Evaluation of the dynamic's adsorption of polar components during the wettability restoration of carbonate rocks from Brazilian pre-salt reservoirs and their preservation for relative permeability tests

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Abstract. In the rock aging process for relative permeability assessment, it is essential to understand the adsorption dynamics of polar components over time, as these are the main molecules responsible for rendering the wetting properties of the rock. In this study, two carbonate rock facies representative of Brazilian Pre-salt reservoirs were evaluated. Wettability restoration was performed using two methods: dynamic and static aging. In the dynamic method, 2.0 pore volumes (PV) of dead oil were injected 13 times at a flow rate of 0.1 mL/min, with effluent collection every 0.25 PV. For static aging, aliquots were collected during the initial days and subsequently every seven days, totaling a 30-day aging period. To assess the adsorption dynamics of polar components, Total Acid Number (TAN) and Total Base Number (TBN) values were determined for each facies under each aging condition. The results demonstrated variations in the adsorption behavior of both polar components throughout the injections and immersion periods in each aging process, enabling correlation with the time required to restore the original wettability.

1. INTRODUCTION

In carbonate reservoirs, polar components are the main oil compounds that interact with the rock surface, playing a key role in wettability [9, 2]. This adsorption process may occur differently across the various rock types that constitute a carbonates reservoir [1, 6, 4], directly impacting the generation of relative permeability curves, which in turn influence the characterization and prediction of recoverable oil volumes throughout the reservoir's productive life [12, 8].

Hopkins et al. (2017) investigated the behavior of outcrop carbonate rocks to evaluate the adsorption dynamics of these polar components during the controlled injection of dead oil. Their study revealed a clear dynamic of polar component adsorption during dead oil flow. In the case of Pre-salt carbonate rocks, certain characteristics must be mapped, as they may affect the establishment of comparable wettability conditions. Moreover, the diversity of facies (i.e., stromatolites and grainstones) found in these reservoirs must be fully characterized, as they may exhibit dynamics distinct from those observed in other carbonate rocks [3, 7, 11, 13].

Wettability restoration is required due to the presence of various contaminants introduced during drilling and core sampling activities. These contaminants, along with a significant portion of the original hydrocarbons, are removed during the cleaning process, thereby altering the original wettability of the samples [7]. Wettability restoration involves placing oil, formation water, and rock in contact under controlled conditions, allowing polar components to adsorb onto the rock surface and re-establish the original wettability state [4, 5, 13].

Aging processes either static or dynamic are employed to restore rock wettability, enabling the characterization of flow properties such as relative permeability, oil production, and the effects resulting from wettability alteration or preservation. Both aging methods are essential for understanding the behavior of polar oil components when in contact with carbonate rocks, differing in terms of interactions and flow-related aspects. The dynamic method involves continuous oil injection, enabling the assessment of how polar components interact with the rock during fluid flow, and allowing for a gradual evaluation of wettability restoration over time. In contrast, the static method consists of injections with minimal flow influence, enabling the evaluation of polar component behavior in a scenario where the oil remains in contact with the rock with little to no movement. This static approach serves as

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an upper bound reference for comparison with the dynamic method. Samples from both aging processes were analyzed using Total Acid Number (TAN) and Total Base Number (TBN) measurements, allowing for quantification of polar component adsorption over time. These results enabled comparisons between the two methods to evaluate the wettability state of the rock, as well as the time and volume required for its restoration.

2. METHODOLOGY

The characterization of the adsorption of polar components in carbonate samples from the Pre-salt was carried out by measuring the acid and base numbers obtained from the oil effluents collected during the wettability restoration process, which was performed through both dynamic and static aging. In both aging procedures, oil samples were collected over time to correlate the variation of these indices with the aging process in the evaluated facies. Additional variables were measured to observe flow variations during the injection of dead oil that could be correlated with wettability restoration in each studied facies.

2.1 Selection of Rocks and Fluids Preparation

With the ionic composition of formation water and seawater provided in mg/l, the quantities of substances necessary to prepare each fluid were calculated. Table 1 presents the composition of the fluids used for the tests conducted.

Table 1 – Ionic composition of formation and seawater for the experimental data, (ppm)

	FW, g/l	**SWd, g/l**
NaCl	154.954	31.467
CaCl2x2H2O	84.108	5.402
MgCl2x6H2O	35.581	0.276
KCl	6.046	0.848
BaCl2x2H2O	0.898	-
SrCl2x6H2O	17.289	-
LiCl2	0.547	-
KBr	2.085	0.107
NaHCO3	0.324	0.059

2.2 Oil Characterization

The first activity involved collecting a representative sample, for which a container was heated to a temperature of 58°C for 8 hours. After this period, smaller samples were collected in 1000 ml containers, which were used for characterization tests and other activities.

Table 2 presents the values of viscosity and density for both fluids, crude oil and mineral oil as a function of temperature, where the results validate the data provided by Petrobras. With this data, it is possible to identify that the heating process did not produce significant variations in the density of the sampled oil.

Table 2 – Crude-Oil and Mineral oil Properties

Temperature, °C	Viscosity, mPa.s		Density, g/cm3	
	Crude-oil	Mineral oil	Crude-oil	Mineral oil
15.6	47.0	1.22	0.88	0.75
20.0	33.5	1.16	0.87	0.76
60.0	6.3	4.25	0.84	0.77

2.3 Physicochemical Properties

The assessment of oil properties was fundamental to understanding the adsorption dynamics of polar components in the evaluated rocks. A representative oil sample was collected, and the measured values for the fractions of saturates, aromatics, paraffins, and asphaltenes (SARA) are also presented in Table 3.

Table 3 - Characterization of SARA fractions and polar compounds of crude oil

	Sat	Arom	Res	Asph
Oil	57.4	24.8	16.2	0.2
TAN		0.23		
TBN		3.16		

2.4 Sample Selection

For this work, three representative faces from Brazilian pre-salt reservoirs were selected. The first step was to measure the petrophysical properties of the sample group, using the DV-4000 pore-permeameter, with a confinement pressure of 1000 psi. Table 4 identifies the samples divided into three types of classification with the identified faces: Stromatolites and Grainstone. The same table also displays the saturation values obtained during the preparation of the initial oil saturation, which was performed using an ACES-300 ultracentrifuge capable of generating capillary pressures of up to 120 psi. In this process, formation water was used as the wetting phase to establish the initial water saturation (Swi). To determine Swi through centrifugation, the samples previously saturated with formation water were subjected to a centrifugal force in the presence of EMCA PLUS 7015 mineral oil.

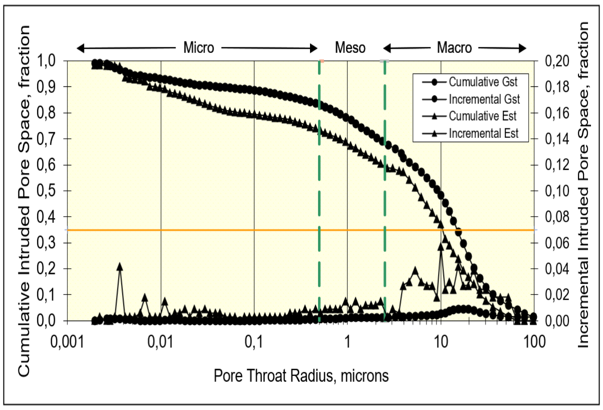

Figure 1 - Pore throat distribution for stromatolite and grainstone facies from Brazilian Pré-salt reservoir

In Figure 1, the cumulative permeability curves indicate that pore throats smaller than approximately 10 microns contribute marginally to total permeability. The main contribution is associated with throats in the range between 10 and 100 microns. The curve for the grainstone sample is shifted toward larger pore throats compared with the stromatolite, indicating that grainstone is supported predominantly by meso- and macropores, enhancing fluid flow capacity. Conversely, stromatolite presents a more restricted pore network dominated by smaller throats, resulting in a sharper decline in cumulative permeability.

Figure 2 complements this observation by showing that the cumulative pore space distribution for grainstone reflects a progressive filling dominated by meso- and macropore throats. The incremental curves clearly exhibit distinct peaks within these ranges, highlighting the dominance of well-connected and effective pore structures. In contrast, the stromatolite sample shows both cumulative and incremental distributions shifted toward smaller pore throats, reinforcing the presence of a less efficient pore network in terms of fluid flow.

The pore classification into micro-, meso-, and macropores, as depicted in Figure 2, highlights that micropores contribute minimally to both permeability and effective storage, while meso- and macropores play a critical role in maintaining effective permeability. Those differences between grainstone and stromatolite may be attributed to diagenetic processes which can be inherent lithological heterogeneity. These results underscore the importance of preserving larger pore structures to ensure efficient flow in carbonate rock samples, particularly in highly heterogeneous reservoirs.

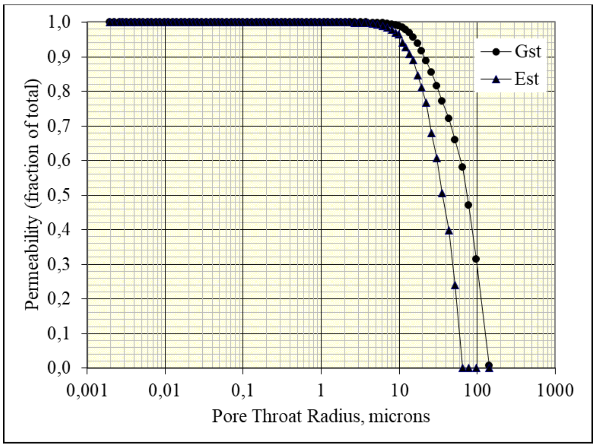

Figure 2 - cumulative permeability distribution for grainstone and stromatolite samples

Table 4 - Petrophysical properties obtained from the samples studied

Sample	L, cm	D, cm	K, mD	Φ, %	VP, ml	Swi, %
Est1	6.2	3.8	52.3	13.0	9.2	22.5
Est 2	5.3	3.7	108.6	17.4	10.3	23.7
Gst1	5.5	3.7	61.1	18.9	11.7	21.6
Gst2	4.5	3.7	107.7	16.3	8.2	19.7

2.5 Wettability Restoration Process through Aging

To carry out the aging process, two traditional methods from literature were chosen: static and dynamic aging. In static aging, each sample in the Swi condition was placed in a holder, and a volume equivalent to 10 pore volumes of dead oil was injected at a flow rate of 0.1 ml/min. Subsequently, the rock was covered with a Teflon film and placed in an aging cell with dead oil until the container volume was complete and then taken to an oven heated to 60°C for at least 30 days. During the aging period, oil samples were collected to measure the indices of polar components (TBN and TAN) adsorbed during this process. In dynamic aging, each sample was placed in the BRZ4-rig and subjected to the temperature and pressure of the test. The aging process was conducted with the controlled injection of two pore volumes of dead oil at 60°C at a flow rate of 0.1 cc/min on alternate days until complete 30 days. During the injections, fractions of 0.25 PV were collected to characterize the polar components adsorbed during each injection. The differential pressure profile of each injection was monitored until complete stabilization.

2.6 Relative permeability using multistep

The relative permeability evaluation method was adapted from the work of Lenormand et al. 2016 [12]. The same flow rates suggested in that study were initially employed. However, adaptation was required for the samples used in this work, as it was not possible to obtain stable differential pressure values at the recommended flow rates. Subsequently, a new sequence of flow rates was defined for the samples under study, ranging from 0.1 to 1.0 mL/min. The selection criteria were based on experimental data obtained in the laboratory, in which each face of the sample was evaluated individually, and the flow sequences were adjusted accordingly. Relative permeability curvas were obtained from processing by CYDAREX software and LET method.

3 Results

With the selection of samples completed, the information presented in Table 3 was compiled. Following the sample preparation under irreducible water saturation conditions, the samples were placed in the BRZ4-rig and subjected to a confining pressure of 3000 psi, pore pressure of 1000 psi, and a temperature of 58°C, which corresponds to the target reservoir conditions.

The dynamic aging process was initiated with the injection of dead oil to displace the mineral oil present in the samples. This procedure was conducted at a controlled flow rate of 0.1 mL/min for at least six pore volumes, while continuously monitoring the differential pressure. Once stabilization was achieved, the collection of effluents began, as described in the previous section.

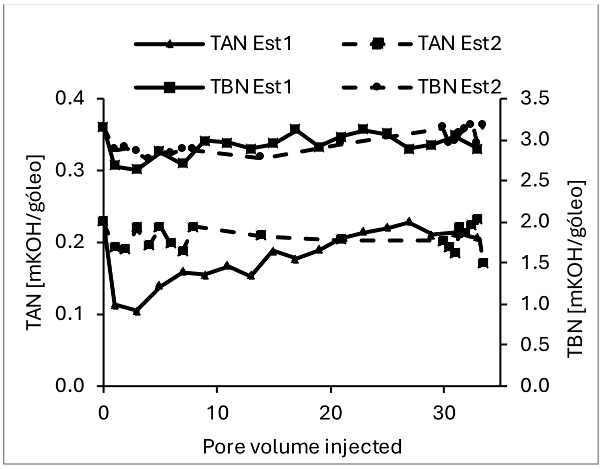

Figure 3 - Evolution of polar component adsorption in Stromatolite rock samples. Solid line represents the dynamic aging process, while the dashed line corresponds to the static aging process.

Figure 3 presents the results of effluent characterization obtained during the two aging processes performed on the stromatolite samples. As observed in the same figure, in the case of static aging, the behavior of these indicators follows different trends due to the limited availability of polar components. As a result, the adsorption dynamics may lead to wettability conditions that differ from those achieved during dynamic aging, in which polar components are continuously replenished, allowing for a more effective adsorption process and potentially complete wettability restoration. Additionally, the figure shows that during dynamic aging, a significant reduction in both TAN and TBN values occurs within the first few injected pore volumes, which can be linked to the adsorption of polar components onto the rock surface, rendering more oil-wetness. In the case of static aging, the behavior of both polar components suggests a rapid stabilization, which may result from two concurrent effects: the initial fast adsorption of polar components and a subsequent decrease in their concentration within the pore space. This reduction in concentration limits further adsorption, ultimately hindering the complete restoration of wettability.

The same type of results is shown in Figure 4 for the Grainstone samples, indicating a distinct adsorption behavior of polar components compared to the stromatolite samples. For both aging processes, a significant decrease in TAN and TBN is observed in the early injected pore volumes and in the first days of oil sample collection using each method. This trend in polar component behavior suggests different rock–fluid interaction mechanisms between the evaluated facies, which may be correlated with the mineralogical composition typically found in Brazilian pre-salt reservoirs.

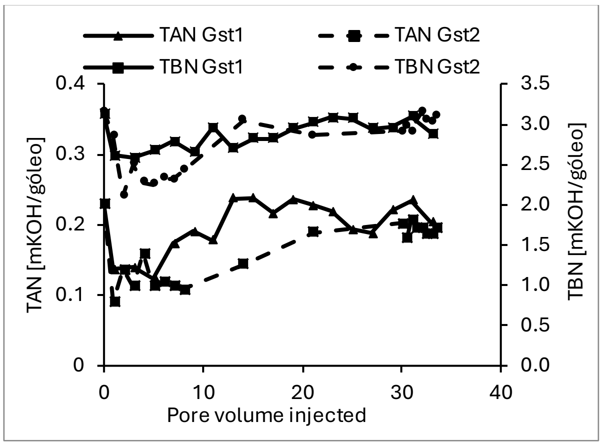

Figure 4 - Dynamic of polar component adsorption in Grainstone rock samples. Solid line represents the dynamic aging process, while the dashed line corresponds to the static aging process.

3.1 Correlation for dynamic and static aging

To evaluate the dynamic aging process throughout the controlled oil injections, the differential pressure was measured at each stage, as shown in Figure 5.

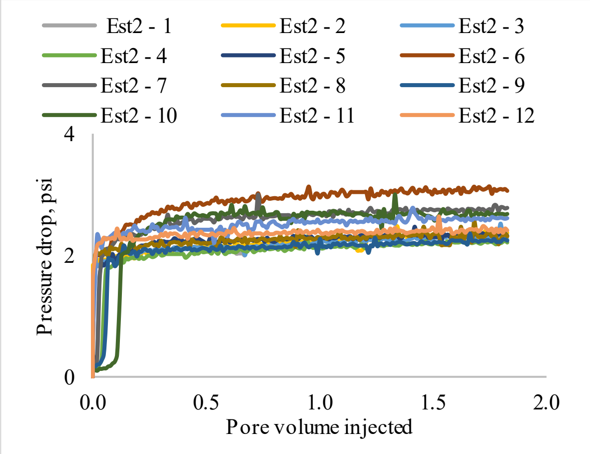

Figure 5 – Pressure drop for the Stromatolite sample for the crude oil injection in the dynamic aging in the dynamic aging.

The data reveal that during the first few pore volumes, there is a rapid stabilization across all injections, indicating that the relative permeability to oil may have reached a steady state. However, during the sixth injection, an increase in differential pressure was observed, followed by a decrease to values similar to those obtained in the initial injections.

When correlating these results with the TAN and TBN values, it becomes evident that this is the point where the trend begins to shift. This suggests that, from the sixth injection onward—or after 18 days of dynamic aging—wettability restoration in stromatolite rocks may be considered to have reached a minimum threshold. The differential pressure results for the grainstone sample, also shown in Figure 6, exhibited a different trend compared to the stromatolite sample.

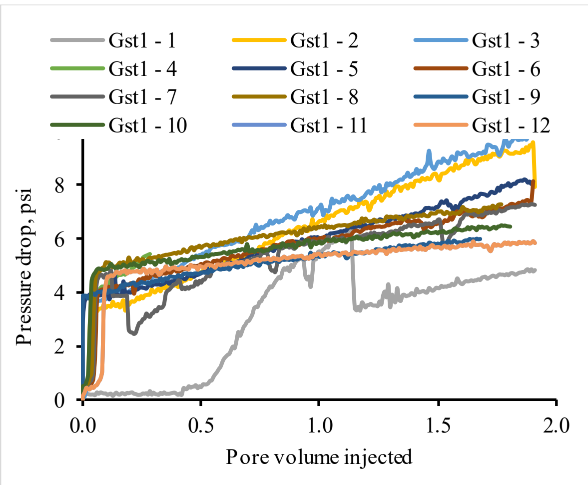

Figure 6 – Pressure drops for the grainstone sample for the crude oil injection in the dynamic aging.

Once the mineral oil was replaced and the first dead oil injection was performed, the differential pressure progressively decreased with each subsequent injection, a trend that continued until the tenth injection. Therefore, for this particular facies, at least 20 pore volumes or approximately 30 days of dynamic aging are required to reach wettability restoration. Two additional injections were conducted to confirm that the differential pressure values had stabilized and would not show significant variations. When correlating these results with the polar component indices throughout the injections, it is evident that the largest pressure variations occurred during the initial oil injections, indicating strong interactions between the polar components and the rock surface, with stabilization occurring toward the end of the injection period.

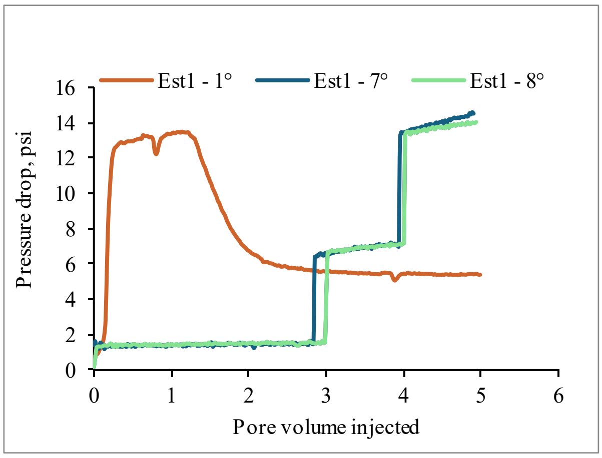

Figure 7 – Pressure drop variation for stromatolite sample in static aging.

The samples restored through static aging were subjected to additional tests to evaluate the behavior of differential pressure across various applied flow rates. Figures 7 and 8 show the behavior of this variable measured at different flow rates for the stromatolite and grainstone samples, respectively. The first injection corresponds to the replacement of the crude oil used during the aging process with model oil, at a flow rate of 0.1 mL/min, which is the standard flow used for removal the mineral oil replacing for oil phase.

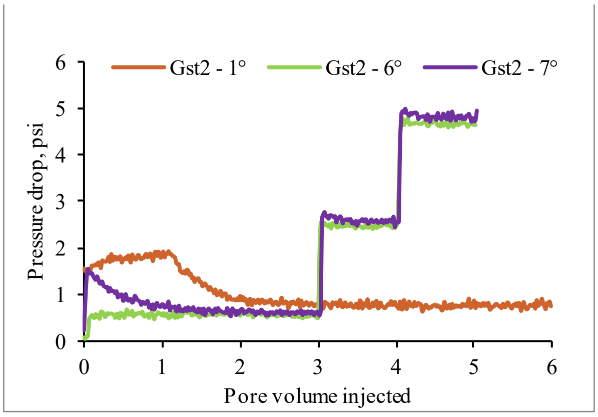

Figure 8 – Pressure drop variation for grainstone sample in static aging.

As can be seen in both figures, there was an initial increase followed by a rapid drop in differential pressure, indicating a swift replacement of the fluids. After the model oil injection, two additional injections were performed using three different flow rates (0.1, 0.5, and 1.0 mL/min) to assess the oil relative permeability immediately after the aging process. The results of these injections showed very similar values for both differential pressure and oil relative permeability fraction, confirming that static aging is a reliable method for restoring wettability in this type of carbonate rock.

3.2 Oil Recovery from multi-step method

Relative permeability experiments were conducted on both samples from the facies under study. Each rock sample was placed individually in the BRZ4-rig, and after each wettability restoration cycle, sulfate-reduced seawater was injected using increasing flow rates, as proposed by Lenormand et al. (2016). Each flow rate stage was monitored over time until complete stabilization was achieved, after which the flow rate was increased, and the process was repeated until the end of the experiment.

During each experiment, the volumes of oil recovered at each flow rate were collected along with the corresponding differential pressure measurements. These data were then processed to generate representative curves of oil recovery and differential pressure as a function of the applied flow rates (Figures 9 and 10). As a result, relative permeability curves were obtained for each of the studied facies.

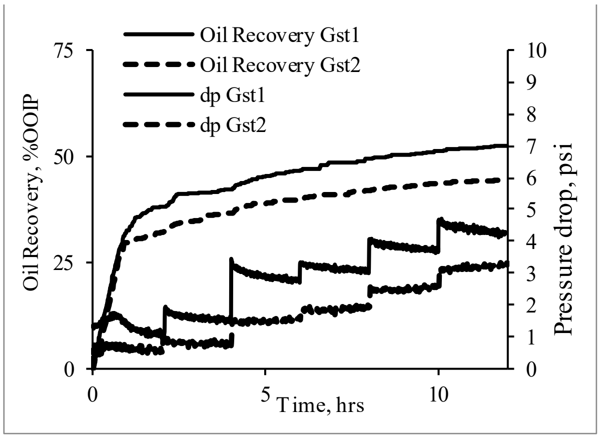

Figure 9 – Oil recovery and pressure drop for Grainstone sample.

It can be observed in both figures that the produced volumes reached similar levels, and the differential pressures were comparable for each evaluated facies. Upon completion of the relative permeability tests, each sample underwent the mild cleaning process and data acquisition to validate the methodology through the measurements reported in the previous section.

Regarding the oil recovery behavior resulting from the evaluated aging procedures, it can be stated that for the stromatolites (Figure 10), there were no significant differences in the recovery levels or in the differential pressures throughout the applied flow rates. Additionally, the figure shows that it was necessary to extend the final flow rates for a longer period, which led to the production of additional oil volumes. This may represent an experimental artifact, since each sample must be individually monitored in terms of both differential pressure and oil volume recovered per applied flow rate. On the other hand, for the Grainstone samples (Figure 9), the oil recovery behavior showed significantly different recovered volumes, which may be attributed to the dynamic interaction of polar components in each aging process characteristic of these facies.

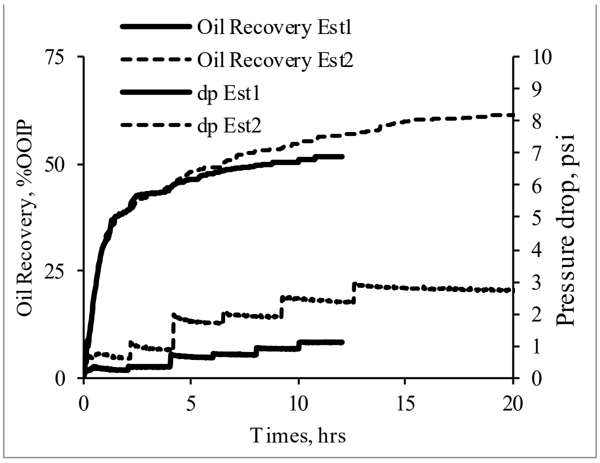

Figure 10 – Oil recovery and pressure drop for Stromatolite sample.

3.3 Relative permeability using a multistep method

To determine the relative permeability curves from the multistep tests, the LET method was applied, in which several parameters are considered. The data were fitted using experimental data adjustment through the biExp multi-step method for all datasets used in each simulation. Figures 11 and 12 present the relative permeability curves obtained for each evaluated facies, representing the behavior of each test and the aging process applied to each sample.

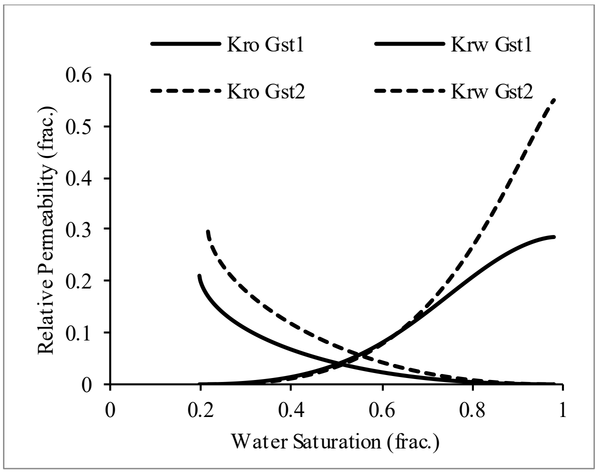

Figure 11 – Relative permeability obtained from both aging processes for Grainstone sample.

In both figures, it is noticeable that the wettability indicated by the shape of the curves shows a slight oil-wet preference, which is a result of the aging process applied. It is important to highlight that for the Grainstone samples (Figure 11), the obtained curves exhibit a slight variation, which contrasts with the data obtained during the evaluation of the relative permeability fractions throughout the aging process. In the case of the stromatolite samples (Figure 12), the curve behavior shows fewer differences among them, which suggests a different interaction of polar components during each aging process.

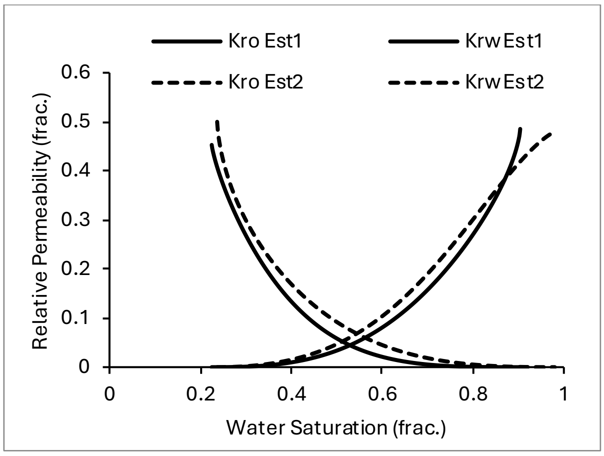

Figure 12 – Relative permeability obtained from both aging processes for Stromatolite sample.

In strongly oil-wet carbonate rocks, the relative permeability to oil (kro) typically exhibits high values. This behavior is primarily attributed to the strong affinity of oil for the rock surface, which promotes the formation of continuous oil films along the pore walls. Under such wettability conditions, oil preferentially occupies smaller pores and maintains a connected flow pathway throughout the porous network, while water is displaced toward the center of larger pores, acting as the non-wetting phase.

However, in highly heterogeneous carbonate rocks—such as those evaluated in this study—the interpretation of kro becomes significantly more complex due to intrinsic microstructural variability. These formations often display a broad spectrum of pore throat sizes, ranging from microporosity to macroporosity, which results in non-uniform fluid distribution and pronounced capillary pressure gradients. In such cases, even under strongly oil-wet conditions, the presence of tight zones and microporous regions—as illustrated in Figures 1 and 2—can locally hinder oil mobility, potentially leading to a reduction in kro.

Therefore, in highly heterogeneous carbonate systems, it is crucial to integrate kro measurements with detailed pore-scale characterization to accurately interpret flow dynamics and validate wettability conditions. This integrated approach is essential for understanding the interplay between rock fabric and fluid distribution, and for establishing reliable relative permeability relationships.

4 Conclusion

The adsorption dynamics of polar components were obtained for stromatolite and grainstone samples, showing significant variations depending on the aging method applied.

The results observed during the dynamic aging process revealed distinct differential pressure levels between the stromatolite and grainstone samples. These differences may be associated with the adsorption dynamics of polar components, suggesting a strong affinity for the rock surface. This interaction can gradually increase the oil-wetness of the rock as more oil is injected during the aging process.

The oil recovery and relative permeability curves obtained for both aged facies exhibited similar trends and characteristics typical of oil-wet carbonate rocks.

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