# Wettability of Coquinas from Morro do Chaves Fm.

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### Abstract

The pre-salt play in Brazil placed the country among the top 10 producers in the world. Such giant reservoirs exhibit complex geology that impacts the pore system and consequently the fluid flow. The study of outcrop analog formations can improve the understanding of the permo-porosity behavior of the pre-salt rocks, once the assessment to geological samples is often more accessible, cheaper and outnumbers the sample collection through costly coring operations in deep water environments. Wettability is one of the rock properties that influence the fluid flow and can only be inferred by lab tests on core samples. In this work, a set of Coquinas samples extracted from Morro do Chaves Fm. was investigated for determining the contact angle between an oil drop and the surface of the studied rocks in a brine-oil system. Apart from those wettability measurements, mineral content and porosity were also estimated, allowing the evaluation of the relationship between the contact angle, mineral fractions and porosity through data analysis assisted by multivariate linear regression. Such a technique resulted in a high accuracy prediction model.

### Introduction

Carbonate reservoirs are the object of studies worldwide due to their significant hydrocarbon concentration. In Brazil, the attention on carbonate reservoirs increased with the pre-salt discovery and continued growing since the oil production from this area has shown to be very favorable. One of the constituent rocks of the pre-salt is the called Coquinas, composed originally of carbonate shells.

The wettability of a system is the property that dictates the solid's preference to be wet for one fluid or another. This property impacts the initial distribution of hydrocarbons in the reservoir. It influences other major reservoir properties as capillary pressure, relative permeability, irreducible water saturation and hence, the final oil recovery as it indicates how they will behave in the presence of the fluid of a recovery mechanism. The wettability in a reservoir in turn, depends on the rock mineral composition, as well as on the oil and brine composition and finally, on the interaction between these three factors. The assessment of reservoir wettability aids the decision for the best oil recovery technique.

Some studies have shown that the oil composition is a key factor in wettability alteration, mainly due to the polar compounds in asphaltenes and resins in its composition (Abdallah *et al*., 2007, Blunt (2017)). Additionally, Blunt (2017) indicates that this alteration in wettability does not occur in all the systems, but generally, in calcite substrates, this alteration tends to be stronger. This finding was also obtained by Costa (2019).

Other studies indicate that reservoir carbonate samples tend to be oil-wet (Treiber *et al*., 1972). Leon (2013) defined the wettability of systems composed of carbonate Coquina samples, brine and mineral oil as fractioned, tending to oil-wet.

This work aims to determine the wettability to the Coquinas outcrop samples in their natural state, from the Morro do Chaves Formation, in the Sergipe-Alagoas basin, which is equivalent of the Coquinas from the pre-salt of the Santos and Campos basins. The wettability was measured in a system composed of reservoir oil and synthetic brine by the contact angle method. Additionally, this study looked for a relation between the contact angle value and the mineral composition.

### Geological Background

The present work uses coquina rock samples from Morro do Chaves Formation. The carbonate rocks present in the Fm. Morro do Chaves are generally described as coquinas, with grain sizes varying from sand to pebble, grain or supported matrix, with absence or abundance of carbonate cement (Buckman et al., 2017; Hoerlle et al., 2017; Luna et al., 2018; Luna et al., 2015; Rigueti et al., 2020; Tavares et al., 2015).

The study of Fm Morro do Chaves (bioclastic deposits) is proven essential because of the similarities from those rocks, called coquinas, with others carbonate deposits of some Brazilian pre-salt basins. The definition of the term coquina, produced by Schäfer (1972), characterizes this lithotype as accumulations produced solely by shells or pieces of shells deposited by the action of a transport agent. However, as noted by Tavares et al. (2015) for the Morro do Chaves coquinas and other similar deposits, the coquinas are not only composed of shells and their fragments, but siliciclastic material is commonly present.

According to Rigueti et al. (2020), the main siliciclastic grains present concurrently with the shells and fragments are quartz, feldspar, and igneous and metamorphic lithoclasts. Tavares et al. (2015) and Corbett et al. (2016) also mention the presence of pyrite and clay minerals, resulting from the reworking of shales interspersed with thick packages of coquinas. Despite being rocks composed of fragments of miniature animal shells, the laws of sedimentation prevail over biological laws, so that physical processes are more impactful in the composition of the rock than biological selection (Schäfer, 1972).

## Methodology

*Wettability measurements*

The wettability of the Coquinas was accessed by the contact angle (θ) method, which analyzes the interaction between a slice of rock, and two fluid phases, measuring the angle formed between the rock sample surface and a drop of one phase, being surrounded by the other phase. The angle is measured through the denser phase. In this work, the systems were composed of brine (5% NaCl), dead oil from the Campos basin and Coquinas samples of around 0.85 cm in length and 3.8 cm in diameter. The characteristics of the oil used in the experiments are listed in Table 1.

Table 1 - Physical properties of the oil used in the experiments.

| | |
|---|---|
| Density (g/cm³) | 0.916 |
| API° | 23 |
| Viscosity (cP) at 25°C | 54.81 |

The experiment was performed in two samples of each rock, for validation purposes at room temperature.

First, the sample was cleaned and dried in the oven at 60°C. Then, it was saturated with brine and submerged in this very brine, in a glass vessel. A drop of oil was released with a syringe below the sample, without touching it. A digital camera took a picture of the system soon after the oil drop reached the sample bottom face (Fig 1). To check the system stability, two other shots were taken in a two-hour interval between them, and the angles were measured in all the three pictures using the DSA4 software from KRUSS (Fig 2). The final θ value was an average of the two samples of each rock. The wettability classification followed that of Fanchi (2010), shown in Table 2.

*Gas Porosimetry*

Gas porosimeter Ultrapore 300 (Fig. 3) was used to calculate the porosity. This equipment is based on Boyle's law (Eq. 1) that relates the volume-pressure-temperature variation of gas in two different situations.

$$\frac{P1V1}{T1}=\frac{P2V2}{T2} \qquad (1)$$

Where $P$ is the pressure in Pascal, $V$ is the volume in m³ and $T$ is the temperature in Kelvin.

The Ultrapore 300 equipment has a graphical interface called Winpore software, which receives the samples' weight, diameter, and length as input; and output the total volume, grain density, and effective porosity.

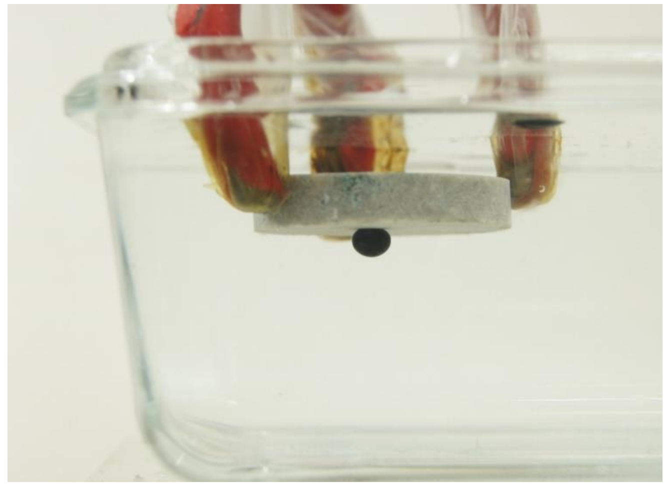

Figure 1: The system composed of a coquina sample (2-AC), brine and an oil drop.

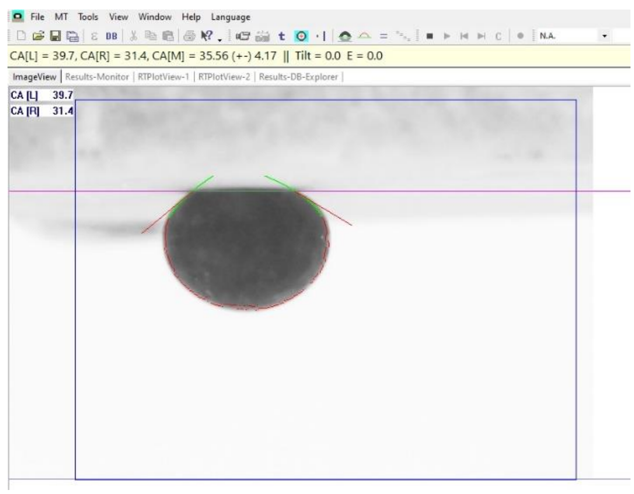


Figure 2: The contact angles measure using the DSA4 software

Table 2: Wettability classification after Fanchi (2010).

| Contact Angle (degree) | Wetting Condition |
|---|---|
| 0-30 | Strongly Water-wet |
| 30-75 | Moderately Water-wet |
| 75-105 | Neutrally-wet |
| 105-150 | Moderately Oil-wet |
| 150-180 | Strongly Oil-wet |

*Mineral Content Evaluation*

Figure 3: UltraPore 300 equipment.

X-ray powder diffraction measurements were carried out using a D2 PHASER (Bruker AXS) instrument using Cu Kα radiation equipped with a diffracted-beam monochromator (Fig. 4). A glass sample holder was carefully filled with the fine powder samples. The surface of the packed powder was pressed and smoothed with a piece of flat glass. The experiment was made at room temperature, and the diffraction patterns were recorded with the following measurement conditions: 2θ from 5° to 70°, 2θ step scan of 0.02°, and counting time of 2 s/step. The total scan time for each sample was 115 min. The voltage and current to the x-ray source were pre-set to 30 kV and 10 mA, respectively. XRD patterns were collected in Bragg-Brentano geometry. An AXS KORUNDPROBE - A26-B26-S disk was used for calibration of the D2 PHASER equipment. We used commercial software EVA and TOPAS to identify and quantify the mineral phases, respectively.


Figure 4: D2 PHASER X-ray Diffractometer from Bruker AXS used in the analysis.

*Multivariate Linear Regression Analysis*

The multivariate linear regression (MLR) is a data analysis technique for obtaining a model for predicting a response variable (Y) that depends on one or more ($x_1 \dots x_n$) measured independent variables (predictors). The typical MLR model is represented by Eq. 2:

$$Y = a_1.x_1 + a_2.x_2 + \dots + a_n.x_n + b \qquad (2)$$

Where $a_i$ are the coefficients for each predictor $x_i$ and $b$ is the slope.

In this work, the MLR analysis was performed using Excel/ ANOVA software.

**Results**

The results of the mineral content of the Coquinas samples obtained through XRD are listed in Table 3. Calcite is the major content of those rocks, while quartz exhibits a great variation. Other minor contents as orthoclase, microcline, pyrite and illite are also found in those rocks.

Table 3: Mineral content of Coquinas samples estimated through XRD.

| Sample | Calcite (%) | Quartz (%) | Ortoclase (%) | Microcline (%) | Pyrite (%) | Illite (%) |
|---|---|---|---|---|---|---|
| 1-A | 45.63 | 45.21 | 0 | 7.03 | 1.78 | 0.35 |
| 1-C | 61.95 | 30.19 | 6.59 | 0 | 1.27 | 0 |
| 2-AA | 98.34 | 1.39 | 0.26 | 0 | 0 | 0 |
| 2-AC | 99.23 | 0.77 | 0 | 0 | 0 | 0 |
| 2-AD | 98.82 | 1.18 | 0 | 0 | 0 | 0 |
| 2-BA | 97.01 | 2.45 | 0.53 | 0 | 0 | 0 |
| 2-BC | 98.75 | 1.10 | 0 | 0 | 0.15 | 0 |
| 2-BE | 97.98 | 1.85 | 0 | 0 | 0.16 | 0 |
| 3A | 95.83 | 2.20 | 0.06 | 0 | 1.91 | 0 |
| 11-A | 54.14 | 37.05 | 2.38 | 0 | 6 | 0 |

Gas porosimetry experiments provided quantitative information regarding porosity and grain density of the studied rocks, as displayed in Table 4.

All the samples were classified as moderately water-wet and presented their contact angle values within a narrow range. These samples exhibited a water-wet behavior, which agrees with the literature that most clean rocks (with a low clay content) are naturally water-wet (Blunt, 2017). The measured θ values were close due to similar mineralogical composition. Fig. 5 shows a trendline of the system to become more water-wet once the contact angle decreases as the calcite to quartz ratio increases. The different dot colors are related to each sample' porosity. Such *a* linear trend resulted in a coefficient of determination ($R^2$) of 0.818.

Table 4: Porosity and Grain Density obtained through gas expansion porosimetry.

| Sample | Porosity (%) | Grain Density (g/cm³) |
|---|---|---|
| 1-A | 5.23 | 2.66 |
| 1-C | 6.06 | 2.66 |
| 2-AA | 8.87 | 2.70 |
| 2-AC | 7.61 | 2.70 |
| 2-AD | 7.62 | 2.70 |
| 2-BA | 13.82 | 2.69 |
| 2-BC | 9.16 | 2.71 |
| 2-BE | 2.69 | 2.71 |
| 3A | 4.33 | 2.71 |
| 11-A | 20.35 | 2.67 |

Table 5 shows the contact angle value obtained for the Coquinas samples in their natural state, namely, cleaned and saturated with brine.

Table 5: Contact angle value and wettability classification.

| Sample | θ ± .0.05 (degree) | Classification |
|---|---|---|
| 1-A | 41.47 | Moderately water-wet |
| 1-C | 40.80 | |
| 2-AA | 38.80 | |
| 2-AC | 36.20 | |
| 2-AD | 37.00 | |
| 2-BA | 40.40 | |
| 2-BC | 37.30 | |
| 2-BE | 36.90 | |
| 3A | 39.40 | |
| 11-A | 40.80 | |

The crossplot shown in Fig. 5 highlights the great influence of the mineral content on the contact angle. To improve the quantification of such a relationship, an MLR was applied to predict the contact angle based on the mineral fractions inferred by the XRD. Those MLR analyses showed that when considering only the two major mineral fractions, calcite and quartz, the coefficient of determination ($R^2$) of such prediction is 0.666 (Fig. 6 – I). If other mineral fractions are included as predictors, the $R^2$ increases to 0.840 (Fig. 6 – II). When adding porosity as a predictor, the $R^2$ increases up to 0.983, as can be observed in Fig. 6 - III. The coefficients of the MLR are presented in Table 6.

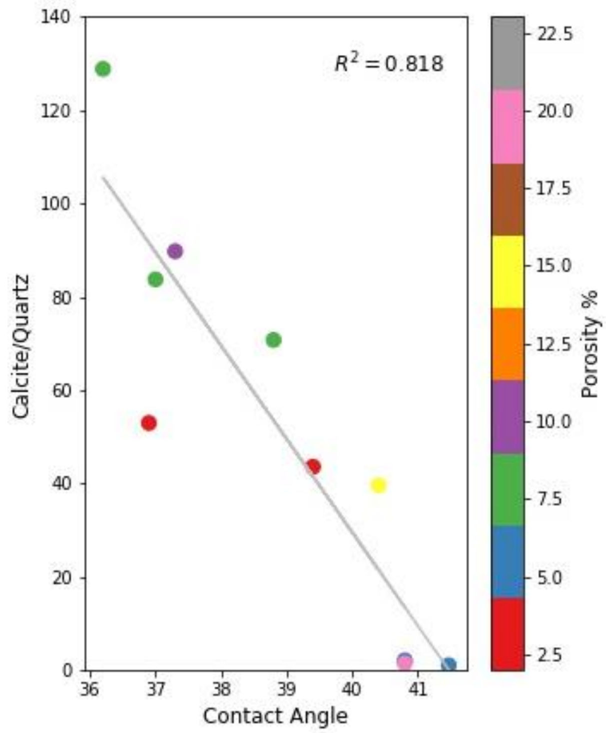


Figure 5: Calcite/quartz content relation with the contact angle of the Coquina samples. Higher ratios correspond to smaller angles. The third axis corresponds to the porosity of each sample.

**Conclusions**

The results differ from what was reported by Leon (2013), which classified the Coquina samples studied as presenting a fractioned wettability with a preference to be oil-wet. One factor that significantly influences this conflicting result is the difference in the oil used in the experiments: the mineral oil used in the mentioned work were much less dense (0.84 g/cm$^3$) and less viscous (24 cP at 23° C) than the crude one used in this work. Moreover, the wettability on this work was measured in the natural state and not after an aging process (Costa, 2019). That procedure might alter the rock wettability, mainly in the presence of such a heavy oil.

Once the same fluids were used during our experiments and no aging process was applied, the contact angle variations in those experiments were regarded solely to differences in rock properties between the samples.

Illite was the only mineral fraction that was not considered for the MLR approach. However, only one sample presented such mineral and even so as minor content. The addition of porosity (case III) improved the prediction accuracy as it provides the quantification of the fluid volume that interacts with the solid part of the rock.

The influence of pore geometry was not addressed in this work but may cause deviation in the predictions.

However, in case III, only two samples are likely to deviate from the expected line, and even though those misfits result in only a relative error of 1%.

The MLR model presented in this work is adequate for the rocks and environmental conditions applied to the samples during the experiments. Different fluids, pressure, temperature, and mineral content might influence the contact angle and affect the coefficients.

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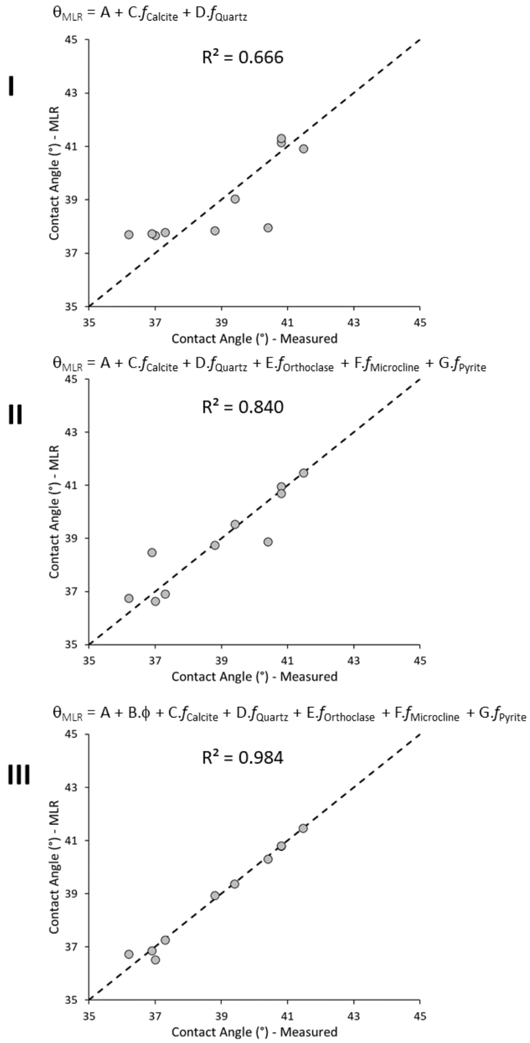


Figure 5: Crossplot showing the results of MLR technique for predicting the contact angle versus the measured values. Cases I, II and III refer to different sets of predictors. The MLR equations are showed in top of the graphics. Coefficients A, B, C, D, E, F and G are listed in Table 6. $f_i$ refers to the mineral fraction denoted by subscript *i*. The dashed line is a reference where measured and predicted values were expected to coincide.

Table 6: Coefficients of MLR equations of the different cases showed in Figure 5.

| *Coefficients* | I | II | III |
|---|---|---|---|
| A | 111.1456 | 17614.9 | 15516.89 |
| B | | | 0.245593 |
| C | -0.7339 | -175.779 | -154.816 |
| D | -0.81266 | -176.062 | -155.332 |
| E | | -174.192 | -152.245 |
| F | | -182.484 | -159.04 |
| G | | -174.16 | -152.71 |