least 30 PV of seawater was injected at 2 ml/min to restore the original salinity. Then WP crude oil was used to re-establish an S_w of 26.5%. After 10 days aging, the core was flooded with 4 PV seawater followed by 4 PV 1,500 ppm dilute seawater (see Figure 6b). The effluent brine pH stayed close to neutral. The pressure drop for R6/C7 was higher than for R6/C6 but the secondary oil recovery was only 28.8 % OOIP. Injection of 1,500 ppm brine caused gradual increase in pressure drop but there was very little additional oil recovery. Thus, after 6 restorations, Core 2060/4 gave low secondary recovery and did not respond to tertiary mode injection of dilute brine. Another example

of reservoir rock that responded well to initial changes in salinity but ceased to respond after repeated flooding cycles was reported previously (Tang and Morrow, 1999).

For R7/C8, flooding the core with seawater gave 56% OOIP recovery at 8.3 PV injection at a water/oil ratio of 150. After cessation of injection for 3 days, further injection of 7.2 PV seawater resulted in 12% OOIP additional in recovery (Figure 7a). The core was then flooded with WP oil to an initial water saturation of 39% for R7/C9. Injection of 4.5 PV seawater gave 80% OOIP (Figure 7b). Flooding the core with WP oil resulted in re-establishing 39% connate water in preparation for testing the possibility that spontaneous imbibition contributed to the additional oil production shown in Figure 7a. However, when the core was removed from the core holder, it was in two friable pieces. An imbibition test on one of the pieces showed no spontaneous displacement of oil over 2 weeks. These observations further demonstrate complex changes in core properties.

Core 2060/1

In total, three restorations and associated cycles were performed. The air permeability of the core was measured before each restoration. LC crude oil was used for R1 and WP crude oil for R2 and R3 (Table 4).

Two floods shown in Figure 8 were performed to assess the change of oil recovery by seawater flooding and after exposure to dilute brine. For R1/C1 (Figure 8a), oil recovery by seawater flooding was comparable with that of R1 for Core 2060/4. Tertiary mode oil recovery by injection of 0.1 seawater gave 13% OOIP extra oil. Further injection with 0.01 seawater gave a linear response with 4.3% OOIP additional oil recovery after injection of 4 PV. The ΔP was almost constant for seawater flooding. When the brine was changed to 0.1 seawater, the ΔP first increased suddenly from 2.4 to 27 psi, and then decreased continuously down to 12 psi during the course of 4.1 PV of 0.1 seawater flooding. The sudden increase in ΔP observed for this core was not observed for Core 2060/4. During the injection of 0.01 seawater, the ΔP stayed at about 12 psi. The effluent pH was neutral throughout the flood.

Prior to R1/C2, the core was flooded with 25 PV seawater at 2 ml/min to replace the low salinity 0.01 seawater in the core. No oil was produced and no clay production was observed during this process. When the core was flooded with LC crude oil to establish the initial water saturation for R1/C2, the retained initial water saturation was 56.9% even after 8 PV of oil flooding. Recovery efficiency by displacement with seawater was very high (84.8% OOIP, Figure 8b). The pressure drop across the core was much higher than for R1/C1 seawater flooding. The effluent brine pH was close to neutral. Although the secondary oil recovery in %OOIP by seawater flooding for R1/C2 was much higher than that for R1/C1, the actual volume of recovered oil in volume was about the same for both cycles (*cf.* Figs. 8a and 8b). Even though ΔP was large during flooding with low salinity brine in R1/C1, the air permeability measured before R2 was the same as that measured before R1.

The core was cleaned and then was saturated with seawater and left to equilibrate for 10 days. The brine permeability was 103 md, as compared 81 md after the first cleaning. A small amount of fines was observed in the effluent brine. The effluent brine pH was neutral throughout the flood.

For R2/C3, WP crude oil was used to establish an initial water saturation of 28% and then the core was re-aged. During 3.3 PV seawater flooding, the ΔP decreased gradually from 6 to 2 psi. The oil recovery was 55.5% OOIP and still increasing with a water/oil ratio of 20 (Figure 9a). After injection of 15 PV of 1,500 ppm dilute seawater, the water/oil ratio decreased and the oil production rate tripled during injection of the first PV of 1,500 ppm seawater. The recovery response, without corresponding increase in pressure drop, is unusual. After the onset of low salinity injection, 11% OOIP extra oil was recovered to give a total oil recovery of 66.5% OOIP (Figure 9a). The pH remained close to neutral throughout the flood.

Secondary recovery for R3/C4 by injecting 6.5 PV seawater was 62.9% OOIP (Figure 9b). Then the core was flooded with 8 PV of 1,500 ppm dilute seawater and the total oil recovery was 73.6% OOIP. Over 10% OOIP extra oil was recovered by dilute seawater flooding (Figure 9b). During secondary recovery, the ΔP across the core ranged from 1.4 to 3.8 psi. Dilute seawater flooding triggered an increase in ΔP of over 20 psi. The ΔP was accompanied by a 10.7 % OOIP increase in oil recovery. The pressure stayed high (~ 25 psi) before it suddenly decreased to about 3 psi, ΔP was accompanied by a small amount of gas production. The effluent pH remained close to neutral. Secondary oil recovery for R3/C4 was higher than for R2/C3 (Figure 9b), further indicating that rock properties after low salinity flooding could not be restored by cleaning and re-aging after low salinity flooding.

CONCLUSIONS

Low salinity flooding of poorly sorted and cemented reservoir sandstone cores that had abundant kaolinite gave large increases in oil recovery in both secondary and tertiary modes. The results provide further evidence of the potential for low salinity flooding as an improved oil recovery process, but also demonstrate the complexity of crude oil/brine/rock interactions that control oil recovery. Sequential waterfloods showed that low salinity flooding caused changes in core properties from one flood cycle to the next (initial water saturation re-established by oil flooding) and from one restoration (cleaning and re-aging with crude oil) to the next. After low salinity flooding, re-aged cores gave greatly increased recovery for injection of high salinity brine but no tertiary response to low salinity brine. A variety of behavior with respect to oil recovery, establishment of initial water saturations, and pressure drop was observed.

Because of the possible change in the characteristics of the core, the comparison of results from one cycle to another must be treated with caution. Ideally, comparative tests are needed on duplicate core plugs with closely similar properties. Closely reproducible

secondary and tertiary responses for duplicate outcrop cores have been reported (Zhang and Morrow, 2006). The current lack of suitable outcrop or availability of sufficient homogeneous reservoir core presents a serious obstacle to systematic investigation of the effect of injection brine salinity on oil recovery. The results support the general observation for high salinity connate water (Zhang and Morrow, 2006) that reservoir cores show greater response to flooding with low salinity water than the outcrop rocks studied to date.

ACKNOWLEDGEMENTS

This work was supported by BP, Total, Shell, Statoil, and the Enhanced Oil Recovery Institute of the University of Wyoming.

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Table 1. Reservoir core samples

Core No.	Depth	L, cm	D, cm	ϕ , %	Original k_g , md	BET surface area, m ² /g	Cation exchange capacity, meq/g
2060/1	2060	7.859	3.914	27.4	394.6	-	-
2060/4	2065.04	7.15	3.885	26	479	-	-
2065/1	2065.04	7.429	3.919	27.6	461.7	1.48 ± 0.02	0.0144
2065/3B	2065.22	6.137	3.883	20.0	885.7	-	-

Table 2. Crude oil properties

Crude oil	C ₆ asphaltenes, wt%	Acid #, mg KOH/g oil	Base #, mg KOH/g oil	ρ at 22°C, g/ml	μ_o at 22°C, cp	μ_o at 60°C, cp
LC	3.2	0.16	1.82	0.9023	56	18
WP	6.3	1.46	2.49	0.9125	111.2	20.1

Table 3. Synthetic seawater composition

composition	NaCl	KCl	CaCl ₂	MgCl ₂	Total dissolved solids (TDS)	μ_w at 60°C, cp
Concentration, g/L	28.0	0.935	1.19	5.368	35.493	0.6

Table 4. Initial water saturation, test fluids and final oil recovery for each test

Restoration/Cycle #	Crude oil	S_{wi}	Brine injected	R_p , %OOIP
Core 2065/1				
R/C1	LC	0.330	seawater 0.1 seawater	57.7 65.3
Core 2065/3B				
R1/C1	WP	0.105	seawater	64.5
R1/C2		0.112		69.1
Core 2060/4				
R1/C1	LC	0.216	seawater	50.9
R2/C2		0.287	0.1 seawater	66.7
R3/C3		0.252	0.01 seawater	80.6
R4/C4		0.287	Seawater 0.1 seawater 0.01 seawater	75.3 78.0 79.3
		0.335	NaCl solutions 35,000 ppm 3,500 ppm 350 ppm	62.9 69.3 80.0
R6/C6	WP	0.265	seawater dilute seawater (1,500 ppm)	58.1 59.4
R6/C7			seawater dilute seawater (1,500 ppm)	28.8 30.0
R7/C8		0.24	seawater	68.5
R7/C9		0.39		80.3
Core 2060/1				
R1/C1	LC	0.331	Seawater 0.1 seawater 0.01 seawater	54.0 66.9 71.2
R1/C2			0.569	seawater
R2/C3	WP	0.280	seawater dilute seawater (1500 ppm)	55.5 66.5
R3/C4		0.246	seawater dilute seawater (1500 ppm)	62.9 73.6

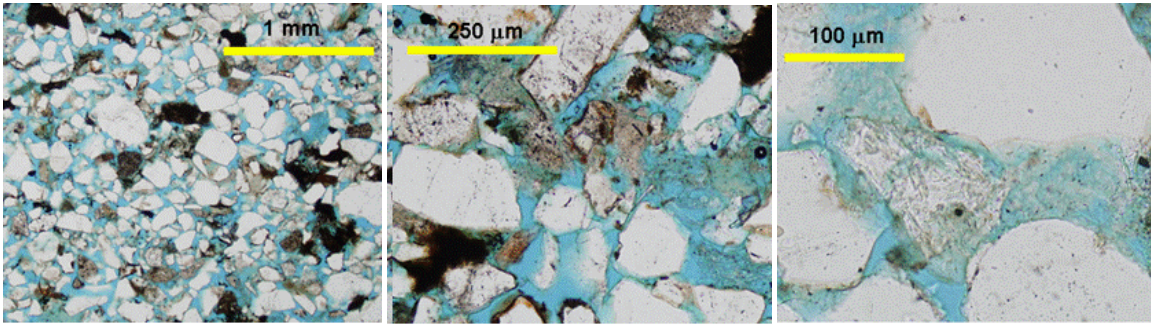
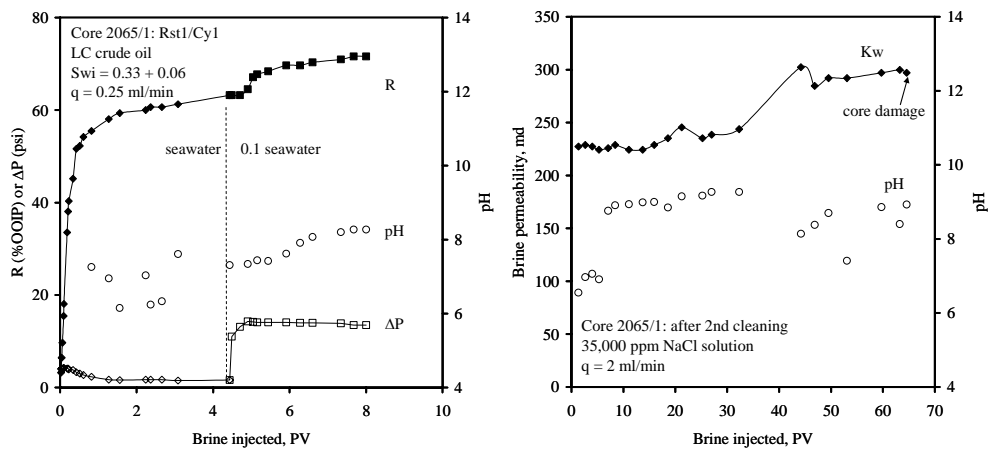


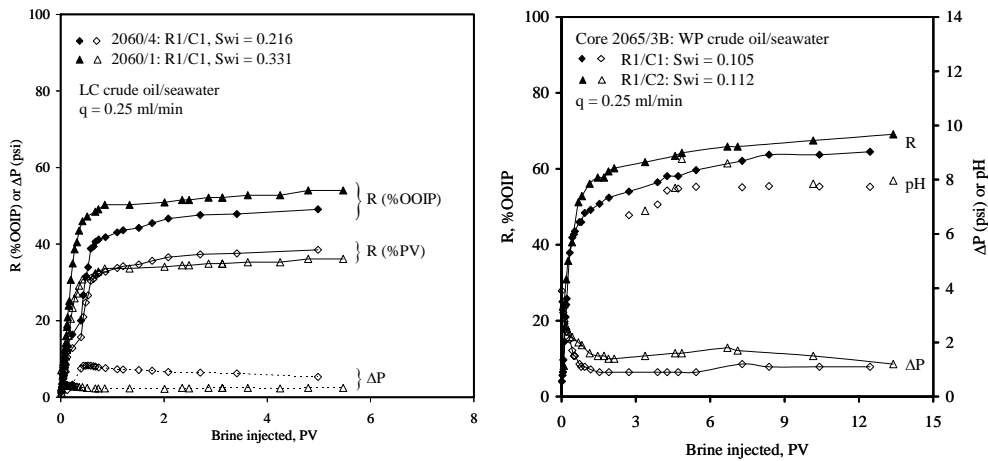
Figure 1. Thin section at various magnifications.



(a) Waterflood recovery after imbibition.

(b) Brine permeability

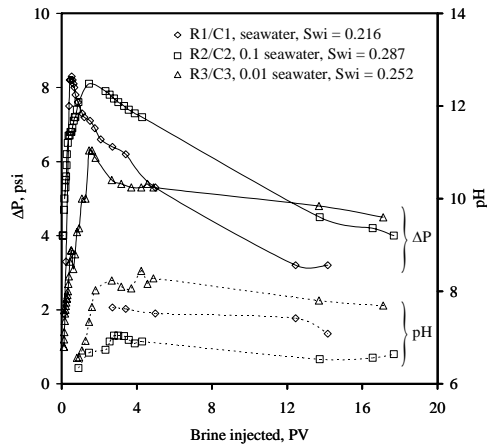
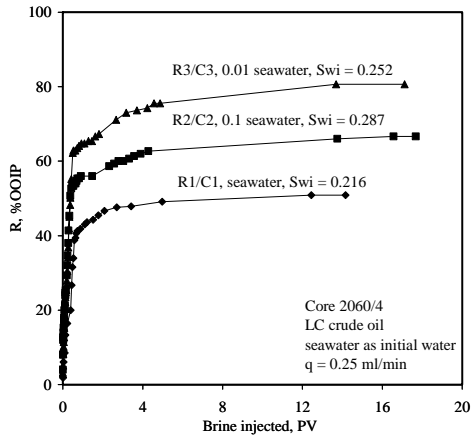
Figure 2. Waterflood recovery and water permeability to brine for core 2065/1.



(a) Cores 2060/4 and 2060/1.

(b) Core 2065/3B.

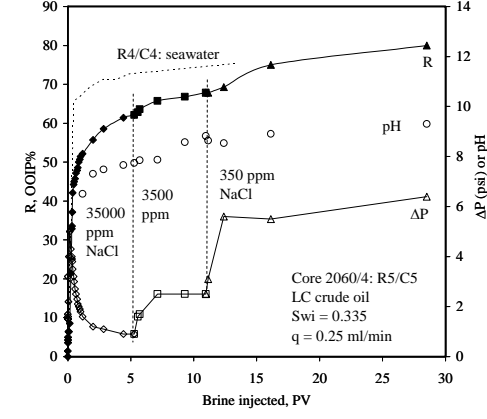
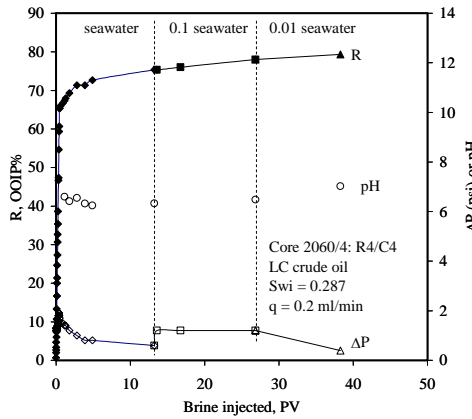
Figure 3. Secondary recovery by injection of seawater.



(a) Secondary recovery.

(b) Pressure and pH

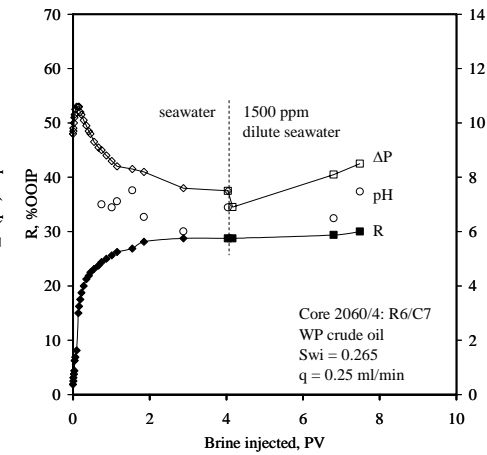
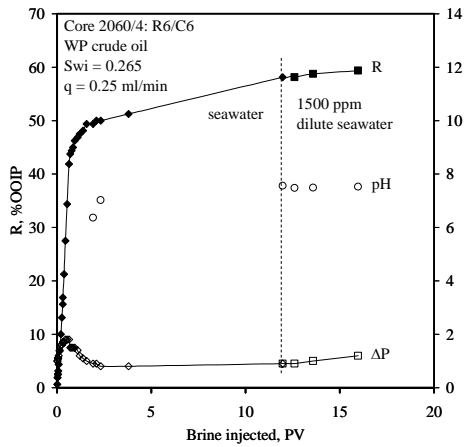
Figure 4. Effect of injection brine salinity on secondary recovery for core 2060/4.



(a) Flood with seawater and dilutions.

(b) Flood with NaCl solution.

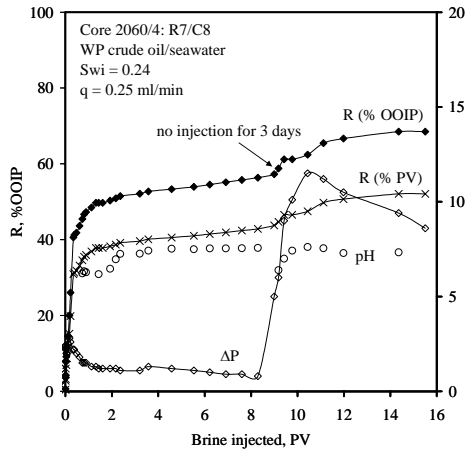
Figure 5. Response to sequential reduction in salinity for Core 2060/4.



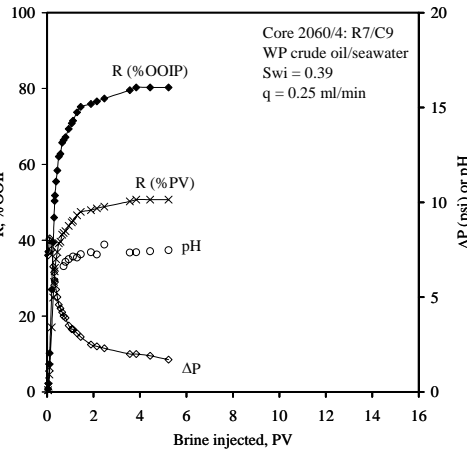
(a) Insensitivity to tertiary mode recovery.

(b) Decrease in secondary mode recovery.

Figure 6. Consecutive cycles after 6 restorations for Core 2060/4.

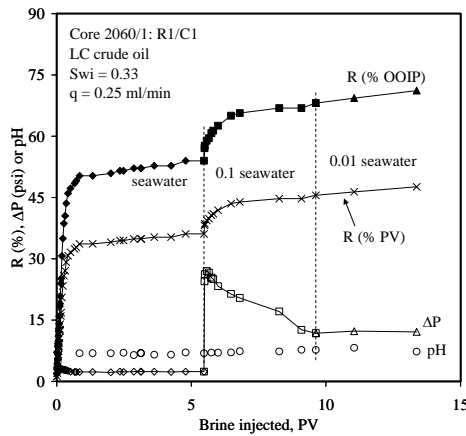


(a) Seawater injection for R7/C8.

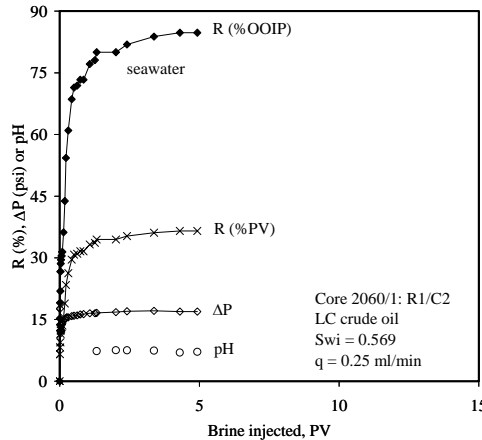


(b) Sea water injection for R7/C9.

Figure 7. Oil recovery by injection seawater after the 7th restoration (core became fractured and highly friable).

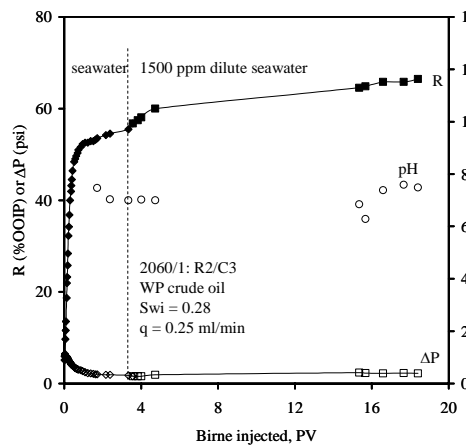


(a) Tertiary mode low salinity flooding.

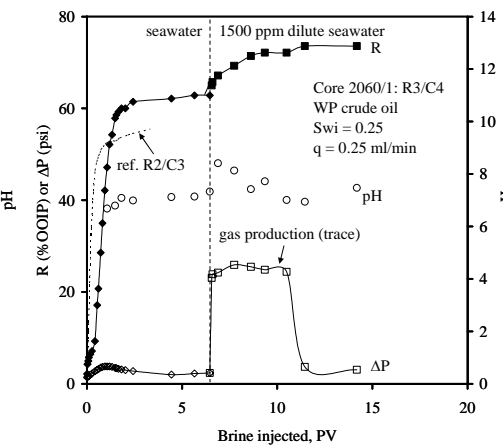


(b) After low salinity flooding

Figure 8. Response to sequential reduction in salinity.



(a) R response with no increase in ΔP (unusual).



(b) Sustained pressure drop during tertiary recovery

Figure 9. Differences in response to tertiary mode low salinity brine flooding.