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EVALUATION OF OIL RECOVERY BY LOW SALINITY WATER INJECTION (LSWI) ON OIL-WET CARBONATES FROM PRE-SALT

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Abstract. *The LSWI technique is defined by reducing specific ions in the injection water in order to increase oil recovery. For carbonate reservoirs, that have complex characteristics and intermediate or preferential wettability to oil, this technique is attractive and results in wettability alteration, an important factor in increasing oil recovery. The objective of this research was therefore to evaluate the recovery of oil in carbonate reservoirs rocks by reducing the concentration of sodium chloride in the injection water under pre-salt reservoir conditions. Coreflooding tests were conducted with reservoir conditions of 8230 psi and 69°C. The injection fluids were: formation water (FW), conventional seawater (SW) and seawater with changes in the concentration of sodium chloride and sulfate. The results returned that the most promising injection waters were: desulfated seawater depleted of NaCl ($SW_{Ds}0NaCl$), which resulted in total increases of 5.6% in oil production, and seawater depleted of NaCl (SW0NaCl), which resulted in total increments of 3.5%. Used as a final recovery, the excess of sulfate in the injection water was not efficient. In this case, FW and SW are good options for increasing oil recovery. In conclusion, the LSWI technique is efficient in increasing oil recovery in carbonate reservoirs.*

Keywords: *Low salinity water injection, carbonate reservoirs, enhanced oil recovery, sodium chloride, sulfate.*

1. INTRODUCTION

The low salinity water injection (LSWI), a promising technique, has been improved given its prospective of savings, ease of application and greater potential for recovery when compared to other methods (THOMAS, 2001). Oil reserves are largely made up of carbonates which have a major influence on the O&G industry as they contain large volumes of oil and natural gas worldwide. In carbonate reservoirs, this technique becomes even more attractive due to the extension to the large amount of oil that cannot be recovered by conventional methods (ALVES *et al.*, 2007; BELTRÃO *et al.*, 2009; DERKANI *et al.*, 2018; SCHLUMBERGER, 2020).

In carbonate reservoirs, oil recovery is characterized by low sweep efficiency due to the great variation in porosity and permeability of the porous medium, in addition, wettability is defined as being preferential to oil or neutral, where only 30 to 40% of the original oil in place (OOIP) can be recovered by means of water injection (CHANDRASEKHAR *et al.*, 2016). Therefore, through past studies, one of the main factors for a low recovery rate is the wettability of the rock (GUIMARÃES, 2018), since wettability controls the location, flow and distribution of fluids in a porous medium. When the rock has preferential wettability to water, oil recovery by water injection will be high, with little additional oil production after initial production. However, for rocks with preferential wettability to oil, water inrush occurs much earlier, with most of the oil being recovered over a long period of simultaneous oil and water production. Water injection processes are less efficient in reservoirs that are oil wet compared to reservoirs with preferential water wettability (ANDERSON, 1986).

The present work aims to complement research related to LSWI by analyzing the reduction of sodium chloride in the injection water, making the recovery method more attractive in cases where the reservoirs have on oil-wet characteristic. For this, coreflooding tests in real conditions of Brazilian pre-salt reservoirs were conducted to evaluate this technique.

2. EXPERIMENTAL PROCEDURE

The methodology used in this research started with the rock sample characterization and fluid preparation. Subsequently, the samples were prepared at initial water saturation condition using formation water and crude oil, followed by the wettability restoration and finally, the coreflooding tests. At the end of each test, the rock samples were cleaned to restore their initial characteristics.

2.1 Sample Characterization and Fluid Preparation

The core samples used during the experiments were from a Brazilian pre-salt reservoir in the Santos Basin. Table 1 shows the rock properties.

Table 1. Rock sample properties.

Sample Nomenclature	L (cm)	D (cm)	m (g)	Φ (%)	PV (cm³)	k (mD)
TC-01	4.90	3.79	121.8	17.6	9.76	9735
TC-02	4.61	3.79	116.1	16.7	8.71	5235
TC-03	7.51	3.78	174.5	22.9	19.4	40.6
TC-04	6.55	3.82	166.5	19.0	14.3	12.3

The fluids used in this work were: crude oil, recombined oil (RO), formation water (FW), seawater (SW), desulfated seawater (SW_{Ds}), seawater depleted of NaCl (SW0NaCl), desulfated seawater depleted of NaCl (SW_{Ds}0NaCl), seawater depleted of NaCl with the addition of sulfate ion (SW0NaCl+SO_4^{2-}) and desulfated seawater with a 50% reduction of NaCl (SW_{Ds}0.5NaCl). The main characteristics of crude oil are: density (865.8 g/L), viscosity (21.1 cP) and molar mass (218.2 g/mol). Table 2 shows the chemical composition of the FW and the SW compositions used in the tests.

Table 2. Formation water and Seawater compositions used in g/L.

Salts	FW	SW	SW_{Ds}	SW_{Ds}0NaCl	SW0NaCl	SW_{Ds}0.5NaCl	SW0NaCl+SO_4^{2-}
HCl, 37% (mL)	0.88	-	-	-	-	-	-
NaCl	217.6	23.5	23.5	0	0	11.7	0
$CaCl_2.2H_2O$	13.4	1.47	1.47	1.47	1.47	1.47	1.47
$MgCl_2.6H_2O$	4.95	10.6	10.6	10.6	10.6	10.6	10.6
$SrCl_2.6H_2O$	9.49	0.04	0.04	0.04	0.04	0.04	0.04
$Na_2B_4O_7.10H_2O$	1.40	-	-	-	-	-	-
KCl	5.33	0.72	0.72	0.72	0.72	0.72	0.72
LiCl	0.56	-	-	-	-	-	-
$BaCl_2.2H_2O$	0.05	-	-	-	-	-	-
KBr	1.41	-	-	-	-	-	-
Na_2SO_4	0.09	3.90	0.10	0.10	3.90	0.10	7.80
$NaHCO_3$	1.29	0.19	0.19	0.19	0.19	0.19	0.19
TDS	**245.2**	**34.5**	**30.5**	**7.06**	**10.9**	**18.8**	**14.8**

In addition to the brines recombined oil was also used. The recombined oil is characterized by a mixture of oil with simplified gas composition to represent the conditions of the fluid within the reservoir. For the preparation, it was necessary to perform a simplification of the gases that would be used, reaching the final composition of the commercial gas shown in Table 3. The final composition used was adjusted to the amount of Gas/Oil Ratio (GOR) granted. To prepare 1 L of recombined oil, 500 mL of crude oil and 185.4 mL of gas were required. The fluids were placed in a single vessel, with the aid of a positive displacement pump. The mixture was then mechanically stirred for 24 hours while an electrical resistance heated the system up to the reservoir temperature.

Table 3. Gas composition at recombined oil.

Components	CO_2	N_2	C1	C2	C3	iC4	**GOR (m^3 std/m^3 std)**
Concentration (Mol%)	28.09	0.48	60.27	4.57	3.74	2.84	**187.67**

The reservoir samples underwent cleaning process with aviation kerosene, heptane, and deionized water and then to eight hours of vacuum, to remove the air in the porous medium. The following stage was the rock's saturation with FW (S_{FW}) and crude oil. After the samples were completely saturated with FW (S_{FW}), they were desaturated with oil until initial water saturation (S_{wi}) was achieved. Finally, the samples were aged for at least 14 days to restore the original wettability condition.

2.2 Experimental Apparatus Preparation

The coreflooding tests were performed according to the scheme in Figure 1. The digital data collection system analyzed the production data with software support. The software used was developed by the Laboratory of Miscible Recovery Methods (LMMR) and was responsible for the acquisition and storage of data during the execution of the entire test.

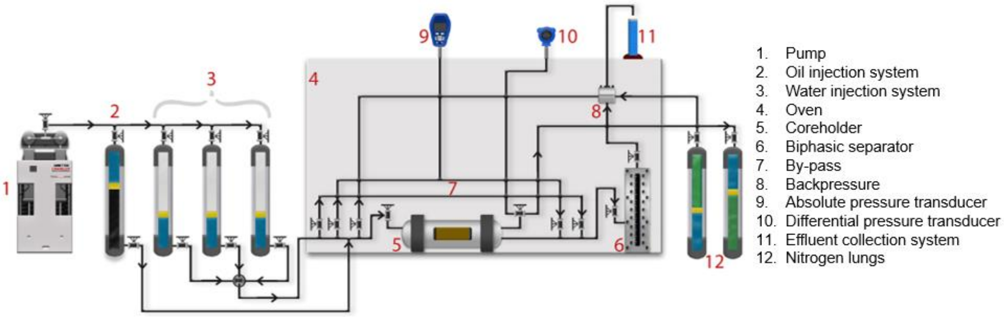

Figure 1. Experimental Apparatus.

The tests were divided into two main series: the first included three tests; the second included two tests with different brine concentrations. The first series of tests analyzed FW as the first injected water and the second series evaluated SW. Figure 2 shows the water sequences used in coreflooding tests.

Figure 2. Water sequences utilized in the coreflooding tests.

3. RESULTS AND DISCUSSIONS

In the first series of tests, it is possible to observe FW as the first injected water; In addition, the waters used as tertiary and final recovery have a reduction in sodium chloride and changes in sulfate ion. In the second series, it is possible to observe the effect of SW as the first injected water and a 50% reduction in sodium chloride used as tertiary recovery. The same rock sample was used in two experiments, allowing the comparison between the tests, except for TC-01/02.

3.1 First series of coreflooding tests

In addition to analyzing the sodium chloride ion in the injection water, one of the objectives of the first series of experiments was to evaluate the formation water and its effects on oil recovery. Formation water was used because this water is in balance in the reservoir and can be considered a non-reactive fluid. Its injection would result in something like the primary recovery of the reservoir, since its use is essential to know the base behavior of the rock samples under study and contribute to a better analysis of the brines used in the tertiary and final recovery.

- **Test 1, Test 2 and Test 3**

In the first test, the water sequence used was: FW, followed by SW_{Ds}, and then followed by SW0NaCl. In this case, a pair of samples (TC-01/02) was used. The samples used in this test have high average values of S_{wi} (S_{wi} = 62.3%). This can be related to high permeability channels in the porous medium, which consequently would result in low sweep efficiency (BRATTEKAS AND SERIGHT, 2017). **Figure 3** provides the oil recovery curve for Test 1.

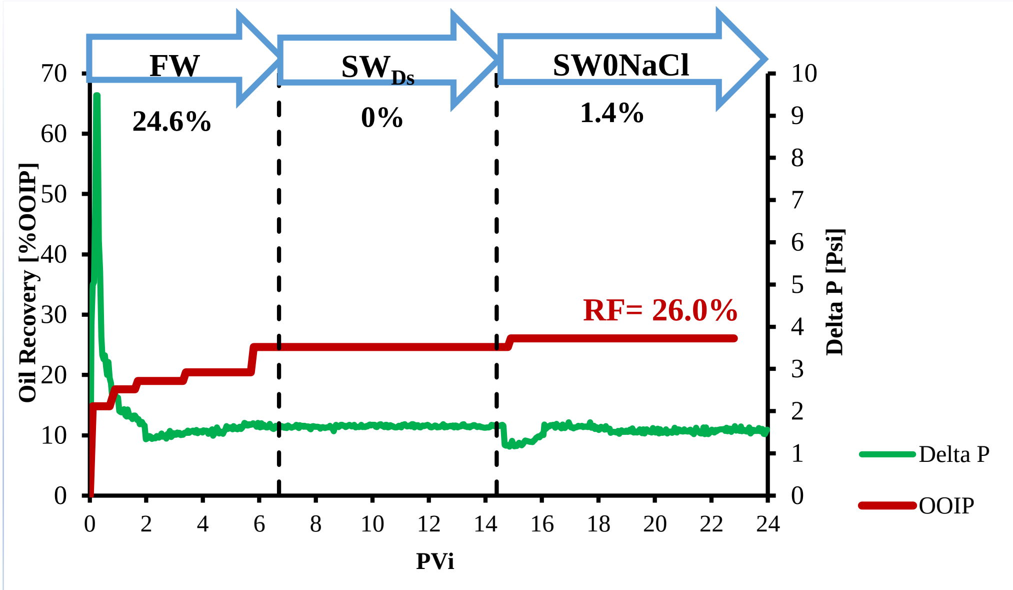

Figure 3. Oil recovery graph – Test 1.

The FW injection resulted in a recovery of 24.6% OOIP. At the beginning of the oil displacement by the FW injection, 14.8% of OOIP was recovered; it then began producing more water and less oil, which is represented by the small increases after the initial recovery. When the injected water was changed to SW_{Ds}, no increase in oil recovery was observed. This behavior could be attributed to the small proportion of sulfate in its composition compared to other waters, since this ion acts as an ion exchange catalyst and helps change the water wettability of the rocks.

As for the third water used (SW0NaCl) there was an increase of 1.4% OOIP, totaling 26.0% of OOIP in Test 1. The reduction of NaCl in the last water resulted in positive effects on oil recovery, strengthening the hypothesis shown in the literature about the easier interaction of potential ions with the rock surface when reducing non-active ions. One can also note that the third water has a higher concentration of sulfate (3.9 g/L) when compared to SW_{Ds} (0.1 g/L), which may also have helped in oil recovery. According to Zhang & Sarma (2012) however, values of up to 1.8% in recovery can also occur due to errors and operational variables.

The differential pressure curve shows a fast peak at the beginning, which can be explained by the rock/fluid pressure interaction, but remained stable between one and two psi, which may suggest that this injection sequence did not cause much interaction between the seawater, oil, and rock.

Figure 4 shows the recovery curve from Test 2. In this test, the injection was started with FW, followed by SW0NaCl, and SW0NaCl+SO_4^{2-}. The sample used was TC-04 (S_{wi} = 35.7%). The selective reduction of sodium chloride and the alteration of sulfate were analyzed. The water used as tertiary recovery had 0.1 g/L of sulfate, while the water used to analyze the final recovery had 7.8 g/L of sulfate so this test also allowed for observing the influence of SO_4^{2-}.

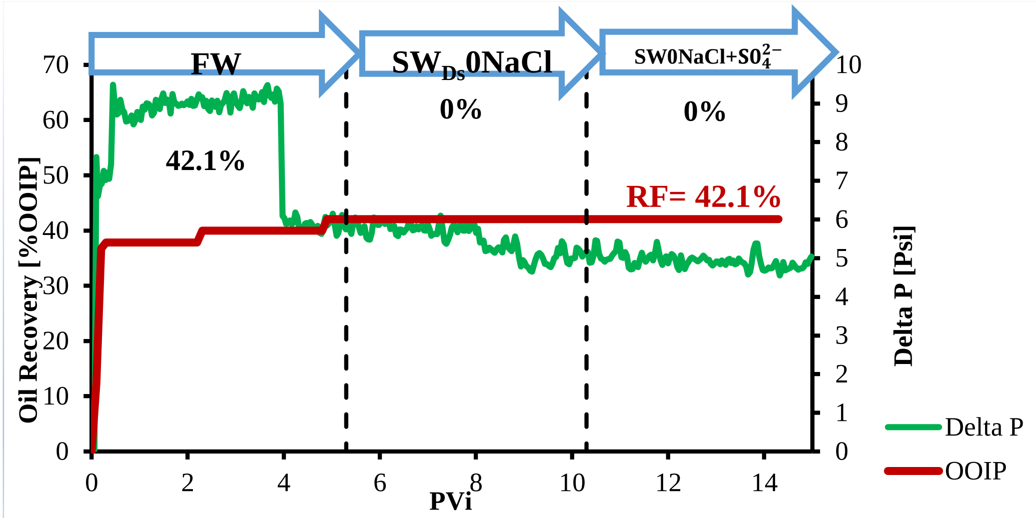

Figure 4. Oil recovery graph – Test 2.

The FW was injected and resulted in 42.1% OOIP. There was a rapid production of oil during the injection of this water in the rock, which was not possible to observe in the pair used in Test 1. Oil production reached the plateau with five VP's, and then stabilized until the final recovery was obtained. As tertiary recovery, SW_{Ds}0NaCl was used but the effects were unsatisfactory. However, its application should not be ruled out, since numerous parameters may have influenced the achievement of this result, such as the mineralogy and the characteristics of each rock. We therefore indicate that this water be analyzed in another test with another rock sample.

As final recovery, the water used was SW0NaCl+SO_4^{2-} and no efficacy was observed. The final recovery factor for Test 2 was 42.1% OOIP. A hypothesis that could explain the result obtained would be the large amount of sulfate in the water used. There is still no agreement on the best amount of sulfate ion in the injection water. The use of sulfate has already been demonstrated in the literature as an ion exchange catalyst that helps to change wettability, but some studies show that the excess of this ion may not be efficient to increase oil recovery (LIMA, 2016).

During the FW injection, there was a great pressure variation that may have occurred due to the dissolution of minerals in the porous medium, which helped in the displacement of oil and made the surface more water wet (PUNTERVOLD and AUSTAD, 2008; BEDRIKOVETSKY *et al.*, 2009; SHABANI *et al.*, 2019a). According to Tale *et al.*, 2020, both precipitation and dissolution tends to decrease as the water dilution increases.

Figure 5 shows the recovery curve from Test 3, which used the same sequence from Test 2; being FW, followed by SW_{Ds}0NaCl and finally SW0NaCl+SO_4^{2-}. The purpose of this test was to evaluate a different face and observe the effect of the reduction of NaCl with the sulfate in the injection water. The sample used in this test was TC-03 (S_{wi} = 24.6%).

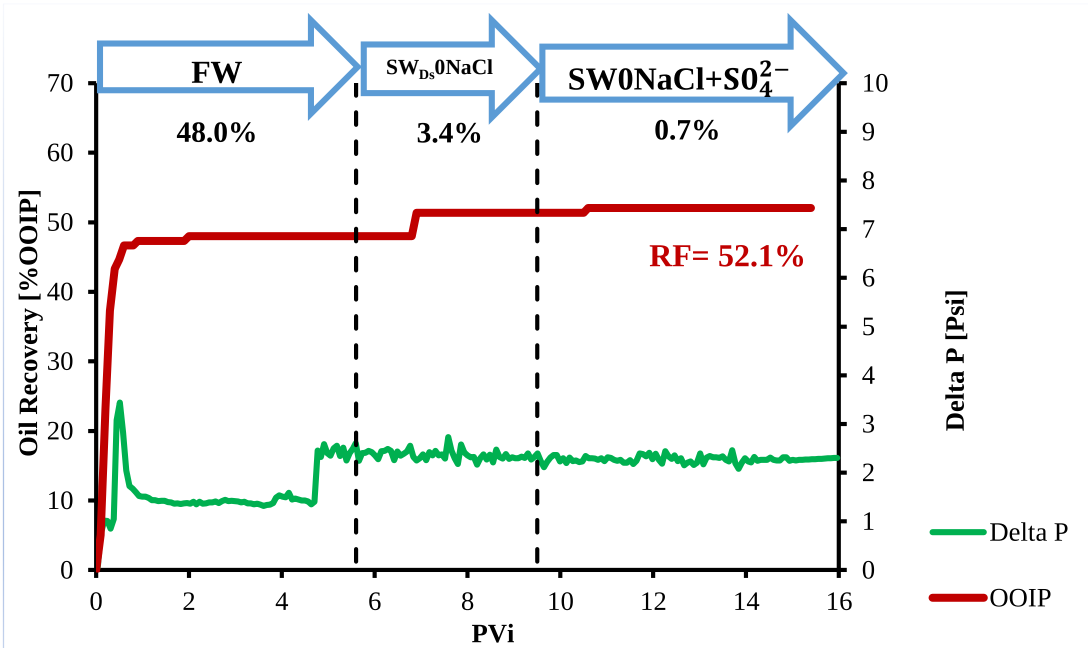

Figure 5. Oil recovery graph – Test 3.

An additional oil recovery of 48.0% OOIP was achieved due to FW injection. This value was close to that found in the previous test. The graph shows that in less than one porous volume injected, more than 45.0% of OOIP had already been recovered and the plateau was reached in roughly two PVi's. For tertiary recovery, SW_{Ds}0NaCl was used, which resulted in an increase of 3.4% OOIP. This occured because when there is a large amount of NaCl on the rock surface, it makes it impossible to interact and approximate the active ions on this surface, which helps change the wettability and consequently increase oil recovery. According to Austad *et al.*, 2013, when injecting a low salinity brine, a diffusion process of the active ions on the rock surface is prominent and induces the wettability alteration. When there is a reduction of non-active ions, it is easier for the active ions in the injection water to change the wettability conditions of the rock, which will result in an increase in recovery, as was observed. For the sample used in this test, the injection of this water provided positive effects on oil recovery. In Test 2 this water did not present the same results, so it is worth noting that each test is unique and that the samples used in both tests are different, which will consequently affect the results.

The last water used was SW0NaCl+$S0_4^{2-}$ and the increase in recovery was 0.7% OOIP. The final recovery factor for Test 3 was 52.1% OOIP. The hypothesis that was also presented in the previous test, and that can explain such an occurrence, is that excess sulfate ion may not be effective. This water was used in tests with different rock samples and resulted in little or no oil recovery, which may indicate that its composition is not really efficient for the operational conditions and lithology used.

In general, Test 3 exhibited better oil recovery results than Test 2. The sample used in Test 3 had higher permeability and porosity values than that of Test 2, so, this can be a parameter for the best results observed and the fluid flow can be facilitated with these definitions. There were no major variations in the pressure gradient during the test, highlighting a decrease level that could relate to the stabilization of the production after the injection of formation water. Otherwise, the pressure remained constant between two and three psi, and it was not possible to observe dissolution or precipitation phenomena.

3.2 Second series of coreflooding tests

The second series of tests are very similar to the first, although it initiates with SW, aiming to observe the effects of seawater with different compositions on the oil recovery of carbonate reservoir samples. The waters indicated as desulfated have 0.1 g/L of sulfate, and the SW, SW0NaCl have 3.9 g/L and the SW0NaCl+$S0_4^{2-}$ have 7.8 g/L. This water is promising, especially from an economic standpoint, as seawater itself is used as an injection, obtaining greater economic returns in the project when compared to other techniques given its availability and ease of use. Each rock sample was used in two different tests, so it is essential that the cleaning process is effective. The S_{wi} of each sample was calculated again.

- **Test 4 and Test 5**

Figure 6 shows the recovery curve of Test 4, performed with sample TC-03 (S_{wi} = 26.2%) using the sequence: SW, SW_{Ds}0.5NaCl and, SW0NaCl.

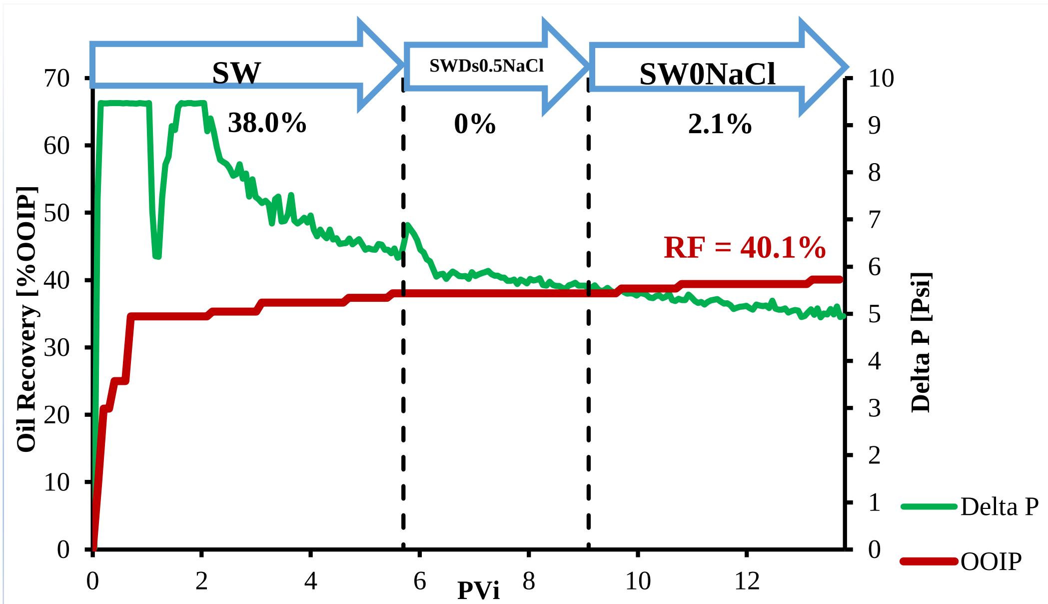

Figure 6. Oil recovery graph – Test 4.

The water used as secondary recovery was SW and resulted in a 38.0% of OOIP. During the entire injected volume, increases in oil recovery were observed, which indicates a continuous reaction between the rock and the brine. SW takes a longer time to reach the maximum oil production compared to the tests where FW was injected as the first water. This behavior indicates that SW promotes ionic interaction that causes the change in wettability. According to Esene *et al.* (2018) and AlHammadi *et al.* (2018), the change in wettability to a favorable state is the main factor that causes greater oil recovery with low salinity water injection in carbonates.

After changing the injection water to SW0.5NaCl, there was no additional oil recovery. This result can be attributed to a hypothesis that the 50% reduction of sodium chloride failed to provide active ions with greater access to the rock surface, helping to change the original wettability of the rock. In Test 3, the rock sample used was the same and the water that had a complete reduction of NaCl showed good tertiary recovery results. This means that, for TC-03, it is necessary to reduce the greatest amount of the NaCl ion.

The water used as final recovery was SW0NaCl and an increase of 2.10% of OOIP was observed, totaling a final recovery factor of 40.1%. As noted in the graph, in less than one PV one can already notice a small increase in oil production, which demonstrates the great potential of injecting this water. The increase in production over the injected volumes shows that there was an interaction between the brine and the rock. This point should be highlighted, since this water has been shown to be efficient in its use.

The pressure differential curve was high at the beginning and this may have occurred due to the migration of fine grains and clogging of smaller pore throats, which influence the displacement of fluid. This sample is characterized by very fine granulometry, which supports the hypothesis presented above. During the porous volumes injected, the pressure decreased, which makes it easier for brines to flow when they contain lower concentrations of NaCl. As observed in the beginning of the test, high pressures were achieved, reaching the limit value of the transducer used.

Figure 7 illustrates the results obtained in Test 5. This test used the sequence: SW, followed by SW_{Ds}0NaCl, and then SW0NaCl +SO_4^{2-}. The sample used was TC-04 (S_{wi} = 37.2%). SW was analyzed as secondary recovery in a rock sample, which was different from the previous test.

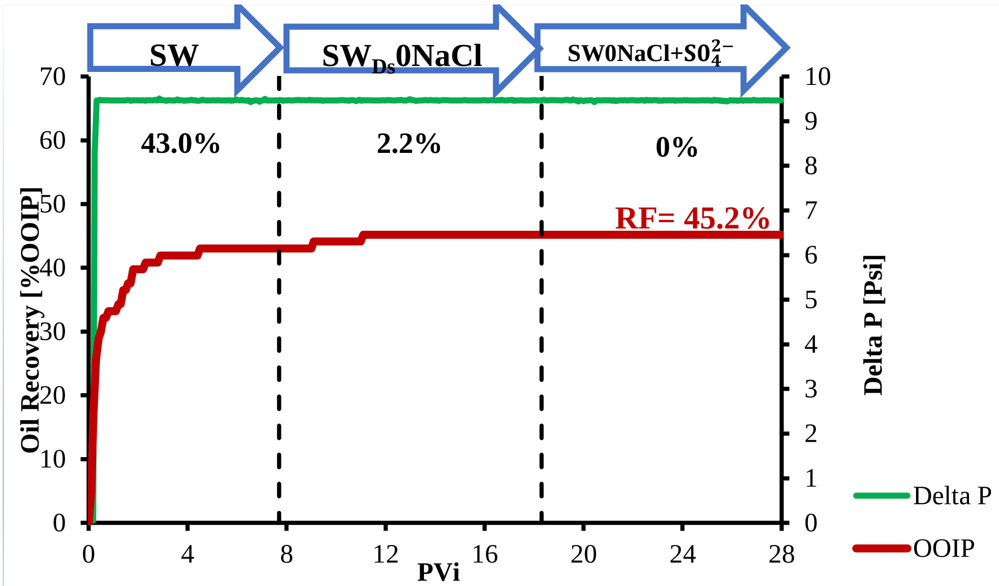

Figure 7. Oil recovery graph – Test 5.

With the SW injection, 43.0% of OOIP was recovered. Oil production increased along the injected porous volume of SW indicating that, after the aging process the sample reached the preferential wettability of the oil. As expected, SW showed effects related to its interaction with the rock. The literature shows that SW has great potential to change the wettability of the rock. SW holds a large concentration of active ions and smaller proportions of non-active ions when compared to the formation water.

The water used as tertiary recovery was SW_{Ds}0NaCl, and an additional recovery of 2.2% of OOIP was obtained. With approximately one PV of this water injected, it was already possible to observe increases in recovery. This water showed good results due to its interaction with the rock. The literature shows that the reduction of sodium chloride in the injection water enables the access of the active ions to the surface, helping to change the wettability and consequently increase the oil recovery factor (FATHI *et al.*, 2010, 2011, 2012). In Test 3 this same water was also successful in this mode, which proves that SW_{Ds}0NaCl exhibits efficiency when used as a tertiary recovery. However, in Test 2, which also used the TC-04 sample, SW_{Ds}0NaCl did not increase the oil recover. A hypothesis that may explain this could be that, during the injection of FW, the test was marked by high pressure values, which may indicate that there may have been some change in the porous medium of the rock and that consequently influenced the effectiveness of the water subsequently injected.

To analyze the final recovery, SW0NaCl+SO_4^{2-} was used, and there was no increase in oil recovery, totaling a recovery factor of 45.2%. The proposal to increase the amount of sulfate in the last injection water did not prove effective for this type of lithology and operational conditions.

In relation to the pressure differential curve, the transducer used to perform this measurement has a maximum scale of 9.5 psi and was limited for further measurements when this value was exceeded. This would be a hypothesis to represent what happened in Test 5. The rock used in this test has low permeability, when compared to the others used in this work, and generally this occurs with rocks of the same characteristic, which means that this test was defined by the high pressure differential.

4. CONCLUSIONS

The present work evaluated the oil recovery through the injection of low salinity water in carbonate rocks wettable to the oil of the Brazilian pre-salt. The reduction of sodium chloride in the injection water was the main point observed. The influence of the sulfate ion was also observed when this ion was changed in the injection water. The parameters were defined to represent the real conditions of the reservoir under study.

The main results obtained were: After the injection of FW and SW, the most promising waters were: SW_{Ds}0NaCl (tertiary recovery), which resulted in a total increase of 5.6% in production and SW0NaCl (final recovery), which resulted in total increments of 3.5%; SW0NaCl+SO_4^{2-} was not efficient in the tests, which indicates that the excess of sulfate in the last injection water is not a good strategy for the lithology and operational conditions; In Tests 3 and 5, SW_{Ds}0NaCl was used as tertiary recovery and proved effective (2.2 and 3.4% OOIP, respectively), the rock samples used in these tests were different, which shows the potential of using this water; The amount of oil produced with few porous injected volumes of FW is much greater than with SW, which indicates that oil production occurs faster and with less injection of fluid than when compared with seawater, because FW is a non-reactive fluid and simulates primary reservoir recovery; Based on the experiments, the results obtained showed that the reduction of non-active ions Na^+ and Cl^- were effective in the recovery of oil in carbonates.

5. ACKNOWLEDGEMENTS

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