Core-Scale Simulation of Low-Salinity Spontaneous Imbibition in Carbonates: Oil Recovery by Wettability Alteration at Experimental Condition

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Abstract. Smart water has successfully improved oil recovery in numerous laboratory and field applications, where the primary mechanism is often attributed to wettability alteration. In carbonate reservoirs, modification of brine composition can shift the rock surface from oil-wet toward more water-wet conditions, promoting spontaneous imbibition of the aqueous phase and enhanced oil recovery. This study presents a numerical investigation of smart water spontaneous imbibition using IORCoreSim software, where wettability alteration is explicitly linked to the amount of SO_4^{2-} adsorbed on the carbonate surface through an anion exchange model. The novelty of this work lies in the quantitative coupling of sulfate adsorption to wettability alteration and the consistent simulation of a wide range of brine compositions within a unified modelling framework. A total of eleven spontaneous imbibition experiments on carbonate cores, reported in the literature, were modelled using experimentally defined core dimensions, rock/fluid properties, and brine compositions. The cases include (1) imbibition brines with varying NaCl concentrations and (2) NaCl-depleted brines with 0 to 4 times the seawater sulfate concentration. The model reproduces the main oil recovery trends across all cases, with simulated ultimate recoveries typically within ~0 to 6% of experimental values, although matching the transient production behaviour remains more challenging. The results demonstrate that sulfate adsorption can account for the observed wettability alteration trends, particularly in sulfate enriched and NaCl depleted systems. It should be noted that the model does not include other potential smart water mechanisms such as mineral dissolution/precipitation or scaling. Overall, this work demonstrates that coupling wettability alteration to sulfate adsorption provides a practical and physically grounded framework to interpret smart-water imbibition trends in carbonate systems.

1 Introduction

Spontaneous imbibition (SI) of Smart Water is the main recovery mechanism in carbonate reservoirs, where a wettability alteration towards a more water-wet rock takes place. When Smart water spontaneously imbibition occurs, SO_4^{2-} will adsorb into the positive water-wet surface sites, whereas Ca^{2+} complexes with carboxylates in the oil. Subsequently, some of the organic materials are released from the surface and contribute to a higher oil recovery [1, 4].

Modified seawater has been regarded as a “smart” EOR fluid in carbonate reservoirs due to its capability of increasing the water-wetness of the rock surface. It is suggested that the wettability alteration is due to the interaction among the rock surface and the potential determining ions Mg^{2+}, Ca^{2+} and SO_4^{2-} present in seawater [1, 3].

Numerous studies have investigated the impact of brine composition on spontaneous imbibition in carbonate rocks. Modified seawater has been shown to increase oil recovery by altering rock wettability toward a more water-wet state [5, 6]. Further enhancement of the EOR effect has been reported by reducing Na^+ and Cl^- concentrations and increasing SO_4^{2-} content in the imbibing brine [2, 7].

A one-dimensional study on SI model including SO_4^{2-} adsorption and key transport mechanisms, showed that wettability alteration shifts the system from oil-wet to more water-wet behavior [8].

Buckley–Leverett-based SI model developed for coupling with reaction–diffusion equations, captured key experimental trends and the impact of brine composition on oil recovery [9].

A reactive transport model for smart-water flooding in carbonates showed that oil recovery increases with SO_4^{2-} concentration [10].

A workflow was proposed to a core-to-field modelling, starting with geochemical-equilibrium and was demonstrated a core-scale history matching (<3.9%

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error) and performed scaled-up 5-spot simulations, finding stable EOR indicators (<0.5% variability). It was shown that Low Salinity Water (LSW) effects can be effectively captured by tuning relative permeability curves [11].Other authors performed numerical simulations using lab core-flood data to model ion-exchange between low-salinity brines and carbonate surfaces. History matched oil recovery and pressure response, attributing increased recovery to wettability change captured by shifting relative permeability curves. Sensitivity analysis demonstrated that timing of LSW injection, flow rate, and temperature significantly influence EOR performance [12].

A review of both experimental and numerical core-scale studies of SI using low-salinity water identified that while lab-scale fracture-matrix SI is well studied, numerical models explicitly incorporating co-/counter-current dynamics are still missing. It was highlighted the need for models coupling dynamic wettability, ion transport, and fracture-matrix interactions [13].

Despite this progress, a key gap remains in quantitatively linking ion adsorption—especially sulfate—to wettability alteration within a fully coupled simulation framework. Many existing models either simplify the underlying mechanisms or reproduce experimental observations through parameter tuning, making it difficult to assess whether the governing processes are correctly represented.

In this study, spontaneous imbibition under laboratory experimental conditions representative of carbonate core-scale experiments is modelled using the IORCoreSim simulator. The simulations are based on experimental conditions (temperature ~90°C, pressure ~10 bar, and seawater-based brine compositions), ensuring consistency with previously reported laboratory measurements. The simulator enables dynamic coupling between multiphase flow, ion transport, and wettability alteration, allowing rock–fluid properties to evolve as a function of brine composition.

The primary objective of this work is to investigate whether sulfate adsorption alone can explain the observed oil recovery trends in smart water spontaneous imbibition experiments. Wettability alteration is explicitly coupled to the amount of SO_4^{2-} adsorbed on the rock surface, providing a mechanistic representation of the process.

The central hypothesis is that sulfate-driven wettability alteration is sufficient to reproduce the experimentally observed recovery behaviour across different brine compositions, without invoking additional mechanisms such as mineral dissolution, precipitation, or scaling. By systematically modelling multiple smart water scenarios, this study aims to assess the capability and limitations of a sulfate-based wettability alteration model to reproduce both recovery trends and transient imbibition behaviour.

2 Methods

In this work, wettability alteration is modeled as a transition from an initially less water-wet system toward a more water-wet condition. This transition is assumed to primarily affect capillary forces, which are reflected in the capillary pressure curves. Although wettability also influences relative permeability, the limited experimental data available does not allow for reliable independent parameterization of relative permeability functions for each wettability state. Therefore, a simplifying assumption was adopted whereby relative permeability curves remain fixed, while wettability alteration is represented through interpolation between capillary pressure curves.

The main objective of this work is to simulate the anion exchange model for wettability alteration of carbonate reservoirs. The reservoir simulation software IORCoreSim was used for its capability of fully couple multiphase, multicomponent and strong handling of chemical interactions between rock and fluid. The simulation model was able to capture the behaviour of the Smart water spontaneous imbibition, where wettability alteration towards a more water-wet system is linked to the amount of sulface (SO_4^{2-}) adsorbed on the rock surface [14].

The main input parameters necessary to run the simulator model are as follows:

(1) Core properties and dimensions (porosity, permeability, diameter, length) – Table 1.

(2) Fluid properties (density, viscosity, oil/water interfacial tension) – Table 2.

(3) Saturation functions (relative permeability, capillary pressure).

Table 1. Core dimensions and properties.

L (cm)	D (cm)	Φ (%)	K (mD)	S_{wi} (%)
7	4	48	3.5	10

Table 2. Fluid properties.

Fluid	μ (cP)	ρ (g/cm^3)	σ (mN/m)
Oil	2.3	0.801	13
Water	1.09	1.05	

It should be emphasized that interfacial tension (σ) is a property of the oil–water system rather than of an individual fluid. Therefore, σ represents the interaction between oil and water phases and is treated here as a system property.

Here it was decided to use the modified Corey correlation [15] to develop the relative permeability curves for water and oil.

$$k_{rw} = k_{rw}^{*}\left(\frac{s_w - s_{wi}}{1 - s_{or} - s_{wi}}\right)^{n_w} \quad (1)$$

$$k_{ro} = k_{ro}^{*}\left(\frac{s_o - s_{or}}{1 - s_{or} - s_{wi}}\right)^{n_o} \quad (2)$$

where:

- *krw* and *kro* are the relative permeabilities of water and oil, respectively;
- *krw** and *kro** are endpoint relative permeabilities;
- *Sw* and *So* are water and oil saturations;
- *Swi* is the initial water saturation;
- *Sor* is the residual oil saturation;
- n_w and n_o are Corey exponents controlling curve shape.

Since there is not enough information to independently determine the functions for both the initial system and a more water-wet system, it was decided to keep the curves constant and alter Pc instead. Corey exponents of oil and water for this study are presented in Table 3.

Table 3. Corey exponents and permeability end-points.

K_{rw}	K_{ro}	n_w	n_o	S_{wi}	Sor
0.6	1	4.7	2.2	0.1	0.13

Although relative permeability is expected to vary with wettability alteration, a single set of relative permeability functions was assumed for all wettability states. Specifically, the Corey exponents (nw and no), relative permeability curves (krw and kro), and endpoint saturation (Sor) were kept constant. Therefore, interpolation was performed only between the capillary pressure (Pc) curves (Figures 1 and 2).

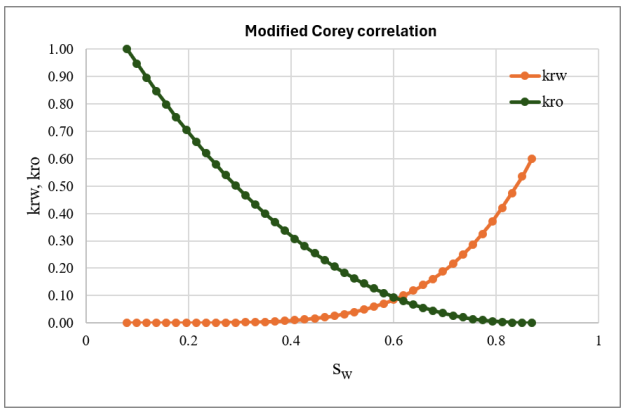

Fig. 1. Relative permeability curves used in this study.

As for the relative permeabilities, the capillary pressure curve model used was the modified version of the Skjaeveland correlation by Skjaeveland *et al.* (2000), due to its flexibility. The capillary pressure correlation is given by:

$$P_c = C_L(s_w - s_L)^{-E_L} - C_R(s_R - s_w)^{-E_R} + C_0 \quad (3)$$

where C_L and C_R are capillary pressure parameters, whereas S_L and S_R are the minimum and maximum saturation parameters respectively. Furthermore, E_L is the first capillary pressure exponent, while E_R is the second capillary pressure exponent. The constant C_0 is a fitting parameter that accounts for different shapes and curvatures of the Pc-curves.

Figure 2 illustrates the capillary pressure curves that will be used in the model, namely "J1" for the initial wetting system and "J2" for a more water-wet system respectively. Modified Skjaeveland's correlations used to establish the curves are shown in Table 4.

Table 4. Modified Skjaeveland's correlations for Pc-curves.

	C_L	C_R	C_O	E_L	E_R	S_L	S_R
J1	0.014	0.013	-0.011	0.51	0.75	0.060	0.88
J2	0.0163	0.012	0.012	0.51	0.73	0.070	0.88

For modelling purposes, it is often convenient to convert the capillary pressure function into a dimensionless scaled J-function. The J-function is generally used to get the same shape of the Pc-curves when the experiments have different permeability (k) and porosity ($\emptyset$). The capillary pressure can be J-function according to the following equation:

$$J = \frac{1}{c_f}\frac{P_c}{\sigma}\sqrt{\frac{k}{\emptyset}} \quad (4)$$

where Pc is the capillary pressure, σ is the oil–water interfacial tension, k is permeability, ϕ is porosity, and Cf is a unit conversion factor (e.g., Cf = 0.3183 for Pc in *bar*, σ in *mN/m*, and k in *mD*).

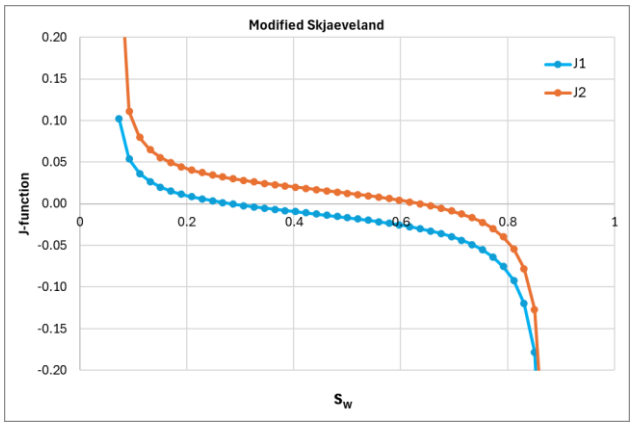

Fig. 2. Capillary pressure curves used in this study.

The decision to interpolate only the capillary pressure curves while keeping relative permeability functions constant was made for both practical and physical reasons. From a physical standpoint, capillary pressure is more directly linked to wettability through interfacial forces and contact angle effects, making it highly sensitive to wettability alteration. In contrast, relative permeability depends on multiphase flow behaviour and pore-scale connectivity and requires extensive experimental data to be accurately defined for multiple wettability states.

From a practical perspective, the available experimental dataset does not provide sufficient information to uniquely determine separate sets of relative permeability functions corresponding to different wettability conditions. Introducing variable relative permeability without proper calibration could introduce non-physical behavior and increase model uncertainty. Therefore, the adopted approach ensures a controlled and physically consistent representation of wettability alteration, focusing on capillary-driven mechanisms which dominate spontaneous imbibition processes.

- Imbibing brines (ionic compositions):

  - In this work will be shown how an anion exchange model can capture the behaviour of conducted experiments of Smart water SI [2]. Simulations will be carried out based on Smart Water compositions published by the author [2] (Table 5).

  - The compositions illustrated in the Table 5 represent the case where the imbibing brine has a varying concentration of NaCl with the definition "SWXNa". SW is an abbreviation for seawater, where "X" stands for "X" times the NaCl concentration of ordinary SW. Note that for the case "SW0Na", the NaCl concentration is not completely zero.

  - It will also be simulated the cases where the brine is depleted in NaCl and with 0-4 times the sulfate concentration in seawater. The Table 5 shows these experiments have the definition "SW0NaXS", where "0S" represents zero sulfate concentration, and "4S" implies four times the sulfate concentration in ordinary seawater.

Table 5. Brines composition.

Ions concentration (mol/L) of the imbibing brines							
Brines	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3	Cl^-	SO_4^{2-}
SW-pure seawater	0.45	0.01	0.045	0.013	0.002	0.526	0.024
SW0Na	0.05	0.01	0.045	0.013	0.002	0.145	0.024
SW0.05Na	0.07	0.01	0.045	0.013	0.002	0.145	0.024
SW0.1Na	0.09	0.01	0.045	0.013	0.002	0.165	0.024
SW0.25Na	0.15	0.01	0.045	0.013	0.002	0.225	0.024
SW0.5Na	0.25	0.01	0.045	0.013	0.002	0.325	0.024
SW0Na0S	0.002	0.01	0.045	0.013	0.002	0.125	0
SW0Na1S	0.050	0.01	0.045	0.013	0.002	0.125	0.024
SW0Na2S	0.098	0.01	0.045	0.013	0.002	0.125	0.048
SW0Na3S	0.146	0.01	0.045	0.013	0.002	0.125	0.072
SW0Na4S	0.194	0.01	0.045	0.013	0.002	0.125	0.096

3 Simulation Model

The simulation model used in IORCoreSim links wettability alteration to the concentration or adsorption of a single component. In this case, the wettability will be altered according to the amount of SO_4^{2-} adsorbed on the surface in an anion exchange process. Initially, all the ions in the formation water will compete against the positive and negative surface sites. Since formation water contains zero concentration of sulfate, ions adsorbed on the positive surface sites are exchanged with Cl- and HCO3-.

Since sulfate is assumed to be the wettability alternating component, the system moves towards a more water-wet state as the amount of sulfate adsorption increases. The adsorbed amount of sulfate (ρ^s_{SO4}) is directly linked to an interpolation parameter (Fm), which interpolates between two sets of saturation functions. The first saturation function represents the initial wetting of the system, whereas the last saturation function defines a more water-wet system. As mentioned before, it was decided to use the same relative permeability curves for the different wetting systems, so that the interpolation only occurs between the Pc-curves.

Table 6 shows the Fm and adsorbed amount of sulfate ($\rho SO4s$) used in IORCoreSim (ncmisc keyword).

Table 6. *Fm* and adsorbed sulfate used in IORCoreSim.

Case	*ρSO4s*	*Fm*
SW0Na0S	0	0.017
SW	0.019	0.443
SW0.5Na	0.033	0.474
SW0.25Na	0.045	0.507
SW0.1Na	0.054	0.528
SW0.05Na	0.058	0.618
SW0Na	0.062	0.641
SW0Na1S	0.062	0.641
SW0Na2S	0.073	0.618
SW0Na3S	0.078	0.739
SW0Na4S	0.081	0.936

4 Results and Discussions

This section presents the history matching between simulated and experimental oil recoveries during spontaneous imbibition tests. The comparison is based on oil recovery as a function of time, allowing evaluation of both transient recovery behaviour and final recovery levels. The results are interpreted in the context of Smart Water mechanisms in carbonate reservoirs.

It is important to note that the primary dataset used for history matching consists of recovery curves only, as no additional experimental measurements (e.g., ion concentration profiles, wettability indices, or in-situ saturation data) were available for calibration. Therefore, the assessment of model performance relies mainly on its ability to reproduce recovery trends and dynamics.

4.1. SWXNa Brine Series

The Figure 3 illustrates the matching of simulated and experimental oil recoveries during spontaneous imbibition of "SWXNa" brines. As is apparent from the figure, they all showed deviations in the time it takes to reach plateau – simulations reached the final recovery faster.

When the NaCl concentration of the imbibing brine is reduced, the oil recovery gradually increases. The plateau recovery for the brine depleted in NaCl (SW0Na) is 50%, which is an 8% increase compared to ordinary seawater (SW). Thus, SW depleted in NaCl should act as smart water compared to ordinary SW. The anion exchange model can predict the experimental recoveries, even though the sulfate concentration is kept unchanged.

All cases presented some effect of high imbibition velocity. This may be a limitation of the anion exchange model. However, even though there is a slight difference in the imbibition rates, the simulated curves capture the most important recovery trends of the experimental data.

In these cases, the concentration of sulfate is constant, but recovery increases during the experiment. There must be another mechanism that explains the extra oil recovered from the core in an anion exchange process. Thus, the anion exchange model can predict experimental recoveries, even though the sulfate concentration is kept unchanged.

Good agreement in final recovery is observed for SW, SW0.05Na, SW0.25Na, and SW0.5Na. However, discrepancies in early-time behavior suggest that mass transfer kinetics or wettability alteration rates may not be fully captured by the anion exchange model.

An important observation is that recovery increases even though sulfate concentration remains constant. This indicates that additional mechanisms—such as ionic strength effects, electrical double layer expansion, or multi-ion exchange processes—may contribute to the observed recovery. Therefore, while the anion exchange model reproduces the overall recovery trend, it may not fully describe all active mechanisms.

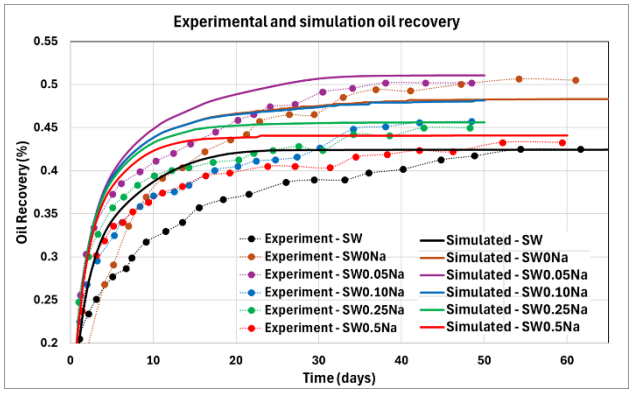

Fig. 3. Results from all SWXNa brines composition.

4.2. SW0NaXS Brine Series (Sulfate Variation)

Figure 4 presents the matching results for the SW0NaXS brine series, where sulfate concentration varies while NaCl is minimized.

For the case SW0Na0S, a recovery of approximately 21% is obtained, representing the initial wettability state without active wettability alteration. The model reproduces this case well, indicating that the base system is properly represented.

When sulfate is introduced (SW0Na1S), recovery increases significantly to approximately 50%, showing the strong impact of sulfate ions in promoting wettability alteration toward a more water-wet state.

For higher sulfate concentrations (SW0Na2S, SW0Na3S, SW0Na4S), the following behaviors are observed:

- The incremental recovery gains become progressively smaller, suggesting a diminishing return effect at high sulfate concentrations.

- The model generally captures the final recovery levels, but again exhibits faster dynamics compared to experimental data.
- Differences between simulated and experimental curves increase slightly at higher sulfate concentrations, indicating possible limitations in representing multi-ion competitive adsorption or saturation of adsorption sites.

Compared to the SWXNa series, the agreement in transient behavior is slightly weaker for higher sulfate cases, suggesting that the model may be more sensitive to sulfate concentration changes than captured in its current formulation.

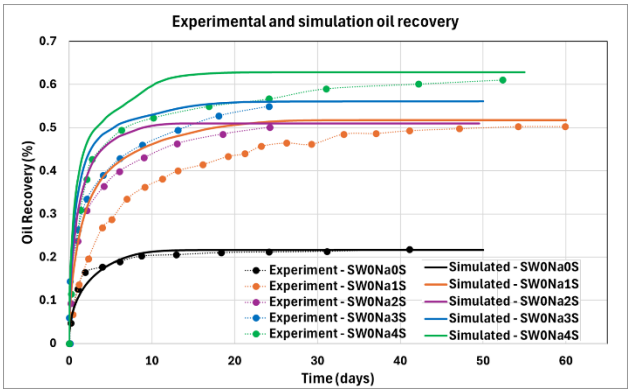

Fig. 4. Results from all SW0NaXS brine composition.

A clear distinction can be made between final recovery matching and transient recovery behavior. The model consistently reproduces the ultimate oil recovery levels, indicating that the equilibrium state (i.e., the final wettability condition) is well represented. However, discrepancies arise in the transient response, as simulated recovery curves tend to reach the plateau earlier than the experimental data. This suggests that the model may overestimate the imbibition rate and relies on simplified representations of ion-exchange kinetics, while also neglecting diffusion-limited transport effects that can slow down the process. Consequently, although the agreement in final recovery is good, it does not guarantee that the displacement dynamics and underlying physical mechanisms are accurately captured.

An important limitation of the present modeling approach is the potential non-uniqueness (non-identifiability) of the solution.

Different parameter combinations - such as capillary pressure shape, reaction rates, and adsorption capacity - may produce similar final oil recoveries while exhibiting different transient behaviors. Therefore:

- Matching only the final recovery can lead to non-unique solutions
- The early-time mismatch suggests that multiple parameter sets could explain the data equally well
- Additional constraints (e.g., ion concentration profiles, wettability measurements) would be required for unique calibration

This limitation should be considered when interpreting the predictive capability of the model.

Conclusions

The main objective of this study was to evaluate whether an anion exchange model implemented in IORCoreSim can reproduce wettability alteration during spontaneous imbibition of Smart Water in carbonate reservoirs.

The results show that the anion exchange model can reproduce key trends in experimentally observed oil recovery [2]. In particular, the simulations capture the increase in oil recovery associated with higher sulfate concentrations in the imbibing brine. This behavior is consistent with the hypothesis that sulfate adsorption is linked to wettability alteration toward more water-wet conditions. However, it should be noted that the model results do not uniquely demonstrate this mechanism but rather provide a representation that is consistent with the observed recovery trends.

The model generally provides a reasonable match of final oil recovery, while discrepancies are observed in the transient recovery behavior, with simulated curves reaching the plateau earlier than the experiments. This suggests that the model may not fully capture the dynamics of the imbibition process, particularly with respect to mass transfer and reaction kinetics.

The history matching process indicates that reproducing transient behavior is more challenging than matching final recoveries. In this study, agreement with experimental data was achieved primarily by adjusting the capillary pressure curves and the amount of adsorbed sulfate on the rock surface. However, such adjustments may not be unique, and different parameter combinations could potentially lead to similar recovery responses.

Several factors may limit the predictive capability of the current model formulation. These include the representation of ion diffusion, the anion exchange capacity (Z^+), as well as the effects of temperature and oil composition. The results suggest that recovery rates may be influenced by transport limitations, such as diffusion of sulfate ions into the core, although this interpretation is not directly validated by the available data.

Overall, the model provides a useful framework for interpreting Smart Water effects in spontaneous imbibition, but its predictive capability remains constrained by simplifications in the representation of transport processes and wettability alteration mechanisms.

Outlook & Future Work

Future work should aim to improve both the physical realism and predictive capability of the model. In particular:

- Sensitivity analysis should be performed to quantify the influence of key parameters such as ion diffusion coefficients, anion exchange capacity (Z^+), and capillary pressure scaling on model predictions.

- Uncertainty assessment is needed to evaluate the robustness of the conclusions, especially given the non-uniqueness of history matching.
- The model should be validated against independent experimental datasets, including cases with varying temperature, oil composition, and rock properties.
- Additional observables, such as ion concentration profiles, effluent chemistry, or in-situ wettability indicators, could provide stronger constraints on the underlying mechanisms.
- Finally, extending the model to include coupled processes such as mineral dissolution/precipitation and relative permeability evolution would help assess whether these effects are required to reproduce transient imbibition dynamics.

Acknowledgments

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