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Individual and Symbiotic Interfacial Contribution of Ions to Hydrophilic Enhancement of Oil-Bearing Dolomite: Implication to Ion-Engineered Waterflooding

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Abstract

The ion-specificity of minerals' wettability is an active research area of particular importance in ion-engineered waterflooding as a promising enhanced oil recovery method. In this process, the wettability of the oil-brine-rock (OBR) system is changed by designing the ions of injected water. Though the contribution of ions to the wetting character of carbonates, particularly dolomite ($\text{CaMg}(\text{CO}_3)_2$), has been investigated by various studies, the contribution of ions still needs to be resolved. Through a systematic experimental investigation, the present paper sheds light on the contribution of the main constituent ions of natural brines to retrieving the water-favoring virtue of oil-bearing rocks majorly composed of dolomite. The static wettability measurements showed distinct affinity of individual surface-active ions to the dolomite/water interface, following the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+}$. To clarify the effect of mixed electrolytes, results of experimental scenarios showed the assisting role of sulfate and, to a lesser extent, nitrate to restore the hydrophilic virtue of oil-aged dolomite samples, irrespective of the divalent cations, which was also mirrored to incremental oil displacement upon enriching those anions in dynamic core flooding tests. The cooperation of SO_4^{2-} and NO_3^- anions yielded optimal wettability alteration in static experiments and maximum oil mobilization in core flooding tests. Insights provided here improve our knowledge of the ion-dependent wettability response of dolomite with implications to diverse fields of surface science, particularly for the rational design of brine composition to acquire optimal performance of water-based EOR operations.

Keywords: Wettability, Dolomite, Brine, Ion-engineered Waterflooding, Oil Recovery.

Introduction

Wettability defines the relative tendency of two different fluids to cover a solid surface [1]. There are ubiquitous cases where wettability takes the determining role, for example, multi-phase transport of fluids through porous substances and surface-release of organic matters upon remediation of subsurface aquifers [2]. In the past two decades, the ion-specific wetting response of rock wettability has drawn much interest from academia and technological communities concerning environmental science and the petroleum industry [3-5]. Amongst, ion-engineered waterflooding (IEWF) has been employed as a well-established and environmentally friendly water-based approach for improving oil recovery through diluting and/or adjusting the ionic composition of the solution injected into underground oil reservoirs [6]. Particularly to carbonates, comprising a major portion of the earth's crust, IEWF often refers to augment divalent cations, sometimes termed potential determining ions

(PDI), of the solution used for flooding those kinds of rock [7]. There is a wealth of publications on identifying factors involved in the variation of surface characteristics of carbonate rocks, particularly limestone and chalk, when being treated by ion-adjusted saline solutions, which has been critically and concisely reviewed by Hao et al. [8]. In terms of affecting mechanisms on carbonate rocks wettability alteration, there exist various mechanistic studies describing the process in depth by running experimental studies [9-10]. Comparatively, little is known about the contribution of ions to the dolomite/water interface. An experimental survey by Al-Hashim et al. revealed the positive surface charge of dolomitic rocks upon immersion in a broad set of brines synthesized by manipulating Persian Gulf seawater [11]. Moosavi et al. pointed out accelerated wettability alteration of oil-conditioned dolomite samples once exposed to PDI-richer solutions [12]. Notably, dolomite turned negatively charged in both studies at high sulfate

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concentrations. Contact angle (CA) and imbibition experiments by Rashid et al. emphasized sulfate's catalytic role in altering dolomite wettability by magnesium cations [13]. However, in a conflicting study, Shariatpanahi et al. deduced a low affinity of sulfate toward dolomite in the presence of Ca^{2+} and Mg^{2+} cations [14]. A recent molecular study by Bai et al. has verified the key role of sulfate in facilitating the desorption of polar organic molecules and, subsequently, wettability alteration of dolomite substrates toward hydrophilic state [15].

As reviewed above, most IEFW literature on carbonates has been devoted to calcite. Less has been paid to the particular role of ions in driving the wetting affinity of oil-bearing dolomites surrounded by a saline environment. Furthermore, former studies have mostly considered Ca^{2+} , Mg^{2+} , and SO_4^{2-} as wettability-modifying ions, widely neglecting the impact of other major components of natural saline solutions, like nitrate (NO_3^-). Motivated by this lack of knowledge, an integrated experimental investigation, including static wettability measurements and dynamic oil displacement tests, was carried out here in an attempt to illuminate individual and combined action of a set of ions in shifting the wetting character of oil-aged dolomite to a more water-favoring condition. The focus was primarily on the competitive interfacial contribution of sulfate and nitrate to assist divalent cations in improving water wetness and incremental oil production from dolomite rocks. In the remainder of this manuscript, we first have a brief overview of chemicals utilized and procedures applied for performing experiments. Measurements are then thoroughly analyzed with an in-depth discussion on likely interactions between ions and the rock/brine interface. Eventually, we conclude by summarizing the main findings of this study.

Materials and Methods

Materials

An asphaltenic crude oil, produced from a carbonate reservoir in southwest Iran was used in the following experiments, with the main specifications reported in Table 1.

Brine solutions were prepared by dissolving certain amounts of salts: NaCl, CaCl_2 , MgCl_2 , Na_2SO_4 , NaHCO_3 , and NaNO_3 in deionized water. All salts, with purity of 99.9%, were purchased from Merck Chemical Co. (Darmstadt, Germany) and used without extra purification. Formation brine (FB) with salinity of 179000 ppm was synthesized according to the ionic composition of connate water in the Ahwaz Bangestan reservoir, reported in Table 2. Diluted Persian Gulf seawater (dSW), with a salinity of 5000 ppm, was taken as the base injecting brine upon which 30 extra solutions were derived by adjusting Ca^{2+} , Mg^{2+} , SO_4^{2-} and NO_3^- ions

concentration. In all solutions, total salinity was maintained equally by adjusting the amount of dissolved NaCl. In what follows, the naming convention "wSxCyNzM" was adopted for defining solutions synthesized, where symbols (w, x, y, z) denote the ratio of (S as SO_4^{2-} , C as Ca^{2+} , N as NO_3^- and M as Mg^{2+}) ions, respectively, in terms of their composition in the reference brine, dSW. For scrutinizing the individual role of wettability-determining ions, a set of solutions, namely, NaCl, NaCl- Ca^{2+} , NaCl- Mg^{2+} , NaCl- NO_3^- , and NaCl- SO_4^{2-} , were prepared only containing the individual ion (Na, Ca^{2+} , Mg^{2+} , NO_3^- , SO_4^{2-}) along with NaCl dissolved for attaining same salinity, 5000 ppm. For ease of analysis, the base concentration of NO_3^- was taken the same as SO_4^{2-} in the dSW solution. As reported in Table 2, all saline solutions are nearly at the same pH level, ~7.

Core and Slab Preparation

Three core samples, A, B, and C, were drilled from a carbonate outcrop block in southwest Iran, with petrophysical characteristics listed in Table 3. The X-ray diffraction analysis revealed that all rock samples comprise dolomite ($\text{CaMg}(\text{CO}_3)_2$) mineral. Thin pellets with a diameter of 3.75 cm and thickness of 3-5 mm were further extracted by cutting circular sections. They were polished using ultra-fine sandpaper to minimize the effect of surface roughness on contact angle tests. Cores and rock slices were cleaned with a toluene solvent within a soxhlet apparatus to eliminate organic contaminants. Rock samples were then flushed with methanol to dissolve any salt deposition in the pores to avoid unwanted intrusion into their ion-dependent wettability response. Ultimately, they were fully dried in an oven overnight at 100 °C and then saturated by FB.

Contact Angle Test

The sessile drop technique assessed the brine-dependent wetting state of rock slices extracted from core plugs. Following a traditional laboratory practice [13], [16-17], a customary setup (sketched in Fig. 1) was employed for recording the contact angle of an oil droplet placed on a horizontally held rock pellet inside a container filled with a certain saline solution. Contact angle was measured at following consecutive stages: (1) immersing rock slabs for 3 days in FB to establish initially water-wet CA, denoted by θ_w ; (2) aging rock pellets for 2 weeks in crude oil to mimic oil-wet conditions in carbonate reservoirs, with CA of θ_o ; and eventually (3) placing oil-aged pellets in a solution with known composition and continually recording contact angle throughout the soaking process until achieving stabilized CA, θ_f . Uncertainty of CA data was estimated by replicating each measurement for 3 different oil droplets, an approach conventionally employed in former relevant studies [18].

Table 1 Crude oil properties.

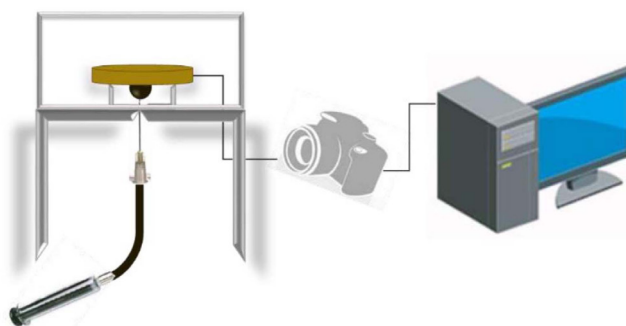
Density at 25 °C (g.dm ⁻³)	Shear viscosity			Acid number (mg KOH/g)	Asphaltene (wt/wt %)	Waxes (wt/wt %)
	at 10°C	at 20°C	at 30°C			
0.861	13.94	8.54	5.12	0.1	7.5	0.4

Table 2 Ionic composition (mol.dm⁻³) and pH of saline solutions (with total salinity of 5000) used in the experiments.

Solutions name	Na ⁺	Cl ⁻	SO ₄ ²⁻	Mg ²⁺	Ca ²⁺	NO ₃ ⁻	pH
FB	2.3211	3.1210	0.0054	0.1199	0.2861	0.0000	-
dSW	0.7100	0.8270	0.043	0.081	0.015	0.0000	7.0
NaCl-Ca	0.0801	0.0916	0.0000	0.0000	0.0028	0.0000	7.0
NaCl-Mg	0.0603	0.0913	0.0000	0.01545	0.0000	0.0000	7.1
NaCl-NO ₃	0.0900	0.0736	0.0000	0.0000	0.0000	0.0082	7.3
NaCl-SO ₄	0.0820	0.0657	0.0082	0.0000	0.0000	0.0000	7.4
NaCl-NaCl	0.8556	0.0856	0.0000	0.0000	0.0000	0.0000	7.6
2S2C0N0M	0.7658	0.0659	0.0082	0.0000	0.0028	0.0000	7.1
1S2C0N0M	0.0783	0.0759	0.0041	0.0000	0.0028	0.0000	7.2
0S2C2N0M	0.0763	0.0739	0.0000	0.0000	0.0028	0.0082	7.0
0S2C1N0M	0.0782	0.0799	0.0000	0.0000	0.0028	0.0041	7.1
1S/N2C0M	0.0729	0.0539	0.0082	0.0000	0.0028	0.0082	7.1
2S/N2C0M	0.0747	0.0599	0.0082	0.0000	0.0028	0.0041	7.2
0.5S/N2C0M	0.0691	0.0420	0.0082	0.0000	0.0028	0.0164	7.3
2S0C0N2M	0.0568	0.0713	0.0082	0.0155	0.0000	0.0000	7.4
1S0C0N2M	0.0586	0.0813	0.0041	0.0155	0.0000	0.0000	7.3
0S0C2N2M	0.0566	0.0484	0.0000	0.0155	0.0000	0.0082	7.3
0S0C1N2M	0.0585	0.0544	0.0000	0.0155	0.0000	0.0041	7.2
1S/N0C2M	0.0531	0.0594	0.0082	0.0155	0.0000	0.0082	7.2
2S/N0C2M	0.0549	0.0654	0.0082	0.0155	0.0000	0.0041	7.2
0.5S/N0C2M	0.0494	0.0474	0.0082	0.0155	0.0000	0.0164	7.2
0S1C1N1M	0.0679	0.0825	0.0000	0.0077	0.0014	0.0041	7.1
0S2C2N2M	0.0502	0.0795	0.0000	0.0155	0.0028	0.0082	6.9
1S1C0N2M	0.0550	0.0811	0.0041	0.00155	0.0014	0.0000	7.2
1S0C2N1M	0.0669	0.0659	0.0041	0.0077	0.0000	0.0082	7.5
2S2C0N1M	0.0634	0.0683	0.0082	0.0077	0.0028	0.0000	6.8
1S/N1C0M	0.0753	0.0753	0.0082	0.0000	0.0014	0.0082	7.0
2S1C0N1M	0.0667	0.0686	0.0082	0.0077	0.0014	0.0000	6.8
1S1C0N1M	0.0685	0.0786	0.0041	0.0077	0.0014	0.0000	6.8
0S1C0N1M	0.0702	0.0886	0.0000	0.0077	0.0014	0.0000	6.8
0.5S/N1C1M	0.0592	0.0447	0.0082	0.0077	0.0014	0.0164	7.3
0S1C2N1M	0.0665	0.0766	0.0000	0.0077	0.0014	0.0082	7.2

Table 3 Petrophysical properties of rock samples.

Cores (s)	Length (cm)	Diameter (cm)	Porosity (%)	Pore volume (ml)	Permeability (md)	S _{wc}
A	7.91	3.74	15.5	13.48	9.5	0.29
B	7.49	3.75	10.4	8.61	10.5	0.23
C	8.25	3.77	17.1	14.21	13.7	0.22

**Fig. 1** The setup is used for contact angle measurement.

Displacement Experiment

A core flooding test was carried out to investigate the composition-dependent performance of saline solution for oil displacement using an injection setup sketched in Fig. 2. This apparatus, equipped with three accumulators, enables successive injection of different solutions into a core sample. After cleaning and drying, as explained before, the irreducible (connate) water saturation, reported in Table 3, was established by adequately flooding the brine-saturated samples with crude oil. The injection operation was conducted by mounting each core sample in the holder under a confining pressure of 500 bar, equivalent to the overburden stress under underground conditions. Afterward, oil-flooded cores were left in crude oil for 2 weeks in a sealed container to restore the oil-wet. From the preliminary static contact angle measurements, a set of brine solutions was selected for further evaluation through a dynamic oil displacement test. The impact of ionic composition was assessed dynamically by injecting specific solutions at secondary and tertiary modes of oil displacement. In all cases, the flooding experiment was initiated by injecting a saline solution into the oil-aged plug at a rate of 0.1 mL.min⁻¹, followed by injection of 1S1C0N1M brine (except for coreflooding II). From a technical and economic viewpoint, using 1S1C0N1M is justified because of the ease of preparation via the least manipulation of the readily available seawater. The operation was eventually terminated after reinjection of the saline solution utilized at the primary stage. The injection was continued at each stage until no extra oil was recovered. Through this special flooding scenario, rock samples were left for 2 days at the

end of each step to establish equilibration of the rock/brine system. Injection sequences for corresponding experiments are summarized in Table 4.

Results and Discussion

In this section, we primarily analyze static wettability measurements to examine the ability of different aqueous solutions to shift the affinity of the oil-aged dolomite to the water-favoring condition. In the next part, the dynamic wettability alteration is probed based on the oil displacement efficiency of candidate solutions.

Static Wettability Tests

The Wettability Alteration Index (WAI), defined below [16], quantifies the extent of the wettability shift of an oil-bearing rock slab to a water-favoring state by exposing it to a saline solution:

$$WAI = \frac{\theta_f - \theta_0}{\theta_w - \theta_0} \tag{1}$$

with WAI close to unity means entire wettability reversal, whereas zero denotes the inability of the brine solution to alter the oil-wet state.

Role of Individual Ions

The relative affinity of ions toward the crude-aged dolomite was assessed by monitoring WAI variation upon soaking samples in the solutions composed of a certain surface-active ion and NaCl as the background, salinity adjusting electrolyte (Fig. 3).

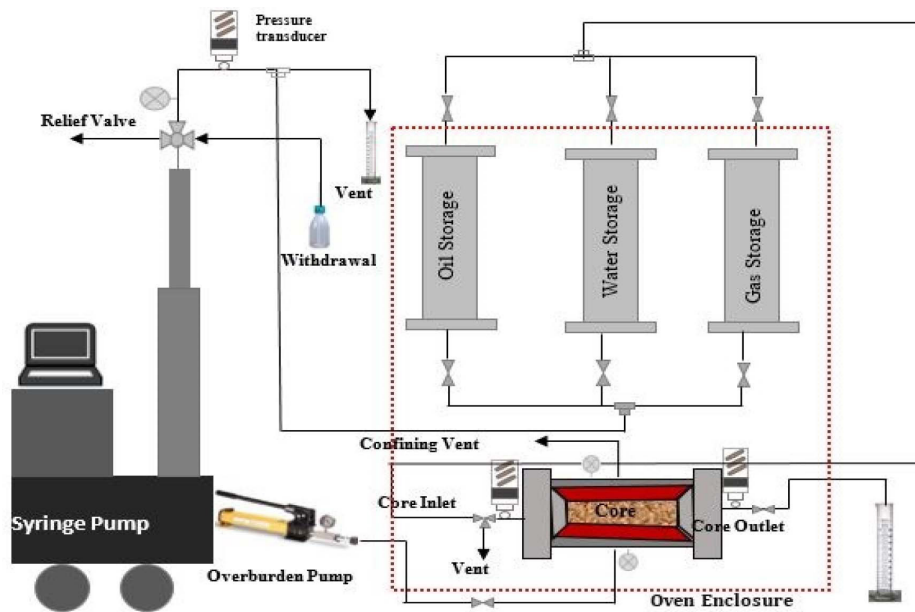


Fig. 2 Schematic of the core flooding apparatus.

Table 4 Summary of core flooding scenarios.

Experiment ID	I	II	III	IV	V	VI
Core ID	B	A	C	B	A	C
Injection sequence	0S1C0N1M → 1S1C0N1M → 0S1C0N1M	1S1C0N1M → 2S1C0N1M → 1S1C0N1M	2S1C0N1M → 1S1C0N1M → 2S1C0N1M	0S1C2N1M → 1S1C0N1M → 0S1C2N1M	0.5S/N1C1M → 1S1C0N1M → 0.5S/ N 1 C 1 M	0.5S/N2C0M → 1S1C0N1M → 0.5S/ N 2 C 0 M

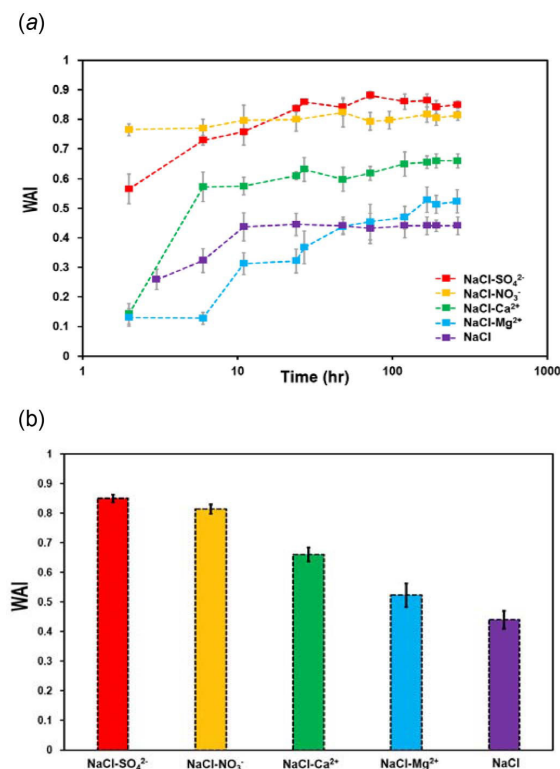


Fig. 3 (a) Time evolution and (b) ultimate value of WAI obtained upon exposing dolomite slabs already aged in crude oil to solutions composed of a single surface-active ion NaCl as the background electrolyte, all at the same salinity, 5000 ppm.

Needless to say, sodium and chloride ions are commonly perceived as indifferent to carbonate/water interfaces, only interfering in the surface behavior of PDIs [3], [19–21]. In all treated cases, wettability change happens within the early 10 hrs; then WAI levels off to a stabilized value maintained by the end of the soaking process. As reported in Fig. 3, using NaCl-SO₄²⁻ and NaCl-NO₃⁻ solutions comparably and appreciably retrieve the water-preference of dolomite pellets, with ultimate WAIs of 0.85 and 0.8, respectively. In comparison, the wettability of dolomite samples shifts moderately by applying NaCl-Ca²⁺ (WAI = 0.66) and, to a lesser extent, upon immersion in NaCl-Mg²⁺ brine, with WAI of 0.52. Amongst, treatment slabs by NaCl solution turned out ineffective, with WAI of 0.44, in agreement with the results of an analogous study by Moosavi et al., who observed the insignificance of that solution in restoring wettability of calcite at the same salinity (5000 ppm) [12]. In sum, SO₄²⁻ and NO₃⁻ anions demonstrate a stronger tendency for retrieving water-wetness of oil-aged dolomite compared to Ca²⁺ and Mg²⁺ cations, with ultimate WAIs following the order: SO₄²⁻ > NO₃⁻ >> Ca²⁺ > Mg²⁺. Electrostatic attraction induced by the positively charged surface of dolomite, as reported by Al-Hashim [11], drives preferential adsorption of anions and, thus, higher surface activity. Under the influence of nitrate and calcium, wettability transits faster to the hydrophilic state than their counterparts, i.e., sulfate and magnesium, as implied by recent nano-scale studies indicating the easier penetration of the former ions to carbonate/water interface [22, 23].

Role of Ions in Brine Mixture: the Particular Contribution of Sulfate

Following the preceding discussion on single-PDI solutions,

we now consider the simultaneous influence of ions, particularly SO₄²⁻ in this part, on the wetting preference of dolomite pellets upon immersion in a brine mixture. From WAIs presented in Fig. 4 and 5, increasing sulfate concentration, regardless of the Ca²⁺ and/or Mg²⁺ content, enhances the water-favoring virtue of dolomite slabs. It has been corroborated, both experimentally and theoretically [22–25], that sulfate anions are naturally inclined to approach carbonate/water interface so that shielding positively-charged binding sites. Local surface-charge neutralization of carbonates by adsorption of sulfate allows divalent cations (Ca²⁺ and Mg²⁺) to come close to the mineral surface and potentially release surface-lodging organic compounds upon associating with their charged moieties, typically carboxylate headgroup [18]. It conceptually describes the so-called multi-ion exchange (MIE) mechanism, originally proposed by Austad and co-workers [26–27]. As schematically illustrated in Fig. 6, this mechanism involves the cooperation of sulfate and divalent ions to facilitate surface desorption of oil compounds, thereby retrieving the hydrophilic character of crystalline carbonate substrates [28]. It clearly justifies the higher WAI result by using 1S1C0N1M (and also 2S1C0N1M, Fig. 4) than those of merely having sulfate (NaCl-SO₄²⁻, Fig. 4) or divalent cations (0S1C0N1M), Fig. 5.

At a closer look (Fig. 4 and 5), the present data reveal the prevailing role of sulfate in the wettability reversal of oil-aged dolomite, which has been already pointed out by Shariatpanahi et al., who worked on the ion-specificity of calcite surfaces [14]. As shown in Fig. 4, introducing SO₄²⁻, in the case of 1S1C0N1M, markedly increased WAI compared to what was acquired by the sulfate-free solution, 0S1C0N1M. WAI raises unity by adding more sulfate, i.e., using 2S1C0N1M solution. The positive correlation of WAI to the sulfate concentration is also observed for surface treatment by solutions containing either Ca²⁺ or Mg²⁺ cations (Fig. 5).

It follows from Fig. 5 that the wettability treatment of dolomite is quite cation-sensitive. Regarding the time-evolution of wettability alteration, as shown in Figure 5(a), WAI comparatively grows faster for treatment by solutions containing Ca²⁺ (1S2C0N0M and 2S2C0N0M) than those with Mg²⁺, which was already interpreted based on the disparate ability of those cations for piercing into the surface-covering water film of mineral. Despite the stronger affinity of sole calcium toward the dolomite surface, as previously recognized in Fig. 3, the 1S0C0N2M solution turned out more effective than 1S2C0N0M in enhancing water-preference of dolomite (Fig. 5), reflecting greater surface activity of magnesium combined with sulfate. Likewise, former studies have frequently reported benevolent cooperation of Mg²⁺ and SO₄²⁻ ions in releasing oil compounds from calcite surfaces [24], [27]. It partly stems from the strong tendency of Mg²⁺ cations to associate with polar hydrocarbons, thus releasing those compounds from the carbonate surface [29].

On the other hand, cation-anion pairing could be detrimental through diminishing fraction of freely moving (surface-accessible) SO₄²⁻ anion by recent atomistic investigations [30]. Extensive complexation of Mg²⁺ and SO₄²⁻ ions accounts for the lower treating influence of 1S1C0N2M against 1S1C0N1M, with WAIs of 0.78 and 0.92, respectively. This effect is also notified to a lesser extent upon increasing the concentration of Ca²⁺ cation (Fig. 7).

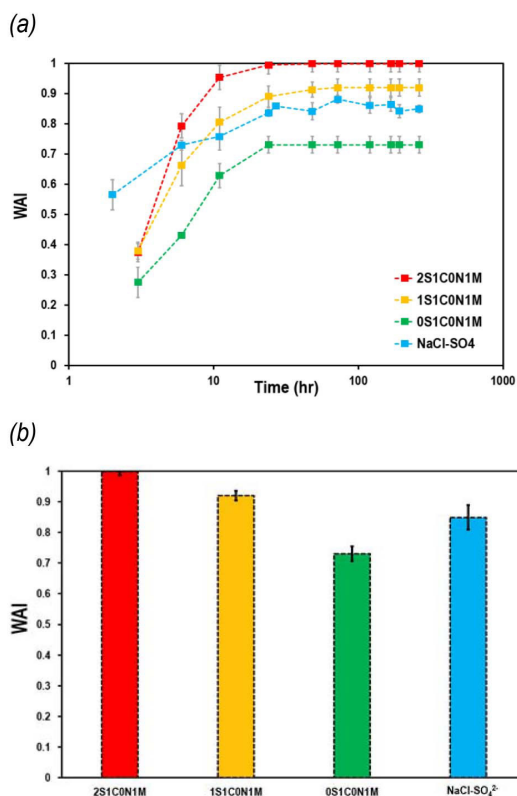


Fig. 4 (a) Time evolution and (b) ultimate value of WAI obtained upon soaking oil-aged dolomite pellets in solutions composed of both Ca²⁺ and Mg²⁺ cations and varying concentrations of sulfate at the same level of salinity. NaCl-SO₄²⁻ solution is provided for the sake of comparison.

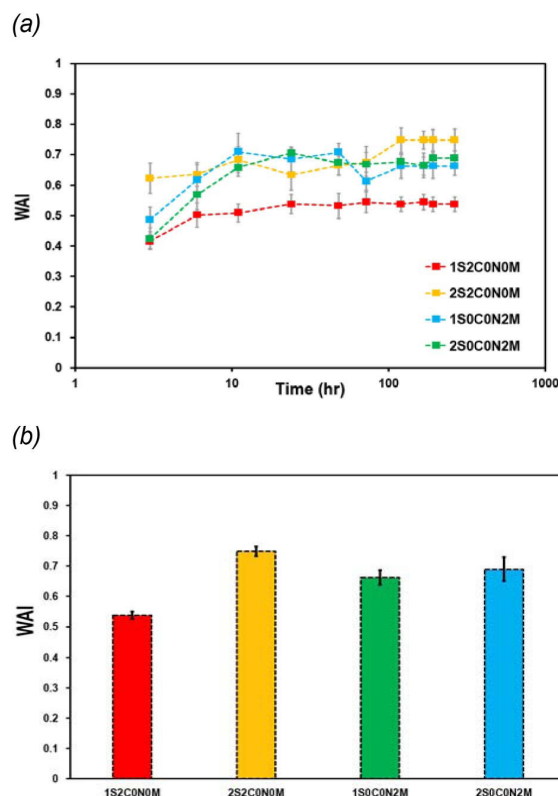


Fig. 5 (a) Time evolution and (b) ultimate value of WAI obtained by immersing oil-aged dolomite pellets in solutions composed of either Ca²⁺ or Mg²⁺ cations and varying sulfate concentrations, all at the same salinity level

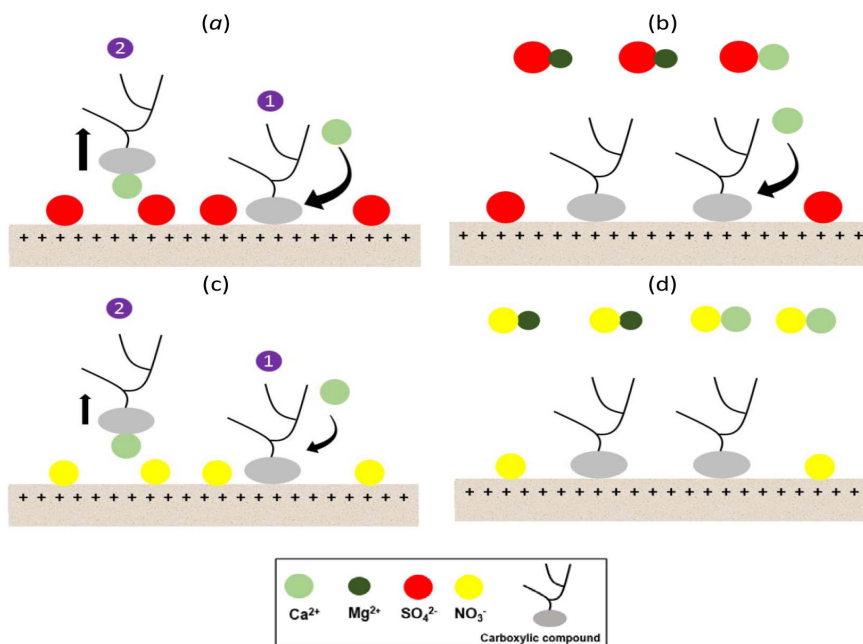


Fig. 6 Pictorial illustration of (a) sulfate-assisted release of carboxylic compounds through association with divalent cations; (b) declining number of surface-accessing sulfates because of extensive pairing with divalent cations, particularly magnesium; (c) relatively weaker influence of nitrate for attracting divalent cations to the dolomite surface and consequently releasing carboxylic compounds to a lesser extent; and (d) surface paucity of nitrate anions as a result of massive association with divalent cations in the bulk space. Panels (a) and (c) involve the complexation and release of hydrocarbon denoted by labels 1 and 2, respectively.

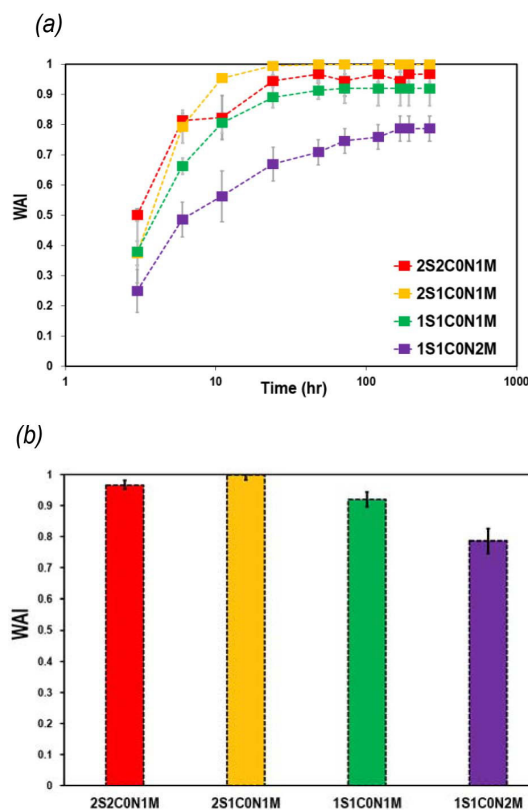


Fig. 7 (a) Time evolution, and (b) ultimate value of WAI acquired by exposing dolomite pellets aged in crude oil to electrolyte solutions composed of varying fractions of Ca^{2+} and Mg^{2+} cations and varying sulfate concentrations at the same salinity level.

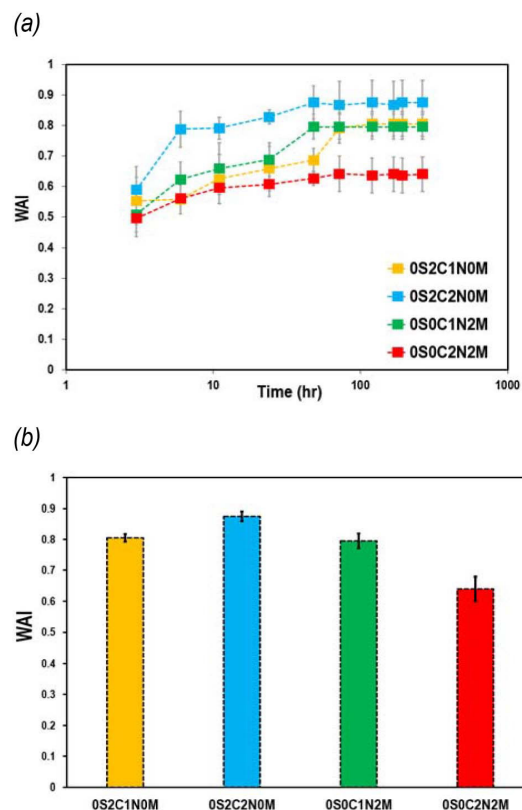


Fig. 8 (a) Time evolution and (b) ultimate value of WAI recorded upon soaking oil-aged dolomite pellets in solutions composed of either Ca^{2+} or Mg^{2+} cations and varying nitrate concentrations, all at the same salinity level.

Role of Ions in Brine Mixture: the Particular Contribution of Nitrate

Following our primitive finding on the significance of nitrate in improving the hydrophilic character of oil-bearing dolomite, we now take a step forward to resolve the mutual interplay of NO_3^- anion and divalent cations (Ca^{2+} and Mg^{2+}) near that kind of mineral. Effect of concentrating NO_3^- in the treating solution appears cation-dependent (Fig. 8): water-wet enhancement in the presence of Ca^{2+} (greater WAI of 0S2C2N0M than 0S2C1N0M) whereas attenuated wettability retrieval when having Mg^{2+} cation (0S0C2N2M vs. 0S0C1N2M). In the co-existence of Ca^{2+} and Mg^{2+} cations in the soaking saltwater, doubling nitrate concentration accelerates the wettability alteration of dolomite. In any case, doubling nitrate concentration accelerates the wettability alteration of dolomite.

In comparison to sulfate (Fig. 5), nitrate seems less effective for activating Aušad's mechanism (Fig. 8) because of its monovalent identity and higher concentration to neutralize the mineral surface. Nitrate anions are less likely to be adsorbed onto the positively charged carbonate/water interface, staying longer in the bulk aqueous space, and more likely to pair with divalent cations, particularly magnesium, as pictorially described in Figure 6. This is the reasoning behind the comparable performance (WAI) of NaCl-NO_3^- (Fig. 3) and 0S1C1N1M solutions in restoring the water-wetness of dolomite samples (Figure 9). As further evidence, Fig. 9 exhibits attenuation of wettability reversal upon enriching Ca^{2+} and Mg^{2+} cations in 0S1C2N1M solution, 0S2C2N2M.

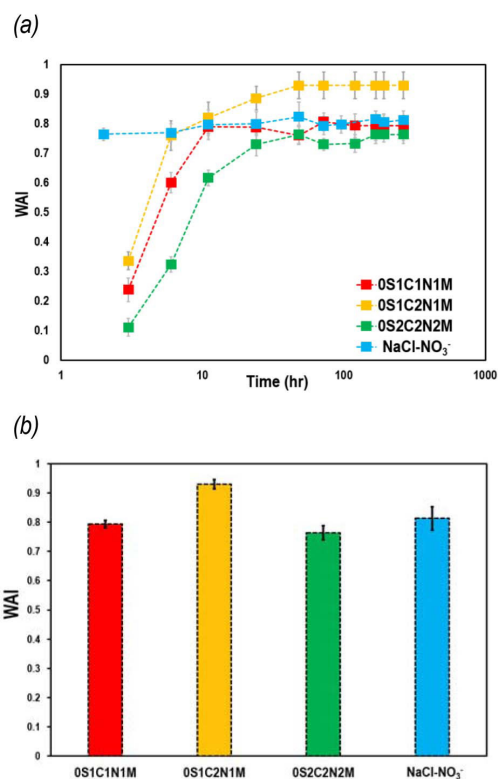


Fig. 9 (a) Time evolution and (b) ultimate value of WAI recorded upon soaking oil-aged dolomite pellets in solutions containing Ca^{2+} and Mg^{2+} cations and varying concentrations of sulfate, all at the same level of salinity. NaCl-NO_3^- solution is provided for the sake of comparison.

SO_4^{2-} and NO_3^- ions show different levels of assisting hydrophilic-retrieval of oil-bearing dolomite. Comparing wettability measurements (Fig. 7 of the Supplementary Information) indicates stronger surface affinity of divalent sulfate anions relative to monovalent nitrate, with WAI values following the order: $2\text{S}1\text{C}0\text{N}1\text{M} > 1\text{S}1\text{C}0\text{N}1\text{M} \approx 0\text{S}1\text{C}2\text{N}1\text{M} > 0\text{S}1\text{C}1\text{N}1\text{M}$; former being of higher capacity for neutralizing dolomite substrate and electrostatically attracting divalent cations. Concerning kinetics of wettability modification, it takes longer to attain equilibration using nitrate-carrying solutions (Fig. 9) relative to what was observed for sulfate-containing brines (Fig. 7), 20 vs. 50 hrs, respectively. In conclusion, the present experiments reveal the less favorable, still remarkable, cooperation of NO_3^- and divalent cations for releasing oil compounds from the dolomite surface, schematically compared to SO_4^{2-} in Fig. 6.

Simultaneous Contribution of Sulfate and Nitrate Anions

In this part, we concentrate on the symbiotic behavior of SO_4^{2-} and NO_3^- anions in regulating the wetting preference of dolomitic rock surfaces surrounded by an aqueous solution. To this goal, rock slabs aged in crude oil were exposed to solutions composed of varying sulfate-to-nitrate concentration ratios: 0.5, 1.0, and 2.0, and like before, all at the same salinity level, 5000 ppm. The brines were synthesized at a constant concentration of sulfate, that is, twice that of the base dSW solution, which showed promising performance in preceding nitrate-free experiments. In the presence of Ca^{2+} , WAIs evolve and achieve a plateau by obeying the order: $0.5\text{S}/\text{N}2\text{C}0\text{M} > 2.0\text{S}/\text{N}2\text{C}0\text{M} > 1.0\text{S}/\text{N}2\text{C}0\text{M}$ (Fig. 10). The same trend holds for solutions with Mg^{2+} (Fig. 11). Nitrate could readily penetrate the mineral/water interface and thus swiftly shield positively charged surface sites on the rock surface due to having a smaller solvation radius than sulfate. With this consideration, nitrate may act benevolently or detrimentally, depending on the amount of sulfate. Partial neutralization of the rock substrate by faster sorption of nitrates could discourage surface attachment of sulfates. On the other hand, nitrates potentially facilitate the desorption of hydrocarbons by covering binding sites not accessible by sulfates. Sulfates are less involved in complexation with divalent cations and could freely approach the mineral surface to a greater extent due to the presence of nitrate in the bulk solution. At high $\text{SO}_4^{2-}/\text{NO}_3^-$ ratios, like $2.0\text{S}/\text{N}2\text{C}0\text{M}$ solution, nitrate concentration is not high enough to compete with sulfates at the interface, therefore taking a positive role by associating with cations in the bulk solution. At comparable concentration ratios, nitrates potentially interfere with sulfates by competing for adsorption spots, which explains the least wettability retrieval using $1.0\text{S}/\text{N}2\text{C}0\text{M}$ solution. At lower sulfate-to-nitrate ratios, e.g., $0.5\text{S}/\text{N}2\text{C}0\text{M}$, ample NO_3^- anions broadly and rapidly occupy vacant dolomite surface sites to assist hydrocarbon desorption and wettability alteration. Overall, a complex interplay of anions and cations and their affinity for rock surface yields the non-monotonic variation of WAI by sulfate/nitrate ratio, shown in Fig. 10 and 11. As evidence of this complicacy, Fig. 10 shows higher WAI due to $1.0\text{S}/\text{N}2\text{C}0\text{M}$ than $1.0\text{S}/\text{N}1\text{C}0\text{M}$. We also notice lower wettability restoration of dolomite by having magnesium (Fig. 11) instead of calcium (Fig. 10) in the treating solution at any sulfate/nitrate ratio.

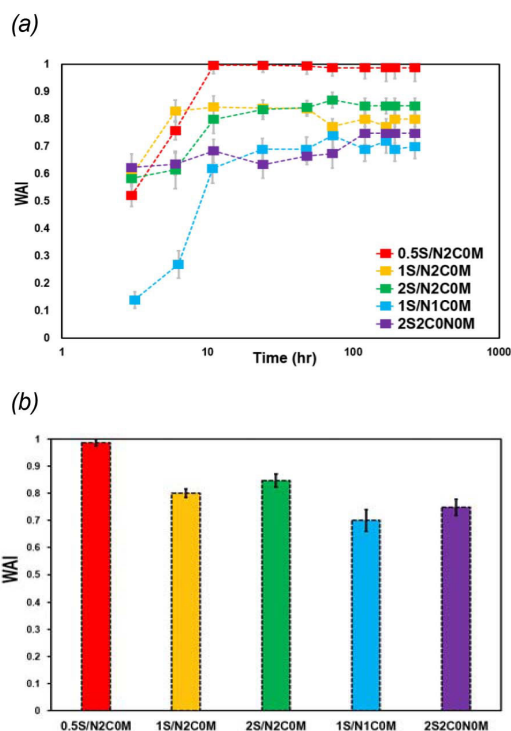


Fig. 10. (a) Time evolution, and (b) ultimate values of WAI obtained upon soaking oil-aged dolomite pellets in solutions composed of Ca^{2+} cation and varying sulfate-to-nitrate ratios. $2\text{S}2\text{C}0\text{N}0\text{M}$ solution is provided for the sake of comparison.

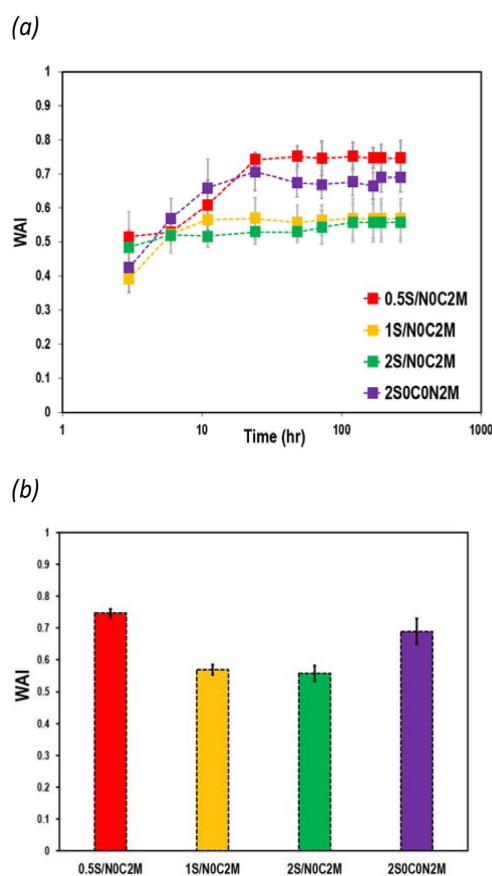


Fig. 11. (a) Time-varying, and (b) ultimate value of WAI upon using soaking solutions solely containing Mg^{2+} and varying sulfate/nitrate ratios.

Oil Displacement Experiments

Thus far, the ion-dependent wetting state of samples composed of dolomite was explored based on static contact angle results. From a practical perspective, the wetting sensitivity of the oil-bearing rocks on ionic composition was probed by conducting an integrated set of displacement tests. Following an innovative core flooding scheme, six core flooding experiments called I to VI, were carried out, each consisting of three sequential stages with the same solutions applied at the first and third steps and injecting the 0S1C0N1M solution at the second flooding stage of all cases but experiment II. Regarding practical (field scale) targets, using 0S1C0N1M is technically and economically justified, which is easily synthesized through the least manipulation of the readily available Persian Gulf seawater.

In all experiments, each injection stage lasted sufficiently, for approximately 3-4 PV, to ensure the attainment of an oil production plateau and stabilized differential pressure across the rock samples. The flooding operation was terminated at each injection stage, and the core was left for equilibration upon achieving maximum oil recovery. By evading the transient response induced by changing ionic environment, this practice allows precise analysis of the additional oil recovered by switching between injection solutions. The following provides a detailed discussion of the results of flooding experiments.

Corefloodings I to III: impact of Sulfate Anion

In this section, attention is paid to the role of sulfate anion in controlling the performance of oil flow in dolomite rocks. For ease of comparison, the resultant oil production by waterflooding experiments I to III as a percentage of the initial oil-in-place (IOIP) against pore volume (PV) injected is collectively displayed in Fig. 12. The adequacy of PV injected is recognized by recording stabilized differential pressure by the end of AAA injection stages (Fig. S2-4 of the Supplementary information). Pressure humps (i.e., rising and falling profiles) at the beginning of the second and third stages arise from the non-continuous (interruptive) injection scenario.

The brine-dependence of oil recoveries (Fig. 12) is distinguished beyond the breakthrough, i.e., at the end of the so-called piston-like displacement mechanism typically lasting less than 1PV [31], where wettability alteration is responsible for the distinct amount of oil mobilized by using different solutions. Consistent with static wettability data discussed before and experiences revealed by former researchers [13, 32], the present dynamic experiments demonstrate oil production improvement upon augmenting the sulfate content of the injecting solutions at the primary displacement stage. Using the sulfate-depleted brine (0S1C0N1M), oil production almost entirely occurs until the breakthrough. Beyond this point, however, Fig. 12 exhibits the steadily increasing oil recovery curves by applying 1S1C0N1M and 2S1C0N1M brines.

In each core flooding experiment, wettability alteration during sequential injections was analyzed regarding the incremental oil mobilized concerning the amount of oil existing at the beginning of each stage, termed the incremental recovery factor (IRF).

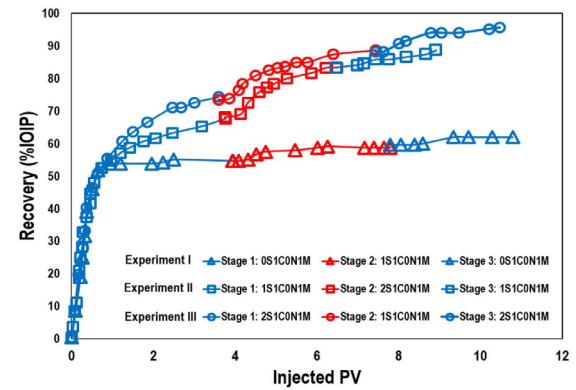


Fig. 12 Oil recoveries (as a percentage of the initial oil in place, IOIP) recorded during sequential injections (stages 1 to 3) in core-flooding experiments I to III.

This way, the pre-breakthrough oil production was excluded from the primary stage. IRFs, plotted in Fig. 13, provide a quantitative basis for correlating oil recovery improvement to the extent of wettability modification at each injection stage. This particular analysis has been vastly neglected in most literature, and it is recommended to be adopted in future studies.

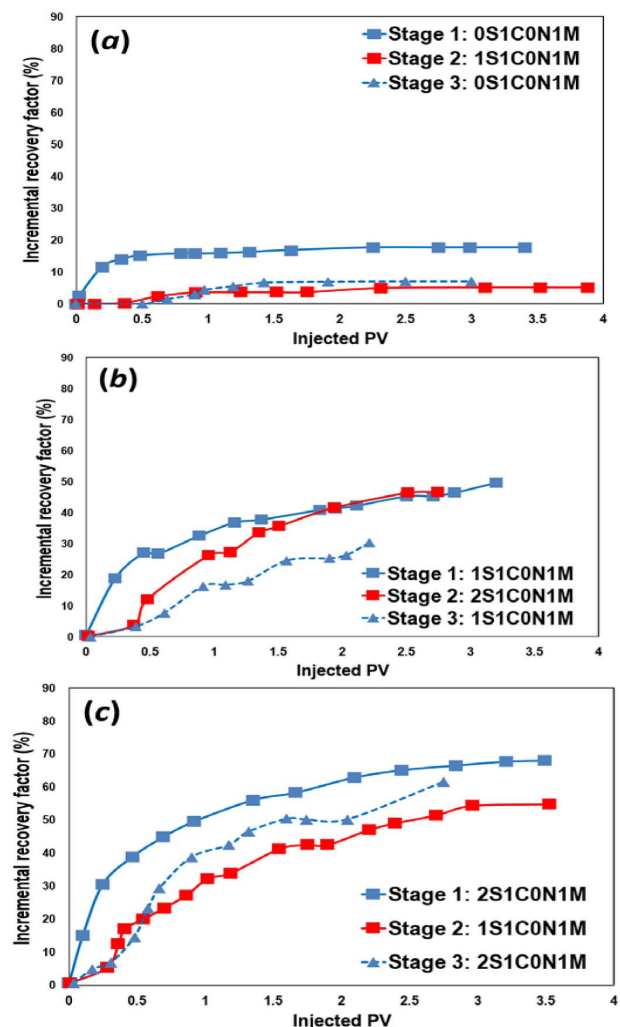


Fig. 13 Incremental oil produced at successive injection stages in core flooding I to III, plotted in panels (a) to (c), respectively.

In all instances (Fig. 13), primary injection steps yield the highest incremental oil production in proportion to the displacing solutions' tendency to enhance the water-wetness of rock samples; that is, the higher the sulfate concentration, the more oil will be recovered, which was learned from static CA measurements. The assisting role of sulfate is also notable in the sequential injection steps of corefloods II and III. However, Fig. 13 particularly shows a lower performance of the 1S1C0N1M solution relative to the preceding sulfate-depleted solution (0S1C0N1M) for the experiment I and also a subtle improvement of oil recovery when finally injecting the 0S1C0N1M solution again. This peculiarity emerges from the intricacy of fluid transport in porous media driven by a vast spectrum of rock and fluid interactions acting in different temporal and spatial scales, which is far more complex to be interpreted merely based on the static wettability tests. As widely observed in previous works [16], the effect of changing the ionic composition of the injecting solution does not appear instantly. Instead, for example, it takes a finite system-dependent duration to detect the incremental oil mobilized by switching to the 1S1C0N1M brine in experiment I. Generally speaking, incremental oil produced by applying a specific solution seems related to the operation history: the sequence and ionic composition of the already injected solutions. In support of this hypothesis, Fig. 13 shows the inequality of incremental oil produced using a saline solution, for example, 1S1C0N1M, at different flooding tests.

Corefloodings IV and VI: Role of Nitrate Anion

The contribution of nitrate anion to oil flow in dolomite samples was investigated by conducting a set of core floodings, namely IV to VI. The same nitrate-containing solution: 0S1C2N1M, 0.5S/N1C1M, or 0.5S/N2C0M was applied at the primary and third steps while injecting the 1S1C0N1M brine in between, like before. Incremental oil recovery data, together with the results of experiment III, are presented for comparison in Fig. 14. Figures S5-7 of the Supplementary Information also show differential pressures measured across core samples. As shown in Fig. 14, ~20% extra IOIP was produced by using 2S1C0N1M instead of 0S1C2N1M brine at the primary flooding stage, highlighting the stronger activity of sulfate relative to nitrate throughout the secondary mode of oil displacement. At the same time, the highest displacement performance results from injecting 0.5S/N1C1M or 0.5S/N2C0M solutions, both equally yielding IRF of nearly 88%. Despite the comparable wettability modifying ability of all solutions mentioned above, with WAI values within the range of 0.9-1.0, they give rise to disparate oil displacement efficiencies as a result of the dynamic wetting response of the dolomite core samples throughout the injection process, which tightly depends on ion exchange at the rock/brine interface coupled to the complex multi-phase oil/water flow through the rock porous medium. Given these interconnected factors, one cannot simply interpret the flooding results by relying on static wettability measurements. Conducting dynamic experiments, therefore, is crucial for tuning brine composition in a waterflooding operation. Overall, from the present core flooding experiences, solutions comprising sulfate and nitrate anions bring optimal secondary oil displacement in dolomite.

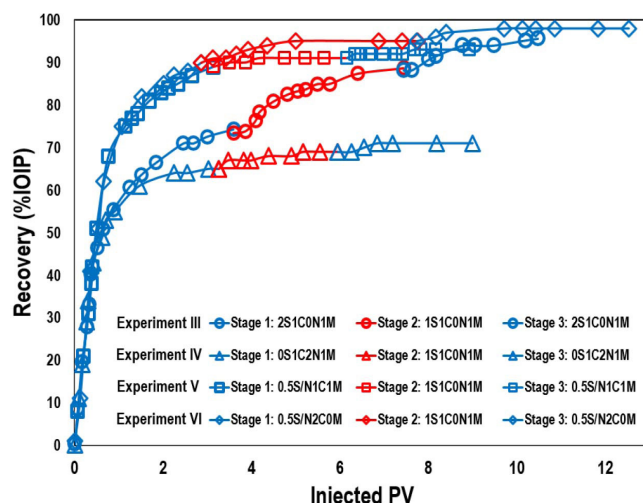


Fig. 14 Oil recoveries (as a percentage of initial oil in place, IOIP) were monitored during sequential injection (stages 1 to 3) in coreflood experiments IV to VI. Results of experiment III are presented for comparison.

For the subsequent injection stages, carried out at tertiary displacement mode, Fig. 14 shows the steep rise of the recovery curve by experiment III. However, using nitrate-containing solutions results in comparable and less pronounced incremental oil production at the second and third injection stages.

We now evaluate the oil-mobilizing efficacy of flooding stages in terms of IRFs obtained in each experiment (Fig. 15). At first glance, Fig. 15 shows the slightly higher post-breakthrough recovery, which amounts to an additional IRF of 5%, obtained at the primary flooding step upon using 0.5S/N2C0M instead of 0.5S/N1C1M. This subtle recovery improvement, not easy to detect from oil recovery curves in Fig. 15, signifies the beneficial contribution of calcium to facilitate mobilization of residual oil by more robust interfacial activity of that cation compared to magnesium inferred earlier from static CA tests. Overall, by plotting IRFs acquired at primary injection stages against corresponding WAI values obtained by static wettability tests (Fig. S8), we infer a roughly direct correlation between the extent of oil displacement and the degree of wettability alteration by a specific solution.

Not specific to the primary flooding step, the effect of ionic composition is felt throughout the subsequent injection stages. When using the same solution, 1S1C0N1M, Fig. 15 shows that the incremental oil recovered at the second injection stage, that is, 10, 36, and 48 %IRF following 0S1C2N1M, 0.5S/N1C1M, and 0.5S/N2C0M solutions, respectively, follows an order similar to what observed for the primary injection step. An analogous trend is also noticed for the last (third) flooding stage, indicating that the optimal combination of sulfate and nitrate anions generally leads to the oil mobilization enhancement from dolomite rocks, with an effect lasting beyond the primary injection step.

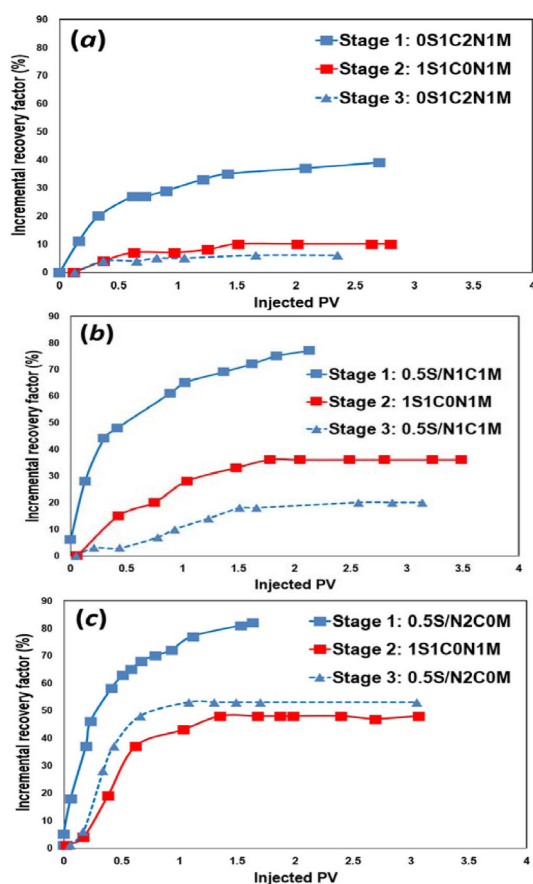


Fig. 15 Incremental oil recovered at successive injection stages in core flooding IV to VI, plotted in panels (a) to (c), respectively.

Conclusions

Through an integrated series of static wettability and dynamic core flooding experiments, the interfacial contribution of a set of surface-active ions, as major constituents of natural brine, was assessed by exposing oil-aged dolomite rocks to various saline environments. Contact angle measurements revealed sole ions' distinct ability to restore the hydrophilic character of dolomite samples, following the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+}$. Compared to calcium, we pointed out the stronger role of magnesium cation in combination with sulfate. Like what is commonly believed for calcite, our experiments revealed the beneficial cooperation of divalent cations with sulfate and nitrate in driving the wettability reversal of the crude-aged dolomite to a more water-favoring state, which was interpreted based on the well-known Auštað's model. Because of a greater charge valence (2-), sulfate appeared more effective in neutralizing the dolomite/brine interface, encouraging divalent cations to approach the mineral substrate. Noteworthy, the co-existence of sulfate and nitrate promotes wettability alteration of dolomite in a non-monotonic manner as a function of their concentration ratio, which was explained by referring to their competition for occupying surface binding sites in conjunction with the likelihood of complexation with divalent cations in the bulk solution. Following insights gained by static wettability tests, dynamic experiments demonstrate the prevailing role of sulfate in controlling oil displacement by brine injection into dolomite rocks. We also observed the higher sweep efficiency of sulfate-containing solutions compared to brines

with nitrate and the best performance acquired by combining those anions. In general, for dolomitic samples used in this study, the performance of oil displacement by a specific saline solution was connected to its wettability-modifying strength deduced by static contact angle measurements. Lastly, we should highlight the history-dependent effect of ionic composition in dolomites' waterflooding, explaining the unequal oil recovered by applying the same solutions at different injection orders.

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