Modeling Oil Recovery in Brazilian Carbonate Rock by Engineered Water Injection Using Numerical Simulation

Fabio Bordeaux-Rego 1,*, Jose Adriano Ferreira 2, Claudio Alberto Salinas Tejerina 2 and Kamy Sepehrnoori 1

1 Center for Subsurface Energy and the Environment, The University of Texas at Austin, Austin, TX 78712, USA; kamys@mail.utexas.edu
2 Galp Energia S.A., 1600-209 Lisboa, Portugal; jose.adriano.ferreira@galp.com (J.A.F); claudio.tejerina@galp.com (C.A.S.T.)
* Correspondence: bordeaux@utexas.edu

Abstract: Waterflooding remains the most commonly used method to improve oil recovery. Although the injected brine type is mainly dependent on its availability, few of its characteristics can be controlled during project design. Published laboratory work indicates that the adjustment of injected brine composition can cause an increase in oil production by wettability alteration. This research objective is to propose a novel four-step framework for modeling improved oil recovery by Engineered Water Injection from laboratory to numerical simulation for carbonate formations. We use a geochemical-based model that estimates contact angles to predict wettability alteration. The steps are (1) screening criteria, (2) geochemical evaluation, (3) wettability alteration modeling, and (4) coreflood history-match. We validate our framework by conducting history-match simulations of Brazilian Pre-Salt corefloods. Incremental oil recovery factors are between 5 to 11%, consistent with those reported during experiments. The reduction in residual oil saturation varied from 3 to 5%. This work is a new systematic procedure to model oil recovery using a comprehensive approach that is fundamental to understanding the underlying wettability alteration mechanisms by Engineered Water Injection.

Keywords: wettability alteration; engineered water injection; carbonate rocks; improved oil recovery; geochemistry

1. Introduction

The most used method to maintain a petroleum reservoir pressure after primary production is to inject water into the formation, well known as waterflooding. This secondary oil recovery technique is still the most commonly used method globally. The main reasons are high efficiency in displacing crude oils and reliable injectivity into hydrocarbon-bearing formations. Recently, increasing attention has been given to control the injected brine composition to improve oil recovery. This Enhanced Oil Recovery (EOR) method is known as Smart Water, LoSal, Advanced Ion Management, Designed Waterflooding, and Modified Salinity Flooding. We refer to this method as Engineered Water Injection (EWI) in this work.

The initial potential of any EOR technique resides in evaluating the reservoir regarding the range of technical parameters based on historical success (screening criteria). For the specific case of EWI, most of the screening criteria are determined by conventional waterflooding range (e.g., enough permeability for injection, light to medium gravity oil, preferable low heterogeneity). If most of the parameters lie within the preferable range, then a specific EOR technique is considered for the subsequent investigation phase. Conventionally, in reservoir engineering, the following steps are laboratory evaluation, simulation modeling, and well pilot test. They are executed to decrease technical uncertainties for final field implementation. Modeling EWI mechanisms is fundamental to predict oil recovery in field-scale simulations, including economic and uncertainty evaluation [1].

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Our objective is to elaborate a framework for simulation modeling of EWI based on laboratory work in this work. We initially establish state-of-art for main laboratory observations that impact improved oil recovery. Then, we link the experimental interpretations with proposed mechanisms available in the literature. In this respect, our review objective is to cover the main published work describing the EWI effect. Please refer to an extensive review of laboratory work and proposed mechanisms [2–5]. Finally, we propose our framework method and verify it using the wettability alteration model proposed by Sanaei et al. [6] and Bordeaux-Rego et al. [7] to predict oil recovery. We use laboratory data from Lima [8] from Brazilian Pre-Salt Carbonate experiments as an example that has never been modeled previously, as far as the authors know.

Experimental Observations and Mechanisms

Evidence from laboratory experiments suggests that EWI can increase oil recovery compared to conventional high salinity waterflooding, with an incremental recovery range of 5% to 15%. In the 1990s, Morrow and collaborators conducted systematic experiments to evaluate injected water salinity on oil recovery in Berea sandstone cores. The results from contact angle and Amott tests illustrated that decreasing the injected brine salinity led to a favorable change in rock wettability conditions. Additionally, the authors showed that decreasing water ionic strength and the ion type substantially impact oil recovery [9–11].

Wettability is the ability of fluid to spread onto a surface. For petroleum engineering, it describes a phase’s capacity to contact the porous wall [12]. In a strong water-wet condition, small and large pores are occupied by water and oil, respectively. The oil-rock-brine contact angle (measured from the aqueous phase) is lower than 60 degrees. For strongly oil-wet, the contact angle is higher than 120 degrees. With a contact angle between 60 and 120, the middle condition is known to be the intermediate-wet. Mixed-wet is when the rock has a similar affinity with oil and water due to mineral heterogeneity. In this case, during Amott tests, both oil and brine imbibe in the core. To model mixed-wet conditions in reservoir simulation, different wettability conditions can be assigned for each gridblock. However, this approach is hardly encountered in the literature.

Wettability alteration is usually described as when rock initially wet to a phase (e.g., oil) changes its wetness preference state to another (e.g., water). Experimental observations show that, as porous media becomes more water-wet, the large pores become gradually saturated to water. Thus, water relative permeability end-point usually becomes smaller than oil. There is a non-monotonic reduction on trapped oil saturation (minimal between oil and water-wet conditions), and water-oil capillary pressure can switch signs. Thus, an improvement in oil displacement is expected according to fractional flow theory.

In subsequent years, most experimental works were focused on quantifying wettability alteration. The two most common ways to measure wettability are indirect (e.g., Amott and USBM tests) and direct (e.g., contact angle in oil/rock/brine system). Besides, corefloods are evaluated to observe how wettability alteration impacts oil recovery mimicking fluid displacement similar to field conditions. Laboratory procedures to establish the core initial conditions can vary considerably even though the wettability quantification methods are well known. Nevertheless, a few recurrent observations can be highlighted from previous publications. We observe that often reported conditions for EWI evaluation during experiments are the extended aging period at reservoir condition (at least two weeks) for wettability restoration, high concentration of monovalent and divalent cations in connate water, elevated temperature (above 60 °C), presence of acidic components in oil, and substantial presence of key minerals (e.g., calcite or clays). In most cases, variations of those conditions lead to significant oil recovery changes.

Moreover, brine dilution has been shown to be relatively successful in sandstones [13–15]. However, it was evidenced that changing specific ions concentration is more relevant for improved oil recovery in carbonate rocks. Contradictory results were reported for brine dilution in carbonates. For example, substantial oil recovery was shown with brine dilution in a Middle Eastern formation [16] but no enhancement in other carbonates [17]. Austad
and collaborators conducted systematic research on EWI \[18–20\]. The authors concluded that increasing sulfate and decreasing sodium concentration might be beneficial for altering wettability towards a water-wet condition in chalks. Those results motivated researchers to investigate the impact of potential determining ions concentration in oil recovery from carbonate \[21–23\].

Researchers proposed some underlying mechanisms as an explanation for the wettability alteration phenomenon. Examples are: double layer expansion \[24\], calcite dissolution \[25\], and multi-ion exchange \[26\]. However, those models had relatively low success in predicting several experimental observations \[15\]. For example, experiments conducted under chemical equilibrium showed that the EWI effect could occur even without calcite dissolution \[27\]. Indeed, multiple mechanisms may contribute to improved oil recovery. The major challenge is to develop a modeling approach that includes the main mechanisms observed in experiments.

Some attempts have been made to relate zeta-potential (ZP) measurements and oil recovery. ZP of rock-brine and oil-brine systems are widely used as a reference to quantify specific surface-to-ion interactions. For example, the results from Al-Mahrouqi et al. \[28\] and Song et al. \[23\] suggest that the assumptions made by Austad and collaborators regarding specific ion interactions (SO\(_4^{2−}\) and Na\(^+\)) can be confirmed using ZP data. Empirical models, for instance, the Bond-Product-Sum (BPS), had relative success in quantifying the wettability alteration trends and their relation to ZP values for limestone \[29\]. However, Korrani and Jerauld \[15\] suggested that BPS cannot model the EWI effect in many other cases. The authors report that the EWI mechanisms are ignored or independently addressed through previous modeling approaches.

Based on the increasing number of reported ZP measurements, more attention was given to understand the interfacial phenomena and geochemistry involving the rock-oil-brine system \[30–34\]. Sanaei et al. \[6\] proposed a mechanistic model to relate surface chemistry and disjoining pressure to quantify contact angle from ZP measurements. In summary, the approach applies surface complexation modeling to predict surface potentials, required to calculate the disjoining force between two parallel surfaces (rock and oil) separated by an aqueous phase using Extended-DLVO theory. Bordeaux-Rego et al. \[7\] proposed improvements to the model suggested by Sanaei for a better wettability prediction and reported a review of main surface chemistry and interfacial phenomena aspects related to wettability. The authors succeeded in predicting dozens of contact angles using ZP to calibrate surface complexation reactions. The modeling approach is distinct from previously published ones because it includes the main EWI mechanism such as double-layer expansion and multi-ion exchange (e.g., the effect of specific ion composition in brines, oil acidic content, and rock mineralogy). However, no attempt was made to validate the proposed model against coreflood experiments. One of the goals of this work is to cover that gap and test if the model is applicable in reactive-transport flow in porous media.

2. Materials and Methods

In the following, we describe the suggested framework to model EWI from laboratory data in numerical simulation. As we develop the procedure in the following sections, we use and discuss Lima’s \[8\] data as an example of typical experimental work found in the literature. The reader should refer to Lima’s \[8\] laboratory design for details on the laboratory data. As Lima \[8\] concluded, capillary pressure is not relevant for the coreflood design due to significant viscous forces in relation to capillary forces (capillary number) and application of bump-flow technique. The imbibition experiments evidence minor oil recovery after prolonged periods. Besides, oil- and water-wet relative permeabilities measurements are usually not performed due to elevated time consumption and cost. Thus, the curve estimation concerning wettability is required using history-matching approaches. Other approaches to estimate relative permeability and capillary pressure based on pore structure (e.g., geometry, pore size distribution, and tortuosity) can be found
in the literature \[35,36\]. The author did not attempt to model oil recovery using numerical reservoir simulations.

**Engineered Water Injection Modeling**

The proposed method does not depend on the type of wettability alteration model used and should follow the subsequent steps:

(I) Experimental screening criteria. Although the laboratory work might indicate successful oil recovery, evaluation of experimental conditions is required to determine if the work is suitable for simulation (e.g., the minimum amount of experimental data, equilibrium conditions, and assumptions).

(II) Geochemical evaluation. Several chemical reactions might affect fluid flow inside porous media. It is essential to identify if, for example, rock dissolution or precipitation is affecting brine composition. The assistance of a geochemical simulator is recommended.

(III) Wettability alteration modeling. Quantifying initial and altered wettability using a mechanistic and tunable model is fundamental because most simulators are based on the interpolation of relative permeability and capillary pressure curves to predict oil recovery. Please, refer to Appendix A on how we perform wettability quantification in this work using contact angle estimation. Further details on the application will be given in the next section.

(IV) Coreflood history-match. Oil displacement from waterflooding is important to evaluate the effectiveness of wettability alteration at conditions similar to field-scale. The assistance of a reactive-transport simulator is recommended.

Other necessary steps are not listed here but should be considered for a complete EWI project design. Some examples are upscale of history-matched relative permeability and capillary pressure to field scale, execution and simulation of single- or inter-well tracer test, and field optimization & strategy development.

## 3. Results and Discussion

### 3.1. Experimental Screening Criteria

Table 1 lists the most critical parameters and the range to which EWI is admitted to be feasible. Also, we give the values from Lima \[8\] core samples. Additional limits are not listed in Table 1 because we consider having a secondary and minor effect during LSW. Table 1 is limited to only carbonate formations (screening criteria for sandstones usually differ from carbonates).

| Parameter                        | Range                                      | Lima \[8\]                               |
|----------------------------------|--------------------------------------------|------------------------------------------|
| Permeability                     | Feasible for waterflooding                | 100 to 300 mD                            |
| Porosity                         | Feasible for waterflooding                | 11 to 19.3%                              |
| Temperature                      | Light to medium gravity                    | 65°C                                     |
| Oil viscosity                    | Active oil (TAN/TBN above 0.1 mg of KOH/g) | 0.15 mg of KOH/g of dead oil             |
| Connate brine concentration      | High concentration of monovalent and divalent cations (salinity above 40,000 ppm and divalent above 1000 ppm) | Approximate 70,000 ppm of Na\(^+\) and 7400 ppm of Ca\(^{2+}\) |
| Core aging                       | At least two weeks                         | Dead oil and formation brine for 18 days at 90 °C |
| Initial Wettability              | Intermediate- to oil-wet                   | Spontaneous imbibition tests indicate cores preferentially wet to oil |
| Mineralogy                       | Predominant calcium carbonate (calcite, dolomite) | Average 55% calcite, 38% dolomite, and 7% quartz in mass |
| Water availability for injection | Na\(^+\) lower than formation water with a reasonable concentration of potential determining ions (Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)^{2-}\)) | Desulfated seawater is the base case with varying concentration of SO\(_4\)^{2-} with fixed Ca\(^{2+}\) and Mg\(^{2+}\) |
Lima [8] core data is a good candidate for EWI with all parameters within the preferable range. According to Pizarro et al. [37], the Santos Basin Pre-Salt fields are ultra-deep offshore formations located Southeast of Brazil, composed of carbonate reservoirs and low to medium gravity oils (API from 26 to 31) at temperatures of about 65 °C and the considerable formation depth (approximately 16,000 to 21,000 ft). The reservoir is initially equilibrated with the formation brine. The initial water for injection is seawater depleted in sulfate to avoid souring. Additional observations to take into consideration in this step are:

- Oil viscosity should be low enough to avoid an unfavorable mobility ratio. At this point, it is reasonable to estimate end-points for relative permeability to predict the mobility ratio as a first assessment.
- The temperature should be above 60 °C to improve wettability alteration. Austad and collaborators have shown through imbibition experimental work that increasing temperature leads to improved oil recovery but not necessarily due to oil expansion or light hydrocarbon release (gas). The most probable reason is that increased temperature accelerates the rock-brine-oil interface’s chemical reaction [25].
- Hydrocarbon-containing polar components are important because it is assumed that the rock-brine-oil interactions are dependent on the charged surface of the oil. The usual way to measure polar component’s content is through acid and base numbers. Apolar oils (or inactive) are known to produce initial water-wet conditions even after aging [20].
- Rock mineralogy needs to be defined because rock-brine geochemical interaction directly affects pore brine composition. For example, anhydrite (CaSO\(_4\)) in the formation has been shown to increase sulfate concentration and change rock wettability even for brines with no injected sulfate in them [38].
- Seawater is considered potential injection water for EWI in carbonates because of its high concentration of key ions needed for wettability alteration (sulfate, calcium, and magnesium) and relatively low sodium content. Due to the risk of souring (production of H\(_2\)S from microorganism activity), it is common to inject seawater depleted of sulfate (produced from sulfate removal units installed in the rig). However, it is remarkably known from the literature that as sulfate concentration increases, the rock condition becomes more water-wet. Thus, the impact of different water compositions needs to be correctly addressed as an opportunity for incremental oil recovery as it might justify economically the use of biocides to avoid H\(_2\)S formation.
- High heterogeneity might be an issue for oil sweep efficiency and is not addressed during corefloods. Its impact on oil recovery efficiency needs to be considered through waterflooding simulation with variable geological properties distribution in field-scale (e.g., permeability layers, fractures, and faults).

### 3.2. Geochemical Evaluation

Several geochemical reactions can affect pore brine concentration and rock-fluid interactions as a consequence of contrast between equilibrated formation brine and injected water. The main geochemical phenomena that should be considered during EWI modeling are listed below:

- Mineral dissolution and precipitation. As mentioned previously, soluble minerals such as anhydrite and gypsum (CaSO\(_4\)) can increase sulfate and calcium concentration if their saturation index to the injected brine is undersaturated. Severe dissolution can affect pore structure and increase local porosity. However, it is believed to be a near wellbore occurrence. Also, mineral precipitation can consume a significant amount of key ions that affect wettability alteration and can cause scale deposition.
- Ion adsorption and exchange. Ion adherence or replacement on a mineral surface can occur when chemical equilibrium is disrupted. It depends mainly on the contrast of connate and invaded water composition, rock mineralogy, and organic matter content [39]. Usually, in petroleum formations, this phenomenon occurs when the porous media contains clays. If significant, it can contribute either to brine ionic con-
centration changes, induce fines migration, and clay swelling. Kozaki [40] conducted EWI corefloods in Berea sandstones showing an increase in calcium and magnesium effluent concentration that can only be explained because of Na\(^+\)/Ca\(^{2+}\) and Na\(^+\)/Mg\(^{2+}\) pairs exchange in clay surfaces.

- Gas solubilization in the aqueous phase. Carbonic gas (CO\(_2\)) can solubilize in water, increase carbonic acid (HCO\(_3^-\)), and dislocate the carbonate system’s equilibrium condition. It can significantly decrease solution pH, resulting in more carbonate minerals dissolution (e.g., calcite and dolomite) and increasing calcium and magnesium concentration. Oxygen gas (O\(_2\)) solubilization in water can induce mineral redox reactions. For instance, pyrite (FeS\(_2\)) oxidation can produce large amounts of sulfate, which might be transformed later into H\(_2\)S. Hence, it is mandatory to determine if the experiment is conducted under an open or closed system (effect of atmospheric CO\(_2\) and O\(_2\)). In the field, the system is considered closed. However, live oil and gas contamination during water injection might alter the chemical equilibrium to undesirable conditions. Oxygen scavenger can be used to avoid adverse redox chemical reactions.

Lima [8] carbonate cores samples are separated into two facies-type: stromatolite and grainstone. The mineralogy comprises calcite, dolomite, and quartz with an average weight of 55%, 38%, and 7%, respectively. PHREEQC geochemical simulator [41] is used to evaluate the possible precipitation of anhydrite and gypsum because of the high concentration of sulfate in some of the injected brines. Although Lima [8] tried to evaluate possible precipitation of anhydrite and gypsum, the simulation was conducted without considering the equilibration with atmospheric CO\(_2\), which might significantly impact the results. Furthermore, we investigate the possible dissolution of calcite and dolomite.

Formation brine (FW) and four seawater variations (initial sulfate concentration, SW, four times sulfate, SW4S, depleted on sulfate, SW0S, and depleted on sodium, SW0NaCl) were considered for injection, and their ionic composition is shown in Table 2. PHREEQC simulations were conducted assuming batch equilibration of calcite, dolomite, and quartz with the selected brines at reservoir temperature (65 °C) and considering atmospheric gas carbonic (pCO\(_2\) = −3.5). The main reactions considered for the carbonate system (including gypsum) are shown in Equations (1)–(5). Debye–Hückel correlation is used for activity coefficient.

\[
\begin{align*}
\text{CO}_2(g) + H_2O & \leftrightarrow H^+ + HCO_3^-, \\
\text{CO}_3^{2-} + H^+ & \leftrightarrow HCO_3^-, \\
\text{CaCO}_3 & \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}, \\
\text{CaMg}((\text{CO}_3)_2) & \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}, \\
\text{CaSO}_4 & \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-},
\end{align*}
\]

**Table 2.** Formation brine and variations of seawater composition.

| Ion (ppm) | FW    | SW0S  | SW    | SW0NaCl | SW4S  |
|----------|-------|-------|-------|---------|-------|
| Na\(^+\) | 68,980| 10,924| 11,498| 1399    | 12,783|
| Cl\(^-\) | 127,467| 21,808| 20,721| 5147    | 16,491|
| K\(^+\)  | 3458  | 390   | 390   | 390     | 390   |
| Ca\(^{2+}\)| 7410  | 439   | 439   | 439     | 439   |
| Mg\(^{2+}\)| 1674  | 1376  | 1376  | 1376    | 1376  |
| SO\(_4^{2-}\) | 39    | 119   | 2800  | 2800    | 11,200|
| Total dissolved solids | 209,046| 35,207| 37,375| 11,702  | 42,679|
| Ionic strength (mol/L) | 4.86  | 0.70  | 0.70  | 0.22    | 0.72  |

Figure 1 shows the mineral composition results after equilibration of formation brine in six different fractions (1.0, 0.8, 0.6, 0.4, 0.2, and 0.0) with variations of seawater from Table 2. Quartz is omitted because it is stable and does not dissolve or precipitate (constant
7.0 wt. %). The trends show relatively stable calcite dissolution and dolomite precipitation (dolomitization) for all brine mixtures. No scale deposition is observed. The only exception is for mixtures of sulfate concentration four times above seawater (SW4S), showing that a substantial amount of gypsum precipitated (no anhydrite). Thus, for now on, we discard SW4S as candidate brine to be injected because of possible scale deposition and sulfate consumption.

Figure 1. Mineral assembly after equilibration of several formation brine fractions with different Scheme.

3.3. Wettability Alteration Modeling

The wettability alteration model’s careful selection, among the several ones proposed in the literature, is fundamental for a good prediction of oil recovery. We listed the underlying mechanism proposed in the literature to explain the wettability alteration of carbonate rocks concerning oil and water. For simulation purposes, the model needs to represent the significant impact of changing water composition on wettability. Lima [8] coreflood results show similar trends observed in other experimental work listed previously. For example, oil recovery increases as sulfate concentration increases, sodium concentration decreases, and ionic strength decrease, indicating the EWI effect.

We apply the model proposed by Sanaei et al. [6] and Bordeaux-Rego et al. [7]. The method consists of first computing interfacial forces between oil and rock surfaces that are separated by an aqueous phase (the disjoining pressure). We assume van der Waals, electrostatic, and structural forces are the only interactions in the system. The electrostatic contribution’s surface potential is computed from surface complexation modeling (SCM). We then estimate the contact angle from the augmented Young-Laplace equation assuming a sessile drop shape. A schematic of the contact angle in the porous media is shown in Figure 2. More details of the proposed model can be found in the Appendix A.

Figure 2. Schematic of (a) oil trapped inside a pore and (b) contact angle in rock-brine-oil interface [7].
The reasons to select this model are: (1) it uses SCM as an adsorption isotherm to consider specific ion interaction, (2) it considers the effect of salinity or ionic strength in all terms, (3) and it is tunable if zeta-potential and contact angle measurements are available. The model’s limitations reside in computing contact angle for oil-wet regions ($\theta > 120$) and having a large number of parameters. In order to lessen this issue, we keep all parameters used in this model similar to as proposed by Sanaei et al. [6] and Bordeaux-Rego et al. [7] shown in Appendix A. Wettability alteration by calcite dissolution as a possible mechanism is not considered since the mineral assemblage is stable for all mixtures (Figure 1). We compute the ion adsorption at mineral and oil surfaces considering SCM using PHREEQC simulator [41]. We use the same brine, oil, and mineralogy composition for surface potential and contact angle estimation for all simulations. However, since Lima [8] did not measure zeta-potential for rock and oil, we use the SCM equilibrium constants and reactions proposed by Bordeaux-Rego et al. [7] that matched of Al-Mahrouqi et al. [28] zeta-potential data (Appendix B). The simulation equilibrium condition is the same as presented in the previous section. Rock and oil surface site densities are assumed to be $1.0 \text{ site/} \eta \text{m}^2$. Rock and oil surface areas are presumed to be equal to 2.5 and 0.1 $\text{m}^2/\eta \text{g}$, respectively. In addition, we use the same DLVO parameters suggested by the authors.

Figure 3 shows details on the electrostatic behavior (rock and oil surface potentials) for different mixtures of formation brine and seawater variations (SW0S, SW, and SW0NaCl). Oil surface potential show similar trends for all mixtures, with values from $-3.3 \text{ mV}$ (100% formation brine) to $-40.0 \text{ mV}$ (100% SW0NaCl). These results indicate that the decrease in absolute values is strongly correlated to ionic strength reduction (linear trend). However, for the rock surface, the potentials indicate the effect of sulfate and sodium adsorption ions on the surface. Values range from 15.5 mV (100% formation brine) to $-29.5 \text{ mV}$ (100% SW0NaCl). This result is reasonable since only rock surface is assumed to have adsorption of $\text{SO}_4^{2-}$ and $\text{Na}^+$ ions.

Figure 4 shows the calculated contact angle for mixtures of formation brine and the three seawater schemes (SW0S, SW, and SW0NaCl). In addition, we include experimental contact angle values reported in literature of Brazilian Pre-Salt formation for FW ($\theta = 93.0^\circ$) [42], SW ($\theta = 63.0^\circ$), and SW0NaCl ($\theta = 55.0^\circ$) [43]. The experimental conditions are similar to our simulations. One can observe that the FW simulation has the most oil-wet condition ($\theta = 85.0^\circ$). SW0NaCl is the most water-wet state ($\theta = 56.6^\circ$) followed by SW ($\theta = 61.9^\circ$). SW0S is the most oil-wet condition for the injected brines ($\theta = 68.6^\circ$), as expected, since it has a low sulfate concentration and high sodium content.
There is a noteworthy discrepancy between the contact angles reported in the experiments and the ones calculated from the modeling approach, especially for the FW brine. The reason can be (1) slight differences in experiment and simulation conditions (e.g., mineralogy and brine compositions), and (2) the model limitation to estimate contact angle in oil-wet regions [7]. However, the most critical aspect is that this modeling approach can capture the wettability alteration trend as expected from laboratory data, even with brines with similar ionic strength and sodium chloride concentrations (e.g., SW and SW0S) and same sulfate content (e.g., SW and SW0NaCl). Note that as the difference between rock and oil surface potential decreases, the contact angle decreases in a similar proportion, as observed by Jackson et al. [21]. All contact angle values lie within the intermediate-wet region.

3.4. Coreflood History-Match

To validate the wettability alteration model’s ability to predict oil recovery, we simulate forced displacement corefloods using UTCOMP-IPhreeqc [44] and a commercial reservoir simulator (we denominate as Simulator A). UTCOMP [45] is a three-dimensional and compositional phase behavior simulator for multiphase transport in porous media developed at The University of Texas at Austin. The simulator has several capabilities, such as model miscible and immiscible gas flooding, chemical EOR, and CO$_2$ storage. IPhreeqc is the interface that allows UTCOMP to perform reactive-transport simulations using all PHREEQC geochemical capabilities.

For UTCOMP-IPhreeqc, contact angles are computed for each grid block directly as interpolation parameter ($\theta_{\text{int}}$) of oil- and water-wet relative permeabilities, according to Equations (6)–(8). Since calculating contact angle is not available in most reservoir simulators, including Simulator A, we propose a method so total salinity concentration in the grid block can be used as an interpolation parameter. We define a simple transfer function relating total salinity concentration to normalized contact angles calculated in the previous section, as shown in Table 3. Observe that the water-wet and oil-wet conditions are assigned at the interpolation parameter equal to 1.00 and 0.00, respectively.

$$\theta_{\text{int}} = \max \left[ \min \left( \frac{\theta(x,t) - \theta_{\min}}{\theta_{\max} - \theta_{\min}}, 1 \right), 0 \right], \quad (6)$$

$$k_{ro} = (1 - \theta_{\text{int}}) \times k_{rW}^{\text{OW}}(S) + \theta_{\text{int}} \times k_{rW}^{\text{WW}}(S), \quad (7)$$

$$k_{rw} = (1 - \theta_{\text{int}}) \times k_{rW}^{\text{OW}}(S) + \theta_{\text{int}} \times k_{rW}^{\text{WW}}(S), \quad (8)$$
where $\theta_{\text{min}}$ and $\theta_{\text{max}}$ are the minimum and maximum computed interpolation parameters, $k_{ro}$ and $k_{rw}$ are the oil and water relative permeability, and suffix OW and WW refer to oil-wet and water-wet relative permeability curves as a function of phase saturation ($S$), respectively. $\theta(x,t)$ is the interpolation parameter of a particular grid block at position $x$ and time $t$.

Table 3. Total salinity concentration and respective interpolation parameter to model wettability alteration in simulator A.

| Brine         | Total Salinity (ppm) | Interpolation Parameter |
|---------------|----------------------|-------------------------|
| SW0S          | 50,000               | 0.00                    |
| -             | 39,500               | 0.26                    |
| SW            | 29,000               | 0.51                    |
| -             | 22,300               | 0.67                    |
| -             | 15,800               | 0.83                    |
| SW0NaCl       | 9000                 | 1.00                    |

Note that the total salinity approach has several limitations and should be carefully used since wettability is directly dependent on specific ions interactions and geochemical reactions. The most important limitations are: (1) total salinity concentration is treated as a tracer that might not represent correctly ionic adsorption/exchange mechanisms, (2) minerals are not able to dissolve/precipitate preventing the source or sink of essential ions, (3) and wettability alteration changes monotonically as the injected brine is being flooded (as shown in Figure 4). However, this last behavior is not always observed in the laboratory [34].

Lima [8] designed several corefloods to test different brine compositions (SW0S, SW, and SW0NaCl). The general experiment procedure consists of initial injection of SW0S for several pore volumes until oil recovery is no longer observed. Then, the new brine is switched and injected until ultimate recovery. Recovery factors and pressure drop were reported along with all experiments. The cores are aged for two weeks with formation brine and crude oil to restore initial reservoir wettability. Irreducible water saturation was measured through centrifuge experiments. Table 4 shows detailed information regarding the simulation of corefloods D65S2-0.1 and D100S2 used as oil recovery and differential pressure history-match examples in this work. Brooks-Corey parameters are the only tuning parameters shown in Equations (9) and (10) (except irreducible water saturation, taken from the experimental data).

\[
k_{ro} = k_{rocw} \left[ \frac{1 - S_w(x,t) - S_{orw}}{1 - S_{iw} - S_{orw}} \right]^{n_{ow}},
\]

\[
k_{rw} = k_{rwro} \left[ \frac{1 - S_w(x,t) - S_{orw}}{1 - S_{iw} - S_{orw}} \right]^{n_{w}},
\]

where $S_{orw}$ is the residual oil saturation, $S_{iw}$ is the irreducible water saturation, $n_{ow}$ and $n_{w}$ are the oil and water exponents, and $k_{rocw}$ and $k_{rwro}$ are the oil and water end-point for relative permeability, respectively. $S_w(x,t)$ is the water saturation of a particular grid block at position $x$ and time $t$.

In one of the experiments (D100S2), a bump-flow technique was conducted. Bump-flows are controlled increases in flow rate (in this case 4 times rise) used to mitigate capillary end-effect. However, the increase in flow rate might decrease the residual oil saturation. According to Lake et al. [12], rocks with wide pore size distribution (e.g., carbonates) might face a reduction of residual oil saturation even when the capillary number ($N_c$) has a relatively small increase. Unlike carbonate, sandstone rocks have a well-defined critical capillary number showing that no change in residual oil saturation is observed below that value even if $N_c$ is increased in some orders of magnitude.
Table 4. D652S and D100S corefloods and simulation parameters and conditions.

| Parameter                          | D652S-0.1 | D100S2 |
|------------------------------------|-----------|--------|
| Porosity                           | 0.12      | 0.18   |
| Permeability (mD)                  | 157       | 237    |
| Length (cm)                        | 6.8       | 5.82   |
| Total Volume (cm³)                 | 77.12     | 66.01  |
| Oil viscosity (cp)                 | 3.18      | 3.18   |
| Oil density (g/cm³)                | 846       | 846    |
| Temperature (°C)                   | 65        | 65     |
| Oil acid number (mg KOH/g of oil)  | 0.151     | 0.151  |
| Water viscosity (cp)               | 1.0       | 1.0    |
| Water density (g/cm³)              |           |        |
| Injection rate (cc/min)            | 0.1       | 0.1 -> 0.4 (bump flow) |
| Injection scheme                   | SW0S -> SW0NaCl | SW0S -> SW0NaCl |
| 1D number of grid blocks           | 50        | 50     |
| 1D number of grid blocks           |           |        |
| Confining pressure (psi)           | 2000      | 2000   |
| Figure 5 illustrates the history-match result for the injection of SW0S followed by SW0NaCl for D65S2 coreflood. Experimental data are shown in circular marks. UTCOMP-Iphreeqc and Simulator A results are illustrated as continuous lines and dashed lines, respectively. The injection brine was switched from SW0S to SW0NaCl at 23 pore volumes. Although results from UTCOMP-Iphreeqc show a much better representation of oil recovery at all injection stages, Simulator A match is also satisfactory to mimic the ultimate recovery. Improved oil recovery from SW0NaCl was approximately 6% compared with SW0S.

Furthermore, we investigate if the effect of wettability alteration (considering the proposed interpolation approach) in Simulator A can be used in conjunction with reducing residual oil saturation from bump-flows. The Bump-flow effect was simulated by reducing the residual oil saturation at low and high capillary numbers. Figure 6 illustrates the history-match results of simulation injecting SW0S and consequently SW0NaCl for the experiment D100S2. The results show an excellent match at low and high flow rates. Observe that the increase in oil recovery is more evident at the lower recovery factor (SW0S), probably because the flooding did not reach residual oil saturation.
The reduction of residual water saturation because of wettability alteration varied from 3 to 5%. End-point and exponents relative permeability parameters showed a more water-wet tendency with a variation on the order of 0.5 and 1.0, respectively. For the increase in capillary number effect (bump-flow case), the decrease in residual oil saturation was 10% to match the coreflood. This result is a critical attribute to consider during the simulation and well-logging residual oil saturation determination since close to the wellbore, the flow rate is usually much higher compared to regions far from the well. The tuned Brooks-Corey parameters for oil- and water-wet conditions of relative permeability are shown in Table 5. The oil recovery factors are between 5 to 11% for both experiments. The results illustrate the importance of other relative permeability parameters (residual oil saturation) and their impact on improved displacement efficiency.

Table 5. Brooks-Corey tuned parameters for relative permeability from experiments D65S1 and D100S2.

| Brooks-Corey Parameter | DS65S1 -0.1 Oil-Wet | Water-Wet | D100S2 Oil-Wet | Water-Wet |
|------------------------|----------------------|-----------|----------------|-----------|
| $S_{orw}$              | 0.38                 | 0.35      | 0.3            | 0.2       |
| $n_w$                  | 1.0                  | 1.5       | 1.2            | 2.0       |
| $n_{orw}$              | 4.5                  | 3.5       | 4.5            | 3.5       |
| $k_{rwo}$              | 0.6                  | 0.5       | 0.6            | 0.5       |
| $k_{rcw}$              | 0.6                  | 0.6       | 0.6            | 0.6       |

4. Summary and Conclusions

We proposed a framework to model Engineered Water Injection from coreflooding experiments using geochemical and reservoir numerical simulations in this work. The framework consists of four steps: experimental screening criteria, geochemical evaluation, wettability alteration modeling, and coreflood history-match. We apply the method using Lima [8] laboratory data of a Brazilian Pre-Salt carbonate as a candidate for Engineered Water Injection. We conclude that:

- Experiment design can considerably affect rock-fluid geochemical interactions. It is essential to perform chemical equilibrium calculations before reactive-transport simulation to represent what to expect from the results. For the specific example used in this paper, sulfate consumption and possible scale deposition occur when high concentrations of sulfate were equilibrated with the mineral assembly.
• The proposed wettability alteration model by computing contact angle can be used to history-match oil production and differential pressure. Besides, the proposed method to use total salinity concentration as a proxy of contact angle is less accurate but gives acceptable results.

• It is essential to highlight that the brine used in this work has very similar ionic strength but gives considerably different wettability conditions. This result evidence that double-layer expansion alone would not explain the results observed. Modeling of combined mechanisms is required to predict improved oil recovery accurately.

Although the proposed framework and validation were applied to a carbonate rock candidate for Engineered Water Injection, future work should also evaluate different rock types (e.g., clayed sandstones) and carbonates with different lithologies. In addition, we suggest further investigation on the impact of scale-up the wettability alteration effect in relative permeability to address the applicability of the proposed methodology in field cases.

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Appendix A

Sanaei et al. [6] and Bordeaux-Rego et al. [7] proposed the following wettability alteration model. The contact angle can be estimated by integrating the Young-Laplace Equation (assuming no capillary forces) as shown in Equation (A1).

\[ 1 - \cos \theta = \frac{1}{\sigma} \int_{h_0}^{h_{\infty}} \Pi \, dh, \]  

(A1)

where \( \sigma \) is the water/oil interfacial tension (20 dynes/cm), \( \Pi \) is the disjoining pressure, and \( h \) is the distance that separates both surfaces. The subscript “0” denotes the separation thickness, and “\( \infty \)” denotes the distance tending to infinity.

The disjoining pressure is composed of the contribution of van der Waals (\( \Pi_{vdW} \)), electrostatic (\( \Pi_{edl} \)), and structural (\( \Pi_s \)) forces (Equations (A2)–(A6)).

\[ \Pi_{tot} = \Pi_{vdW} + \Pi_{edl} + \Pi_s, \]  

(A2)

\[ \Pi_{vdW} = -\frac{A}{6\pi h^3}, \]  

(A3)

\[ \Pi_{edl} = \frac{\varepsilon_0 \varepsilon_\kappa^2 [2\psi_{0,1}\psi_{0,2} \cosh(kh_0) - (\psi_{0,1}^2 + \psi_{0,2}^2)]}{2[\sinh(kh_0)]^2}, \]  

(A4)

\[ \Pi_s = \alpha A_s \exp \left( -\frac{h_0}{h_s} \right), \]  

(A5)

\[ \alpha = \frac{1}{1 + \left( \frac{BNa}{1 + Ns} \right)}, \]  

(A6)
where $A$ is the screened Hamaker constant (Equation (A7)), $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the water relative dielectric constant, $\kappa$ is the Debye length (Equation (A8)), $\psi(0,i)$ is the surface potential, $A_s$ is the structural coefficient ($5.5 \times 10^{10}$ kPa), $h_s$ is the decay length (0.03 nm), $Na$ is the sodium activity, and B is assumed to equal to 1.5.

$$A_h = A_{\nu=0}(2kh) \exp(-2kh) + A_{\nu>0}, \quad (A7)$$

where $A_{\nu=0}$ is the zero-frequency contribution, $A_{\nu>0}$ is the dispersion energy contribution calculated from Lifshitz theory.

$$\kappa^{-1} = \left( \frac{\varepsilon_0 k_B \varepsilon^2}{2e^2 N_A T} \right)^{0.5}, \quad (A8)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature (338 K), $e$ is the electronic charge, $N_A$ is Avogadro’s number, and $I$ is the ionic strength given in Equation (A9).

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2, \quad (A9)$$

where $c_i$ and $z_i$ are molar concentration and charge number (valence) for ion $i$, respectively.

The surface potential in Equation (A4) can be obtained using surface complexation modeling. After computing the surface potential, we estimate the separation distance between rock and oil ($h$). To do so, we solve Equation (A2) numerically for disjoining pressure equal to zero. Finally, with all the unknowns in hand, we can compute the contact angle using Equation (A1).

**Appendix B**

We apply the following surface reactions and respective equilibrium constants [log(k)] for oil and carbonate as an ion adsorption isotherm to define the surface potential used to estimate the contact angle summarized in Tables A1 and A2.

**Table A1. Oil surface complexation reactions and logarithm of equilibrium constants [log(k)].**

| Reaction                      | log(k) |
|-------------------------------|--------|
| $-\text{NH}^+ \leftrightarrow -\text{N} + \text{H}^+$ | -5.0   |
| $-\text{COOH} \leftrightarrow -\text{COO}^- + \text{H}^+$ | -4.2   |
| $-\text{COOH} + \text{Ca}^{2+} \leftrightarrow -\text{COOCa}^+ + \text{H}^+$ | -3.8   |
| $-\text{COOH} + \text{Mg}^{2+} \leftrightarrow -\text{COOMg}^+ + \text{H}^+$ | -3.8   |

**Table A2. Carbonate surface complexation reactions and logarithm of equilibrium constants [log(k)].**

| Reaction                      | log(k) |
|-------------------------------|--------|
| $\text{CaOH} + \text{H}^+ \leftrightarrow \text{CaOH}_2^+$ | 11.3   |
| $\text{CaOH}_2^+ + \text{SO}_4^{2-} \leftrightarrow \text{CaSO}_4^- + \text{H}_2\text{O}$ | 1.1    |
| $\text{CaOH} + \text{HCO}_3^- \leftrightarrow \text{CaCO}_3^- + \text{H}_2\text{O}$ | 6.8    |
| $\text{CO}_2\text{H} \leftrightarrow \text{CO}_2^- + \text{H}^+$ | -3.35  |
| $\text{CO}_2\text{H} + \text{Ca}^{12} \leftrightarrow \text{CO}_2\text{Ca}^+ + \text{H}^+$ | -3.6   |
| $\text{CO}_2\text{H} + \text{Mg}^{12} \rightarrow \text{CO}_2\text{Mg}^+ + \text{H}^+$ | -3.6   |
| $\text{CO}_2\text{H} + \text{Na}^+ \rightarrow \text{CO}_2\text{HNa}^+$ | 2.7    |

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