IBP2185_18
INTERFACIAL TENSION AND CONTACT ANGLE IN OIL-BRINE-ROCK SYSTEMS AT HIGH TEMPERATURE AND PRESSURE

Célia Melo[1], Nilo Kim[2], Osvair Trevisan[3]

Abstract

Low salinity water injection has been shown to improve oil recovery from carbonate rocks. Studies of contact angle and interfacial tension (IFT) could check this technique. Pendant drop method was used in this work to analyze how contact angle and interfacial tension vary according brine concentration at high pressure and temperature. Density tests were made to decrease the error associated at IFT measurements. These tests were realized at 25°C and atmospheric pressure, at 25°C and 5000psi (34.47 MPa) and at 124°C and 5000 psi (34.47 MPa).
IFT and contact angle tests were performed in brines with similar concentration of seawater and seawater diluted two, ten, fifty, and one-hundred times diluted, at the conditions already righted; in this way it was possible to understand how brine composition and characteristic as temperature and pressure influenced the system.
With this experimental work it can be inferred that interfacial tension values increase with decreasing of salinity. IFT values are strongly affected by characteristics as temperature and pressure. Contact angle values shown a preferable wettability to water for dolomite rock in the presence of low salinity water.

Keywords: Low salinity; pendant drop; interfacial tension; contact angle.

1. Introduction

Carbonate reservoirs make up more than half of the world's oils reserves (Alotaibi et al., 2010). However, the oil recovery from carbonates is well below 30% due to low water wetness, natural fractures, low permeability, and heterogeneous rock properties (Austad et al., 2012). This type of reservoirs at high temperatures tend to be oil-wet or mixed wet, thus is understood – and economically viable – to conduct detailed research (Chandrasekhar et al., 2016).
Low salinity water injection is one of the emphasized techniques in the oil recovery. This technique could improve oil recovery reversing the rock wettability to a water-wet state. This technique has been studied in laboratory as advanced recovery method by, among others, Yousef et al. (2011) and Zhang et al. (2006). According to this brief literature review, wettability is one of the most important parameters which control the fluids porous distribution.

[1] MSc, student – IST/Cepetro/Unicamp
[2] DSc, Researcher – Cepetro/Unicamp
[3] Professor – DEP/FEM/Unicamp

Ionic change is one acceptable proposed mechanism because carbonate rock wettability changes to water-wet by the ionic interactions between oil, rock and brine with low salinity.
In reservoirs of petroleum capillary forces are the result of the combined effect of the surface and interfacial tensions of the rock and fluids, the pore size and geometry, and the wetting characteristics of the system (Ahmed, 2000). Capillary pressure can be calculated by Laplace equation, represented further as Equation 1, considering pressure, interfacial tension and radius related to the drop.
In this work it was used the pendant drop method through Attension Theta software version 4.0.1 to evaluate in which way do contact angle and interfacial tension in a system oil-brine-rock vary according to different salinities and ionic concentrations.
Interfacial tension and contact angle are two important parameters to perform a better way to calculate capillary pressure.
It was tested in laboratory different seawater concentrations under similar reservoir parameters, 124°C and 5000 psi (34.47 MPa).

2. Methodology

2.1. Core Sample Preparation

To perform this work, Silurian dolomite rocks from the Thornton formation, USA, were used. The rocks were supplied in a cylindrical form with 2 inches diameter and 610 mm length. High-pressure cell has 33 mm of diameter, so it was necessary to remove a 1-inch (25.4mm) diameter plug from the rock cylinder using a core cutting machine, rotating 40-48 rpm, diamond tip and water as the cooling fluid. Then, with a diamond circular saw, chips of approximately 8 mm thickness were cut. As the surface of each dolomite pellet presented irregularities, a polishing equipment, was used at 600 rpm, applying water as cooling fluid, for sanding in one direction (0°) and then in another direction, orthogonal (90°), using a sandpaper with particle size of 1200. To measure the roughness of this polished surface, a rugosimeter was used, resulting in an average of three measurements, equal to 31.35 μm.
For this laboratory work it was used rocks with 10% of initial water saturation. The methodology to use in this process of saturation was as follow. This process begins by rocks weight measurement; then rocks are saturated with formation water 10 times diluted into a cylinder (composition of water formation are described in Table 1), pressurized at 2000 psi (13.79 MPa) for 24 hours. After that, rocks are weighed and placed in silica gel desiccators to ensure the desired saturation (10%); there is no defined time for this process which depends of rock characteristics, quantity of samples and capacity of silica to absorb water. Once the desired mass is reached a balance of the fluid distribution is made remaining the rocks stored for a while. The rocks are again placed in a saturation cylinder with dead oil at 2000 psi (13.79 MPa); it is placed in the oven at 124 ° C for ten days.

2.2. Brines Preparation

To perform this work it was used different brines consisting in formation water (FW), seawater (Sw) and its dilutions, 2, 10, 50 and 100 times diluted seawater (denoted by Sw2x, Sw10x, Sw50x, and Sw100x, respectively).
The preparations of those brines consist in mixing the chemicals reagent with deionized water based in each composition described on Tables 1 and 2.

Table 1. Composition of formation water.

Component	g/L
NaCl	165.0854
KCl	7.4741
$MgCl_2$:$6H_2O$	4.1777
$BaCl_2$:$2H_2O$	0.0073
$CaCl_2$:$2H_2O$	16.8624
$NaHCO_3$	0.0293
Na_2SO_4	0.0738
eq.NaCl (ppm)	187354

Table 2. Composition of seawater diluted and non diluted.

Components	Sw (g/L)	Sw2x (g/L)	Sw10x (g/L)	Sw50x (g/L)	Sw100x (g/L)
NaCl	23.4721	11.7360	2.3472	0.4694	0.2347
$CaCl_2$:$2H_2O$	1.4669	0.7335	0.1467	0.0293	0.0146
$MgCl_2$:$6H_2O$	10.5508	5.2754	1.0551	0.2110	0.1055
KCl	0.7245	0.3623	0.0725	0.0144	0.0072
$SrCl_2$:$6H_2O$	0.0396	0.1978	0.0040	0.0008	0.0004
Na_2SO_4	3.9165	1.9582	0.3916	0.0783	0.0392
$NaHCO_3$	0.1927	0.0963	0.0193	0.0039	0.0019
eq.NaCl (ppm)	34378	17189	3437	687	343

In Table 1 and 2, eq.NaCl is the equivalent concentration in ppm if only exist NaCl in composition instead of other salts.

2.3. Reservoir Oil Preparation

A sample of dead oil at laboratory, packaged in a vessel of 50 liters. An aliquot of one liter was appropriately taken and stored separately. The sample was then heated to approximately 60°C, mixed, vacuum filtered using an 8 μm paper filter, placed in a steel container and pressurized at 5000 psi (34.47 MPa).

The characteristic of dead oil are represented in Table 3, these characteristics are important to understand further the obtained values of IFT and contact angle.

.

Table 3. SARA analysis, acid number and molecular weight of dead oil.

SARA analysis, acid number and molecular weight results	
Saturated (%)	97.35
Asphaltenes (%)	0.34
Resins (%)	0.37
Aromatics (%)	1.94
Acid number (mg/g KOH)	1.32
Molecular weight (g/mol)	287.56

2.4. Experimental Setup

For the different tests of contact angle and interfacial tension, the Pendant Drop method was applied, as represented in Figure 1.

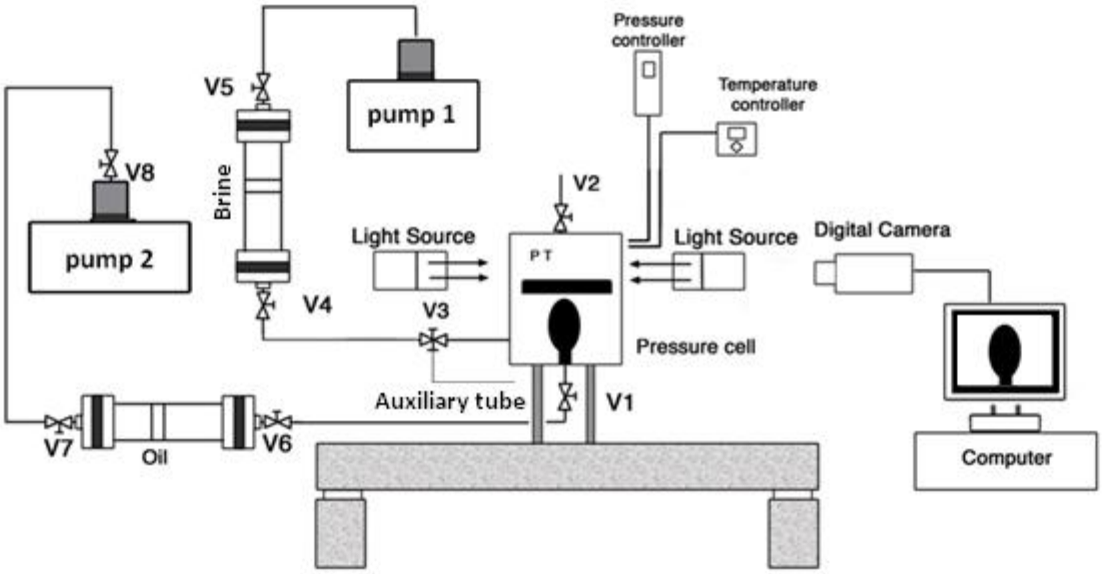

Figure 1. Test diagram.

After the experimental apparatus is assembled, through the valves V3 and V4, the high-pressure cell is filled up with brine; to make sure the cell is completely full brine has to go out for by valve V2, which is then closed. The high-pressure cell is heated up at 124° and pressurized at 5000psi (34.47 MPa). After that, the oil is slowly injected by a needle coupled to the bottom of the cell through valve V1.

Auxiliary tube is used to drain off the air present in the tube line. Light sources are used to improve the images captured by a digital camera which are analyzed by Attension Theta software.

Using Attension Theta software, the interfacial tension between the drop of oil and the brine is measured the instant before the drop detaches from the needle, which is coupled to the bottom of the cell; after that when drop is fixed to the bottom surface of the dolomite rock, contact angle is measured. For each experiment, 10 drops of oil were released, repeating the experiment 3 times over with different samples of dolomite for each sample of brine.

2.5. Attension Theta

Interfacial tension and contact angle values was measured by Attension Theta software 4.1.0 version. To perform the test the software has to be calibrated with density values of the used fluids.

Attension Theta use Young-Laplace equation (Equation 1) to calculate IFT and contact angle values by tracing an envelope in the oil drop, calculating its form factor accurately as represented in Figure 2. The software automatically reverses the images captured by digital camera to calculate IFT values.

$$\gamma = \frac{\Delta\rho \times g \times R_0}{\beta} \qquad (1)$$

Where, γ = surface tension; β = shape factor; $\Delta\rho$= difference in density between fluids at interface; g = gravitational constant; R_0 = radius of drop curvature at apex.

Notice that the software makes an envelope in a point of contact between rock, brine and the drop of oil. The angle is measured inside the drop. Trough Figure 2 (b), CA = 115°, dolomite rock has a tendency to water-wet.
The cell borderlines are represented in red (Figure 2).

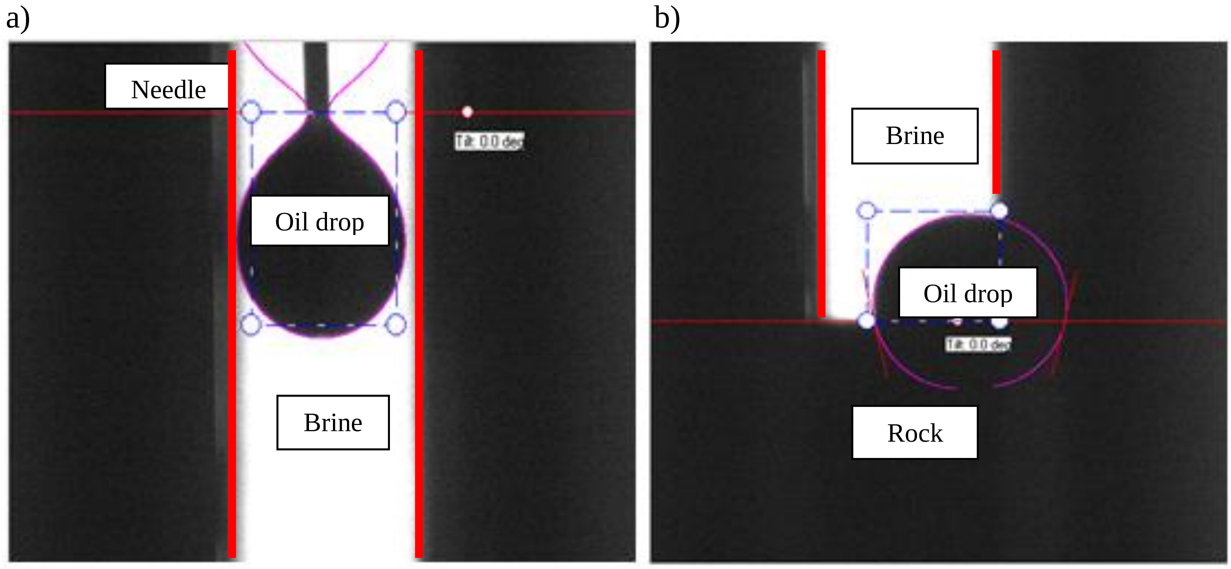

Figure 2. Interfacial tension, (a) and Contact angle, (b) calculation by Attension Theta software.

Density tests were handled in a high pressure density meter. This density meter obtains precise results with up to 5-digit accuracy, through oscillating U-Tube principle. This equipment can operate at considerable ranges of temperature and pressure, adaptable to several experiments. The density meter was calibrated manually for all used conditions in this test.

Table 4. Values of density meter calibration.

	25°C / 5000psi	124°C / 5000psi	124°C / Patm
N-Pentane	0.65631	0.58252	-
Water	1.01180	0.95638	0.93985
Nitrogen	-	-	0.00159

The density tests were conducted under those conditions to mimic reservoir parameters (124°C and 5000psi (34.47 MPa)).
When the high-pressure cell is heated at 124°C and depressurized to atmospheric pressure, IFT were measured to evaluate how pressure affects this system property.
When cell is cooled to ambient temperature (25°C) and pressurized to 5000 psi (34.47 MPa), IFT were measured to evaluate how temperature affects this characteristic.

3. Results

Laboratory tests of contact angle and interfacial tension were performed with brines concentration similar to that of seawater and seawater diluted (2, 10, 50, and 100 times) in conditions similar to reservoir (124°C and 500psi); it was also made IFT tests with seawater at ambient temperature and atmospheric pressure to conclude about temperature and pressure influence in used system.

Figure 3 relate IFT values and the first 10 drops released for the three tests. It was showed the values of the first ten drops released because exists a repeatability of results when all thirty drops are considered; this make possible a detailed analyses of the first 10 released drops.

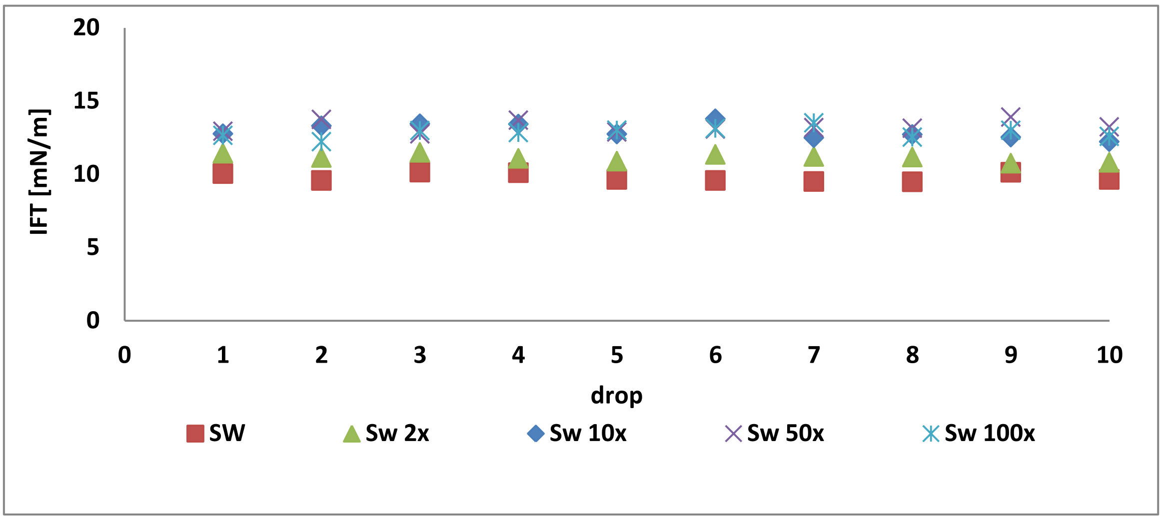

Figure 3. Values of the first ten drops released of IFT.

Through Figure 3 it is possible to conclude about IFT values; these values vary according dilutions. Exists an increasing IFT values when salinity decrease; seawater non-diluted and seawater diluted two and ten times proves these assumption; however system into forward seawater 10 times diluted the ions threshold concentration shown that seawater 10, 50 and 100 times dilutions are similar.
If IFT was measured in distilled water, the values should be higher than Sw diluted Sw 50 and Sw 100 times, because the system is empty of ions considerable
Figure 4 shows IFT values related to dilutions for three tests.

Figure 4. Values of IFT vs. dilutions considering the three tests.

For seawater diluted 2 and 50 times the IFT values, considering the three tests, are similar through Figure 4. In test 1, IFT increase with dilutions except in Sw100 times diluted, however in test 2, IFT values increase except in Sw and Sw10 times diluted; in test 3, IFT values also increase, except in Sw and Sw100 times diluted.

Contact angle in an oil/brine/rock system is used to measure the rock wettability. The principal aim is to figure out which salinity changes the wettability of rock to water wet to obtain a better oil recuperation. When contact angle is lower than 75° the rock is defined as water-wet, if it was between 75° and 115° is neutrally or intermediately wet and if it´s higher than 115° is oil-wet Anderson (1986). Figuring this experiment Attension Theta software measures the complementary angle. Figure 5 shows contact angle values by dilutions function.

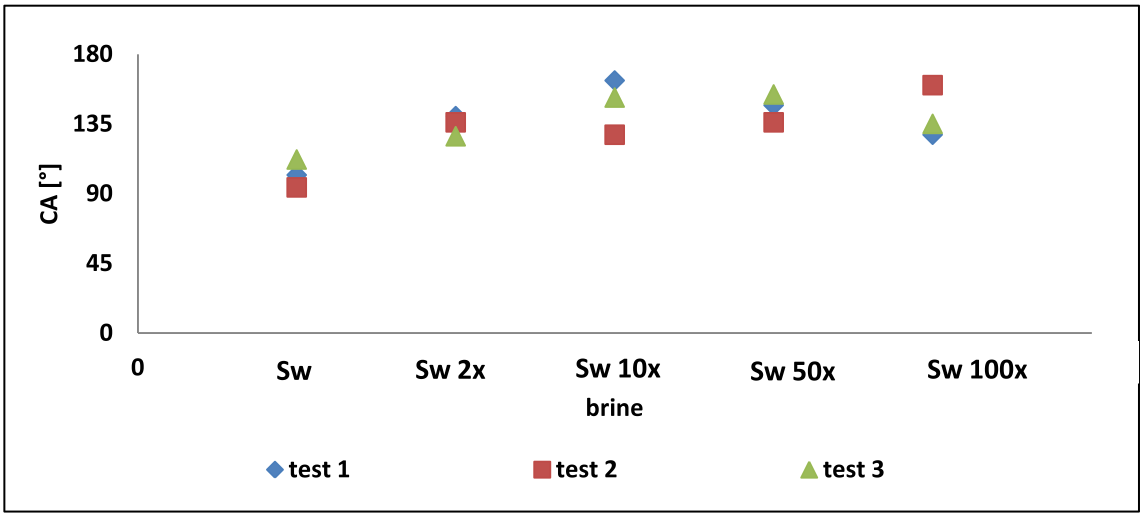

Figure 5. Values of CA vs. dilutions considering the three tests.

Through Figure 5, can be concluded when saline concentration decreases contact angle increases; rock changes the wettability from preferable neutral to water-wet.

Table 6 relates the interfacial tension (mN/m) and contact angle (degrees (°)).

Table 6. IFT (mN/m) and Contact Angle values (°).

	Sw		Sw 2x		Sw 10x		Sw 50x		Sw 100x	
	IFT(mN/m)	CA(°)	IFT(mN/m)	CA(°)	IFT(mN/m)	CA(°)	IFT(mN/m)	CA(°)	IFT(mN/m)	CA(°)
Test I	9.78	102	11.13	140	12.94	163	13.25	147	14.28	128
Test II	12.67	112	10.94	136	12.78	128	13.30	136	12.85	160
Test III	12.96	94	11.44	127	11.14	152	12.88	154	13.17	135

The density values for the different dilutions show that the higher the dilution, the lower the density value, a conclusion that can be achieved for any of the three conditions tested. The condition with the highest density value was in the undiluted brine at 25°C/5000psi, 1,03555 g/cm^3, while the lowest density was registered for the one-hundred times diluted brine at 124°C/5000psi, 0,95256 g/cm^3.

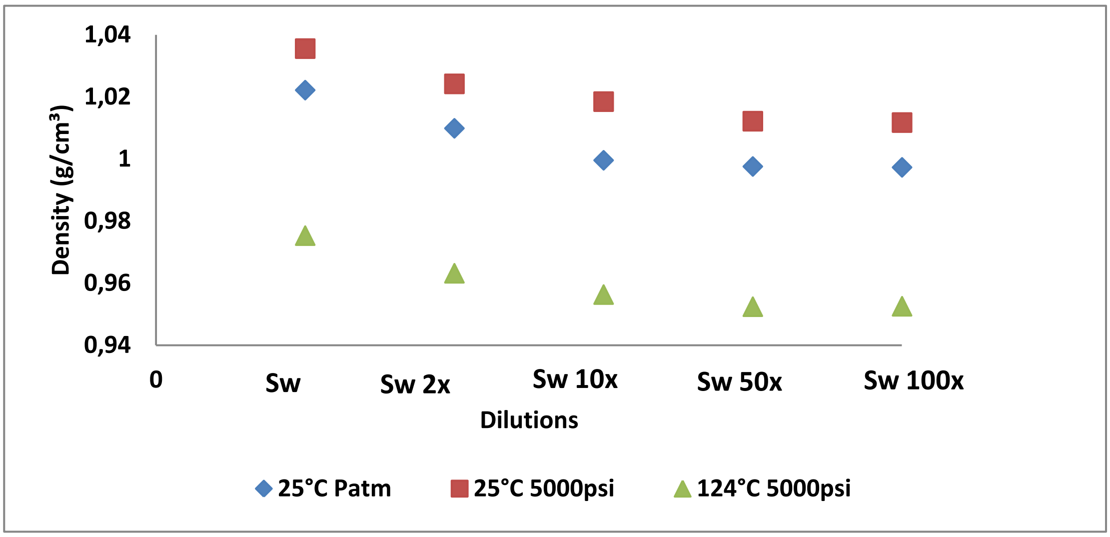

Figure 6. Density values of brine dilutions.

The density values of the oil as showed in Figure 6 were: 0.85347 g/cm^3 for 25°C/Patm, 0.87359 g/cm^3 for 25°C/5000psi and 0.82496 g/cm^3 for 124ªC/5000psi

Table 7. Oil density values.

	25°C Patm	25°C 5000psi	124°C 5000psi
Oil	0.85347 g/cm³	0.87359 g/cm³	0.82496 g/cm³

4. Conclusions

It therefore can be concluded that there exist variations in interfacial tension according to alterations in brine salinity. The lower a given solution’s salinity, the higher the interfacial tension will be.
Once the ionic concentration of the aqueous medium was increased (high polarity), it differentiates itself even more from the organic medium (low polarity).It would be expected that the results would be correlated in opposite ways. The hypothesis used to justify this unexpected behavior is based on the ionization of the oil used, given that it is considerably acidic (TAN = 1, 32 mg/gKOH).
As for the results of the contact angle it was proved that dolomite rock is water wet if we decrease the saline concentration.

5. Acknowledgements

Cepetro – Center for Petroleum Studies, IST – Instituto Superior Técnico, ANP – National Agency of Petroleum, Natural Gas and Biofuels, Unicamp – State University of Campinas, provided the infrastructure for tests. Authors would like to thank to Repsol Sinopec Brasil for funding and supporting this project.

6. References

AHMED, T. Reservoir Engineering Handbook. 2. ed. Houston, Texas: Gulf Professional Publishing, 2000.

ALOTAIBI, M.B., NASRALLA, R.A., NASR-EL-DIN, H.A. Wettability Challenges in Carbonate Reservoirs. In: SPE Improved Oil Recovery Symposium, 2010, Tulsa. Proceeding. USA: Society of Petroleum Engineers, n.1, 2010.

AUSTAD, T., SHARIATPANAHI, S. F., STAND, S., BLACK, C. J. J., and WEBB, K. J. Conditions for a Low-Salinity Enhanced Oil Recovery (EOR) effect in Carbonate Reservoirs. Energy & Fuels, USA, v. 26, p. 569-575, 2012.

CHANDRASEKHAR, S.; SHARMA, H.; MOHANTY, K. K. Wettability Alteration with Brine Composition in High Temperature Carbonate Rocks. SPE Annual Technical Conference and Exhibition, p. 1–17, 2016.

YOUSEF, A.A., AL-SALEH, S., AL-KAABI, A., and AL-JAWFI M. Laboratory Investigation of the Impact of Injection-Water Salinity and Ionic Content on Oil Recovery From Carbonate Reservoirs. SPE Reservoir Evaluation & Engineering, v. 14, n. 5, p. 578–593, 2011.

ZHANG, P. and AUSTAD, T. Wettability and Oil Recovery from Carbonates: Effects of Temperature and Potential Determining Ions. Colloids and Surfaces A: Physicochem. Eng. Aspects, 279, p. 179-187, 2006.