STUDY OF THE SULPHATE ION EFFECT ON OIL RECOVERY DURING LOW SALINITY WATER INJECTION IN DOLOMITES

Guilherme Bueno Aquino de Oliveira
Center of Petroleum Studies/State University of Campinas
Eddy Ruidiaz Muñoz
Center of Petroleum Studies
Alessandra Winter
Center of Petroleum Studies
Osvair Vidal Trevisan
Center of Petroleum Studies/State University of Campinas

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ABSTRACT

The wettability of carbonate rocks is influenced by sulphate ion concentration in formation water. Furthermore, sulphate promotes an increase of oil recovery acting as a catalyst to wettability alteration reaction during low-salinity waterflooding. In spontaneous imbibition tests, oil recovery increments could be observed only above 100°C. Also, capillary forces are dominant in imbibition mechanism, although in coreflooding experiments, viscous forces are higher than the capillary ones. So this paper proposed an investigation of low salinity injection in displacement tests using two temperatures based on Brazilian pre-salt reservoirs (65°C e 110°C). As an attempt to further understands the mechanism behind the presence of initial sulphate four tests were performed with two pairs of rocks. The samples used in this work were dolomite outcrops. Experiments were conducted two times in the same pair of rocks changing only the sulphate concentration in correspondent formation water. A sequence of three brines was injected, starting with sea water followed by two diluted brines (two times and ten times diluted). The injection of twice diluted seawater after seawater flood resulted in gains of 2.8 up to 8.2% of OOIP. A trend in oil recovery anticipation was observed at experiments with a higher concentration of sulphate in the formation water. The final recovery was around 50% and temperature dependence was observed for the tests carried out. In addition, sulphate adsorption was observed by the analysis of effluents by ion chromatography. These results indicated that carbonate reservoirs with lower temperatures could be potential candidates to low salinity water injection. This paper contributes to a better understanding of the sulphate influence in oil recovery and it is relevant to lab-scale experiments validation.

INTRODUCTION

Exploration and characterization of carbonate reservoirs has many technical challenges. Recently, with the introduction of low salinity waterflooding in carbonates, different researches have shown that initial sulphate present in the rock may be relevant for understanding the mechanism behind the additional oil recovery through wettability alteration [1, 2].

Studies contemplating the mechanism of wettability alteration in carbonates are recent [1] and dynamic tests dated the later years, one example is the research presented in reference [3]. Understanding the behaviour of oil production after low salinity water flood is crucial to validate its effects and to compare it as an alternative to desulphated seawater, commonly injected in Brazilian offshore fields.

In the wettability alteration mechanism proposed by Austad in reference [1], magnesium and calcium ions are involved in the reaction that removes the polar compounds adsorbed on the rock surface responsible for the oil wetness condition. In addition, according to this mechanism, the sulphate ion acts as a catalyst to improve these reactions playing a key role in the wettability alteration process.

For the wettability alteration mechanism to occur, the potential determining ions (PDI`s) Mg^{2+}, Ca^{2+} and SO_4^{2-} must have access to the rock surface. Fathi et al. in reference [4] discussed that these active ions have better access to carbonate surface if there are fewer inactive ions (Na^+ and Cl^-) in the double surface layer. This can occur if the density of this ions decreases or if the concentration of PDI`s increased in the injected water.

Figure 1 exhibits the effect of non-active ions depletion in the injected water. In high saline water, a large amount of ions Na^+ and Cl^- is present in the double layer. If the ionic density decreases in the double layer, the active ions (PDI`s) will have better access to the positively charged of carbonate surface, increasing the imbibition rate and oil recovery [4].

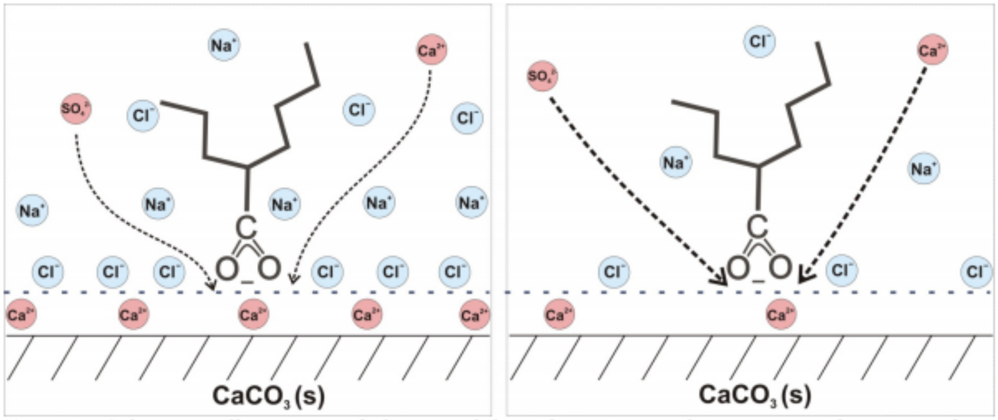

Figure 1 - Schematic illustration of the wettability alteration mechanism at carbonate surfaces. Effect of non-active ion depletion, adapted from reference [5].

Several efforts have been done regarding low salinity effect and the main mechanism behind the method in carbonate rocks. Based on the wettability alteration mechanism proposed by Austad in reference [1], the PDI`s could have relevance in relation to the affinity with the rock surface. Different approaches have been carried out to investigate the shock salinity, brine concentration and dissolution effects.

The anhydrite is one of the most intriguing research points when it comes to an understanding the phenomena involved in the injection of low salinity water. Because it contains the sulfate ion, the effects of its presence in the recovery increments were investigated. In reference [6] the authors hypothesized that the dissolution of the anhydrite would be responsible for the increased production in the study of zeta potential change with chalks. Also, Fjelde and Asen in reference [2] reported results of additional recoveries when sulfate ion was present in water, even if small. Thus, the possible interference of the sulfate in the initial properties of carbonate rocks used in laboratory tests motivated part of this work. However, there is no evidence concerning carbonate rocks with initial sulphate and their influence on EOR studies regarding low salinity waterflooding.

Considering these approaches, this work aims to understand the role of sulphate and its effect on low salinity waterflooding in carbonates. For this, oil recovery tests were carried out at two temperatures in the same cores and a water aging method for anhydrite precipitation was applied to mimic the effect of the initial sulphate on the rock. The suggested method promotes chemical disequilibrium to precipitate calcium sulphate (anhydrite) at 110°C, given that the solubilisation of the salt decays with increase in temperature.

PROCEDURES

To study the effect of initial sulphate on oil recovery in carbonate reservoir, several activities were carried out to mimic reservoir wettability and water/oil saturation conditions. The carbonate rocks samples were outcrops of dolomites from the Thornton Formation, USA. According to semiquantitative X-Ray Diffraction (XRD) analysis, the Silurian outcrop rock is mainly dolomite with no clay or anhydrite evidence. The first step in the sample preparation was cleaning it with solvents to remove salts and any possible impurities, and after that a routine of petrophysics measures was carried out and summarized in Table 1.

Table 1 - Rock properties.

Sample	D (cm)	L (cm)	Dry weight (g)	κ (mD)	Φ (fr)
GB1	3.36	4.64	123.01	309.6	0.154
GB2	3.36	4.73	127.75	164.2	0.142
GB9	3.36	3.79	136.97	81.7	0.119
GB15	3.36	3.80	126.53	274.1	0.168

The oil sample used was a representative specimen of a pre-salt reservoir. The density under the test conditions, SARA chemical analysis and the acid number were determined and summarized in Table 2.

Table 2 - Crude oil composition.

Asphaltenes (%)	**Resins (%)**	**Aromatics (%)**	**Saturates (%)**	**TAN, mg/g KOH**	**Density, g/cc**	**Viscosity, cP**
1.57	16.68	5.59	76.15	0.055	0.863	13.9

Brine sequences were selected based on the variation of seawater concentration. The brines used was: formation water (FW), formation water with initial sulphate (FWIS), seawater 2 times diluted (SW2D) and seawater 10 times diluted. The composition and salt concentration of each brine used in this work are indicated in Table 3.

Table 3 - Ionic composition, total dissolved solids (TDS) and ionic strength of the brines used in the tests.

Ion (mg/L)	**FW**	**FWIS**	**SW**	**SW2D**	**SW10D**
Na^+	58006	58448	10758	5379	1075.8
Li^+	126	126	0	0	0
K^+	3984	3984	399	199.5	39.9
Ca^{2+}	8930	8930	412	206	41.2
Mg^{2+}	393	393	1283	641.5	128.3
Ba^{2+}	2.8	2.8	0	0	0
Sr^{2+}	118	118	8	4	0.8
Br^-	320	320	67	33.5	6.7
Cl^-	110519	110519	19353	9676.5	1935.3
SO_4^{-2}	80	1001	2712	1356	271.2
HCO_3^-	55	55	105	53.76	10.5
Ion Strength (mol/dm^3)	0.337	0.339	0.07	0.039	0.007
TDS (mg/L)	182.5	183.9	35.1	22.9	3.5

To mimic the initial sulphate present in the core, a methodology was applied to prepare the samples. The procedure was initiated by promoting a saturation of 100% of the sample using FWIS. To further guarantee the anhydrite precipitation, the cores saturated with FWIS were aged in a pressurized vessel at 110°C for 24 hours.

To minimize the parameters of test an initial water saturation (Swi) of 10% was stablished for all the samples. To perform this preparation, it was applied the procedure described in reference [7]. According to this methodology, the rocks were saturated with the 10 times diluted FW and achieved the Swi through evaporation. Finally, the rocks in Swi condition were placed in individual hermetic containers for 3 days to allow internal fluids redistribution.

The rocks were saturated with oil after achieving the Swi condition. The samples were placed in core holders and a vacuum pump was connected for 5 minutes – the vapor pressure of water was respected, so it was assumed the maintenance of the initial water saturation. At 50°C, 2 porous volumes of oil were flowed through the samples in each direction. The rocks completely saturated were disposed inside an oven at 110°C. The aging lasted 2 weeks in order to get rocks more oil wet.

Four tests were designed in order to study the effect of the initial sulphate on dolomite cores. The research variables were defined as: salt concentration on the injected solutions, temperature and initial sulphate concentration on the rock. The experimental planning can be seen in Table 4 and was coded as follows: index T indicates test temperature and the letter S indicates that FWIS was used to saturate the samples.

In previous experiments with carbonates on our laboratory, the author [8] adopted the bump flow method: after the injection at a constant flow of 0,1 cm³/min, the flow rate was increased by a factor of four. The author observed a higher production than the commonly obtained for sandstone. The difference in residual oil saturation (Sor) observed in [8] for carbonate reservoir rocks were between 9% and 15,8% OOIP - when raising flow rate and consequent capillary pressure increase. The capillary desaturation curve (CDC) for carbonates differs from the sandstone ones, increases in capillary number result in a considerably lower Sor. So, for these experiments, we did not adopt bump flow.

The rock samples were investigated in pairs. In all experiments the coreflooding sequence starts with SW, then it was switched for SW2D as tertiary mode and in ultimate mode was injected SW10D. Four porous volumes of each brine were injected at 0.1 ml/min and this flow rate was constant throughout all experiments. A pressure gauge measured the differential pressure while the experiment was performed. The effluent production of one of the tests was collected for ion chromatographic analysis. The experimental conditions were the same for all tests besides petrophysical parameters.

Table 4 - Experimental planning of tests and the rock samples used in each one of them. Also, the sequence of brines injected.

Test Code	Sequence	Rock Pair
T65	S2: SW -> SW (2x dil) -> SW (10x dil)	GB1-GB15
T65-S	S2: SW -> SW (2x dil) -> SW (10x dil)	GB1-GB15
T110	S2: SW -> SW (2x dil) -> SW (10x dil)	GB2-GB9
T110-S	S2: SW -> SW (2x dil) -> SW (10x dil)	GB2-GB9

RESULTS

Four corefloods were performed, and the results are plotted in the following images. The graphs show the oil production (percent of original oil in place, %OOIP) against the pore volume injected (PVI), the differential pressure (Psi) was plotted in the secondary axis.

In order to minimize different conditions between the tests, the number of porous volumes injected was standardized in four. If the criteria of 4 PVI had already been reached and there was an important recovery of oil, the production was expected to stabilize for at least 3 measurements (0.3 PVI).

Figure 2(a) shows the result of the oil recovery from a dolomite core evaluated at 65°C and without initial sulphate. The seawater injection shows a recovery of 49.7% of OOIP. In tertiary mode, an additional of 4.3% OOIP was achieved and 0.8% OOIP was recovered with the SW10D. A second coreflood was performed at 110°C in order to evaluate the temperature effect under the same scheme of injection. Figure 3(a) shows that SW produced 41% of OOIP followed by 8.2% and 2.0% of OOIP with SW2D and SW10D respectively.

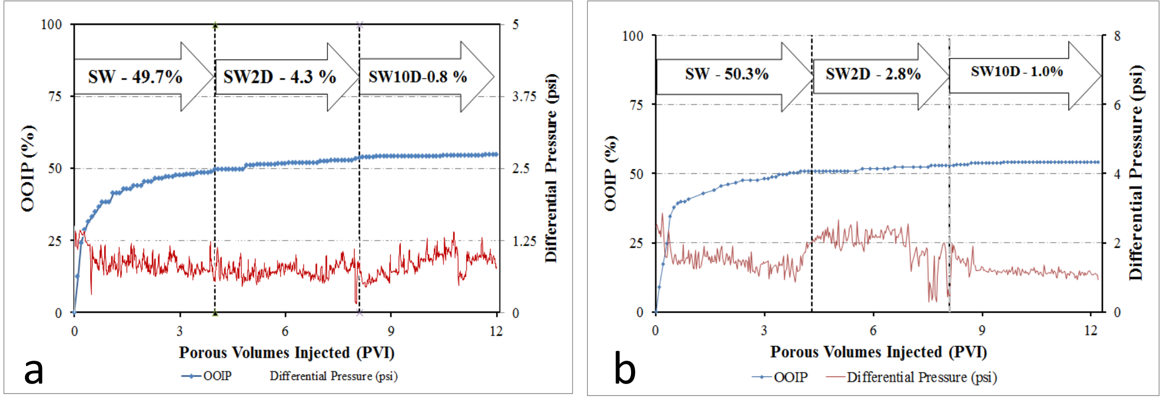

Figure 2 - Oil Recovery of dolomite evaluated at 65°C, (a) core without initial sulphate (Swi using FW), (b) core with initial sulphate (Swi using FWIS).

After concluding the coreflooding in the samples without initial sulphate, the cores were cleaned with solvents and prepared using FWIS in order to mimic the presence of initial sulphate in the cores. Figures 2(b) and 3(b) shows the effect of initial sulphate on the oil recovery evaluated at the same temperature conditions. For the samples with initial sulphate the seawater injection recovered around 50% of OOIP in both temperatures evaluated.

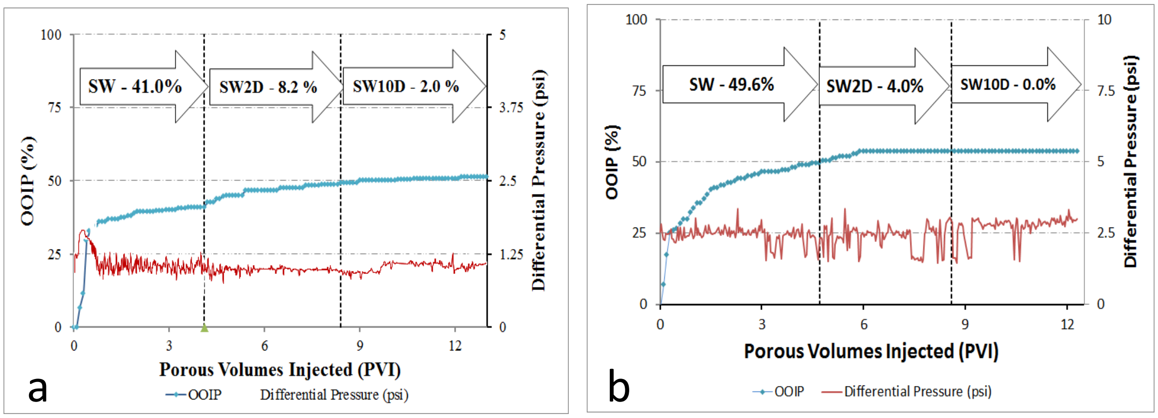

Figure 3 - Oil Recovery of dolomite evaluated at 110°C, (a) core without initial sulphate (Swi using FW), (b) core with initial sulphate (Swi using FWIS).

DISCUSSION

The results show an important recovery with the seawater injection, up to 40% OOIP in all cases. The final oil saturation was between 51.2% and 54.8% for the 4 tests performed. The twice-diluted seawater (SW2D) injection promoted a significant recovery in all test, from 2.8% to 8.2% of OOIP. These increments can be attributed to the salinity depletion. The use of a brine with a half concentration of salt resulted in more access to the rock surface by active ions, once there are fewer non-active ions in the double surface layer [4].

Negligible amounts of oil were obtained at ultimate recovery due to injection of seawater ten times diluted. In this condition the large reduction in total concentration of ions provided also significant depletion of PDI`s,

Comparing the two tests performed at 65°C (Figures 2(a) and 2(b)) it is possible to observe the same trend of recovery with the seawater injection, less than 1% of OOIP difference between them. The seawater two times diluted showed an increase on oil recovery in both cases. The final recovery of these two tests was very close, around 54% of OOIP. As is noticed in the Figures 2(a) and 2(b), there is no evidence of additional recovery linked to the presence of initial sulphate in the core at 65ºC.

The effect of initial sulphate could be noticed in the experiments performed at 110ºC. Figure 3b shows an oil recovery of 49.6% of OOIP in the core with anhydrite presence. These results represent an increase of 8.6% of OOIP compared to the core without initial sulphate (Figure 3(a)). Also, due to the presence of anhydrite, is possible to observe an increase in the production rate. Although the ultimate oil recovery reach close values, the production plateau achieved around 6PVI for T110-S instead of 11PVI in T110.

In order to investigate the affinity of sulphate in the rock surface, effluents from test T65 were analyzed by ion chromatography. Figure 4 shows the sulphate concentration along the coreflooding at 65ºC. It is possible to observe an adsorption of sulphate while SW is flooded. In Figure 4 the concentration of effluents goes below the baseline of the seawater relative concentration of sulphate (red line). After changing the brine, there is still some adsorption taking place in the core, which may be linked to the wettability alteration mechanism releasing extra oil. With the last injection, there is a reduction in the sulphate concentration, which indicates the anhydrite desorption, therefore, there is negligible or none additional oil produced with this brine concentration.

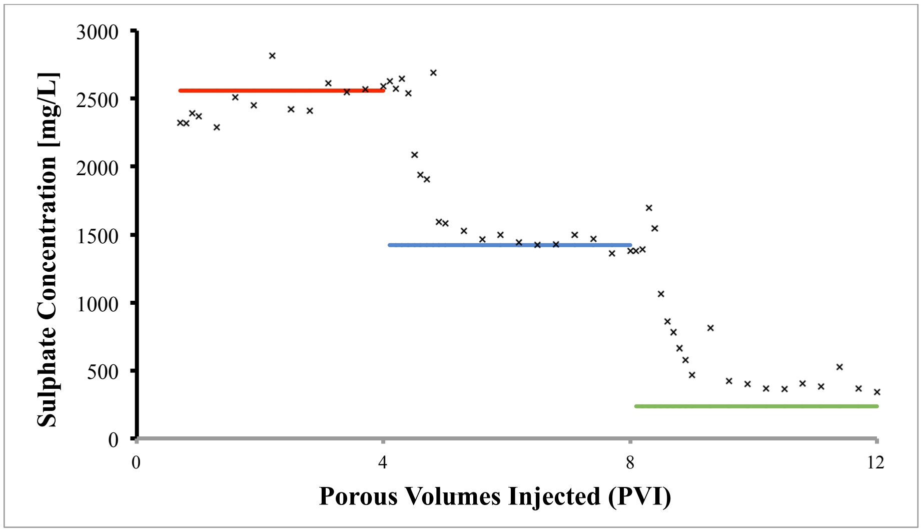

Figure 4 - Sulphate chromatographic analysis of the effluents for the test T65. Red baseline – sulphate concentration of SW, Blue baseline - sulphate concentration of SW2D and Green baseline – sulphate concentration of SW10D.

CONCLUSION

The sulphate ion is one of the potential determining ions based on wettability alteration mechanism and it plays a key role in the low salinity injection on carbonates rocks as dolomite. The following aspects could be observed in this work:

- The depletion of total salt concentration of seawater shows an increase on oil recovery of 2.8% to 8.2% of OOIP for two times diluted seawater.
- Additional oil recovery due to the presence of initial sulphate in dolomite rocks shows temperature dependence. An increment of less than 1% of OOIP was observed at low temperature (65ºC), while an increment of 8,6% of OOIP was observed at 110ºC.
- The presence of initial sulfate in dolomite rocks can contribute to increase the oil recovery during low salinity waterflooding strategies, showing better results at high temperatures.

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