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Amin Ahmadi
 Department of Petroleum
 Engineering, Mahshahr Branch,
 Islamic Azad University,
 Mahshahr, Iran

Mirhasan Moosavi
 Department of Petroleum
 Engineering, Masjed Soleiman
 Branch, Islamic Azad
 University, Masjed Soleiman,
 Iran

Potential evaluation of low salinity water flooding for improved oil recovery in carbonate reservoirs

Amin Ahmadi and Mirhasan Moosavi

Abstract

Flooding by low salinity water is a promising technology for improving oil recovery (IOR). However, this method is an efficient method for many sandstone reservoirs, the potential for low salt water injection in carbonate reservoirs is still not well established. Therefore, the purpose of this study is to investigate the improvement of oil recovery by low water salting in carbonate reservoirs by water injection in existing cores. Totally four flooding tests were conducted on three limestone cores (A, B, C) and one chalk core (D), to evaluate the low salinity effect due to presence of anhydrite and different temperature. The concentration of SO_4^{2-} is one of the key factors determining the wetting properties. It is stated that different parameters such as salinity and composition of initial formation brine are able to affect dissolution of CaSO_4 . Observing traces of SO_4^{2-} during core cleaning in effluent of all limestone cores, indicate that the increased oil recovery with low salinity brine could be result of dissolution of anhydrite. Thus, in both cores A and B, the enhanced recovery about 4%, by switching the brine from FW to Diluted FW is due to low salinity and temperature effect on dissolution of anhydrite. The dissolution of anhydrite normally increases as the temperature decreases. We observed also an increased recovery for core C, when switching from SW to diluted SW, even the core was saturated and aged with a crude oil with $\text{AN}=0.08$. The core with low acid number tends to be more water-wet and it has a lower potential of increased recovery. Lowering the salinity of injection brine increases the reactivity of the surface's active ions SO_4^{2-} and Ca^{2+} . The dissolution of anhydrite takes place in the injection front. SO_4^{2-} , which is the catalyst for wettability alteration process are always present in the injection front in a viscous flooding process. A tertiary low salinity flooding was not to change the wetting condition of the cleaned chalk that did not contain any anhydrite. Thus, the recovery did not change. We should note that the low salinity effect is only be observed in the carbonate rock containing a mineral that can release sulfate ions.

Keywords: Improved Oil Recovery, Low salinity water flood, Wettability Alteration, carbonate reservoir.

Introduction

Oil production enhancement by low-salinity water flooding in carbonate formations has been the subject of intense speculation. Several mechanisms are attributed to enhanced oil recovery by low-salinity water flooding in carbonate formations. The main mechanism revolves around wettability alteration by interaction of Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and RCOO^- carboxylic group in the electrical double layer (EDL) near the surface of carbonate pores. In carbonate formations, the carbonate rock surface attains a positive charge in presence of formation brine. The positive charge results from carbonate dissolution in brine, which also increases the solution pH (Navratil 2012) [6]. In presence of oil, the brine-soluble acidic components of the oil (carboxylate ions, R-COO^-) are attracted to the positively charged carbonate rock surface. Some of these acidic oil molecules attach to the positively charged carbonate surface, which makes the surface oil-wet. This is why restoring core wettability is critical factor in any IOR/EOR experiments. In presence of brine, the positively charged carbonate surface is amenable to *anion exchange*, which might be the reason for wettability alteration by the seawater in seawater flooding. In the latter, the sulfate, calcium and magnesium ions (SO_4^{2-} , Ca^{2+} , Mg^{2+}) compete with the carboxylate (R-COO^-) ions (Austad *et al.*, 2012) [7-8] to *partially alter* the rock wettability from oil wet to water wet. Wettability alteration is a complex issue which, in addition to the brine ionic composition, also depends on reservoir temperature. Austad *et al.* (2006) [4] conducted experiments using cores from Ekofisk, Valhall, and Yates fields to improve spontaneous imbibition of water into oil-saturated samples. They observed that the presence of SO_4^{2-} improved the spontaneous imbibition regardless of the

Correspondence
Amin Ahmadi
 Department of Petroleum
 Engineering, Mahshahr Branch,
 Islamic Azad University,
 Mahshahr, Iran

wetting conditions. Furthermore, studies on low-salinity water flooding in carbonate reservoirs, with reduced Na^+ , indicate that Ca^{2+} , Mg^{2+} , and SO_4^{2-} play a major role in the wettability alteration (Fathi *et al.*, 2012, Austad *et al.*, 2012, Awolayo *et al.*, 2014) [8, 7, 9]. Gupta *et al.*, 2001 reported an increase in oil recovery through experiments involving carbonate cores using Advanced Ion Management (AIMSM), where it adds/removes different ions from the injected water. Al-Harrasi *et al.*, 2012 [10] conducted low-salinity water flood experiments on different carbonate cores. In their study, carbonate cores were used for both core flooding and spontaneous imbibition experiments at 70°C. Synthetic brine was mixed with distilled water in four ways (diluted twice, 5 times, 10 times, and 100 times). From these experiments, it was reported an increase of 16-21% in oil recovery. Study by Zekri *et al.*, 2012 [11] reported contact angle change with time with low-salinity brine, both on limestone and sandstone cores from Libyan oil reservoirs. Several brine injection concentrations were used in the experiment to examine the effect of salinity in oil recovery by varying sulfate concentrations. The study concluded that wettability alteration is the main mechanism to increase recovery in carbonate formations by low-salinity water flooding. Zahid *et al.*, 2012 [12-13] experimental results show improved oil recovery during low-salinity water flood in carbonate reservoirs. Their experiments were conducted with live oil both at ambient and high temperatures (90°C). It was also observed no effect of low salinity water flooding on oil recovery at ambient temperature. However, an increase in oil recovery was

observed with runs at high temperatures (90°C). Moreover, due to the increase in pressure drop, migration of fines or dissolution effects may have occurred and may contribute to the increase in oil recovery. Evaluating the potential of low-salinity water to enhance the oil recovery from reservoir limestone is the main objective of this study. To reach the goal, four core flooding tests were conducted at reservoir temperature with initial formation water between 7%-10%.

2. Materials and Methods

2.1 Materials

Totally two different brines were used in this paper as initial and displacement fluid. The Brines were made from deionized water (DIW) and the available reagent-grade salts in laboratory. The brines were diluted through a 0.22µm Millipore filter prior to uses. The terminology and the specification of those brines are as follows:

- Formation water (FW) was used as initial formation water in both chalk and limestone cores. FW contains Ca^{2+} , Mg^{2+} , but doesn't contain SO_4^{2-} .
- 100 times diluted FW by distilled water, was used as a low-salinity formation water.
- Seawater (SW) was used to evaluate the surface reactivity of the core's surface.
- 10 times diluted SW was used as low-salinity seawater
- Furthermore, seawater with half amount of tracer (SW1/2T) was used as reference fluid in ion chromatograph and. The composition of the brines is listed in table 1.

Table 1: Composition of brines

Ions	HCO_3^-	Cl^-	SO_4^{2-}	SCN^-	Mg^{2+}	Ca^{2+}	Na^+	K^+	TDS[g/L]	IS[mol/L]
FW[mol/l]	0.003	3.643	0.000	0.000	0.076	0.437	2.620	0.000	208.94	4.158
SW[mol/l]	0.002	0.525	0.024	0.000	0.045	0.013	0.450	0.010	33.39	0.657

In this study we have used three reservoir limestone cores and as a reference carbonate rock, we have used one outcrop chalk core. The limestone cores, were taken from different section of a well. All the core plugs had a diameter of 3.80 cm and

lengths of 8.1 except core B, which has a length of 8.4 cm. The permeability of the cores were low, about 0.3-1mD. The porosity of the cores was between 17% to 18%, which was measured in laboratory.

Table 2: Limestone and Chalk core data

Core ID	Length (cm)	Diameter (cm)	Porosity $\phi\%$	Permeability k_a , mD
A	8.1	3.8	18	1.2
B	8.1	3.8	17	1.1
C	8.1	3.8	17	0.8
D	8.0	3.8	45	4.2

Three different crude oils were used in the experiments. All of the oils were examined macroscopically and no wax or other deposits were observed. To remove water and solids from the oils, they were centrifuged and filtered through a 5µm Millipore. The Acid numbers are measured by a modified version of ASTM D664. The base numbers are determined by

a modified version of ASTM D2896. Both methods were developed by Fan and Buckley (2006). Density and viscosity of the crude oil were measured at 20°C by Anton Parr DMA 4500 Density Meter and Physica Parr UDS 200 Spectrometer, respectively.

Table 3: Chemical and physical properties of crude oils

Oil ID	AN mg KOH/g Oil	BN mg KOH/g Oil	Density $\text{g/cm}^3@20\text{ C}$	Viscosity cp @20 C
Oil A	0.08	0.34	0.824	4.3
Oil C	0.34	0.45	0.821	4.2
Oil B	0.70	0.42	0.818	3.8

3. Experimental setup and procedure

The oil saturated and aged core was placed in a rubber sleeve and mounted in the core holder with a confining pressure of

20 bar. HPCL piston pump was used as a driving force for flooding of the core. It pumped distilled water from a water reservoir into two piston cells to displace the different

injection brines. A manifold valve on top of piston, made it easy to switch the flow of two different brines into the core. The brine was flowing directly from the piston cell to the Hassler core holder containing the core. Using a valve system on the outlet of the Hassler core holder controlled the outlet flow from the core holder. Fig.4.3 is schematic illustration of flooding setup.

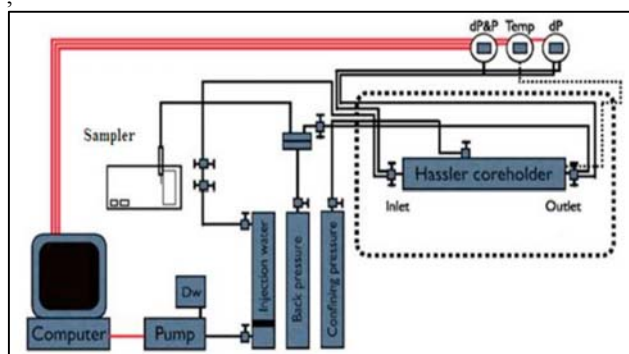


Fig 1: Schematic illustration of flooding setup. (Peimao Zhang *et al.*2006) [4]

A back pressure was applied on the core, to avoid oil boiling. The injection brine was injected with rate 0.01 ml/min \approx 0.6 PV/day. The core holder was placed in an oven which supplied high temperature during the test. The produced fluid was collected in a buret, and oil recovery was measured as a percentage of OOIP versus injected pore volumes (PVs). During the tests some samples of produced brine were collected to be analyzed for sulfate, calcium and magnesium in ion chromatograph.

4. Results and Discussion

Test #1 on (core A)

Core A with $S_{wi}=7\%$ was saturated and aged with a crude oil with $AN=0.7$.

The core flooding in this test was performed at 110°C , first with FW and then with diluted FW. As it has been discussed earlier, the FW doesn't contain any sulfate, thus it doesn't cause wettability alteration in the rock. The result, which is presented in Fig. 2 shows that the flooding with FW gave an ultimate recovery about 65% of OOIP after 5 PVs FW injected. Then, in order to verify low salinity effect on the limestone core, the injection brine was switched to the 100 times diluted FW. The oil recovery increased from 65% to 69% OOIP.

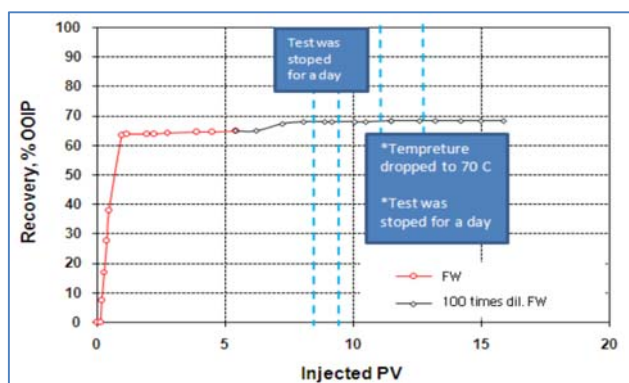


Fig 2: Viscous flooding of limestone core A. The core was flooded first with FW and then with 100 times diluted FW with a constant rate 0.01ml/min (=0.6PV/day)

Fig. 3 shows the differential pressure over the core versus PV injected. A reduced pressure drop was observed during oil mobilization and the injecting diluted FW.

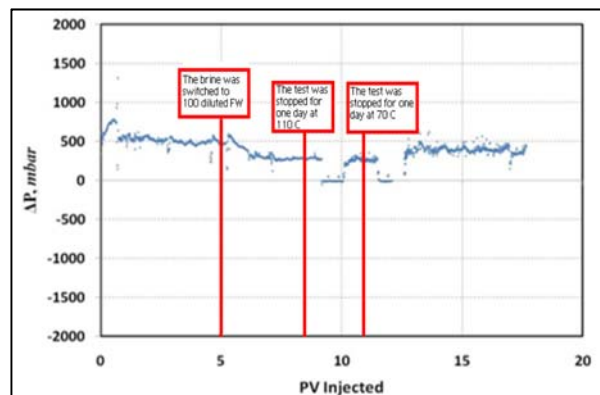


Fig 3: The differential pressure over the limestone core A versus PV injected. ΔP decreased as the 100 times diluted FW remobilized oil.

Effluent brine samples were analyzed for SO_4^{2-} concentration in ion chromatograph. The results are plotted versus PVs injected, Fig.4. The concentration of sulfate gradually decreased from 0.8 mMole/L to 0.3m Mole/L and even more to 0.1 mMole/L after switching FW to diluted FW. After reaching ultimate recovery by injecting 8PVs of brines, the flooding was stopped for one day in order to observe any change in sulfate concentration. By restarting the test, an increase in the concentration of sulfate in the effluent was observed.

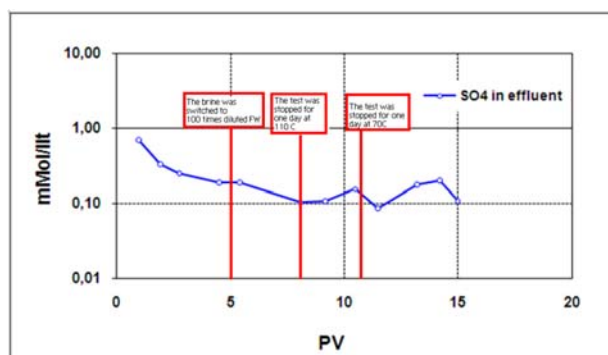


Fig 4: Concentration of SO_4 in the effluent of core A versus PV injected. A reduction in concentration of sulfate is observed when the brine was switched from FW to 100 times diluted FW.

After injecting 11 PVs the injection was stopped for one more day and the temperature was reduced to 70°C . This was done to monitor any changes in dissolution of CaSO_4 . By further flooding at 70°C , a jump in both ΔP and concentration of sulfate was observed, but no increase in oil recovery was observed. The dissolution of sulfate after first shut in period (10 PVs) at 110°C , is lower than the dissolution of sulfate after the second shut in period (13 PVs) at 70°C , indicating that the dissolution of CaSO_4 increased with decreasing temperature.

Test #2 on (core B)

Limestone core B with $S_{wi}=8\%$ was saturated and aged with $AN=0.73$ mgKOH/g, the same as core B. Initially the core was flooded with FW at constant temperature 90°C . The ultimate recovery of 68% was reached after 6 PVs injected, Fig.5.4. Then the injection brine was switched to 100 times

dilute FW. An increase in oil recovery from 68% to 72% was observed. The ΔP decreased as the diluted FW remobilized more oil, Fig.5. The test was stopped after injecting 9 PV brines in total.

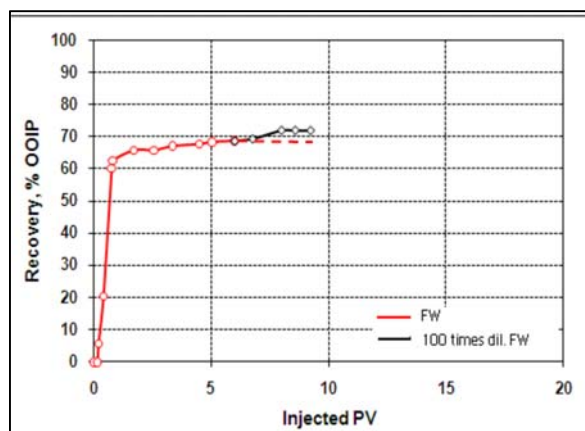


Fig 5: The viscous flooding of limestone core B at 90 °C. The core was flooded first with FW and then with 100 times diluted FW with a constant rate 0.01 ml/min (=0.6 PV/day)

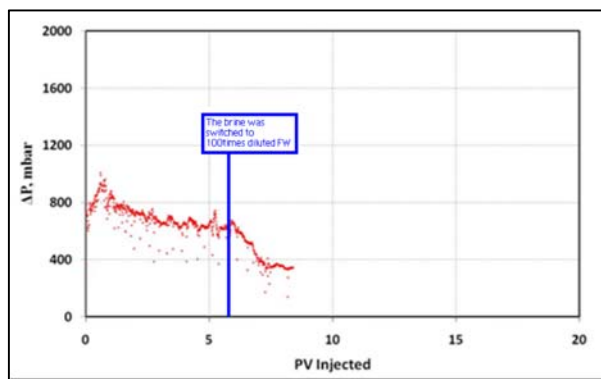


Fig 6: The differential pressure over core B versus PV injected. The ΔP decreased as 100 times diluted FW remobilized oil

Test #3 on (core C)

Limestone core C with $S_{wi}=7\%$, was saturated and aged with crude oil with low acid number about $AN=0.08$. The core C was flooded first with SW at temperature 110 °C which gave an ultimate recovery of 60% after 3PVs injected, Fig. 7. The flooding brine was then switched to 10 times diluted SW. An increase in recovery from 59% to 61% was observed due to low concentration of Ca^{2+} and $NaCl$ ions in diluted seawater. The test was stopped after injecting 10PVs of brines.

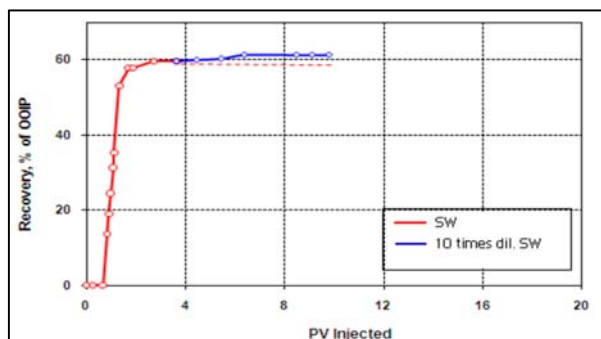


Fig 7: Viscous flooding of core C at 110°C. The core was flooded first with SW and then with 10 times diluted SW with a constant rate 0.01 ml/min (=0.6 PV/day)

Test #4 on (core D)

The Chalk core D containing no anhydrite with $S_{wi}=10\%$ was saturated and aged with crude oil with $AN=0.34$ mgKOH/g. Initially, the core was flooded with FW at temperature 110°C. The ultimate recovery was about 55% after injecting 7PVs, Fig. 8. Then the brine was switched to 100 times dilute FW, but no improved recovery was observed after injecting 14PVs. By cleaning the chalk core, it was confirmed that the chalk core did not contain any anhydrite which can release sulfate ions.

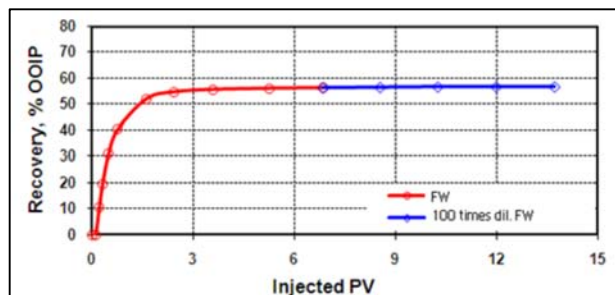


Fig 8: Viscous flooding of Chalk core D containing no anhydrite at 110 °C. The core was flooded first with FW and then 100 times diluted FW

5. Conclusion

According to the results of the current work, the following conclusions can be reached:

1. The low salinity brine, increased the recovery in carbonate, which contained anhydrite.
2. Sulfate ions are dissolved in the injection front when the low salinity brine invaded the rock.
3. The amount of non-active salt ($NaCl$) is very low in the diluted FW, which promotes increased reactivity of SO_4^{2-} and Ca^{2+} . Thus, diluted FW can be used as smart water to enhance the oil recovery.
4. Increasing the temperature will also increase the reactivity of SO_4^{2-} and Ca^{2+} .
5. In the cores containing anhydrite, the dissolution of $CaSO_4$ can increase by using diluted seawater which contains lower concentration of Ca^{2+} than seawater.

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