Journal of Petroleum
Science and Technology

CORE FLOOD STUDIES TO EVALUATE EFFICIENCY OF OIL RECOVERY BY LOW SALINITY WATER FLOODING AS A SECONDARY RECOVERY PROCESS

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ABSTRACT

Various researches on laboratory and field scale illustrate that manipulating the ionic composition and the ion concentration of injected water can affect the efficiency of water flooding and the interaction of injected water with rock and other fluids present in porous media. The objectives of this paper are to investigate parameters that affect low salinity water flooding; mainly the effect of injecting water salinity on and the potential of low salinity water flooding for oil recovery in secondary recovery mode are studied. The effect of pH and differential pressure across the core are used to explain the mechanism of fine migration phenomena. The recovery results of formation water injection were compared for the seawater, formation water with a salinity of 0.1 and 0.01, and when divalent ions were removed from the formation water with a salinity of 0.01 to investigate the effect of divalent ions on oil recovery. Different types of crude oil were used for investigating the effect crude oil properties on oil recovery. Seawater injection resulted in lowest oil recovery of 2.6% and the reduction of water salinity of formation water from 0.1 to 0.01 resulted in an improvement of 4% and 7.7% in oil recovery respectively. Removing divalent ions from the injected water decreased the improving effect of low salinity water flooding. In addition, both types of crude oil responded to low salinity flooding and no straight correlation was seen between acid number and the improving effect of low salinity water flooding.

Keywords: Low Salinity, Water Flooding, Core Flood, Oil Recovery, Secondary Recovery

INTRODUCTION

By now, water flooding has widely been applied in the world to improve oil recovery. It has been observed that the injection of dilute brine can increase oil recovery as compared to high salinity water injection. The study of variables that affect displacement mechanisms has been the subject of research interest for several decades. Among the many identified factors that affect oil recovery by water flooding, the composition of injecting water has been shown to the most important factor because it is the only parameter that can be manipulated [1,2].

The connate water composition has a predominant effect on the fluid distribution in porous media and determines wettability states induced by the adsorption from crude oil [3-5]. When the connate water has relatively high

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Article history
Received: January 09, 2013
Received in revised form: July 21, 2013
Accepted: August 17, 2013
Available online: March 10, 2014

salinity, the injection of dilute brine gave economically significant increase in oil recovery, which may be because of mixing with connate water and the creation of a favorable condition for oil production.

Crude oil type and rock type (particularly the presence and distribution of clays) both play an important role in the effect that brine chemistry has on waterflood oil recovery. The crude oil/ brine/rock interactions that determine displacement efficiency are highly complex [6,7].

Numerous hypotheses have been devised to explain the increase in oil production associated with low salinity water injection, including increasing pH leading to in situ saponification and interfacial tension reduction, emulsion formation, clay migration, and wettability alteration [8,9].

A solution with lower salinity affects the dispersion of clay and silt in the formation. The clay and silt, upon dispersion, become mobile and follow the paths taken by the greatest proportion of the flowing water. These paths are the domains of high permeability, and the mobile clay and silt become lodged in the smaller pore spaces of these domains and reduce the flow of water through these pore spaces. The permeability of the domains where clay and silt are lodged is accordingly reduced, and the water is forced to take other flow paths. As a result, the permeabilities in these domains within the formation become more uniform. A reduction in permeability in the more permeable domains improves the mobility ratio of waterflood. Premature breakthrough is thus reduced, and the efficiency of the waterflood is improved [10].

A pH increase is associated with dilute brine injection in numerous laboratory tests. The pH increase could be explained by carbonate dissolution and cation exchanges [11]. During the dissolution of carbonate, an excess of OH^- gives increased pH. Cation exchange occurs between clay minerals and the invading low salinity brine. An exchange of H^+ in the liquid phase with cations previously adsorbed at the mineral surface leads to a decrease of H^+ concentration inside the liquid phase. This could also result in a pH increase.

Multi ion exchange is another mechanism that explains how low salinity water flooding influences the oil recovery. Multi-component ion exchange (MIE) takes place between adsorbed crude oil components, the clay mineral surface, and the cations in the brine, when low salinity brine, which contains low concentrations of Mg^{2+} and Ca^{2+}, are injected. Divalent cations from the injected brine exchange with either cationic organic complexes or with bases, due to the change in ionic equilibrium. The clay surface becomes more water-wet as a result of the removal of polar organic compounds and organo-metallic complexes from the clay surface. This also increases the oil recovery.

In 2009, Ligthelm et al. proposed the LS mechanism to be the expansion of the electrical double layers that surround the clay and oil particles and increase in the level of zeta potential [6]. It was suggested that a decrease in the ionic strength by lowering the salinity in the brine would increase the electrostatic repulsion between the clay particles and the oil. Once the repulsive forces exceed the binding forces via the multivalent cation bridges, the oil particles may be adsorbed from the clay surface, which leads to a change in wetting phase towards increased water wetness. If the electrolyte concentration is further reduced, the electrostatic forces within the clay minerals starts to exceed binding forces, which may lead to formation damage.

In this study, in addition to oil recovery data, the pH of aqueous solution flowing out from cores during core flood experiments was studied to determine the capability of ion exchange between rock and the injected water.

EXPERIMENTAL

Materials

Core Material: in this study, five reservoir core samples with designations of A1 to A5 were used. Core samples were obtained from the sandstone section of an oil reservoir in Iran. The porosity and permeability of cores were measured using coreflood apparatus and high salinity formation brine, Tables 1 and 2 show the mineralogy and rock properties of core plugs respectively. The porosity and permeability ranges were 14-19 Vol.% and 4-27 mD respecttively. As it can be seen in Table 2, the core plugs A1 and A5 have different porosity and permeability with respect to the other plugs. In this study, the reservoir cores were used and the goal was to obtain the maximum number of plugs. These two cores were obtained in different directions with respect to the other plugs and therefore had different properties. The main concern was that all the cores had the same mineralogy to enable the comparison of results.

Table 1: Mineralogy of sandstone cores (wt.%)

Quartz	Albite	Calcite	Dolomite	Kaolinite	Muscovite
67	21	4	2	4	2

Fluids: all the brines were prepared in the laboratory by resolving reagent grade salts in deionized water. Table 3 tabulates the composition of formation brine and sea water. Low salinity water was made by diluting the formation water to salinity of 0.1 and 0.01. In one experiment, divalent ions were removed from the injected water to investigate the effect of divalent ions on oil recovery.

Table 3: Composition of formation water and sea water

Components	Formation Water (mg/l)	Sea Water (mg/l)
Na^+ and K^+	63204	12763
Ca^{2+}	13600	382
Mg^{2+}	2673	1424
Cl^-	127436	22120
SO_4^{2-}	500	3118
TDS (ppm)	207413	39807

Crude oil: two types of crude oils were used for saturating the cores, *crude A* and *crude B*. Filtered stock tank crude oils were used for aging the core samples. Table 4 lists some properties of the oil at room temperature. The acid number of crude oil was measured in the laboratory according to modified ASTM D664 method.

Table 4: Properties of crude oils

Oil Sample	Density (g/cm^3)	Viscosity (cp)	AN/BN (mg KOH/g oil)
Crude A	0.8549	3.15	0.842/0.21
Crude B	0.9203	4.27	1.683/0.42

Table 2: Rock properties of core plugs

Core ID	Length (m)	Diameter (m)	Porosity (%)	Permeability (mD)	S_{wi} (%)	Aging Time (Day)
A1	0.05	0.0379	15.63	4.35	30.71	20
A2	0.0484	0.038	14.62	20.98	29.1	20
A3	0.049	0.038	14.91	27.11	31.4	20
A4	0.0491	0.038	16.8	23.70	31.2	20
A5	0.049	0.038	19.41	3.94	32.1	20

Core Preparation

Core cleaning: the cores were cleaned by Soxhlet extraction using toluene and methanol, and then dried at 100 °C. After drying, the core dimensions, weight, and permeability were measured.

Brine saturation: the core samples were saturated with formation water. After saturation was achieved, base permeability was then measured at three different flow rates and allowed 15 days at 50 °C for ionic equilibrium to be established between the rock and the formation water. Weight method was applied to measure porosity.

Establishment S_{wi}: the initial water saturation (S_{wi}) was established by the injection of dead crude oil into the cores until the irreducible water saturation was reached and no more water was produced from the examined core. The direction of flow was reversed after 2 pore volumes (PV) injection of crude oil to give uniform saturation distribution along the core.

Aging: after establishing S_{wi} by displacement with crude oil, the cores were removed from the core holder and aged in crude oil in sealed Pyrex jars. The cells were sealed and held at 90 °C for 20 days.

Restoration of core: after flooding the core with different brines, in the cases where restoration was needed, the core was restored to its initial state by cleaning the core. The restoration was performed after first flooding experiment by formation water for each core plug. After restoration the core plugs to initial state, they were ready for low salinity water flooding experiments. The restoration was done by the same procedure as described before.

Waterflood Tests

A coreholder apparatus was used in the flooding experiments. The core was placed in the coreholder with a confining pressure of 140 bar according to axial stress of the depth that core prepared. Identical flooding conditions i.e. a temperature of 50 °C, gravity stable displacement, and a nominal flooding rate of 2 PV/day were used in all the floods. Furthermore, a backpressure of 5 bars was applied to avoid the formation of gas by light ends in the crude oil. The pressure drop across the core was carefully monitored in all the experiments. Two floods were performed on each core. The first flood was a continuous injection of formation water (high salinity brine) to remaining oil saturation, while the second flood was a low salinity water injection. Remaining oil saturation after water flooding was considered to be obtained when water cut values were high and stable over time. The produced oil was collected using a fractional collector and the oil recovery was determined as the percentage of original oil in place (percentage of OOIP). The effluent samples were collected regularly and pH was measured and recorded. Table 5 shows the experimental layout of core displacement experiments. Figure 1 shows the schematic of core flooding set up for the experiments.

Table 5: Experimental layout of core displacement experiments at 50 °C

Test	Core ID	1st flood	Recovery (% OOIP)	L.S.W. flood	Recovery (% OOIP)	Crude type
Test 1	A4	FW	48.2	SW	50.8	B
Test 2	A3	FW	50	0.1 FW	54	B
Test 3	A2	FW	49	0.01 FW	56.7	B
Test 4	A1	FW	51.5	0.01 FW (only monovalent ions)	57.5	B
Test 5	A5	FW	49	0.01 FW	56	A

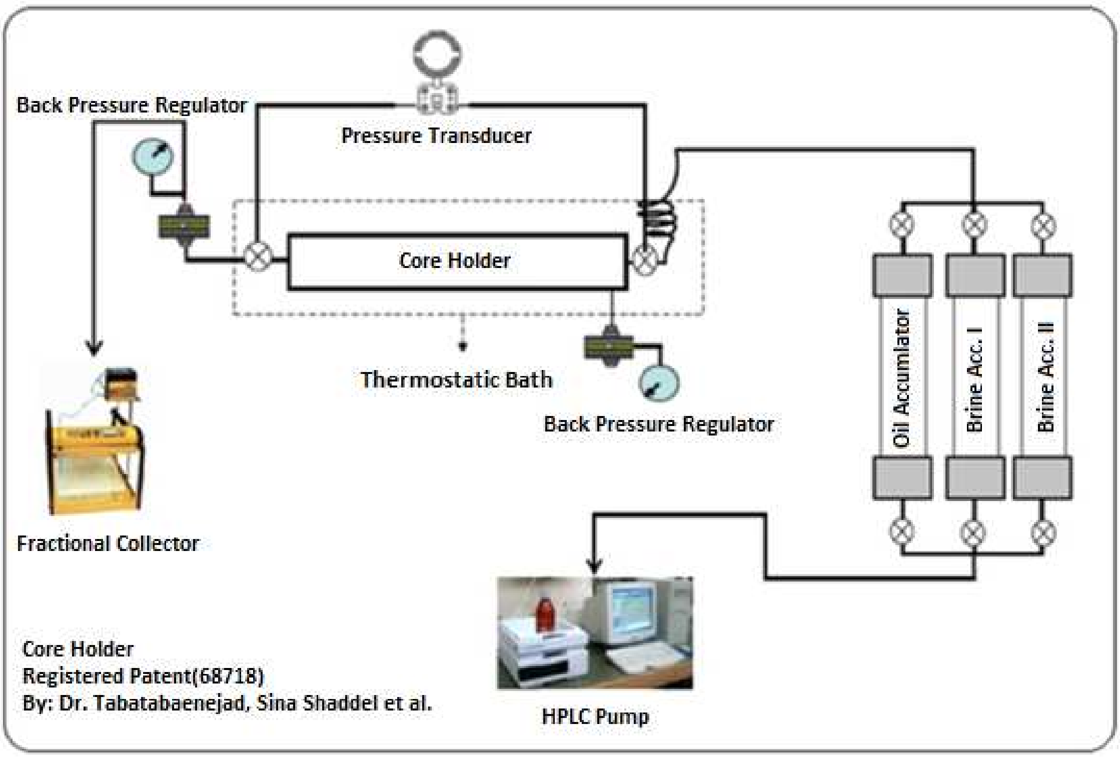

Figure 1: A schematic of core-flood set up

Low salinity waterflood by seawater: in this experiment, seawater was used for flooding in core A4 to compare oil recovery values with those obtained from formation brine injection in secondary recovery mode. Formation water injection resulted in 48.2% oil recovery of original oil in place (OOIP) and seawater injection produced 50.8% oil recovery of original oil in place. The pH of effluent water was in the range of 6.25 to 6.51 and 6.29 to 6.62 for formation water and sea water injections respectively. Figure 2 shows the oil recovery profiles, variation of differential pressures, and the pH of effluent water with respect to the pore volume injected.

Low salinity waterflood by 0.1 formation water: the injection of formation water into core A3 resulted in 50% oil recovery of original oil in place (OOIP) and the pH of effluent water in formation water injection was in the range of 6.58 to 6.84. Then, after restoration, water with salinity of 0.1 formation water resulted in 54% oil recovery of original oil in place and the pH of effluent water was between 6.48 and 6.7. Oil recovery, pressure drop, and the pH of effluent water are shown in Figure 3.

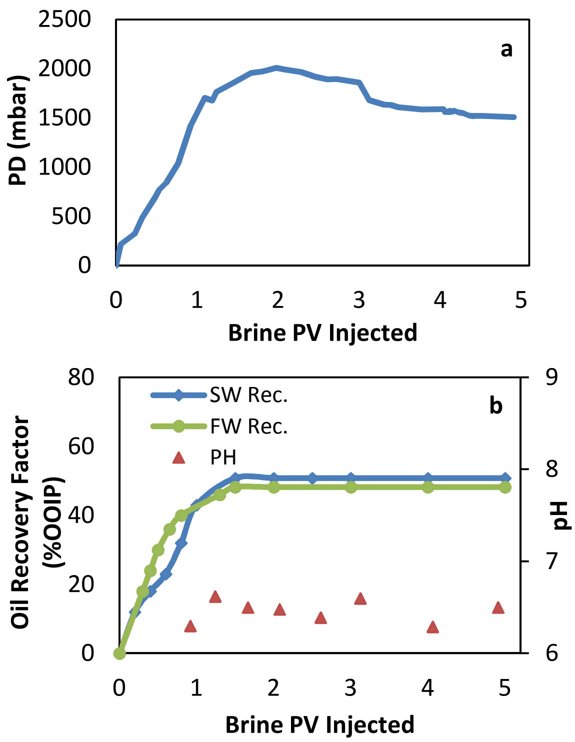

Figure 2: Oil recovery, pressure drop, and pH evolution during secondary recovery experiment on A4

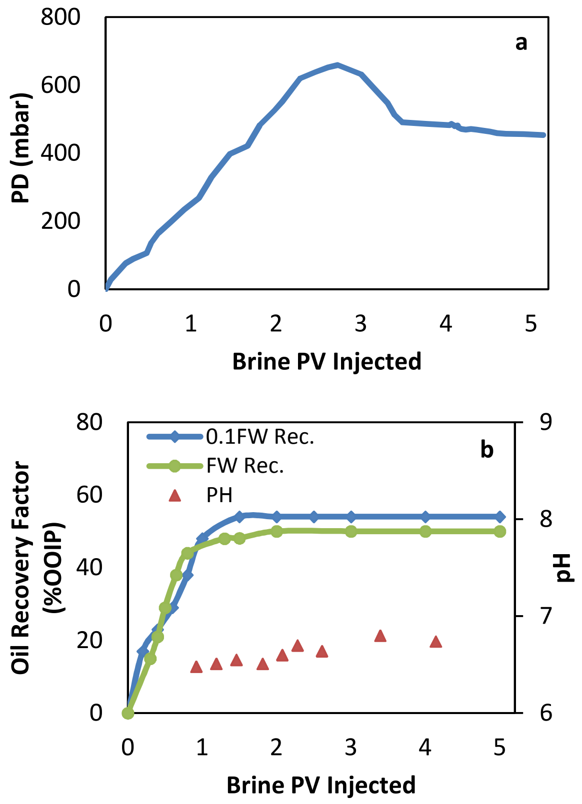

Figure 3: Oil recovery, pressure drop, and the pH evolution during secondary recovery experiment on A3

Low salinity waterflood by 0.01 formation water: formation water injection into core A2 resulted in 49% oil recovery of original oil in place (OOIP) and the pH of effluent water in formation water injection was in the range of 6.32 to 6.61. For investigating the effect of low salinity flooding and reaching optimum injection water salinity, the formation water was diluted to salinity of 0.01 formation water, which resulted in 56.7% oil recovery of original oil in place and the pH of effluent water was in the range of 6.53 to 6.95. Figure 4 shows oil recovery, pressure drop, and the pH of effluent water through the core versus the injected pore volume.

Low salinity waterflood by 0.01 formation water with only monovalent ions: core A1 was flooded with a formation water and the recovery factor was 51.5% recovery of original oil in place (OOIP); the injection of water with salinity of 0.01 formation water which contains only monovalent ions (Na, K, and Cl without Ca and Mg ions) resulted in an oil recovery factor of 57.5%. The effluent water pH for formation water injection was between 6.2 and 6.71 and in further flooding between 5.9 and 6.92. Figure 5 shows the oil recovery profiles, the variation of differential pressures, and the pH of effluent water with respect to the pore volume injected.

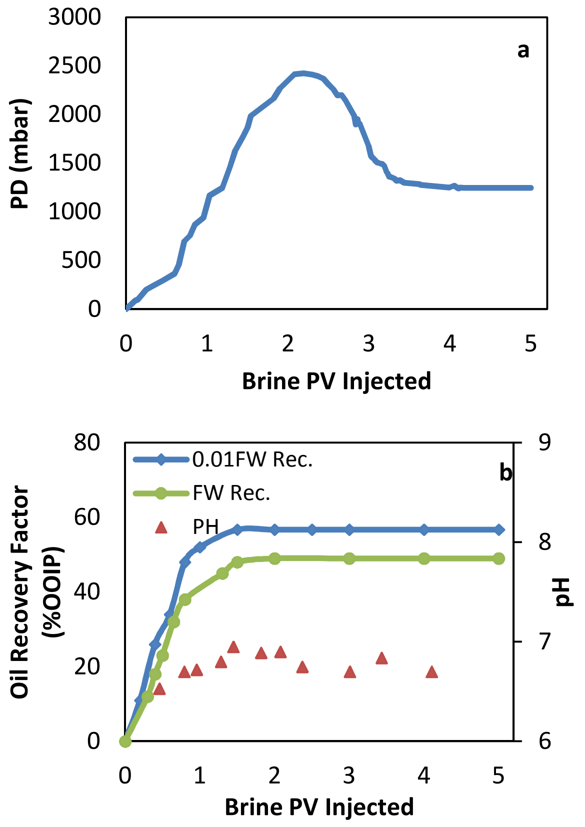

Figure 4: Oil recovery, pressure drop, and the pH evolution during secondary recovery experiment on A2

Low salinity waterflood by 0.01 formation water and crude type A: the core A5 was saturated with crude type A to investigate the effect of the type of crude oil on oil recovery; the other conditions were identical to the other experiments except the type of crude oil. The experiment with crude A resulted in 51.5% oil recovery of original oil in place (OOIP) and the injection of low salinity water with salinity of 0.01 formation water lead to an oil recovery of 56%.

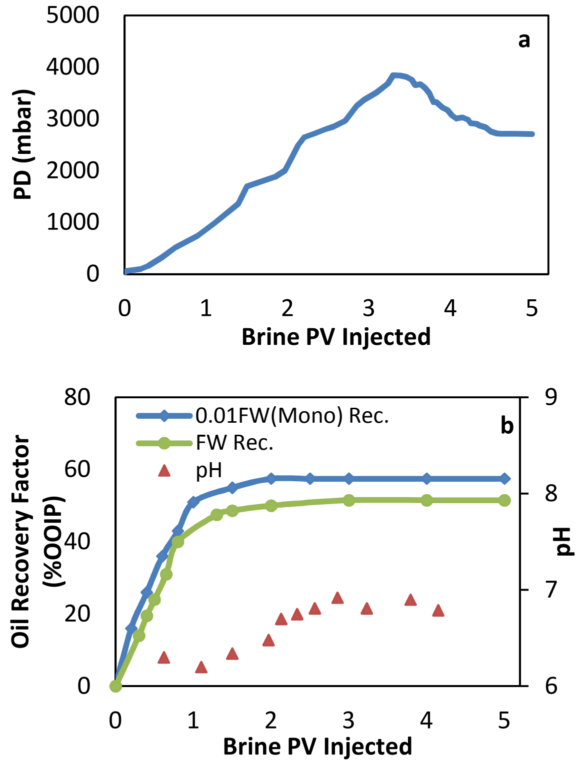

Figure 5: Oil recovery, pressure drop, and pH evolution during secondary recovery experiment on A1

The pH of effluent water for formation water injection and the injection of water with salinity of 0.01 formation water was in the range of 6.8 to 7.22 and 6.2 to 7.03 respectively. Figure 6 shows oil recovery, pressure drop, and the pH of effluent water through the core versus the injected pore volume.

RESULTS AND DISCUSSION

In this section, the obtained results are analyzed. The main purpose of study was the examination of the ability of low salinity water in improving oil recovery in Iranian sandstone in secondary recovery mode. Herein, the results of flooding 5 sandstone cores were compared with formation water injection into them to investigate the effect of low salinity water flooding on oil recovery in secondary recovery mode. The selected cores were well sorted and mainly composed of quartz, albite, and trace amounts of calcite and dolomite; the cores had some amounts of clays which were mainly kaolinite and muscovite. For decreasing the water wetness of cores, an aging period of 20 days at a temperature of 90 °C was chosen.

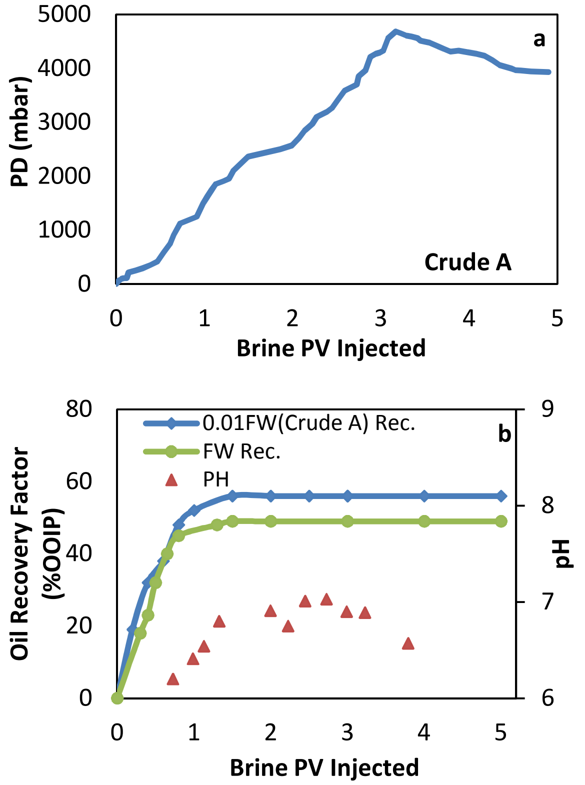

Figure 6: Oil recovery, pressure drop, and pH evolution during secondary recovery experiment on A5

The recovery data by formation water injection for these cores were obtained from another set of experiments. Herein, the results of low salinity flooding of cores in secondary mode are presented and compared with formation water injection data. Because the cores were used once for low salinity flooding in tertiary mode, we believe that interpretation and comparisons between cores must be treated with caution in the case of sequential flooding on individual cores. Interactions between rock/oil/brine may result in identifiable changes in response from one flood to the next. Numerous hypotheses have been devised to explain the increase in oil production associated with low salinity water injection; however, the investigation of the mechanisms by which recovery is increased presents a considerable challenge because they depend on complex crude oil/brine/rock interactions. These cores had low clay content about 6% and limited fine migration was observed in sampling tubes; therefore, we think that this improving effect in oil recovery is a result of multi-component ion exchange between the injected low salinity brine and rock surface, which causes a reduction in ion binding between the crude oil and the rock surface to be the main reason for increasing oil recovery by low salinity water. Multivalent cations at clay surfaces are bonded to polar compounds present in the oil phase (resin and asphaltene) forming organo-metallic complexes and promoting oil-wetness on rock surfaces.

Meanwhile, some organic polar compounds are directly adsorbed onto the mineral surface, displacing the most labile cations present at the clay surface and enhancing the oil-wetness of the clay surface. During the injection of low-salinity brine, MIE takes place, which removes organic polar compounds and organo-metallic complexes from the surface and replaces them with uncomplexed cations [9].

It is generally accepted that the adsorption of polar compounds onto rock surface has a significant effect on the wettability of reservoirs [11-19]. To establish a wide range of the initial wetting conditions, two types of crude oils with different concentrations of polar components, AN and BN, were used. The variation of aging time of a core in crude oil is a viable parameter for obtaining systematic changes in wettability. In this study, two types of crude oils with different concentrations of polar components, AN and BN, were used, namely oil A with AN and BN of 0.842 (mg of KOH/g) and 0.21 (mg of KOH/g) respectively and oil B with AN and BN of 1.683 and 0.42 (mg of KOH/g).

The crude oil designated A has a lower acid number and is used for the investigation of the effect of crude oil on low salinity water flooding. The difference between recoveries of the two types of crude oil can be because of lower acid number of crude A; however, other effective parameters must be surveyed and our hypothesis is not complete because the drastic mechanism is a consequence of many parameters and the interaction of rock/oil/brine which is complex

The instantaneous permeability versus the pore volume of injecting water is shown in Figure 7. The investigation of this graph could help the explanation of probable fine migration phenomena. Reducing the injecting water salinity may cause fine movement in porous media. The reduction of permeability in each step is an indication of fine migration and blockage of pore throats.

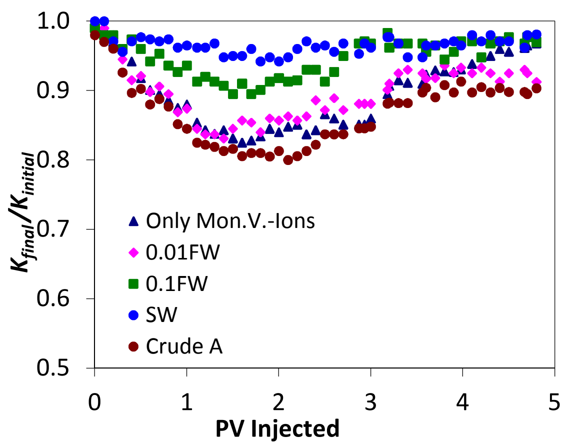

Figure 7: Variation of instantaneous permeability vs. the pore volume injected

The task to take into account the output of the low salinity water IOR-effect is not straight forward as the influence of end-effect may induce some degrees of uncertainty in the measurements of additional oil recovery. The measurement of small droplets of oil at the end steps of oil production from core would cause some uncertainty, since for accurate measurement, several reference tubes with known volumes of oil and formation water were used. The tolerance in measuring the effluent pH and differential pressure was ±0.05 unit and ±0.001

mbar respectively.

CONCLUSIONS

1- Not all levels of low salinity can increase the oil recovery in sandstone reservoirs. An optimum salinity level should not be exceeded to recover more oil. The chem.-istry of the injection water is very important and it shows a significant impact on oil recovery.
2- The extent of the increase in oil recovery by low salinity waterflood is highly specific to crude oil-brine-rock (COBR) interactions and cannot be predicted.
3- The low salinity water shows the potential for improving oil recovery in secondary mode for these sandstone cores.
4- The increase in effluent water pH was not high and the maximum increase in pH was in the case of using crude type A and equal to 1 unit.
5- The maximum improving effect of using low salinity water was in the case of using crude type B and the injection of 0.01 formation water, which improved the secondary recovery by an additional oil recovery of 7.7% of original oil in place (OOIP).
6- Gains of recovery were mainly occurred in the first three pore volumes and were not accompanied by a significant pH increase; however, pressure drop increased. The increase could also occur without additional oil production.
7- In conclusion, increasing pH or fine material migration were not seen during our study but we conjecture that cation exchange between the mineral surface and the invading brine is the primary mechanism underlying the improved waterflood recov-ery observed with low salinity water flooding.

NOMENCLATURE

AN	Acid number
BN	Base number
DP	Differential pressure
FW	Formation water
ID	Identification
L.S.W.	Low salinity water
mD	Millidarcy
MIE	Multi-component Ion Exchange
OOIP	Original oil in place
PD	Pressure drop
PV	Pore volume
S_{wi}	Initial water saturation
SW	Sea water
TDS	Total dissolved solid

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