



## INVESTIGATION OF THE KEY PARAMETERS AFFECTING WETTABILITY OF A BRAZILIAN PRE-SALT CRUDE OIL AND BRINE ON PURE MINERALS THROUGH STATISTICAL ANALYSIS

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### ABSTRACT

Wettability is a fundamental property that defines the fluid's distribution in oil reservoirs. Assessing wettability is required to model flow in porous media. Nevertheless, it involves complex intermolecular and surface forces. Contact angle measurement is a quantitative method to determine wettability. However, rock samples must be prepared to assure results representative of reservoir conditions. This work applies statistical analysis to investigate the relevance of variables involved in sample preparation (aging time, solvent used to remove the excess oil from the surface) and mineral type on the wettability of oil and brine from a Pre-Salt field on pure minerals. Since there is limited experimental wettability data at Pre-Salt conditions, this work aims to assist filling this gap. The results showed aging time and mineral type as the most important parameters for analysis. Furthermore, authors found that greater aging time in oil and point of zero charge of the mineral lead to a more oil-wet behavior.

### KEYWORDS

wettability; contact angle measurement; Pre-Salt reservoirs; rock aging; ANOVA

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## 1. INTRODUCTION

Wettability is of paramount importance to describe an oil reservoir accurately. It affects critical properties, such as relative permeability and capillary pressure, determining the distribution of the fluids in the pore volume and the flow capacity of each phase in the porous medium. Wettability is the result of the balance between complex intermolecular and surface interactions, which include electrostatic, van der Waals, dispersion, and disjoining forces (Donaldson & Alam, 2008).

According to the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), the fields in the Campos and Santos basins have aided in the 25% increase of Brazil's oil production representing over 50% of the total production at the present time (ANP, 2018). However, these reservoirs consist of complex heterogeneous carbonate rocks, light and medium oils, and brine salinities over 200,000 ppm (Pepin et al., 2014; Pizarro & Branco, 2012). This unique environment represents a challenge in terms of wettability assessment and reservoir modeling. While there are descriptions of the Pre-Salt rocks in the literature (Pepin et al., 2014; Teles et al., 2016), there is no detailed data describing their wettability.

Contact angle measurement (CA) is one of the most widely accepted techniques to evaluate the wettability of a rock under reservoir conditions. It derives from the balance between the adhesion and cohesive forces when a drop rests on a solid surface surrounded by an external fluid (Young, 1855). When measured throughout the denser fluid phase (brine), a lower CA represents a greater interaction between this fluid and the solid. Thus, for a drop of oil on a rock surrounded by brine, the lower the contact angle, the more water-wet the mineral is. This is exemplified elsewhere (Haagh et al., 2017). As a result, it is expected that brine will locate preferentially in the smaller pores and oil in the greater ones (Ahmed, 2010). Surfaces with CA values lower than 70 are considered water-wet. Moreover, values between 70° and 110° are intermediate-wet, and values over 110° are oil-wet.

Although its application assumes smooth and homogeneous surfaces, it is used to infer wettability trends (Morrow, 1975). Moreover, to assess the initial wettability under representative

conditions, the rock must be put in contact with reservoir fluids (*i.e.* oil and brine) in a process called aging (Marzouk, 1999). Previous studies compared the CA measured in unaged and aged calcite, quartz, and mica (Seyyedi et al., 2015). They obtained considerable changes after aging, but no evaluation under different aging time was performed. Despite being necessary to achieve meaningful CA measurements, the relevance of aging on the final CA values was never studied in the Pre-Salt environment.

Several works used contact angle to study wettability of oils from diverse formations in the world considering both rocks and minerals (El-Yamani et al., 2017; Rajayi & Kantzas, 2009; Teklu et al., 2015). However, none of these included brines of salinity and hardness as high as that of the Pre-Salt reservoirs. Also, none of them focused on the minerals which are the major components of Pre-Salt rocks (Pepin et al., 2014). A recent study (Al-Khafaji & Wen, 2019) considered the wettability of different crudes on limestone and dolomite rocks as a function of brine salinity. This work contains measurements for oils with varied SARA composition and brines up to 200,000 ppm salinity. They concluded that decreasing brine salinity could shift wettability towards neutral-wet, but this was also a strong function of oil composition. This shows that, as wettability trends generalization is usually not possible, it is important to consider each unique rock-brine-oil scenario to evaluate wettability. Other study (Karimi et al., 2016) also considered wettability alteration of aged calcite by measuring the CA of a high-salinity brine drop under a decane environment. Mineral slabs were aged for ten days in crude oil and the excess bulk oil was removed with toluene. They used low-salinity brine and cationic surfactants to increase the water-wet behavior of the mineral and concluded that magnesium and sulfate ions have a key role in this process. Other publication (Castro Dantas et al., 2014) reported the same effect for the wettability alteration by cationic, anionic and nonionic surfactants. In this case, limestone rocks from Jandaira formation in northeast Brazil were aged for 48 hours in oil, and CA was measured using a crude oil from Ubarana Field (Potiguar Basin, northeast Brazil) and a 20,000 ppm KCl solution. They concluded that all the tested surfactant solutions shifted the rock's wettability from neutral to water-wet.

Some initial wettability measurements using Pre-Salt reservoir fluids were recently published (Facanha et al., 2016). Nevertheless, no systematic study evaluating the impact of the variables involved in contact angle measurement (*i.e.* aging time, bulk oil from the surface cleaning process) were discussed. To the best of our knowledge, no research has discussed how these parameters affect measured wettability to the present date.

In this work, the authors propose a statistical analysis to compare the relevance of three variables (aging time, type of mineral and solvent used to remove the excess oil from the surface of the rock) on the measurement of the CA using Pre-Salt fluids and pure minerals as rocks. In addition, data optimization was applied to identify the equilibrium value for each measurement improving the analysis of the copious results database. This procedure is innovative and represents a valuable tool to define a reliable method for CA measurement under reservoir conditions to obtain wettability trends from a large number of measurements.

## 2. MATERIALS AND METHODS

### 2.1 Experimental methods

Calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and quartz ( $\text{SiO}_2$ ) with 99% purity were supplied by Wards Science. The point of zero charge (pzc) is the pH of an aqueous phase in contact with a solid surface at which the net charge of the solid is zero (Mahmood et al., 2011). The pzc for calcite (9.5 at 20°C), dolomite (7.0 at 20°C) and quartz (3.0 at 25°C) were obtained from the literature

(Kosmulski, 2011; Al Shalabi & Sepehrnoori, 2017). N-hexane, cyclohexane, n-hexadecane and toluene were purchased from Sigma Aldrich with purities over 99%. The dielectric constants for the different substances as found in the literature are shown in Table 1.

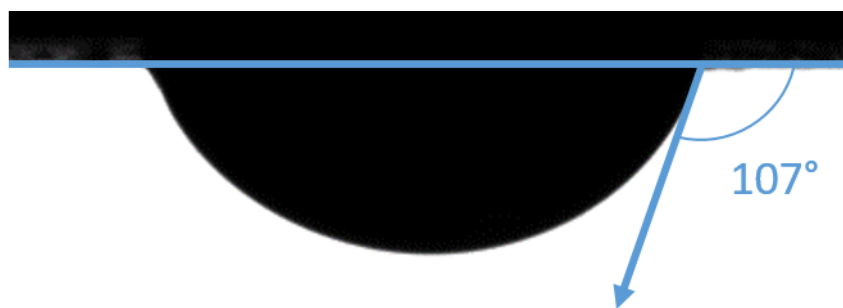
Formation brine with total dissolved solids (TDS) of 226,694 ppm was prepared in the laboratory following the composition of a Pre-salt field. Shell Brasil supplied a sample of crude oil from this field with an API of 26. The ionic composition of formation brine and the SARA analysis of the crude oil for this field can be found elsewhere (Facanha et al., 2016).

Rock slabs with 2.54 cm x 2.54 cm dimensions and 0.3 cm thickness were obtained from the mineral samples. Then, they were immersed for 1 day in formation brine and for 1, 3, 5, 15 and 30 days in crude oil at reservoir temperature (60°C). Afterwards, five drops of a solvent were applied to remove the excess of oil on the surface of the mineral. This excess oil must be removed to allow the contact of the droplet with the aged surface (Seyyedi; Sohrabi; Farzaneh, 2015). Finally, the excess of solvent was removed flushing with formation brine. The solvents tested in this work were n-hexane, cyclohexane, n-hexadecane, toluene, and formation brine.

Contact angle measurements were carried out at 1,000 psi (6.89 MPa) and 60°C using a high pressure and temperature (HTHP) Drop Shape Analyzer (DSA) apparatus designed by Kruss and Eurotechnica. After aging, the rock sample was placed in the equipment's chamber, which was filled with formation brine. Then, the pressure and temperature were stabilized to the desired values.

**Table 1.** Dielectric constant ( $\epsilon$ ) of different substances and source from the literature.

Substance	$\epsilon$	Source
Air	$\cong 1.000$ (25°C)	(Hector & Schultz, 1936)
N-hexane	1.890 (20°C)	(Haynes, 2015)
Cyclohexane	2.015 (25°C)	(Maryott, 1951)
N-Hexadecane	2.090 (25°C)	(Aralaguppi et al., 1991)
Toluene	2.379 (25°C)	(Maryott, 1951)
Water	78.540 (25°C)	(Maryott, 1951)



**Figure 1.** Scheme illustrating the Contact Angle (CA) measurement.

Finally, a drop of oil was injected and images were continuously acquired measuring both left and right contact angles every 30 seconds. The experiments were continued for 24 hours. More detailed description of the experimental procedure can be found elsewhere (Facanha et al., 2016). The contact angles were measured towards the denser phase (brine) as illustrated in Figure 1; thus, a greater contact angle value represents more oil-wet behavior and a lower contact angle value indicates water-wet behavior.

## 2.2 Data analysis methods

To identify the equilibrium CA, the raw collected data was processed using Visual Basic for Applications (VBA) in Microsoft Excel®. This is to avoid misinterpretations of the stable values due to the large volume of data. The total dataset corresponding to each experiment was divided in intervals of 10 measurements each. For each interval, three criteria were used to identify the equilibrium value. First, the amplitude (difference between maximum and minimum values) had to be lower than one. Then, the variance of the values in the interval should be below 0.05. Finally, the slope of the linear regression had to be between -0.05 and 0.05. The stability frequency (SF) for each data point was calculated as the number of preceding measurements that satisfied all three criteria. In addition, the standard deviation (SD) and relative standard deviation (RSD) were calculated to check the consistence of the results within each interval. Finally, the CA and the SF were plotted versus time to aid in the identification of the most stable CA value for each measurement. The reported value was the arithmetic mean of the values in the most stable interval.

The statistical analysis of the experimental data was performed using Statsoft Statistica 7.0®. The

points of zero charge included in section 2.1 were used as input variables for the mineral rock since they are key to determine the electrostatic interactions between the rock and the fluids. Moreover, the solvents used to eliminate the excess of oil from the surface were represented by their dielectric constants (Table 1) representing their polarities. For the use of brine as a solvent, the dielectric constant of water was considered. This does not affect the data analysis because both water and brine have greater dielectric constants than the other substances contemplated in this work. In addition, for the experiments in which no solvent was used, the dielectric constant of air was applied.

A Correlation matrix was constructed as a preliminary tool to check expected patterns and relationships between the independent variables/factors (*i.e.* solvent, mineral and aging time) and the dependent variable (*i.e.* contact angle). Afterwards, a more complete set of statistical tools was used: ANOVA, Pareto Chart of Effects and Multiple Linear Regression to emphasize the statistical significance of the tendencies found in the preliminary analysis.

## 3. RESULTS AND DISCUSSIONS

For each experiment, the equilibrium contact angles were obtained following the procedure in Section 2.2, and the results are summarized in Table 2.

The first statistical tool to be used was the correlation matrix. The matrix considering the mineral type, aging time in brine and oil, solvent used for cleaning surface excess oil and CA as variables is shown in Table 3.

**Table 2.** Contact angle (CA) results on different minerals for the experiment considering different aging times in brine ( $T_{\text{brine}}$ ) and oil ( $T_{\text{oil}}$ ) and solvents to remove the excess oil from the surface.

Mineral	Test	$T_{\text{brine}}$ (days)	$T_{\text{oil}}$ (days)	Solvent	CA (°)
Quartz	1	0	0	None	82
	2	1	3	Brine	93
	3	1	3	N-hexane	180
	4	1	3	Cyclohexane	64
	5	1	3	N-hexadecane	107
	6	1	3	Toluene	60
	7	1	15	Cyclohexane	144
	8	1	30	Cyclohexane	89
Calcite	9	0	0	None	52
	10	1	3	Brine	77
	11	1	3	N-hexane	71
	12	1	3	Cyclohexane	61
	13	1	3	N-hexadecane	92
	14	1	3	Toluene	100
	15	1	15	Cyclohexane	163
	16	1	30	Cyclohexane	114
Dolomite	17	0	0	None	50
	18	1	3	Brine	83
	19	1	3	N-hexane	129
	20	1	3	Cyclohexane	64
	21	1	3	N-hexadecane	103
	22	1	3	Toluene	53
	23	1	15	Cyclohexane	96
	24	1	30	Cyclohexane	143

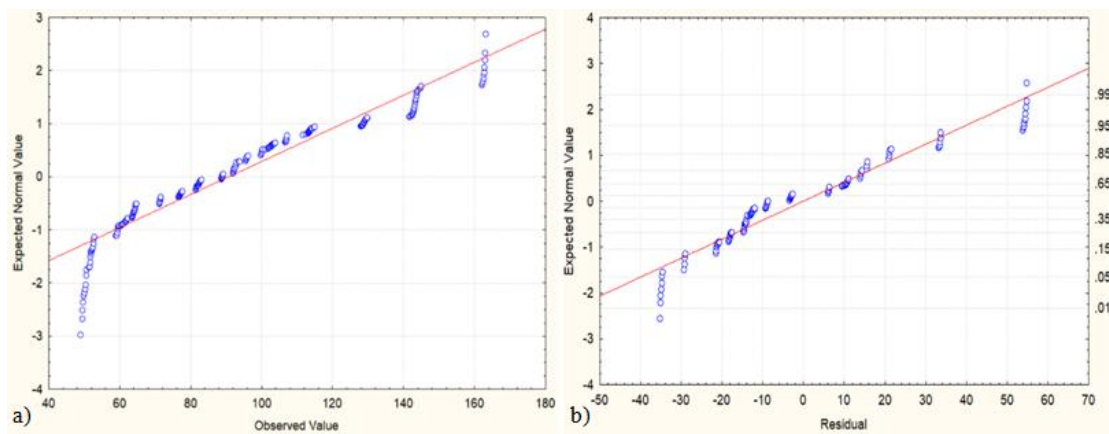
**Table 3.** Correlation matrix considering mineral type, aging days in brine ( $T_{\text{brine}}$ ) and oil ( $T_{\text{oil}}$ ), solvent dielectric constant, and contact angle (CA). Values in red indicate statistical significance with  $\alpha = 5\%$ .

	Mineral	$T_{\text{brine}}$	$T_{\text{oil}}$	Solvent	CA
Mineral	1.00	0.02	-0.03	-0.02	0.00
$T_{\text{brine}}$	0.02	1.00	<b>0.31</b>	<b>0.16</b>	<b>0.37</b>
$T_{\text{oil}}$	-0.03	<b>0.31</b>	1.00	<b>-0.19</b>	<b>0.56</b>
Solvent	-0.02	<b>0.16</b>	<b>-0.19</b>	1.00	-0.08
CA	0.00	<b>0.37</b>	<b>0.56</b>	-0.08	1.00

The matrix fields are Pearson's Correlation Coefficients (PCC) for each pair of variables and the values in bold and red indicate statistical significance with  $\alpha = 5\%$ . It is evident that the aging time in oil had the highest positive correlations with the contact angle, concluding that the higher the aging time, the greater the oil-wet behavior of the rock. This indicates that aging is a crucial part of sample preparation, and longer aging times are

required to establish initial wettability for minerals with greater interaction with the oils, such as calcite with the oil used in this work. This needs to be taken into account to obtain meaningful CA measurements.

The second statistical tool to assess the CA data obtained was the ANOVA. Before the analysis, ANOVA's premises were checked. First, the normality of the population was verified with a



**Figure 2.** (a) Normal Probability Plot of CA data. The straight line is a perfect fit to Normal Distribution; (b) Normal Probability Plot of Residues. The straight red line indicates a perfect fit to Normal Distribution.

Normal Probability Plot, as shown in Figure 2a. As it can be observed in the plot, the CA population contains a few outliers if compared to a Gaussian distribution. Descriptive Statistics actually show that the CA distribution is slightly asymmetrical (asymmetry coefficient equal to 0.67) and platykurtic (Excess Kurtosis equal to -0.34). This deviation of normality was considered to be negligible for the objectives of this study.

Secondly, ANOVA's homoscedasticity (equal variance among populations or subpopulations) premise was analyzed. The subpopulations (*i.e.* set of data obtained from each experiment) which did not fulfill this rule were excluded from the analysis. It is important to highlight that this choice changes the Universe of the study and that parameter estimation of the excluded subpopulations configures a Statistical Induction.

Finally, ANOVA's independent subpopulations premise was fulfilled, since all experiments were randomly performed. Before presenting ANOVA results, it is important to verify the normality of the residues. Figure 2b shows the Normal Probability Plot of the residues, indicating the same slight deviation from normality, which was also

considered negligible.

The ANOVA results are shown in Table 4. As concluded by the correlation's matrix analysis, the aging time in oil proved to be the most influential variable, with the highest  $F$  statistic. The mineral variable also proved to be influential with statistical significance, proving that surface charge determines the CA value obtained. Although the solvent used to remove the excess oil is a relevant parameter, the analysis showed no statistical significance, meaning that there is no direct correlation between the polarity of the solvent and the CA value. This can be explained due to the complex chemical and physical interactions that take part, which include oil solubility, asphaltene precipitation, electrostatic forces and interfacial tension among others.

Performing a Multiple Linear Regression on CA data, the best fit according to Least Squares Method is shown in Equation 1:

$$CA = 54.65612 + 1.92950 M + 7.22438 T_{brine} + 1.86603 T_{oil} + 0.04950 S \quad R^2 \cong 0.38 \quad (1)$$

**Table 4.** ANOVA analysis considering mineral type, aging days in brine ( $T_{brine}$ ), and oil ( $T_{oil}$ ), solvent dielectric constant. Values in red indicate statistical significance with  $\alpha = 5\%$ .

Variable	SS	DOF	MS	F	p-value
Mineral	9627.1	1	9627.06	17.5665	0.000036
$T_{brine}$	1569.4	1	1569.35	2.8636	0.091593
$T_{oil}$	83126.4	1	83126.38	151.6808	0.000000
Solvent	629.5	1	629.52	1.1487	0.284646
Residual	172631.0	315	548.03	--	--
Total	267583.3	319.0	--	--	--

In the linear model above, CA is the contact angle, M is the mineral (point of zero charge),  $T_{brine}$  is the aging time in brine (days),  $T_{oil}$  is the aging time in oil (days), and S is the solvent (dielectric constant). Of the coefficients, only M and  $T_{oil}$  reached statistical significance with  $\alpha = 5\%$  and, because of that, they are highlighted in bold. It should be observed that these coefficients are positive. Therefore, the higher the point of zero charge and the higher the aging time in oil are, the higher the CA will be. This supports the previous discussions showing that calcite results in more oil-wet behavior after aging, followed by dolomite and quartz in agreement with the trends found elsewhere (Seyyedi et al., 2015).

As for the  $R^2$  of the model, one can conclude that roughly 38% of CA values' variability is

explained by the independent variables considered in this study confirming the non-linearity of surface phenomena. This is expected as wettability is ruled by complex interactions including adsorption, acid-base behavior and electrostatic forces (Buckley et al., 1997; Yu & Buckley, 1997) and cannot be isolated into single parameters. Figure 3 illustrates the fitted model (red line) and the experimental data (blue circles). One of the main utilities of the  $R^2$ , in the case of low values (below 0.5), is to suggest a model's complexity enhancement (e.g. adding more independent variables, such the interfacial tension between the solvent and each liquid phase). In any case, it is relevant to point out that the non-linearity does not influence the statistical analyses performed: the result of the Multiple Regression is the best linear model to the observed phenomenon and, regarding that model,

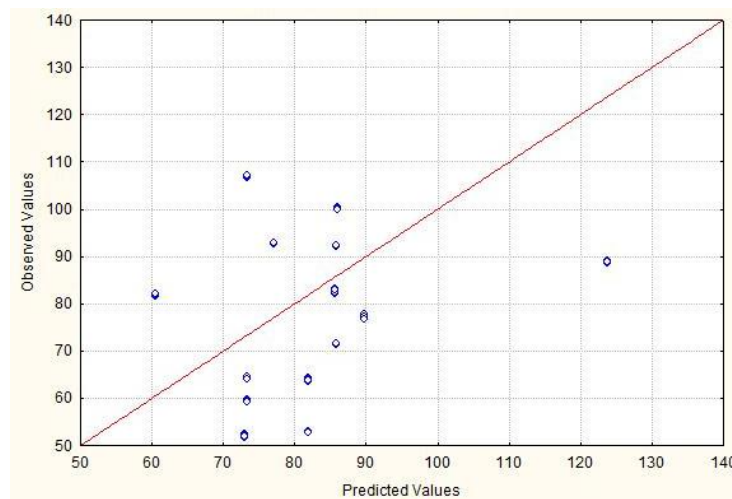


Figure 3. Fitted linear model by Multiple Regression (red line) and the experimental data (blue circles). It is clear to observe the non-linearity of the phenomenon.

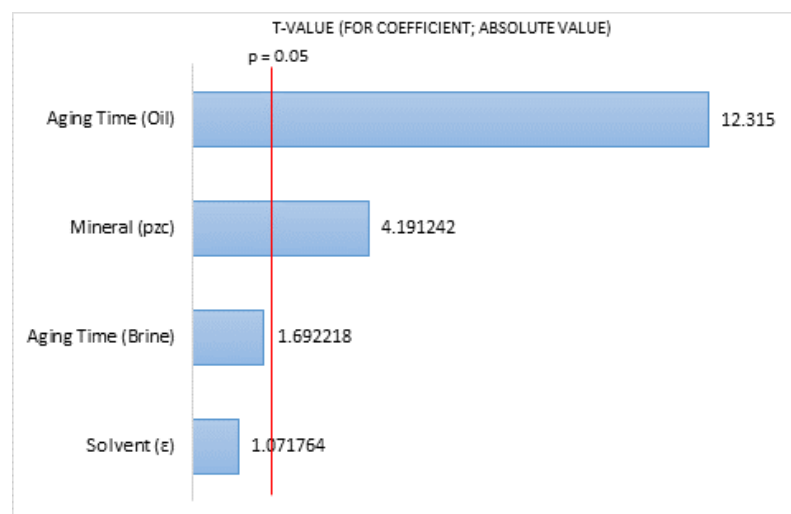


Figure 4. Pareto Chart of Effects for the CA data. The vertical red line highlights the statistical significance threshold (with  $\alpha = 5\%$ ). All bars to the right of the threshold indicate that the corresponding variable is statistically significant.

the most influent independent variables are the ones found by ANOVA.

The last technique to be used was the Pareto Chart of Effects. Figure 4 shows the results. Once again, it is possible to observe that the most influent variable to CA results is the aging time in oil, followed by the mineral (both with statistical significance,  $\alpha = 5\%$ ).

#### 4. CONCLUSIONS

This work presents a statistical analysis to study the influence of mineral, solvent used to remove bulk oil and aging time in oil on the measured CA to obtain wettability. There is no systematic study including these variables, which determine the results of the CA measurement. Thus, this work is novel in proposing a quantification of the relevance of these parameters in CA measurement. In addition, it is the first study showing CA results with Pre-Salt oil and brine using different aging times and bulk oil removing solvents.

The aging time in oil and the mineral type proved to be the most relevant variables to affect wettability. The greater the point of zero charge (*i.e.* for calcite) and the aging time in oil is, the stronger the oil-wet behavior will be. The solvents used for removing the excess oil didn't show a clear trend as the previous parameters. It is relevant to highlight that 75% of the statistical analyses performed identified the aging time in oil and the mineral as the main factors of the experiments, with both reaching statistical significance ( $\alpha = 5\%$ ). Therefore, one can affirm with 95% of confidence that the variation between these variables and the CA is the result of a meaningful relationship.

Moreover, the results confirmed that the rocks were more oil-wet for longer aging times in oil and higher the point of zero charge (resembling to those of Pre-Salt carbonates). This is in agreement with results found in the literature for crude oil and high salinity brines at reservoir conditions. As a result, aging time in oil for over than 15 days is required to obtain meaningful results considering CA measurements in carbonate minerals.

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