Evaluation of the impact of mineralogy on oil recovery using digital petrophysics

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Abstract. Exploring pre-salt oil deposits poses a significant challenge for the oil and gas industry. Carbonate rock reservoirs, being more susceptible to diagenetic actions, exhibit considerable complexity due to the heterogeneity of the porous system. This study investigated the impact of mineralogy on oil recovery using desulfated seawater (DSW). Two coquina samples from the Morro do Chaves Formation in the Sergipe-Alagoas Basin were used, each with different contents of quartz and feldspar. In this context, 3D image analyzes were performed, obtained by micro-CT, at different saturation phases of the rock: dry, saturated in formation water, aged in oil, and in contact with DSW. Image analyzes were conducted using profiles of porosity and fluid saturation present in the pores. To complement the observations, the oil-water contact angle in the aged samples was measured. The results revealed that the presence of terrigenous minerals significantly influences rock wettability and oil recovery. The sample with a higher percentage of these minerals exhibited a shift in wettability from oil-wet to water-wet over time, resulting in an oil recovery efficiency of 31%. Conversely, the sample with a lower percentage of quartz and feldspar maintained a constant oil-wettability and demonstrated a lower recovery efficiency of only 3.22%.

Keywords: oil recovery, carbonate rocks, pore scale, wettability

1 Introduction

The discovery of pre-salt reserves has positioned Brazil as a major player in oil and gas production, ranking as the world's eighth-largest producer [1]. The exploration of these reservoirs, located beneath an extensive layer of salt, faces significant challenges due to their intrinsic complexity, demanding the development of advanced technologies to maximize the production of this commodity [1, 2]. Lacustrine carbonate rocks, including coquinas, are particularly relevant due to their high potential as reservoirs in the pre-salt areas of the Santos and Campos Basins [3, 4]. These deposits, found along the eastern coast of Brazil and in western Africa, are associated with a lacustrine system during the rift basin stage of the Early Cretaceous, coinciding with the opening of the Atlantic Ocean [5]. The risks associated with implementing projects in this context primarily stem from the contrasts in porosity and permeability among various geological units [6]. This heterogeneity in the reservoirs, resulting from greater susceptibility to diagenetic processes, can be observed between different areas and within the same accumulation [6, 7]. Therefore, the complex geometry of the porous system and variations in characteristics between layers can negatively impact oil production [8].

A multidisciplinary study that includes the characterization of petroleum reservoirs, investigation of rock-fluid interactions, and analysis of the mechanisms involved in fluid flow through porous media is essential for optimizing advanced oil and gas recovery techniques [9]. Understanding the dynamics of fluid displacement in structures of difficult comprehension requires approaches that allow for microscale visualization and analysis. Traditional methods, such as laboratory experiments and well log analyses, often encounter significant limitations in the field of petrophysics and reservoir geology [10, 11]. On the other hand, digital rock analysis, especially employing X-ray micro-computed tomography (micro-CT), enables the acquisition of high-resolution images and three-dimensional digitization of core samples and plug samples [7]. This technique allows for the identification of pores, the analysis of pore geometry and type of porosity, the evaluation of formation and specific diagenetic alterations, as well as the understanding of the mechanisms governing fluid displacement in porous media [7, 9].

The application of this methodology in the oil and gas industry has been widely discussed in the literature [7, 9, 11, 12]. Matheus et al. [7] adopted an approach that integrated X-ray computed tomography, petrophysics, and petrology to investigate the geological factors influencing porosity distribution. The study explored the visualization and characterization of the pore network in carbonate rocks from the pre-salt. Applying this tool, Lbedeva and Fogden [12] investigated the relationship between oil recovery and its underlying causes in sand packs containing kaolinite in their composition. In this specific case, a small amount of this clay mineral significantly impacted oil removal efficiency. Alaamri et al.[9] analyzed rock-fluid interaction through spontaneous imbibition and drainage experiments, examining phase distribution in a porous system at the pore scale. The 3D images generated allowed for monitoring all stages of the tests, aiding in the understanding the mechanisms involved in oil displacement. Khishvand et al. [11] further conducted a detailed microscale image analysis to identify potential changes in wettability during different stages of flow tests. Building on this foundation, additional studies on samples analogous to pre-salt formations could significantly contribute to the advancement of exploration in these complex reservoirs.

This study used micro-CT images of two coquina rock samples from the Morro do Chaves Formation, located in the Sergipe-Alagoas Basin, which can be considered analogous to certain reservoirs in the Santos Basin [5, 13]. The impact of mineralogy on oil recovery using desulfurized seawater (DSW) was investigated based on porosity and fluid saturation curves generated from segmented images at all stages of the experiment, including dry, saturated with formation water, aged with oil, and in contact with DSW phases. Preliminarily, the oil-water contact angle was measured on the samples aged with oil to complement the analyses. These data provide a more robust and fundamental understanding of the impact of terrigenous minerals on rock wettability and oil recovery efficiency at the pore scale. The insights gained are particularly relevant and comparable to the conditions found in Brazilian pre-salt reservoirs.

2 Material and Methods

2.1 Rocks

Two coquina samples from the Morro do Chaves Formation in the Sergipe-Alagoas Basin, considered analogs to the coquinas of the Itapema Formation in the Santos Basin Brazilian pre-salt, were utilized in this research. The samples, provided by the Laboratory of Sedimentary Geology (LAGESED) of UFRJ, were cut longitudinally from cores to create 3D slabs, each containing different percentages of terrigenous materials. Sample 94.40 contains a higher proportion of minerals such as quartz and feldspar compared to Sample 162.40.

2.2 Fluids

Crude oil with a density of 0.8884 g/cm³ at 20°C, a viscosity of 42.48 mPa·s at 20°C, and acid and base numbers of 0.37 and 3.79 mg KOH/g, respectively, was used. Additionally, desulfated seawater (DSW) was employed in the experiments to recover oil. Details about this formation water are provided in Table 1.

Table 1. Composition of synthetic desulfated seawater (DSW)

Component (DSW)	NaCl	$CaCl_2{\cdot}6H_2O$	$MgCl_2{\cdot}6H_2O$	KCl	$SrCl_2{\cdot}6H_2O$	$NaHCO_3$	Na_2CO_3
Concentration (ppm)	30.348	2.733	14.220	953.00	27.00	139.00	55.00

2.3 Experimental Procedure

The impact of different proportions of terrigenous minerals associated with carbonates on oil recovery was investigated through a series of 3D image acquisitions using micro-CT at various saturation stages. To mimic multiphase flow dynamics in geological formations, tomographic images were first obtained from the clean and dry samples, allowing for the investigation of porosity distribution. Next, both slabs were saturated with brine and scanned again using micro-CT. To simulate the condition of irreducible water saturation in an oil reservoir, the samples were immersed in crude oil to drain the present water to the irreducible saturation point (Swir). Subsequently, the slabs were subjected to an aging process for 30 days at 60°C, followed by imaging. This procedure, which involves prolonged exposure of the samples to crude oil, was designed to modify the initial wettability of the rock substrate, bringing it closer to a state that more accurately represents reservoir conditions [14]. In a subsequent step, the samples were immersed in desulfated seawater and kept in this state for two hours, followed by the final data acquisition.

2.4 X-Ray Microtomography (micro-CT)

A current approach to non-destructively evaluate the porous space of rocks is to use equipment that generates 3D images, such as a micro-CT scanner, which has its X-ray source. The X-ray beam passes through the material, where some X-ray photons are absorbed depending on the linear attenuation coefficient. The transmitted photons are received by a detector positioned on the opposite side of the sample, resulting in a single 2D attenuation map [15]. The tridimensional geometry of the object is obtained by gradually rotating it. In this rotation, multiple two-dimensional projections are collected at different angles, constructing a tridimensional distribution of attenuation coefficients [16]. Micro-CT images of samples (slabs) were taken by the Enhanced Oil Recovery Laboratory of the Federal University of Rio de Janeiro (LRAP/UFRJ) with a CoreTOM equipment (Tescan/XRE) applying a voxel size of 13.2 µm. The images were reconstructed using Acquila reconstruction software (Tescan/XRE). Image processing was performed with Avizo 9.5 (Thermo Fisher Scientific), using threshold tools to identify and separate the pores from the sample's mineral framework and also the different fluids [17, 18].

2.5 Porosity and Saturation Profiles

Initially, the tomograms distinguished two phases: the mineral phase, with higher attenuation, and the pore phase, with lower X-ray attenuation. It was also possible to segment the aqueous and oil phases occupying the pore space throughout the experiments. The porosity was calculated using the obtained CT scan images of the dry samples by dividing the labeled pore voxels by the total number of voxels. With the values obtained for each slice, porosity profiles were constructed. Similarly, oil and water saturations were measured in each slice along the domain based on segmented images, resulting in the generation of saturation profiles in different scenarios.

2.6 Contact Angle

The oil-water contact angle of the aged samples was measured using the captive bubble method. In this method the droplet is deposited onto the sample surface by 'J' shaped syringe needle, and high-resolution cameras and software (KRÜSS ADVANCE 1.9.0.8) are used to capture and analyze the contact angle [19, 20]. Initially, the rocks were aged in crude oil for 30 days at 60°C, and the contact angles were measured by depositing a drop of oil on the surfaces of the samples, with DSW as the surrounding phase. Subsequently, the aged slabs were submerged in a sealed beaker of desulfurized seawater at 60°C for approximately 6 days, with contact angle measurements repeated to verify any changes in the rock's wettability.

3 Results

3.1 Contact Angle

The wettability of the aged samples was tested using the captive bubble method, as shown in Fig. 1. When the contact angle through the denser phase (θ) is less than or equal to 60 - 75° ($\theta \leq$ 60-75°), it indicates that the denser liquid wets the solid preferentially. If 60 - 75 $< \theta <$ 105 - 120°, the rock is neutrally wet, and when 105 - 120° $\leq \theta \leq$ 180°, the less dense phase wets the solid preferentially [21, 22]. Therefore, a high value of this parameter indicates that the rock is oil-wet, while a low value indicates a more hydrophilic behavior.

The initial contact angle, measured in denser liquid (DSW), on slab 94.40 with an oil droplet surrounded by desulfated seawater was 131.4°. After six days in interaction with DSW, the contact angle changed to 55.6°. Therefore, our results indicate a shift in this trend: initially, the oil droplet spread on the sample, but in the subsequent scenario, the oil droplet formed a sphere, resulting in a contact angle of less than 60 - 75°. Previous studies have shown that the interaction between fluids and carbonate rocks [23], coupled with prolonged exposure, can alter wettability, thereby impacting oil recovery. For slab 162.40, the trend persists over time, with oil wetting prevailing, as indicated by a shift in the contact angle from 138.3° to 150°. In the context of this research, the type of mineral had a significant impact on the alteration of wettability, as observed in previous studies [24]. This property in reservoirs is influenced by intricate boundary conditions at the interfaces within the pore spaces of sedimentary rocks. These conditions significantly impact the movement of interfaces and the displacement of oil [25]. The principal controlling factors are oil composition, brine composition, mineral type, and pressure and temperature conditions [19].

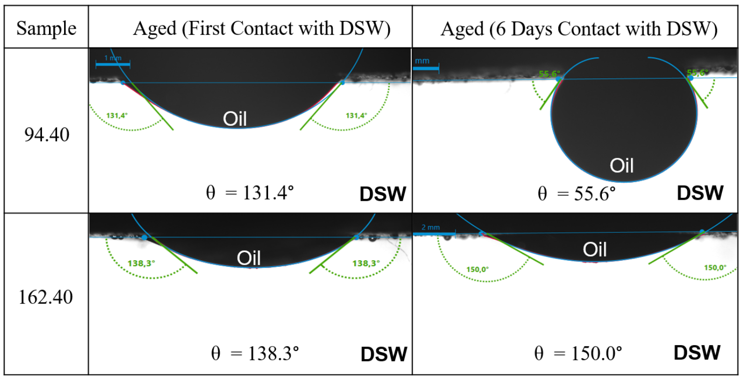

Figure 1. Contact angle of a drop of crude oil on the surface of two carbonate rock samples at different contact times with the surrounding DSW phase.

3.2 Porosity and Saturation Profiles

To provide a more detailed view of the displacement events within the pore space, Fig.2a– 2d present pore-scale fluid occupancy maps from the central regions of Sample 94.40, while Fig. 2e–2h show similar maps for Sample 162.40. Additionally, Figure 3 shows the porosity and saturation profiles of both samples, and Fig. 4 illustrates the average fluid saturations along the vertical slices of the samples after contact with desulfated seawater, as well as the percentage of pore space occupied by oil voxels before and after contact with DSW. Together, these figures provide a comprehensive understanding of the evolution of fluid distributions throughout the various stages of each flow process.

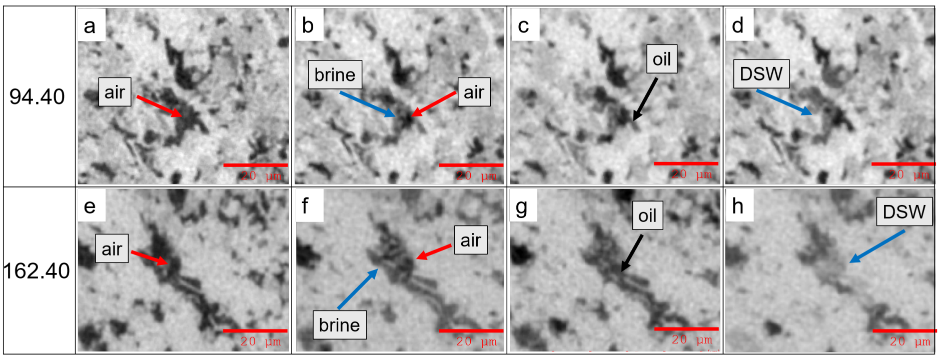

Figure 2. Two-dimensional visualization of pore-scale fluid occupancies at different stages of the experiments. (a and e) Dry rock; (b and f) Brine-saturated rock; (c and g) Aged rock; (d and h) Contact with DSW.

Comparing the results (Fig. 3a), it is observed that the slab with a low percentage of terrigenous material, 162.40, exhibits relatively uniform reduced porosity throughout the sample, with an average value of 4.0%. In

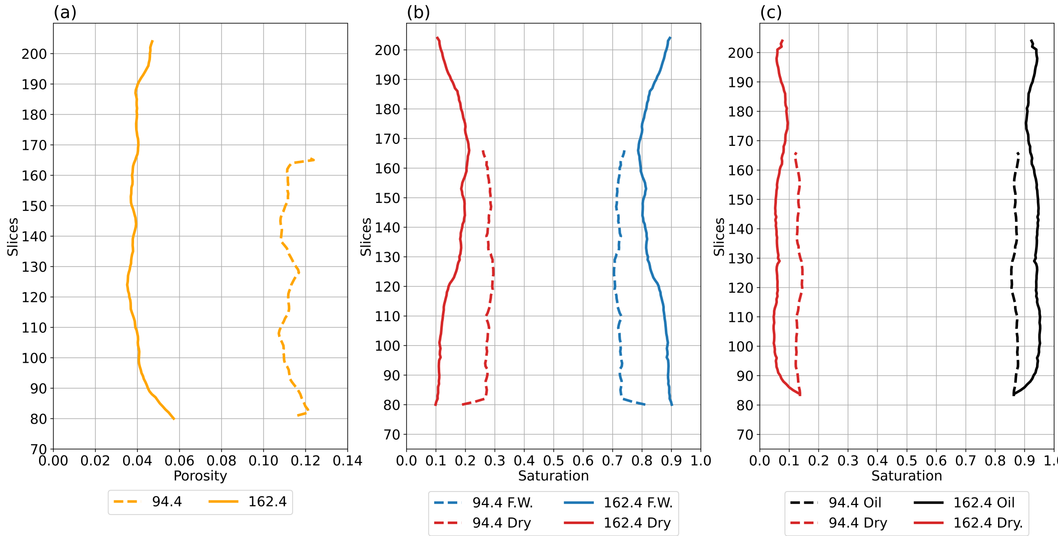

Figure 3. Profiles along the slabs measured using X-ray microtomography: (a) Porosity, (b) Saturation with brine, (c) Saturation after the aging process.

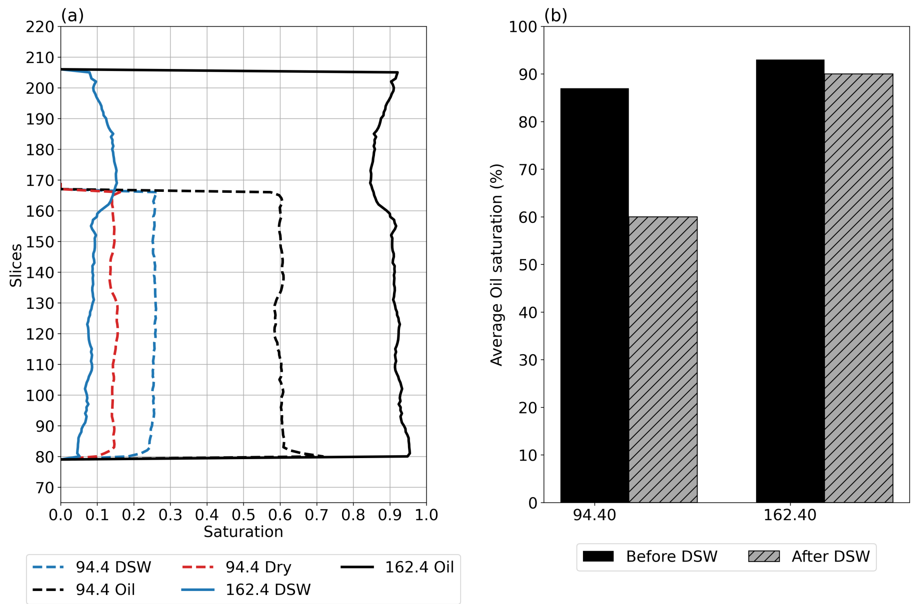

Figure 4. Slice-averaged saturations along the slabs following contact with desulfated seawater (DSW); (b) Average oil saturation before and after contact with DSW.

contrast, sample 94.40, which has a higher percentage of quartz and feldspar, shows greater variations in porosity, with an average porosity value of around 11%.

Figure 3b shows the saturation curves of the samples after contact with formation water (FW). Analyzing the profiles of sample 162.40, despite having lower porosity, it was observed that water advanced well in the sample, occupying a large part of the pore space, probably due to greater uniformity and better pore connectivity. Even though sample 94.40 had a higher average porosity throughout the slices, brine penetrated less into the sample. This may be associated with the possibility that the pore space is more heterogeneous and has smaller pores, reducing connectivity. Additionally, rocks with more terrigenous material, mainly quartz, often exhibit lower permeability, which may be influenced by factors such as fragmentation, grain size, and classification of this mineral [18]. Regarding the aging stage, Fig. 3c, sample 162.40 left only a small fraction of air, resulting in an average oil saturation of 93%, probably because the throats connecting this space have larger diameters, allowing fluid entry. Conversely, the pore space of sample 94.40 made fluid intrusion somewhat more difficult. The saturation curves for slab 94.40 indicate that, while oil filled the spaces previously occupied by water, visible in the resolution, a larger portion of the pores remained filled with air, resulting in an average saturation of 87%.

The higher percentage of terrigenous material in the rock significantly influenced its wettability and oil recovery. Based on the calculation of micro-CT images (Fig. 4), in sample 94.40, the recovery water initially penetrated the pore space effectively, removing a significant portion of the oil and resulting in a final average saturation of 60% for the phase of interest. The transition from oil-wet to water-wet conditions in this sample over time likely facilitated the displacement of the oil phase by desulfated seawater (DSW), resulting in an oil recovery of approximately 31% of the original oil in place. In contrast, the penetration of recovery water into sample 162.40 was less effective, resulting in a final oil saturation of 90% and a low recovery efficiency of only 3.22%. This unsatisfactory performance is likely attributed to the persistence of the oil-wet condition of the slab, which may have hindered the mobilization and removal of oil from the porous system.

In addition, comparing Fig. 3b, Fig. 3c with Fig. 4a, which depicts the final phase of the experiments, it was observed that sample 94.40 exhibits a significant percentage of dry pores, i.e., occupied by air. This observation suggests a tendency for gas trapping, as a portion of the void spaces remained filled with air throughout all experimental stages. However, it did not significantly compromise the recovery efficiency, as the sample still achieved a high oil recovery rate.

4 Conclusions

The study highlighted the significant impact of mineralogy, specifically the presence of terrigenous minerals such as quartz and feldspar, on porosity, fluid saturation, wettability, and oil recovery efficiency. Porosity and fluid saturation profiles were constructed from segmented images obtained via micro-computed tomography (MicroCT), complemented by contact angle analysis of oil-aged samples. The sample with a higher quartz and feldspar content (94.40) exhibited more variable porosity and experienced a shift in wettability over time, transitioning from oil-wet to water-wet conditions. This shift resulted in a reduced fraction of residual oil and an oil recovery efficiency of 31% after two hours of contact with desulfated seawater. Conversely, the sample with a lower mineral content (162.40) demonstrated a lower oil recovery of only 3.22%, primarily due to its persistent oil-wet condition. These findings underscore how variations in mineral composition can significantly alter fluid behavior, impacting the selection of the most effective recovery method to maximize field productivity.

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