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A Comprehensive Simulation Study of Physicochemical and Geochemical Interactions on Immiscible CO₂-LSWAG Injection in Carbonates

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Abstract: Low-salinity water-alternating-CO₂ (CO₂-LSWAG) injection has been widely studied and employed due to its capability to promote enhanced oil recovery (EOR). However, there is no consensus on the dominant mechanisms for oil recovery in carbonates due to the extreme complexity of the oil–brine–rock interactions. This work proposes a comparative investigation of the physicochemical and geochemical effects of continuous CO₂ and CO₂-LSWAG immiscible injections on oil recovery in a carbonate core. Simulations were carried out using oil PVT properties and relative permeability experimental data from the literature. A comparison of SO₄^{2−} and Mg²⁺ as interpolant ions, oil, water and gas production, pressure, and rock and fluid properties along the core and in the effluent was made. The results show a high recovery factor for CO₂ (62%) and CO₂-LSWAG (85%), even in immiscible conditions. The mineral dissolution and porosity variations were more pronounced for CO₂-LSWAG than CO₂. The simulation results showed that Mg²⁺ as an interpolant improves oil recovery more than SO₄^{2−} because Mg²⁺ concentration in the aqueous phase after LSW injection leads to relative permeability values, which are more favorable.

Keywords: immiscible CO₂; CO₂-LSWAG; carbonate; physicochemical simulation; geochemical simulation; interpolants



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1. Introduction

A broad discussion has been observed in recent years regarding greenhouse gas emissions reduction, among which CO₂ is one of the main ones. Several studies have evaluated the capture, use and storage of carbon. The CO₂ geological storage has been investigated from a few different perspectives. For instance, CO₂ injection into depleted oil reservoirs has been considered an alternative for underground gas storage and, simultaneously, to operate as a bioreactor capable of producing natural gas (low-carbon energy) by microbial-mediated CO₂ methanation [1]. Another process that has been widely used as an alternative for reducing CO₂ release to the atmosphere is the reinjection of this gas to improve the oil recovery factor in reservoirs whose primary methods are no longer technically and economically viable.

CO₂ injection is one of the most successful and widely applied enhanced oil recovery (EOR) techniques, achieving a typical incremental oil recovery rate of 15 and 25% when injected after a typical waterflood [2]. CO₂ is preferred to other gases, such as hydrocarbons and N₂, because it presents the lowest minimum miscibility pressure (MMP). CO₂ flooding in miscible conditions leads to oil swelling, oil viscosity reduction, and gas–oil interfacial tension (IFT) reduction due to CO₂ dissolution into the oil, increasing the relative permeability of the oil inside the reservoir pores and, consequently, the oil displacement towards

production [3,4]. However, it has been reported that even in non-miscible conditions, CO₂ flooding still promotes some recovery of residual oil through combining mechanisms related to partial CO₂ dissolution in oil and a reduction in capillary and interfacial forces [5,6]. In addition, immiscible CO₂ injection allows the use of milder operating conditions, which is better operationally and economically and valued in reservoirs whose pressure is lower than the minimum miscibility pressure of CO₂ [7]. Al-Mutairi et al. [8] investigated the injection of immiscible CO₂ in carbonates. They experimentally proved that the wettability alteration due to the CO₂ solubility in the brine could be an oil recovery mechanism. However, continuous CO₂ injection is associated with a high mobility ratio and viscous finger formation, which are undesirable for oil recovery efficiency. For this reason, CO₂ injection has been associated with other fluids, such as in low-salinity water-alternating-gas injection or high-salinity water-alternating-gas injection [9].

In turn, water injection with salt concentration and composition variation, as proposed by LSWI, has been studied since the 1990s [10]. The LSWI technique has been tested and investigated at laboratory and field scales, generally showing positive results compared to conventional waterflooding in sandstones and carbonates [11–16]. Around 80–90% of the carbonate reservoirs, the primary type of worldwide oil reservoir, are not water-wet due to the positive charge of the carbonate surface that adsorbs the negatively-charged crude oil. Thus, the rock wettability alteration, from oil-wet to water-wet or neutral conditions, enhances oil recovery because the water phase interacts preferentially with the rock surface. In addition, this has been the main reason LSWI leads to oil recovery improvement in carbonate rocks [17,18]. LSWI changes the wettability by combining different mechanisms, such as multicomponent ion exchange, double layer expansion, pH increase, fines migration, and rock dissolution. However, an adequate understanding of the wettability mechanisms in carbonates is still lacking. Some contradictory results have been found due to the high complexity of this type of reservoir, which is an additional motivation to investigate each mechanism's contributions under several conditions deeply [19,20].

Low-salinity water-alternating-CO₂ flooding (CO₂-LSWAG) is an EOR technique that has recently attracted scientific and industrial attention. It is very promising because it promotes synergy between the unique advantages of low-salinity water injection (LSWI) and CO₂ EOR. The CO₂-LSWAG technique has a significant economic and environmental appeal since it does not require the purchase of chemicals, and the CO₂ injection into the reservoirs helps mitigate greenhouse gas emissions [21,22]. As stressed by Wilson [23] and Ma and James [16], in addition to improving recovery, the CO₂-LSWAG technique helps deal with operational issues, such as the delayed production observed in conventional CO₂-WAG (CO₂ water-alternating-gas injection). CO₂-LSWAG combines the unique advantages of each fluid with the interaction between CO₂ and LSW that allows CO₂ dissolution into the injected brine. Carbonated brine's in situ formation leads to improved wettability alteration and brine-oil IFT reduction, decreasing the capillary effects [22].

A few works are investigating the performance of the immiscible CO₂-LSWAG technique in carbonate using experimental core flooding tests, as summarized in the review prepared by Ma and James (2022) [16]. Teklu et al. [22] developed an extensive experimental study to compare the miscible CO₂-LSWAG case with the typical seawater (SW) injection for carbonate cores. The core flooding results showed that LSW and CO₂ alternated injection cycle applied after seawater flooding leads to significant incremental oil recovery. Furthermore, contact angle measurements indicated that the CO₂-saturated low-salinity brine led to a higher wettability alteration than SW and LSW brines. In this work, they also evaluated the immiscible CO₂-LSWAG, but, like most of the works in the literature, applied it to sandstone cores. Ramanathan et al. [24] demonstrated that rock aging is a necessary procedure before CO₂-LSWAG core flooding tests. Their tests showed that immiscible CO₂-LSWAG yielded a 36% additional recovery after SW injection in sandstone cores. Neither author focused on examining the mechanisms that lead to wettability alteration in CO₂-LSWAG processes.

More recently, Chaturvedi et al. [25] evaluated the impact of water salinity on the performance of CO₂-LSWAG core injection, but it is unclear whether the injections were above or below the MMP. They reinforced that the salinity strongly affects the CO₂ saturation in water and, consequently, the oil recovery. The authors recommended CO₂-LSWAG injection to develop depleted oil reservoirs. However, they considered only sandstone cores, which are out of this study's scope, and did not perform any mechanistic investigation. Moradpour et al. [9] conducted contact angle, gas solubility in water, emulsion formation, and core flooding experiments to assess the underlying mechanisms of immiscible CO₂-LSWAG injection in carbonates, and found an incremental oil recovery of 25.5% after SW injection. They highlighted the ion exchange mechanism as the primary cause of the wettability alteration, i.e., the oil desorption from the rock surface. Solubility and contact angle results indicated that CO₂ is more suitable for achieving wettability alteration than N₂. Despite their remarkable contributions, Moradpour et al. [9] did not evaluate the effluent ion concentration, which is needed to properly understand the ion exchange mechanism. Other experimental studies have contributed to the CO₂-LSWAG evaluation, such as Kumar et al. [26] and Al-Abri et al. [27], who performed core flooding tests applied to sandstones under immiscible conditions. Complementary steady-state laboratory tests, such as the determination of contact angle, CO₂ solubility in brines, and oil-brine interfacial tension, were conducted to evaluate the mechanisms behind the effective recovery from the dynamic EOR process. They pointed out interfacial tension reduction due to CO₂ solubility in the aqueous phase and the wettability alteration as reasons for additional oil recovery due to LSW injection.

As core flooding experiments are very time-consuming and operationally complex, numerical modeling and simulation have been used to perform comparative, mechanistic, and sensitivity studies on EOR methods. The great challenge for CO₂-LSWAG simulation is to incorporate the complexity of the geochemical interactions resulting from the low-salinity water injection and the lack of a consensus on the mechanism of this EOR method [16]. Only a few numerical studies have been conducted on CO₂-LSWAG injection. Most of them are applied to sandstones, considering miscible CO₂ injection and adopting the wettability alteration as a recovery mechanism for LSWI. Al-Shalabi et al. [28] compared the performance of gas and high- and low-salinity water-alternating-gas injections. They investigated the effect of water salinity on miscible and immiscible WAG injections in a carbonate core using the UTCOMP simulator. They used previous experimental data to validate the simulation results and highlighted that CO₂ controls the residual oil saturation. At the same time, the LSW increases oil production through wettability alteration. However, they did not evaluate the interpolant of relative permeability curves. They focused only on evaluating the oil recovery factor and pressure drop. As reinforced by Ma and James [14], the UTCOMP simulator does not include the modeling package of geochemical reactions like ion exchange and mineral dissolution. Using a similar approach, Dang et al. [21] compared conventional waterflooding, LSWI, miscible CO₂ injection, and miscible CO₂-LSWAG injection in sandstones using the GEMTM compositional simulator with a mechanistic LSW model at the core and field scale. Their results showed the CO₂-LSWAG case to be the best scenario. They concluded that the performance of CO₂-LSWAG depends on the initial wettability condition, the rock composition, the reservoir heterogeneity, the formation and injection water compositions, the miscibility conditions, and CO₂-LSWAG operational parameters, such as flow rate and CO₂-LSWAG ratio. Given the limited numerical investigations considering CO₂-LSWAG under immiscible conditions in carbonate systems, where most worldwide oil reserves are located, this kind of reservoir requires more in-depth research.

In this context, it is worth highlighting that two major types of mechanisms are involved in oil displacement and recovery during CO₂-LSWAG: the geochemical, which is related to rock-fluid interactions, and the physicochemical, which includes all fluid–fluid interactions, such as oil swelling and viscosity reduction due to gas solubilization into the oil [29,30]. In CO₂-LSWAG EOR, both the physicochemical and geochemical coincide [22].

Naderi [31] has done a numerical study of CO₂-LSWAG to evaluate geochemical and physicochemical modeling. He investigated a sandstone rock with traces of carbonate minerals, such as calcite and dolomite, under miscible conditions, compared with other injection configurations, and considered the use of high-salinity water. However, no comparison of geochemical and physicochemical effects on the performance of immiscible CO₂-LSWAG in carbonates is found in the literature. An assessment of how the interpolant ion affects the CO₂-LSWAG injection and the difference in the most important reservoir properties comparing different interpolants also lack in the literature. The effects of using different interpolant ions are weakly discussed, even though they are fundamental when performing reservoir simulation because the interpolant is used to obtain the relative permeability curves for the reservoir during the simulation [32].

This work employed the GEMTM simulator to comprehensively investigate continuous CO₂ and CO₂-LSWAG immiscible injections in a carbonate core. These processes' physicochemical and geochemical alterations that lead to oil recovery were critically discussed. Oil recovery, water and gas production, reservoir pressure, and rock and fluid properties and composition were carefully assessed in the core and the effluent to understand the physicochemical and geochemical effects. Additionally, for CO₂-LSWAG, Mg²⁺ and SO₄^{2−} were unprecedentedly compared as interpolant ions in the relative permeability curves.

2. Materials and Methods

This work studied continuous immiscible CO₂ injection and low-salinity water-alternating-CO₂ injection using the GEM (Generalized Equation-of-State Model Compositional Reservoir Simulator) developed by CMG (Computer Modelling Group) under the same conditions.

Several authors have used this simulator to study enhanced recovery methods. It is essential to highlight the use of this specific tool to evaluate (i) immiscible, miscible, and near-miscible CO₂ injection into sandstones as developed by Hatzignatiou and Lu (1994) [33], Kamali et al. (2015) [34] and Kamali et al. (2017) [35] and near miscible CO₂ injection simulated by Wang et al. (2021) [5]; (ii) low-salinity water injection into carbonates, by Lee et al. (2020) [36], Moradpour et al. (2020) [37], Adegbite et al. (2018) [38], and Esene et al. (2018) [39]; (iii) miscible and immiscible CO₂ water-alternating-gas injection (CO₂-WAG) in carbonate by Hu et al. (2020) [40] and Sampaio et al. (2020) [41]; (iv) and also the low-salinity water-alternating-CO₂ flooding (CO₂-LSWAG), miscible in sandstone by Dang et al. (2016) [21] and Ma and James (2022) [16]. Most of these works validate the simulations of these EOR methods using experimental data from core flooding tests. In general, it is observed that the number of studies focused on the simulation of different immiscible CO₂ injection approaches in carbonates, such as continuous injection or CO₂-LSWAG, is more limited.

The following sections describe the simulation models, including modeling details, fluid properties, rock and grid simulation characterization, the reactional system and operational requirements specification, and relative permeability data. Additional data required for the simulations are also available in the Supplementary Materials, such as the models to calculate aqueous and hydrocarbons phases properties.

2.1. GEM Modeling of Oil Recovery by Immiscible CO₂-LSWAG Injection

The EM simulator presents a numerical formulation to describe multidimensional and multiphase flow in porous media. This tool incorporates the compositional dynamics of the phases through phase behavior and correlations to compute mass transfer. Therefore, it is equation-of-state-based, and fundamentals mass, momentum, and energy balance equations are considered in association with Darcy's law and the mechanical dispersion/diffusion of components that describe flow in porous media. From this association, multiphase multicomponent flow equations are obtained. The conservation equations that cover all oil, gas, aqueous, and mineral components, as summarized by Dang et al. (2016) [21], are presented as follows:

- For oil and gas components:

$$\psi_i \equiv \sum_{\alpha=g,o,w} \Delta T_{\alpha}^u y_{i\alpha}^u (\Delta P^n + \Delta P_{c\alpha}^u - \tilde{\rho}_{\alpha}^u g \Delta d) + \sum_{\alpha=g,o,w} \Delta D_{i\alpha}^u \Delta y_{i\alpha}^u + V \sigma_{i,aq}^n + q_i^n - \frac{V}{\Delta t} (N_i^n - N_i^{n-1}) = 0 \quad (1)$$

where $i = 1, \dots, n_h$ oil and gas components; α represents the phases o (oil), g (gas), w (water), and T represents molar transmissibility of phase α ; y is the mole fraction of component i in phase α ; P is pressure; P_c is capillary pressure, $\tilde{\rho}$ is mass density; g is gravity acceleration; d is depth; D is the dispersion coefficient in phase α ; V is the grid block bulk volume, σ is the reaction rate, q is the injection/production rate; t is time; N are the moles of a component; superscript n is the current time and $n - 1$ the previous time step, the superscript u refers to $n - 1$ for explicit grid blocks and n for fully implicit grid blocks; and the subscript aq refers to the aqueous phase.

- For aqueous components:

$$\psi_j \equiv \Delta T_{w}^u y_{jw}^u (\Delta P^n - \tilde{\rho}_w^u g \Delta d) + \Delta D_{iw}^u \Delta y_{iw}^u + V \sigma_{j,aq}^n + V \sigma_{j,mn}^n + q_j^n - \frac{V}{\Delta t} (N_{ja}^n - N_{ja}^{n-1}) = 0 \quad (2)$$

where $j = 1, \dots, n_a$ aqueous components; the subscript w refers to phase water; $V \sigma_{j,aq}^n$ to the aqueous reactions rates; and $V \sigma_{j,mn}^n$ to mineral dissolution/precipitation reaction rates.

- For mineral components:

$$\psi_k \equiv V \sigma_{i,mn}^n - \frac{V}{\Delta t} (N_k^n - N_k^{n-1}) = 0 \quad (3)$$

where $k = 1, \dots, n_m$ mineral components and the subscript mn refers to the mineral phase.

The reactions listed in Section 2.4 are coupled to these equations and the equations for EOS flash calculations. The chemical equilibrium of intra-aqueous reactions is modeled with chemical equilibrium constants of the reactions, as shown by Dang et al. (2016) [21] and presented below.

$$Q_{\alpha} - K_{eq,\alpha} = 0 \quad (4)$$

where $\alpha = 1, \dots, R_{aq}$ intra-aqueous reactions; $K_{eq,\alpha}$ refers to the chemical equilibrium constant for the aqueous reaction α and Q_{α} to the activity product (Equation (5)).

$$Q_{\alpha} = \prod_{k=1}^{n_{aq}} a_k^{\nu_{k\alpha}} \quad (5)$$

where a_k is the activity of component k , calculated with the B-dot model; $\nu_{k\alpha}$ are the stoichiometry coefficients; and n_{aq} is the number of species in an intra-aqueous equilibrium reaction.

Kinetics of the mineral dissolution and precipitation reactions are also incorporated in the model, as detailed by Dang et al. (2016) [21]:

$$r_{\beta} = \hat{A}_{\beta} k_{\beta} \left(1 - \frac{Q_{\beta}}{K_{eq,\beta}} \right) \quad (6)$$

where $\beta = 1, \dots, R_{mn}$ mineral reactions; r_{β} refers to the dissolution/precipitation rate per unit bulk volume of the porous medium; $\hat{A}_{\beta}$ to the reactive surface area for mineral β per unit of the porous medium; k_{β} to the rate constant of mineral reaction; Q_{β} to the activity product for mineral β dissolution reaction; and $K_{eq,\beta}$ refers to the chemical equilibrium constant for mineral reaction (available in the literature for many minerals).

Considering the individual contributions of the injected fluids, CO_2 and LSW, the simulator can simultaneously capture the recovery mechanisms associated with each one. One of the oil recovery mechanisms related to CO_2 injection is the mineral dissolution and release of ions that may participate in other chemical reactions incorporated into the model

through the geochemical reactions in Section 2.4. The CO₂ distribution between the oil, gas, and water phases is essential to simulate CO₂ EOR. Then, the CO₂ solubility in the water phase is considered by including Henry's law. Regarding the contribution of the injection of low-salinity water, the ion exchange reaction (shown in Section 2.4) and the wettability alteration represented by the shifting of the relative permeability curves from an oil-wet condition to a water-wet condition (presented in Section 2.6) are included.

2.2. Fluid Properties

Experimental composition oil data presented by Sequeira [42] were chosen, as indicated in Table 1. As explained in the Supplementary Materials, PVT characterization data and the MMP, also available from Sequeira [32], were used for tuning the EOS to match the oil behavior through the WinProp simulator developed by CMG.

Table 1. Oil composition [42].

Component	N ₂	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	iC ₄	NC ₄	iC ₅	NC ₅	FC ₆	C ₇₊
Molar composition (%)	0.023	0.136	23.736	0.009	0.064	0.117	0.342	0.822	0.786	2.644	71.323

The composition of the connate water (pH = 6) and the injection water is shown in Table 2. The injection water chosen is a typical composition of seawater, diluted 30 times to obtain a low-salinity brine with a concentration of 1000 ppm. This optimal concentration was selected from preliminary studies [43], in which the brine that maximizes the oil recovery factor for the same scenario investigated in this study was evaluated.

Table 2. Connate water and low-salinity water composition.

Ion	Composition (ppm)	
	Connate Water	Low-Salinity Water
Na ⁺	54,370	11,075
Cl [−]	139,800	18,847
K ⁺	2850	393
Ca ²⁺	19,740	142
SO ₄ ^{2−}	8	24
Mg ²⁺	4070	170

2.3. Rock Properties and Simulation Grid

A homogeneous carbonate core with dimensions 1.5'' in diameter and 12'' in length was selected. The simulation grid was built considering the 30 × 1 × 1 blocks with an injection well at coordinates {1,1,1} and production well at coordinates {30,1,1}, approximating the cylindrical shape of the core to cartesian geometry, as illustrated in Figure 1. As a carbonate system, the volumetric composition of the core was 50% calcite and 50% dolomite, which allows for analyzing the different interactions with each type of mineral. The porosity and permeability data are also summarized in Figure 1.

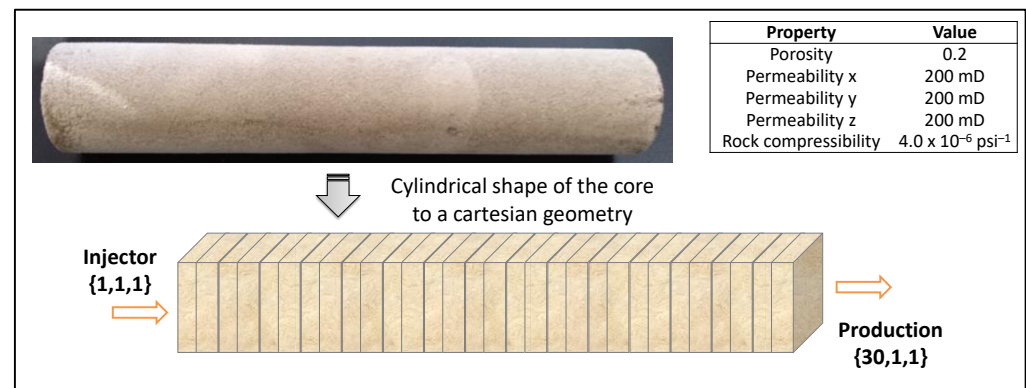


Figure 1. Schematic diagram of the simulation grid indicating the injector well and production well.

2.4. Reactional System

The simulation model includes relevant chemical reactions related to CO₂ injection and CO₂-LSWAG, shown in Table 3. Besides the reactions of salt dissociation, the following reactions are worth mentioning: (1) the carbonic acid formation from the CO₂ dissociation in water; (2) the rock dissolution of calcite and dolomite due to the presence of an acidic medium from the dissociation of carbonic acid; and (3) the ion exchange reactions.

Table 3. Reactional system.

Aqueous Reactions:		
1.	$\text{NaCl} \leftrightarrow \text{Na}^+ + \text{Cl}^-$	$\log K_{eq} (238^\circ\text{F}) = 0.89$
2.	$\text{KCl} \leftrightarrow \text{K}^+ + \text{Cl}^-$	$\log K_{eq} (238^\circ\text{F}) = 1.14$
3.	$\text{CaCl}^+ \leftrightarrow \text{Ca}^{2+} + \text{Cl}^-$	$\log K_{eq} (238^\circ\text{F}) = -0.48$
4.	$\text{MgCl}^+ \leftrightarrow \text{Mg}^{2+} + \text{Cl}^-$	$\log K_{eq} (238^\circ\text{F}) = -0.16$
5.	$\text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	$\log K_{eq} (238^\circ\text{F}) = -2.84$
6.	$\text{MgSO}_4 \leftrightarrow \text{Mg}^{2+} + \text{SO}_4^{2-}$	$\log K_{eq} (238^\circ\text{F}) = -2.67$
7.	$\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}$	$\log K_{eq} (238^\circ\text{F}) = -3.52$
8.	$\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O}$	$\log K_{eq} (238^\circ\text{F}) = 12.03$
9.	$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	$\log K_{eq} (238^\circ\text{F}) = -6.50$
Mineral reactions:		
10.	$\text{H}^+ + \text{Calcite} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	$\log K_{eq} (77^\circ\text{F}) = 0.509$
11.	$2\text{H}^+ + \text{Dolomite} \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$	$\log K_{eq} (77^\circ\text{F}) = -0.272$
Ion exchange reaction:		
12.	$0.5\text{SO}_4^{2-} + \text{CH}_3\text{COO}^- \leftrightarrow \text{CH}_3\text{COO}^- + 0.5\text{SO}_4^{2-}$	
13.	$\text{CaCH}_3\text{CO}^+ \leftrightarrow \text{Ca}^{2+} + \text{CH}_3\text{COO}^-$	
14.	$\text{MgCH}_3\text{CO}^+ \leftrightarrow \text{Mg}^{2+} + \text{CH}_3\text{COO}^-$	

To also take into account the kinetic of mineral reactions, in addition to the equilibrium mineral dissolution/precipitation data shown in Table 3, the kinetic parameters of reactions 10 and 11 were included in the simulation model, as presented in Table 4.

Table 4. Kinetic parameters of mineral reactions.

	Calcite	Dolomite
Reactive surface area (m ² /m ³ of bulk volume of rock)	2989.25	2584.4
Activation Energy (J/mol)	23,500	52,200

2.5. Operating Conditions

The initial operating conditions cover a temperature of 238°F (114.4 °C), initial water saturation of 0.0894, and pressure of 1900 psi. The initial core pressure is below the minimum miscibility pressure (6675 psi), determined experimentally by Sequeira [42]. Consequently, the present study was carried out under conditions of immiscible CO₂ injection. An overview of the operating conditions used in the simulation is shown in Table 5. Injection well and production well constraints are the same for CO₂ continuous flooding, differing only from the non-existence of a water flow.

Table 5. Operating conditions.

Injection well constraints	Water flow rate = 0.0007 bbl/day—reservoir condition CO ₂ flow rate = 0.004 ft ³ /day—reservoir condition Bottomhole pressure = 1950 psi—maximum
Production well constraints	Bottomhole pressure = 1901 psi Surface liquid rate = 0.001 bbl/day—maximum
WAG ratio	1:1
Slug size	0.06 PV
Pore volume	0.003 ft ³

2.6. Relative Permeability Curves

For CO₂-LSWAG injection, two simulations were performed, each one using an interpolation criterion. The first simulation considered the sulfate concentration in the aqueous phase to interpolate the relative permeability curves during the process, varying between the high- and low-salinity relative permeability curves provided as input to the simulation. The second scenario used the magnesium concentration in the aqueous phase as the interpolation agent. Mg²⁺ and SO₄^{2−} were selected because they have been widely discussed as potential candidates for wettability alteration and oil recovery factor improvement in carbonates when injecting low-salinity water [44]. Although Ca²⁺ is also mentioned as a possible ion, its effects are more pronounced at lower temperatures than in the analyzed reservoir [44]. The water–oil relative permeability curves for two salinity levels are shown in Figure 2, based on data available from Dang et al. [45]. It is noteworthy that, for the relative permeability curves corresponding to low-salinity water, the interpolant ions concentrations were considered according to Table 2, that is, for magnesium 170 ppm and calcium 142 ppm. Likewise, for the relative permeability curves corresponding to high-salinity water, the concentration of the interpolant ions was specified for connate water in Table 2, that is, for magnesium 4070 ppm and calcium 19,740 ppm. These values are a reference for the curves shown in Figure 2. During the simulation, when the interpolating ion concentration in a grid block assumes an intermediate value to those reported for high and low salinity, an interpolation of the reference curves is performed to determine the value of the relative permeability. The Supplementary Materials provides a detailed discussion on the interpolation of relative water–oil permeability curves, the gas–liquid relative permeability curves, the three-phase relative permeability model, and the hysteresis effect on the gas permeability curves.

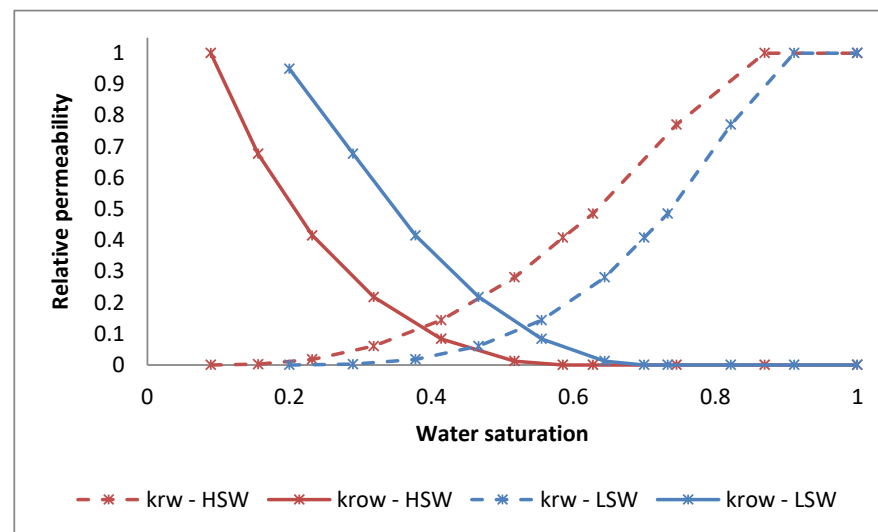


Figure 2. Water–oil relative permeability curves.

3. Results and Discussion

Before starting the simulation of core-scale recovery methods, adjusting the model's parameters to calculate the properties of the hydrocarbon phase is necessary, especially for the study conditions involving CO₂ injection. The results of these adjustments are in the Supplementary Materials.

3.1. Oil Recovery

The comparison presented in Figure 3 indicates that CO₂-LSWAG leads to a higher oil recovery than continuous CO₂ injection, regardless of the considered interpolant. However, it is essential to note that even under injection conditions below the minimum miscibility pressure, a high recovery factor of 62% is reached during continuous CO₂ injection.

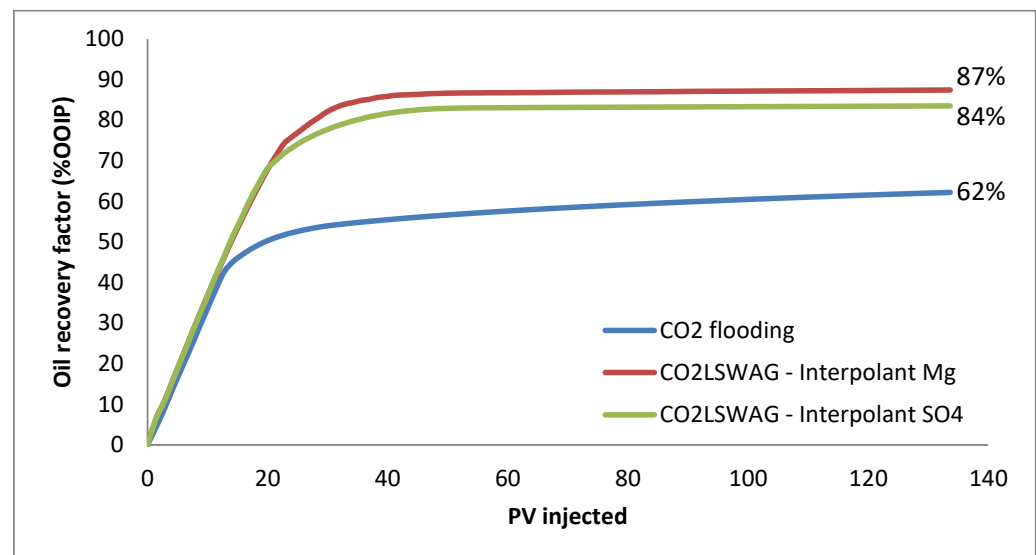


Figure 3. Oil recovery factor for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolant.

Furthermore, based on Figure 3, the three curves show the same behavior up to approximately the injection of 10 porous volumes. From the 10 PV injected, the core average pressure values, shown in Figure 4, become distinct. As the pressure in the production block is kept constant, this curve reflects the pressure difference between injection and

production throughout the displacement. The average pressure corresponding to the continuous CO₂ injection shows a slight decrease, while the curves related to CO₂-LSWAG present an increase in this average value and an oscillatory trajectory due to the alternate fluids injected. Although the pressure variation was not so significant, the maintenance of a greater pressure gradient is a factor that possibly promotes increased recovery via the CO₂-LSWAG method. In addition, in Figure 4, one can observe that at each cycle of CO₂ injection, there is an increase in the pressure gradient. Conversely, when the injected slug is of LSW, there is a reduction in this gradient, indicating the loss of CO₂ injectivity, i.e., a more significant pressure gradient is required to maintain the same injection flow rate. The water cut and gas–oil ratio graphs, also shown in Figure 5, help to identify the water and gas breakthrough in the simulated scenarios.

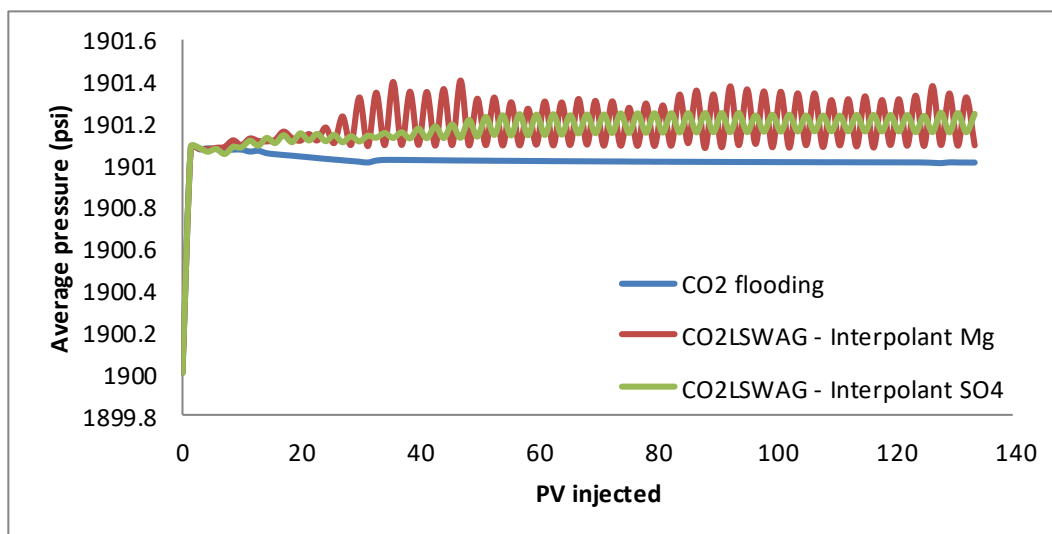


Figure 4. Average pressure for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

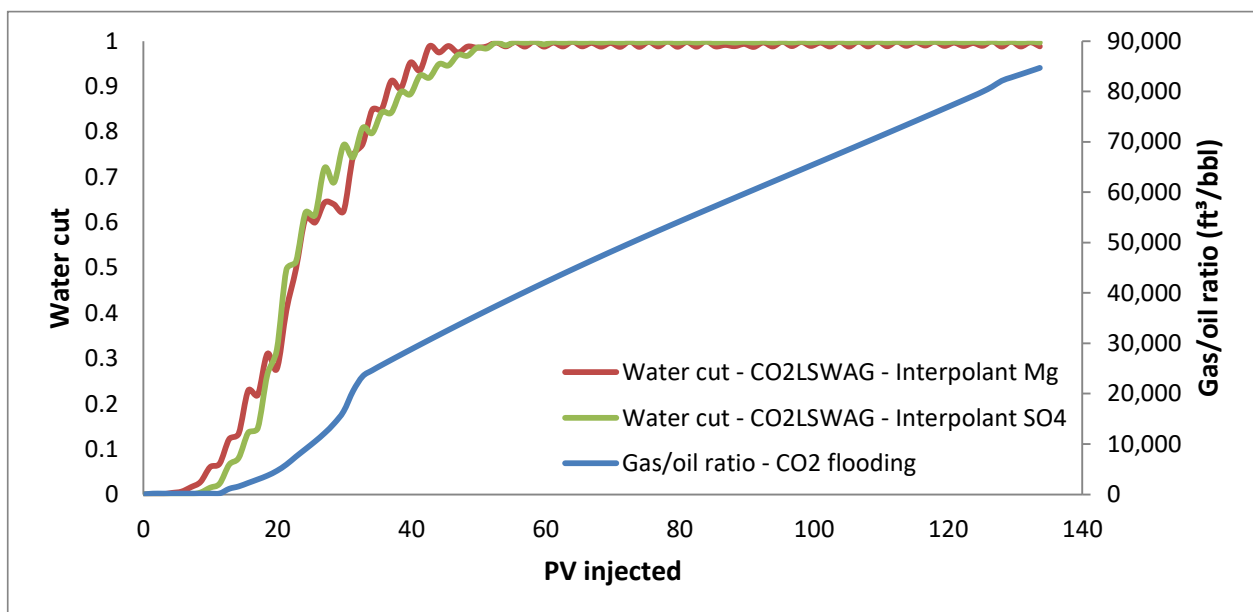


Figure 5. Water cut for CO₂-LSWAG considering Mg and SO₄ as interpolant ions and gas–oil ratio for continuous CO₂ injection.

Regarding CO₂-LSWAG, the water breakthrough occurs at around 30 injected porous volumes, indicated by the increase in the water cut, shown in Figure 5, and by the plateau in the oil recovery curve in Figure 3. Similarly, for continuous CO₂ injection, the gas breakthrough is observed at around 20 injected porous volumes, which is associated with the increase in the gas–oil ratio indicated in Figure 5 and the plateau in the recovery curve in Figure 3. All these parameters allow a general overview assessment of oil recovery but do not provide significant details explaining the additional oil production. For instance, a better understanding of porous medium mechanisms that trigger such results is obtained from analyzing the variation in properties in the simulation blocks. Therefore, the following sections present a more detailed analysis. It is important to emphasize that a microscopic analysis on a pore scale has not been done, but instead on what is happening in terms of measurable properties in the smallest simulation control unit (the grid blocks). Usually, the study of the interactions in the medium is done through experimental measurements in the steady state [9,26,27]. On the other hand, in the present work, the variations are analyzed by simulation during the dynamic displacement process.

3.2. Geochemical Mechanisms

Rock–Fluid Interactions and Mineral Dissolution

CO₂ injected into the core reacts with water to form carbonic acid, which can react with the rock minerals leading to their dissolution. Variations in the mineral (calcite and dolomite) concentrations and the consequent alterations in permeability and porosity were analysed to assess the impact of mineral dissolution in the porous medium. The Supplementary Materials presents the approach considered to compute these effects. Three blocks of the grid were selected, located at the coordinates {1,1,1}, {15,1,1}, and {30,1,1}, representing the injection point, the central point of the core, and the production point, respectively. Comparative results for the porosity variation are shown in Figure 6.

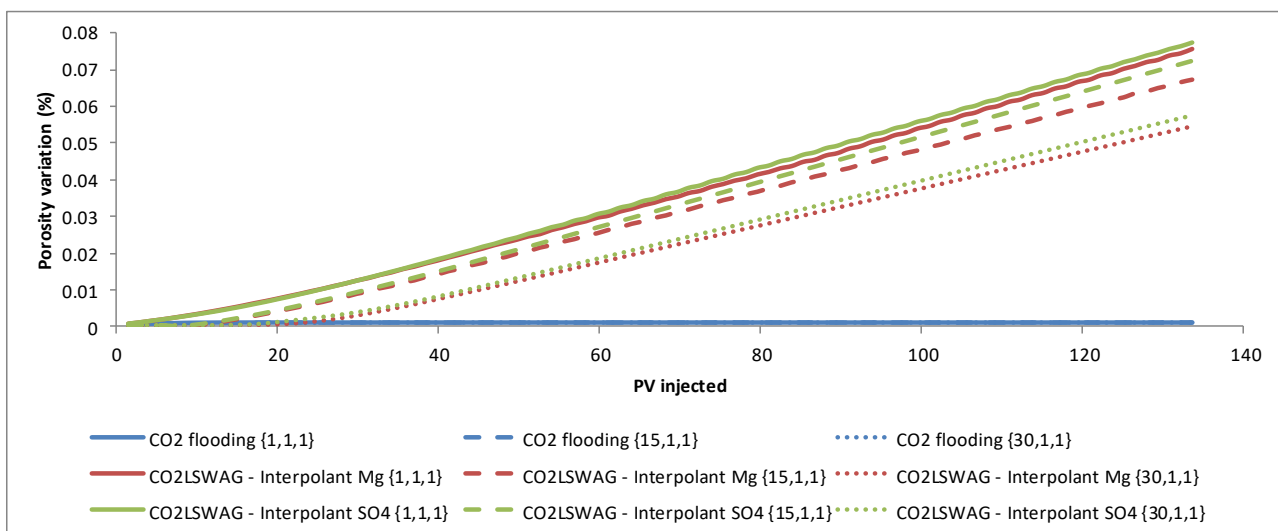


Figure 6. Porosity variation at the coordinates {1,1,1}, {15,1,1}, and {30,1,1}, representing the injection, the central point of the core, and the production.

The formation damage decreases between the inlet and outlet of the core, with the most significant porosity change occurring at the core inlet, at coordinates {1,1,1}, and the least at coordinates {30,1,1}, as a consequence of the interaction time between CO₂, LSW, and the rock. The interaction is gradual as the displacement front of the injected fluids reaches the regions. There is an increasing porosity trend because mineral dissolution predominates in the simulated core flooding tests instead of precipitation. Porosity variations follow the mineral dissolution shown in Figure 7. The results are presented for the {1,1,1} block, which gives a more accentuated mineral variation than the other blocks; following

what was observed for porosity, the scenario with more significant dissolution showed a considerable increase in porosity and vice versa. This scenario is due to the gradual CO₂ concentration increase in the aqueous phase, which is a consequence of the CO₂ contact with the formation water or the formation water + injected water mixture in the cases of continuous CO₂ injection and CO₂-LSWAG, respectively. Figure 8 highlights the CO₂ molality in the aqueous phase from the injection block to the core outlet in the condition of 10 porous volumes injected (before the CO₂ breakthrough). In the initial grid blocks, the CO₂ concentration is higher for both recovery methods evaluated, favoring the mineral dissolution. Figure 8 shows that the CO₂ concentration is higher for the CO₂-LSWAG simulation than for the CO₂ flooding. One of the main reasons for this difference is the salting-out effect. While CO₂-LSWAG is going on, there is a salinity reduction and an increase in CO₂ dissolution. On the other hand, during CO₂ flooding, the aqueous phase is composed of only the formation water, with high salinity compared to LSW. As a result, less CO₂ solubilizes into water.

Although the mineral composition variations are minimal, we can observe some important points:

- For CO₂ flooding, there is practically no variation because only gas is injected. Therefore, the water saturation in the medium corresponds to the initial saturation, which is less than 10%, as shown in Figure 9. In addition, since the formation water has high salinity, the already-mentioned salting-out effect reduces the CO₂ dissolution in water. A small amount of CO₂ solubilizes in water and forms carbonic acid, which is responsible for mineral dissolution.
- CO₂-LSWAG, when sulfate is the interpolant ion, results in more significant mineral variation for dolomite and calcite. The higher variation, in this case, is also associated with water saturation in the core, which is higher than for CO₂-LSWAG, where magnesium is the interpolant ion, as indicated in Figure 9.

For the three scenarios evaluated, calcite dissolution is greater than for dolomite because the dissolution rate of CaMg(CO₃)₂ is slower than CaCO₃ dissolution, according to reactions 10 and 11 in Tables 3 and 4. Xiong et al. (2021) [46] summarize some studies that have discussed these processes and observed the same behavior. Additionally, the authors argue that kinetics control the dissociation and precipitation of dolomite, while thermodynamics control the same reactions for calcite.

No permeability variation was observed in any of the analyzed grid blocks. As previously mentioned, while not negligible, a slight variation in mineral components was identified in Figure 7. Given that this was a core-scale study, insufficient data led to any significant change in the permeability because there is an equilibrium between the mineral dissolution and precipitation reactions indicated by reactions 5, 6, 10, and 11 in Table 3.

As discussed, mineral reactions were more pronounced for CO₂-LSWAG than for CO₂ flooding, indicating that LSW plays an essential role in geochemical interactions. It occurs because the aqueous phase is fundamental to promoting CO₂ dissolution and the formation of carbonic acid. As a result, core properties change. For instance, an increase in porosity increases water saturation and carbonated water formation in situ. CO₂ dissolution in the aqueous phase, as represented in Reactions 8 and 9 of Table 3, results in the H⁺ concentration increase in the medium. In turn, the rise in H⁺ concentration shifts reactions 10 and 11 in Table 3 towards mineral dissolution (right side). This observation also highlights the role of low-salinity water and its interactional effects with the rock for incremental oil recovery in the evaluated system, because CO₂ dissolution in the aqueous phase is necessary to promote mineral dissolution. Moradpour et al. and Teklu et al. [9,22] highlight the rock wettability alteration due to the presence of carbonated water in situ, which makes the rock surface more hydrophilic and, therefore, more water-wet.

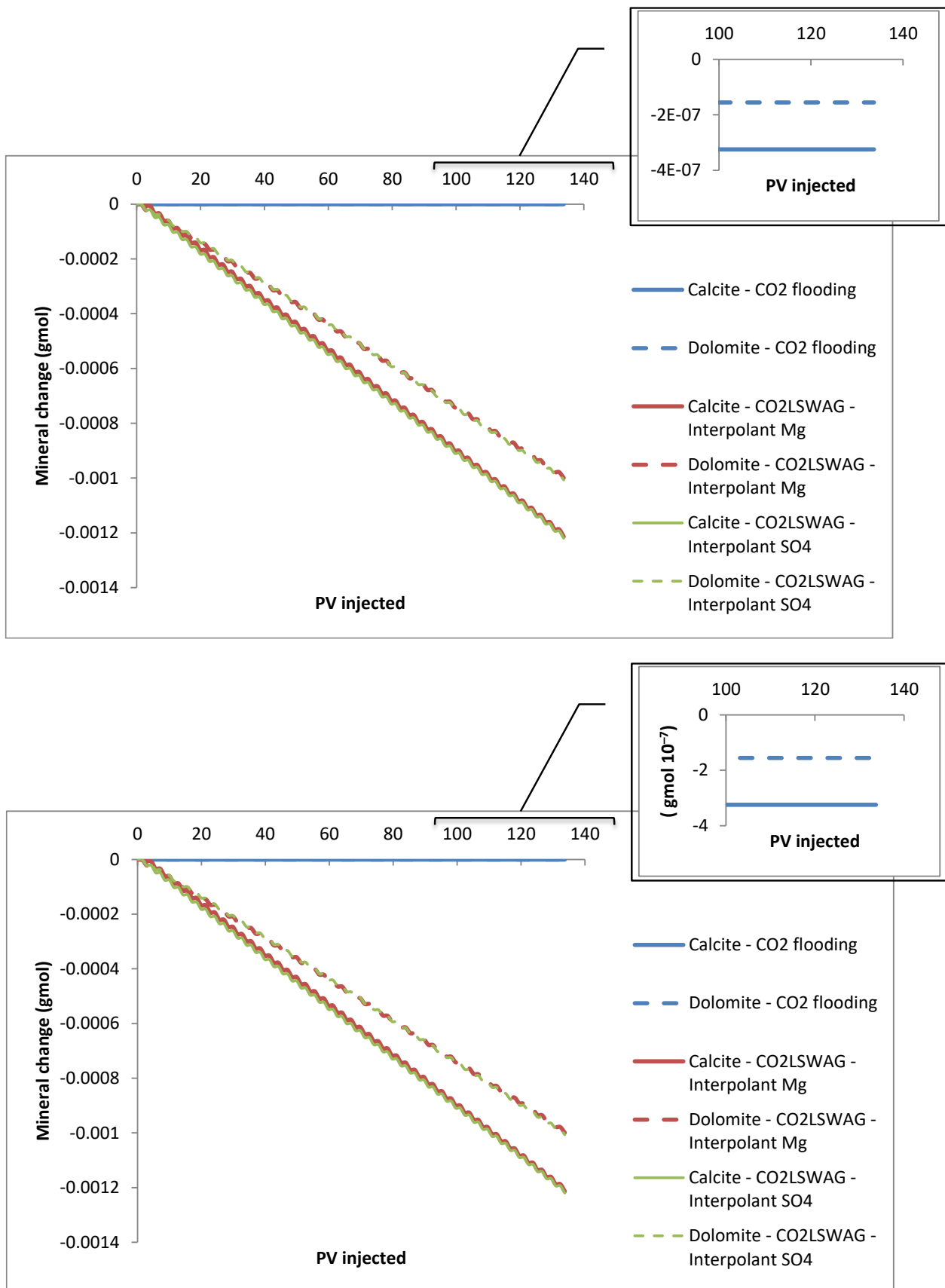


Figure 7. Mineral dissolution for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

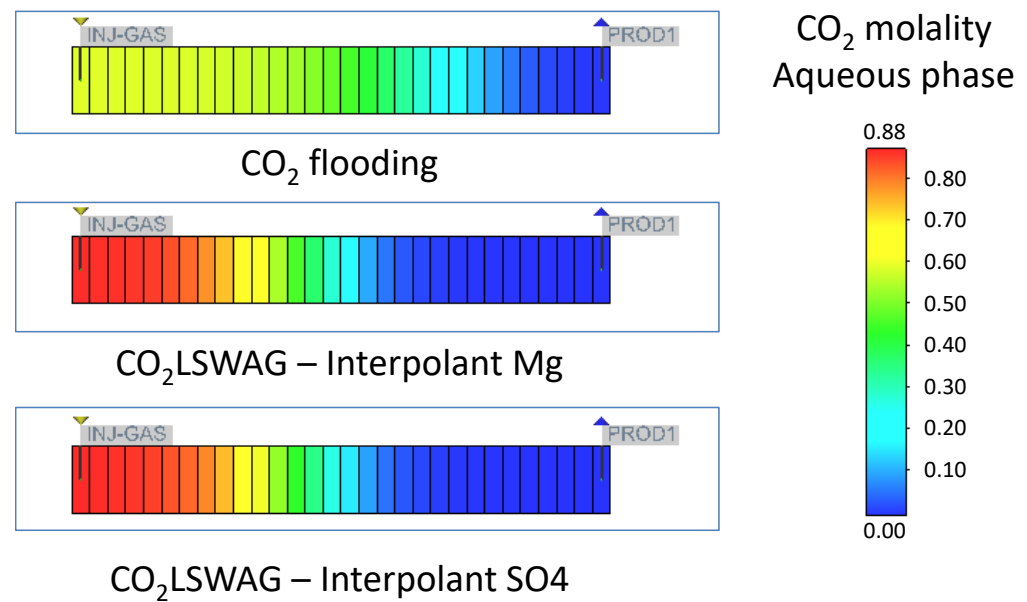


Figure 8. CO₂ molality in the aqueous phase for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants—10 porous volumes injected.

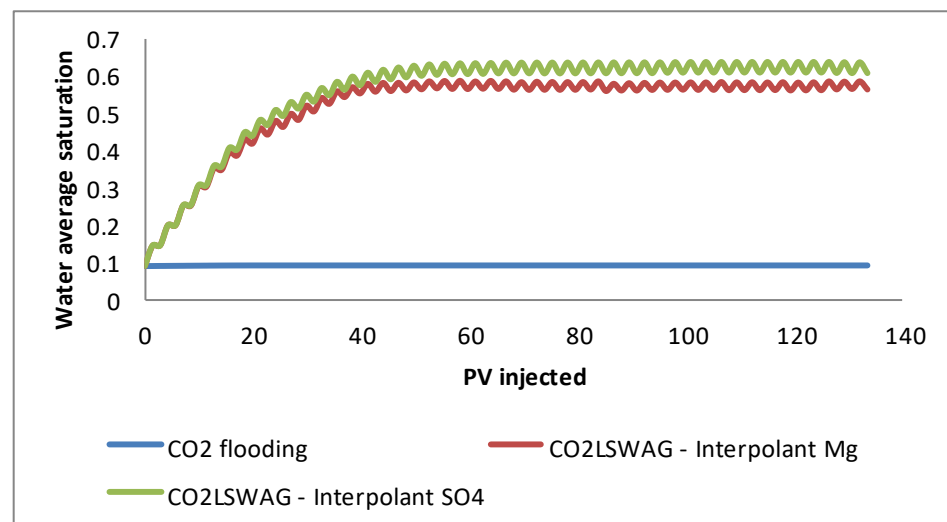


Figure 9. Water average saturation for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

The influence of mineral dissolution on the oil recovery factor is better understood if the interactions between the oil components and the rock sites are analyzed. Carboxylic acids (R-COOH) are the main components of oil adsorbed on the rock surface. We observed two active sites for calcite, $>\text{CO}_3^-$ and $>\text{Ca}^+$, where the symbol $>$ represents the rock surface. For dolomite, in addition to calcite sites, $>\text{Mg}^+$ also appears. The oil polar group (RHCOO^-) interacts with the rock sites with positive charges. Oil is apart from the rock and consequently is recovered when it dissolves, as shown in the diagram in Figure 10. In this paper, the mineral reactions considered are related to carbonic acid formation due to the CO₂ dissolution in water. However, oil recovery by the rock dissolution mechanism and consequent wettability alteration is also discussed by some authors in low-salinity water flooding studies, such as by Mohammadi et al. [47], Al-Shalabi et al. [48], and Hiorth et al. [49]. Nonetheless, the simulation model developed does not capture the wettability alteration by rock dissolution due to LSW injection in the present study. The effect of LSW on wettability is quantified only through the relative permeability curves.

They are set at the simulation beginning but do not consider the CO₂ content in water as an interpolation criterion. Regarding rock–fluid interactions, the simulator only includes the influence of formation damage in the recovery estimates, as the porosity variation was less than 1%. Therefore, despite being observed, the rock dissolution mechanism has no significant effect on oil recovery for the simulated core-scale cases.

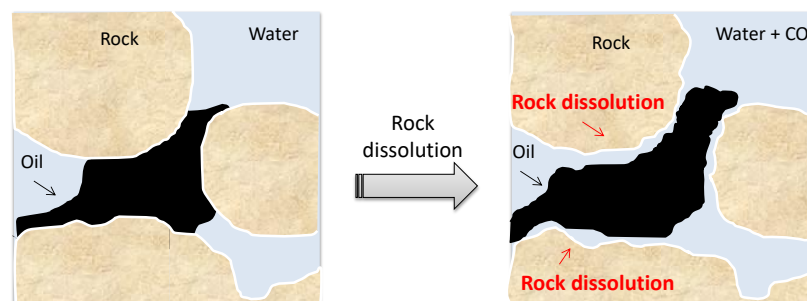


Figure 10. Schematic diagram of rock dissolution due to carbonated water in situ and oil detachment.

3.3. Physicochemical Interactions

3.3.1. Fluid–Fluid Interaction—Effluent Analysis

To evaluate the fluid–fluid interactions and their influence on the oil recovery estimates for the three simulated scenarios, the results obtained for the last block of the grid, located at the coordinates {30,1,1}, were analyzed. This block corresponds to the core’s production, providing data for a more detailed analysis of the effluent.

Figure 11 shows the pH variations during the core flooding test simulation. Initially, the pH of the effluent is equal to that of the formation water, highlighted in Table 2. Two trends related to pH can be observed in the results. In all cases, the pH decreases due to the presence of CO₂ and the formation of carbonic acid. The curve of the continuous CO₂ injection evidences this. During CO₂-LSWAG, as discussed before, there is a more accentuated dissolution of the rock, both calcite and dolomite. Dissolving these minerals increases the concentration of Ca²⁺ and Mg²⁺ ions in the aqueous phase, resulting in a higher pH when compared to continuous CO₂ injection. The rise in the HCO₃ can infer the increase in these ions concentrations, also shown in Figure 11, from reactions 10 and 11 in Table 3, corresponding to mineral dissolution.

Figure 12 shows the concentration variation of the interpolant ions SO₄^{2−} and Mg²⁺ for the three simulations. As there is neither additional water supply nor much mineral dissolution, these ions’ concentration during the CO₂ flooding can be supposed to be constant and equal to that of the formation water. For CO₂-LSWAG cases, there is a reduction in the concentration of the two ions caused by the injection of low-salinity water. As discussed earlier, there is an increase in Mg²⁺ concentration due to the dissolution of calcite and dolomite. However, the impact of this increase is less than that of dilution caused by injected water. According to the results, the reduction of magnesium concentration before reaching the minimum value is more significant than sulfate in both scenarios.

For this reason, the trend for the magnesium concentration to be closer to its concentration in the low-salinity water is adopted as a criterion in the relative permeability curves. A higher oil relative permeability favors oil recovery if the interpolant ion concentration is closer to that established for LSW. Therefore, this variation is the primary reason for the oil recovery factor estimated to be higher when magnesium is the interpolant ion instead of sulfate in CO₂-LSWAG.

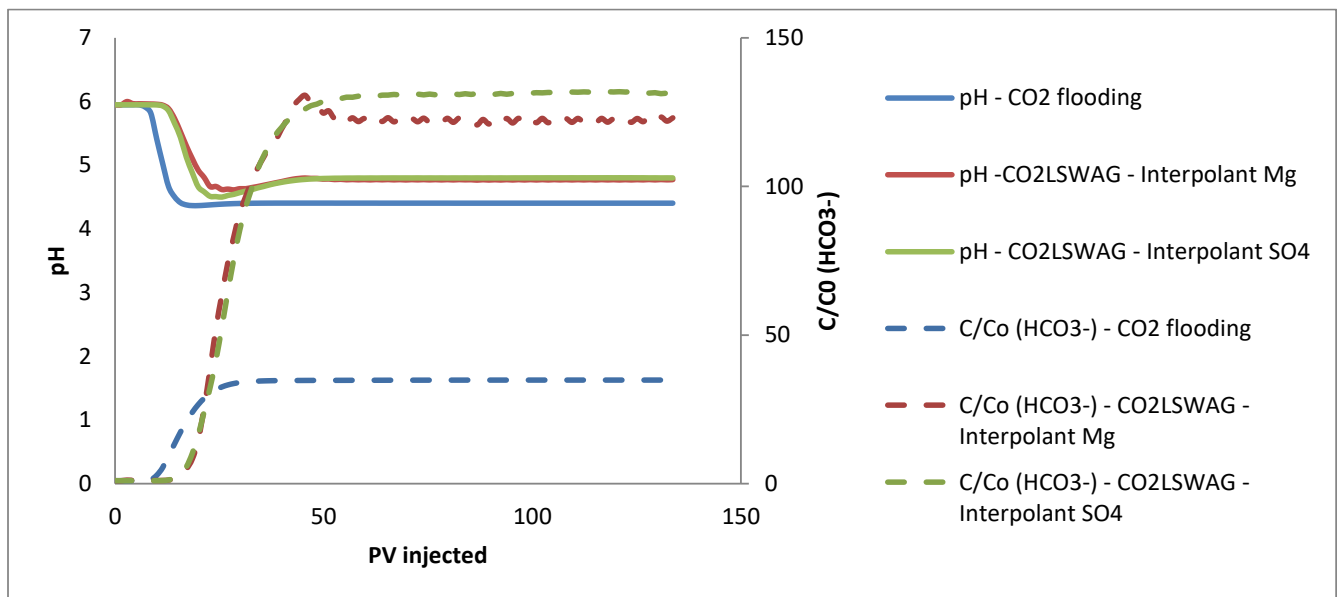


Figure 11. Results of pH and HCO_3^- concentration in the effluent for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

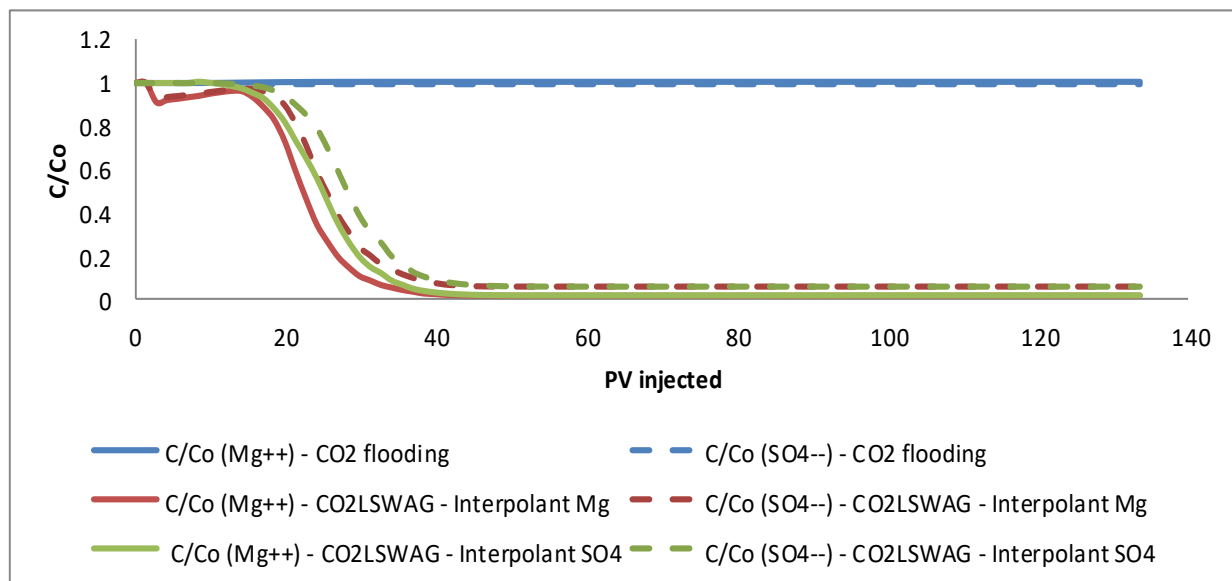


Figure 12. Results of pH and Mg^{2+} and SO_4^{2-} concentration in the effluent for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

Figure 13 shows the effluent salinity curves in line with the results discussed. There is a dilution of the aqueous phase for CO₂-LSWAG due to brine injection with a lower concentration of salts than the formation water initially present in the core. Data on CO₂ solubility in the aqueous phase are also shown. Due to the salting-out effect, the solubility is lower for the CO₂ flooding scenario because the brine has a higher concentration of salts. Although the CO₂ solubility in water reduces the amount of gas that can solubilize in oil, it also leads to mineral dissolution and wettability alteration, which are advantageous, as already mentioned.

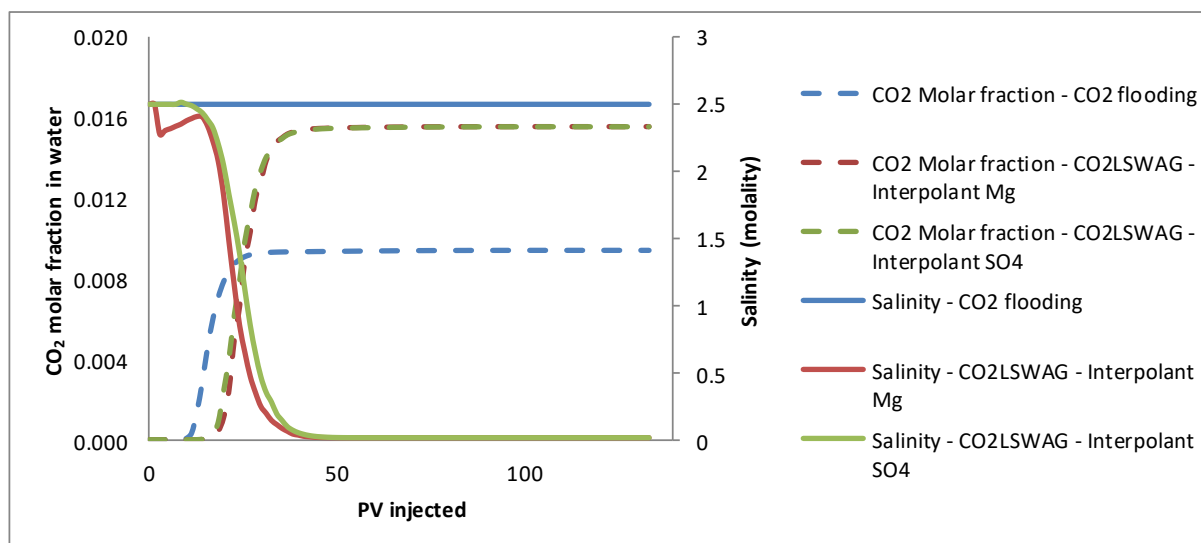


Figure 13. Results of CO₂ molar fraction and salinity of the effluent for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

3.3.2. Fluid–Fluid Interaction—Compositional and Interfacial Properties

In the simulations, CO₂ was injected below the minimum miscibility pressure in continuous flooding and CO₂-LSWAG. Even for an immiscible injection, compositional effects related to CO₂ solubility in the oil can be observed in Figure 14. Experimentally, Bui et al. [50] demonstrated oil swelling at different pressures, including below the MMP. Spivak et al. [51] have already pointed out the contribution of compositional interactions of immiscible CO₂ over time during injection in oil reservoirs. As the CO₂ molar fraction in oil increases, we can observe the reduction in viscosity and oil swelling caused by a density increase. Both variations improve the displacement properties of this phase. The oil swelling is related to the oil volume increase and, consequently, the oil saturation in the core increase, leading to higher oil relative permeabilities [52]. The peaks identified in the curves shown in Figure 14a with an opposite behavior (increase in viscosity and reduction in density) are related to the compositional effects of mass transfer between the oil and gas phases (oil light components extraction), as can be seen for the methane molar fraction variation presented in Figure 14b.

As CO₂ is injected under immiscible conditions, gas dissolution in the oil phase is not beneficial. However, the compositional interaction between CO₂ and the aqueous phase plays a vital role in oil recovery. As Moradpour et al. [24] pointed out, the mobility of displacing CO₂ is enhanced, the viscous fingers are attenuated, and the sweep efficiency is improved.

The effect of interfacial tension reduction is one of the primary mechanisms mentioned in the literature due to CO₂ injection. Figure 15a presents the gas/oil interfacial tension results for the grid block located at the intermediate point {15,1,1} and the core production block located at the coordinates {30,1,1}. Initially, the interfacial tension is null because there is no free gas phase in the core. Figure 15b shows the gas saturation. After CO₂ injection, the saturation is no longer null, and the interfacial tension is quantified. As there is no alternation of fluids injection, the appearance of this phase occurs before the continuous injection of CO₂ for the two grid blocks analyzed. Thus, CO₂ injection controls the physicochemical interactions since the variations in oil, gas, and water properties present similar behaviors for all injections. The only difference observed is related to the time the changes occur, faster or slower depending on whether the injection is continuous or LSWAG. In this context, the injection of LSW only delays the contact of CO₂ with the phases and, consequently, the physicochemical interactions. The results also indicate the presence of CO₂ causing the observed physicochemical alteration in the system. The interfacial

tension values are close for the three simulated cases, tending to the same value in the final simulation time. Comparing the CO₂-LSWAG injection results reveals no difference in the gas/oil interfacial tension. That occurs due to the polar oil components, which interact in the interface with gas, even when the gas saturation is higher for the scenario in which magnesium is the interpolant ion of the relative permeability curves.

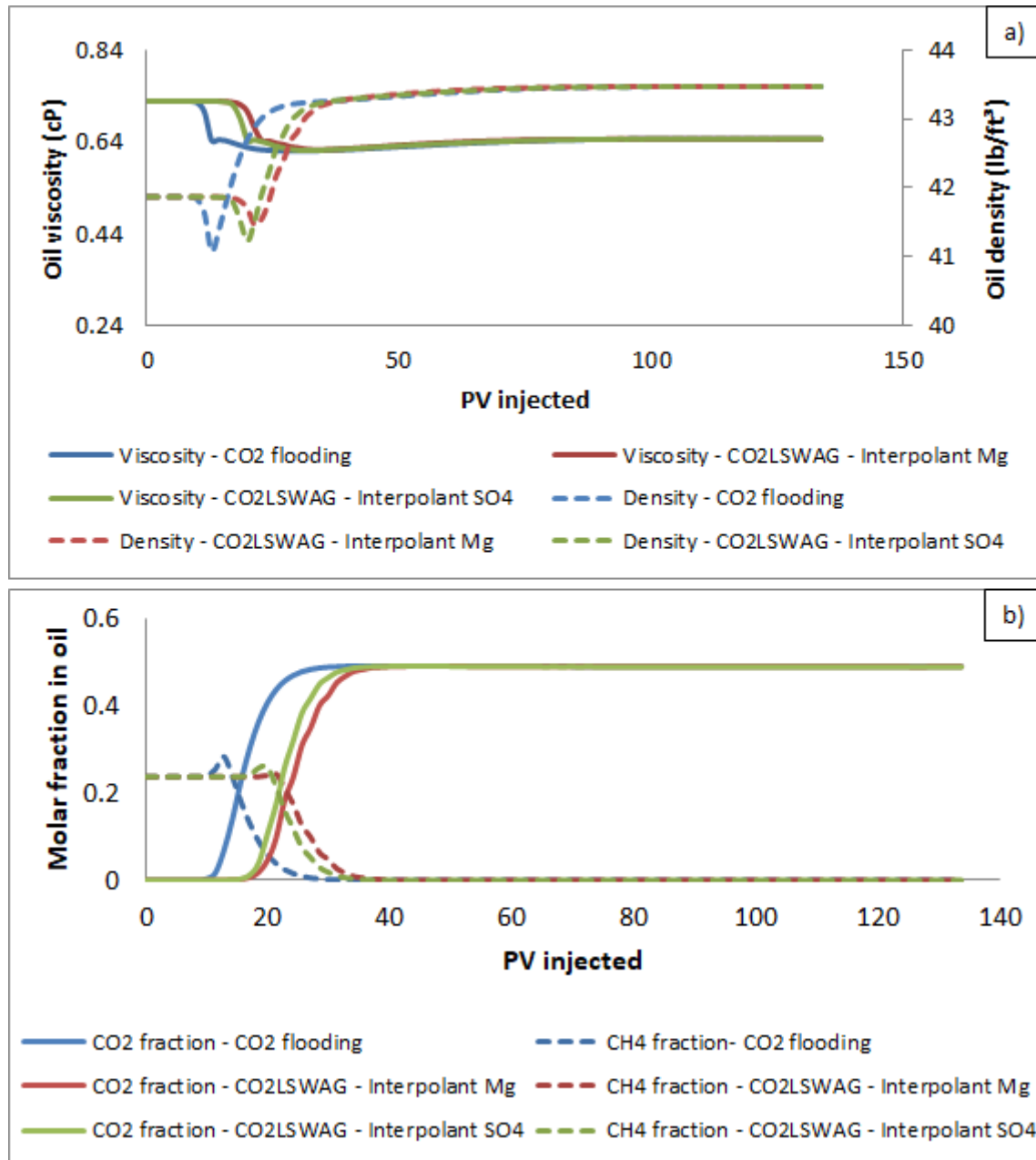


Figure 14. Results of (a) viscosity and density and (b) CO₂ molar fraction and CH₄ molar fraction of oil effluent for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

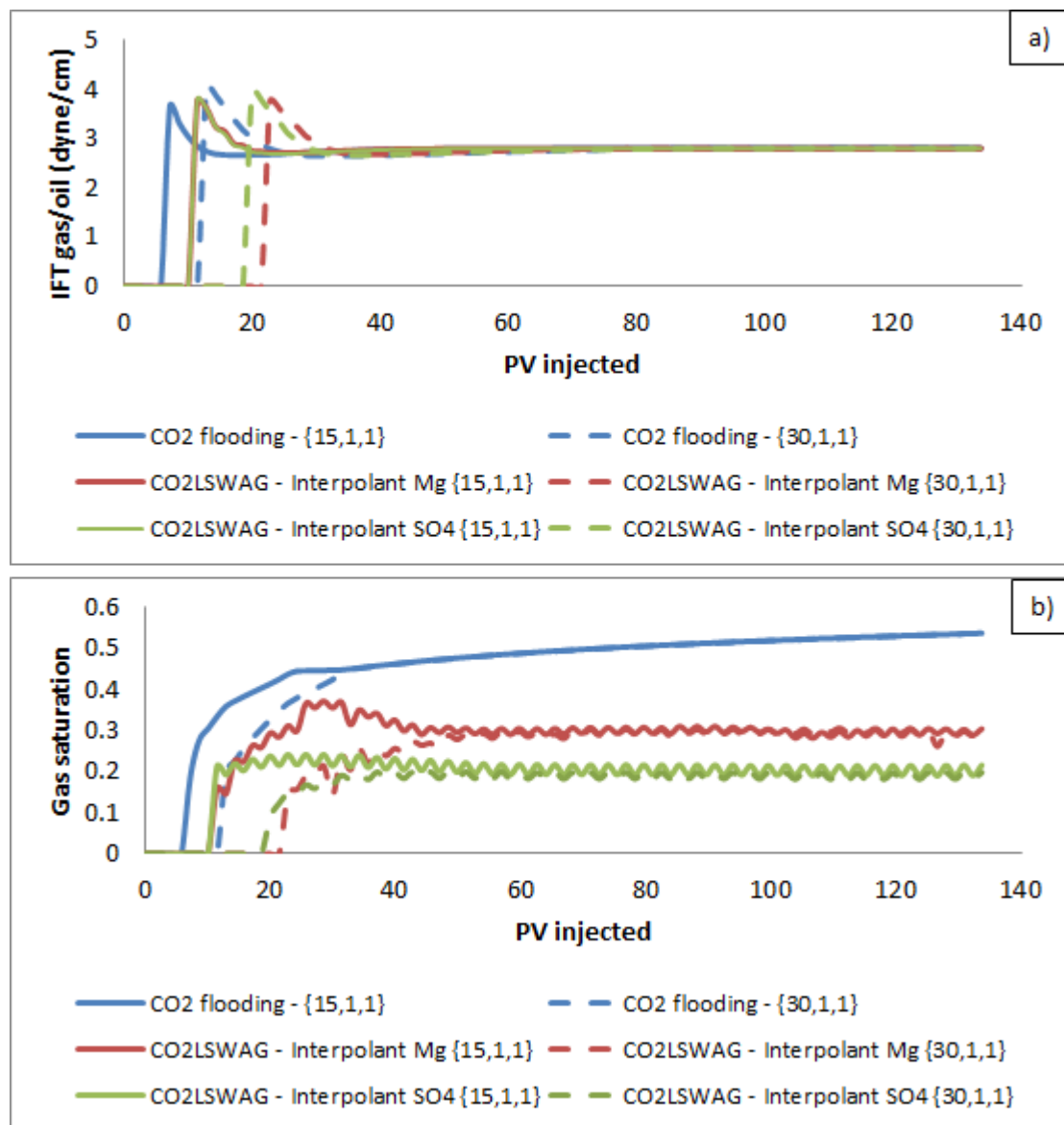


Figure 15. (a) Interfacial tension gas/oil and (b) gas saturation at grid blocks {15,1,1} and {30,1,1} for continuous CO₂ injection and CO₂-LSWAG considering Mg and SO₄ as ion interpolants.

On the other hand, the brine's salinity affects the oil/water interfacial tension. In this system, the polar oil components and the salts in the water interact at the interface. However, salinity assumes the same values for the two simulated CO₂-LSWAG scenarios. It is essential to clarify that when CO₂ solubilizes in the aqueous phase, there is a reduction in the gas–aqueous phase interfacial tension. In addition, due to CO₂ diffusion through the brine, CO₂ migrates to the oil–brine interface, resulting in the interfacial tension reduction of the oil–brine system and, consequently, CO₂ diffusion in the oil [9,22]. All the interfacial effects favor oil recovery and displacement. Moreover, the indirect interaction between CO₂ and oil occurs in the WAG process, in which the slugs alternation can prevent the gas from directly contacting the oil.

4. Conclusions

The present work investigated immiscible CO₂-LSWAG and continuous CO₂ flooding as EOR methods in carbonate systems. Core flooding simulations evaluated the physico-chemical and geochemical interactions of CO₂-LSWAG on carbonates using experimental oil data from the literature. Oil recovery, water and gas production, reservoir pressure, and

rock and fluid properties and composition were carefully assessed in the core and the effluent to understand the contributions behind these obtained results. The main conclusions, based on the results obtained, are summarized in the following:

- Even under injection conditions below the minimum miscibility pressure, continuous CO₂ injection achieves a high oil recovery factor of 62%.
- In addition to the unique advantages of each injected fluid, the detailed investigation of physicochemical and geochemical variations highlights that the interaction of CO₂ and LSW also contributes to additional oil recovery. The reduction of the aqueous phase salinity accentuates this interaction due to a decrease in the salting-out effect. Despite not using experimental recovery data from core flooding tests, the simulations in this paper allow relating the properties to each other and the consequences of these variations in the oil displacement, making a separate assessment of each interaction rock–fluid or fluid–fluid.
- Results show that mineral reactions were more pronounced for CO₂-LSWAG than for CO₂ flooding, indicating the critical role of LSW in the geochemical process, even though the simulation model did not include the mineral dissolution mechanism directly related to the LSW injection. Their effects on core properties, such as porosity increase, are controlled by CO₂ and LSW interaction associated with in situ formations of carbonate water. The difference between the recovery estimates is due to CO₂ dissociation and carbonic acid formation, and this is more noticeable when injecting LSW and the water saturation increases. Furthermore, formation damage was more pronounced for calcite than for dolomite sites in the core, according to the dissolution reaction rate of these minerals.
- CO₂ injection controls the physicochemical interactions, even under immiscible conditions. The presence of CO₂ highly affects the physicochemical properties. Compositional and interfacial effects related to oil recovery improvement can still be observed at pressures below the MMP, such as CO₂ solubility in oil, oil viscosity reduction, oil swelling, gas/oil interfacial tension reduction, and extraction of light hydrocarbons. Oil, gas, and water properties changes present similar behavior for CO₂ flooding or CO₂-LSWAG, differing just because variations occur faster or slower depending on whether the injection is continuous or water-alternating-gas, as the water slugs delay the contact of the injected CO₂ with the phases.
- CO₂-LSWAG simulations using Mg²⁺ as an interpolant improved oil recovery more than SO₄^{2−}. In this case, magnesium ion concentration in the aqueous phase is closer to the LSW condition after dilution by low-salinity water injection and variation due to mineral dissolution. It leads to relative permeability values, which are more favorable for oil recovery when compared to sulfate concentration.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16010440/s1>, Figure S1: Swelling factor and Saturation pressure fitting as a function of CO₂ molar fraction; Figure S2: Gas-liquid relative permeability curve. References [53–57] are cited in the supplementary materials.

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