

Original Paper

Dynamic retention and geochemical interactions during zwitterionic surfactant–ATBS polymer flooding in carbonates under harsh conditions



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ABSTRACT

Surfactant–polymer (SP) flooding in carbonate reservoirs under high-temperature, high-salinity (HTHS) conditions is governed not only by interfacial and rheological properties but also by carbonate geochemical re-equilibration. This paper provides an integrated experimental analysis of chemical propagation, dynamic retention, and effluent-ion evolution to clarify the geochemical mechanisms that influence surfactant and polymer transport under harsh conditions. To isolate carbonate–brine–chemical interactions, three sequential single-phase, oil-free corefloods were conducted on Indiana limestone at 90 °C. Each coreflood progressed through two cycles, including preflush, chemical-slug, and postflush stages, first in seawater (SW) cycle and then in ten-times diluted seawater (10dSW) cycle. Two of these corefloods used the zwitterionic surfactant oleyl polyoxyethylene amidopropyl carboxybetaine (OPAC) alone at 0.5 and 0.1 wt%, while the third coreflood was a surfactant–polymer (SP) case, 0.5 wt% OPAC with a 2000 ppm acrylamide–tertiary-butyl sulfonate (ATBS)-based polymer. Bulk rheology showed that 2000 ppm polymer delivered practical viscosity in both brines, while adding 0.5 wt% OPAC caused only a slight viscosity penalty (~5% on average). In corefloods, surfactant-only solutions behaved essentially as brine, whereas the SP bank provided strong mobility control, with resistance factors of 3.46 in SW and 11.14 in 10dSW and low residual resistance factors of 1.36 and 1.29, respectively. Lowering salinity from SW to 10dSW reduced surfactant retention from 0.284 to 0.198 mg/g-rock at 0.5 wt% OPAC and from 0.191 to 0.084 mg/g-rock at 0.1 wt% OPAC. At 0.5 wt% OPAC, polymer coinjection further reduced surfactant retention to 0.202 mg/g-rock in SW and 0.086 mg/g-rock in 10dSW, while polymer retention remained low at 0.063 and 0.044 mg/g-rock, respectively.

To understand the origin of these salinity- and polymer-dependent retention trends, the effluent inorganic chemistry was examined throughout the flooding sequence. During seawater-salinity surfactant flooding, pronounced deviations of effluent calcium (Ca) and magnesium (Mg) from the injected brine concentrations may indicate active redistribution of divalent ions among the flowing brine, carbonate surface complexes, and surfactant-associated interfacial species. Additionally, upon switching from SW to 10dSW, small surfactant and polymer remobilization peaks coincided with sulfate depletion, suggesting that salinity reduction partly released weakly retained chemicals from the preceding SW cycle while reopening positively charged calcite sites for renewed sulfate uptake during low-salinity re-equilibration. Furthermore, upon arrival of the 10dSW SP bank, a distinct Ca–Mg pulse revealed rapid divalent-ion complexation by the injected chemicals, compensating for release from carbonate surface complexes, and possible mild calcite dissolution. These results suggest that an SW-to-10dSW sequence may be mechanistically attractive for harsh-condition carbonate SP flooding, with the first cycle helping establish favorable interfacial conditioning and the diluted second cycle supporting lower chemical loss and stronger propagation of the SP bank.

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Nomenclature

10dSW	10-times diluted seawater
10dSW PO	Postflush with 10-times diluted seawater
10dSW PR	Preflush with 10-times diluted seawater
AEC	Alkyl ether carboxylate
AFM	Atomic force microscopy
AGES	Alkoxyglycidylether sulfonate
APG	Alkyl polyglucoside
ATBS	Acrylamide-tertiary-butyl sulfonate
CEOR	Chemical enhanced oil recovery
CMC	Critical micelle concentration
EDL	Electrical double layer
ELSD	Evaporative light scattering detector
FTIR	Fourier transform infrared spectroscopy
FW	Formation water
HPAM	Partially hydrolyzed polyacrylamide
HPLC	High-performance liquid chromatography
HTHS	High-temperature, high-salinity

IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IFT	Interfacial tension
IOS	Internal olefin sulfonate
MD	Molecular dynamics
MIE	Multicomponent ion exchange
OPAC	Oleyl polyoxyethylene amidopropyl carboxybetaine
PDIs	Potential-determining ions
PV	Pore volume
RF	Resistance factor
RRF	Residual resistance factor
SP	Surfactant–polymer
SW	Seawater
SW PO	Postflush with seawater
SW PR	Preflush with seawater
UV–VIS	Ultraviolet–visible
XPS	X-ray photoelectron spectroscopy

1. Introduction

Carbonate reservoirs, which contain a substantial fraction of the world's oil reserves, present challenging conditions for oil recovery due to their complex heterogeneity and often oil-wet rock surfaces. As a result, large volumes of residual oil frequently remain trapped within the reservoir. To address these limitations, chemical enhanced oil recovery (CEOR) techniques, particularly surfactant–polymer (SP) flooding, have gained increasing attention. In an SP process, the surfactant lowers the oil–water interfacial tension (IFT) and promotes a shift toward more water-wet rock surfaces, while the polymer increases the viscosity of the injected water, improving the mobility ratio and helping the displacement front sweep the reservoir more uniformly. By combining these effects, SP flooding aims to mobilize trapped oil and sweep it from tighter pores that plain waterflooding would bypass (Ahmed et al., 2023). In practice, the efficiency of SP flooding in carbonate reservoirs is closely linked to the geochemical processes that accompany chemical transport through the pore network. These processes can strongly influence chemical propagation and loss by affecting adsorption, wettability, divalent-ion redistribution, ion exchange, and mineral re-equilibration in the rock–brine system. Geochemical analysis is therefore not a secondary add-on, but a central part of understanding and designing SP floods.

A natural first question in SP design is how much of the injected surfactant and polymer propagates with the advancing bank and how much is retained by the rock. Surfactant adsorption on carbonate surfaces plays a dual role in chemical flooding. A certain level of adsorption is required to modify the solid–fluid interface and promote wettability alteration, as reported in chalk and limestone systems where surface-bound surfactants reduce contact angles and enhance spontaneous imbibition (Standnes and Austad, 2000). At the same time, adsorption reduces the amount of surfactant available to sustain ultra-low IFT along the flow path. When retention is high, the flowing surfactant concentration declines, the IFT-reduction zone shortens, and process economics deteriorate (Bashir et al., 2022). Similarly, polymer retention in SP flooding can also have competing effects. Moderate polymer

retention can be beneficial, as it selectively reduces flow in high-permeability zones and improves sweep efficiency (Mishra et al., 2014; Tan et al., 2022). In addition, polymers may act sacrificially by competing for adsorption sites and reducing surfactant loss (Gbadamosi et al., 2019; Khlaifat et al., 2024). However, excessive polymer retention reduces the viscosity propagated through the reservoir and may lead to increased chemical consumption or injectivity issues (Seright and Wang, 2023).

A second central element is wettability. Many carbonate reservoirs are initially oil-wet or mixed-wet because polar and nonpolar components of crude oil have accumulated on the mineral surface over geological time (Yue et al., 2020). Under such conditions, injected water has difficulty displacing oil from smaller pores. In SP flooding, the aim is to weaken oil–rock adhesion by shifting the system toward a more water-wet state and to facilitate oil mobilization by lowering the oil–water IFT. Among the different surfactant classes, cationic surfactants are often reported as especially effective wettability modifiers in oil-wet carbonates because they can interact with negatively charged acidic oil species and detach them from the mineral surface, forming localized water-wet patches on the rock (Standnes and Austad, 2000; Deng et al., 2021). Zwitterionic surfactants may promote a similar effect through their dual-charge headgroups, which enable interactions with both charged rock sites and polar oil components (Kumar and Mandal, 2019). Recent studies have shown that such surfactants can markedly reduce contact angles and restore water-wetness in carbonate rocks (Gbadamosi et al., 2023; Deng et al., 2024; Zeynalli et al., 2025). In addition, polymers play a different but complementary role by improving mobility control and sweep efficiency, thereby distributing surfactants more effectively throughout the pore space and enabling more widespread wettability alteration (Pal et al., 2018).

A third important factor in SP flooding, in addition to adsorption and wettability, is how variations in brine composition alter the geochemical equilibrium among carbonate rock, brine, injected chemicals, and resident oil. In carbonate systems, changes in salinity and ionic composition may alter surface speciation, the electrical double-layer structure, and the availability of potential-determining ions (PDIs) such as Ca^{2+} , Mg^{2+} , and SO_4^{2-} , thereby

affecting mineral stability, surface or interfacial charges, and the geochemical interactions within the system (Karimi et al., 2016). As SP formulations flow through carbonate rocks, ongoing re-equilibration among dissolved ions, mineral surfaces, and injected chemicals governs how much surfactant and polymer remain available for oil mobilization and sweep. The importance of geochemical interpretation for low-salinity surfactant flooding experiments in limestone has been highlighted by Groenendijk and van Wunnik (2021). They showed that effluent profiles can only be history-matched when calcite dissolution, ion exchange, and divalent-ion-surfactant complexation are included in the model. Moreover, the authors confirmed that a polymer preflush or coinjection suppresses surfactant loss by complexing $\text{Ca}^{2+}/\text{Mg}^{2+}$ in solution and competing for positive surface sites. Complementary coreflooding tests by Alagic and Skauge (2010) further indicated that combining a low-salinity preflush with surfactant flooding prevents re-trapping of mobilized oil and enhances recovery. Their effluent pH and ion-composition trends indicated that dissolution and ion-exchange processes were operating alongside the surfactant flood. On the other hand, a mechanistic low-salinity polymer-flooding study revealed that reducing salinity can improve the stability of the aqueous film between oil and rock and thereby enhance displacement efficiency, resulting in higher oil recovery through the combined effects of polymer mobility control and wettability alteration during low-salinity waterflooding (Jadhawar and Saeed, 2023). Moreover, low-salinity polymer floods by Unsal et al. (2018) confirmed that dilution lowers polymer retention and improves long-term injectivity relative to high-salinity polymer floods. However, their effluent chemistry analysis also revealed that cation exchange during low-salinity injection may release Ca^{2+} and Mg^{2+} from the rock and form divalent-ion-polymer complexes, causing viscosity loss that they capture with a coupled flow-geochemistry model.

Furthermore, the surfactant and polymer also interact with each other, and these interactions are strongly influenced by brine salinity as well as by the ionic nature and molecular architecture of both components. Electrostatic attraction between charged surfactant headgroups and oppositely charged sites on the polymer chain becomes stronger as ionic strength decreases because fewer dissolved ions are available to screen charges on surfactants and polymers at low salinity (Druetta and Picchioni, 2020). In parallel, both molecules may contain hydrophobic segments that tend to associate in water, such that the lipophilic side chains of the polymer can interact with the surfactant tails and form various aggregates (Pal et al., 2019; Ge et al., 2021). When the brine is more saline and electrostatic forces are screened, these hydrophobic associations become the dominant mode of binding, which can change the size and shape of aggregates and, in turn, the viscosity of the SP solution (Lindman et al., 2014).

To help visualize how these processes act together, Fig. 1 presents a generalized schematic of SP flooding in a carbonate rock. Fig. 1(a) shows the initial high-salinity state, in which an oil film rich in polar groups remains strongly attached to a carbonate surface populated by various charged surface complexes and surrounded by brine containing Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- . On the other hand, Fig. 1(b) illustrates the system after injection of a low-salinity SP formulation. For illustrative simplicity, this schematic depicts a cationic surfactant and an anionic polymer as an example of possible SP interactions, although the broader discussion is not restricted to that specific pairing. The red-dashed arrow indicates a possible pathway for progressive oil-film detachment and displacement. First, changes in brine salinity and ionic composition can reduce oil-rock adhesion through several coupled geochemical mechanisms. Lower ionic strength promotes electrical double-layer expansion (1), while changes in ionic composition may favor sulfate-mediated multicomponent ion exchange

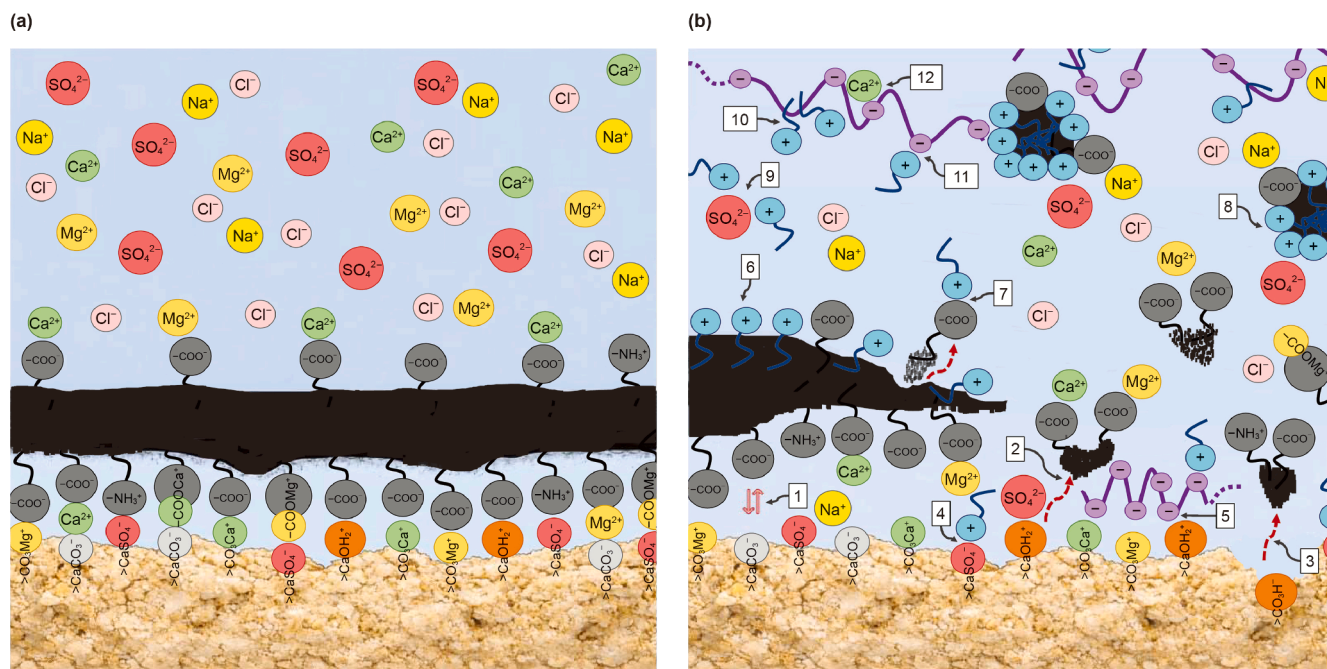


Fig. 1. Generalized schematic (not to scale) of geochemical interactions during SP flooding in carbonate rocks. **(a)** Initial high-salinity state: an oil film coats a carbonate surface populated by various surface complexes in brine containing Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- . **(b)** Injection of a low-salinity cationic-surfactant/anionic-polymer formulation; the red arrow shows the direction of potential oil displacement. Numbers mark key processes: (1) electrical-double-layer expansion pushing the oil film away from the surface; (2) sulfate-mediated multicomponent ion exchange and desorption of polar oil components; (3) mineral dissolution releasing adsorbed oil and exposing a more water-wet surface; (4) adsorption of cationic surfactant on negatively charged sites; (5) adsorption of anionic polymer on positively charged sites; (6) hydrophobic anchoring of surfactant tails on the oil film; (7) ion pairing between cationic surfactant and acidic oil groups; (8) oil-swollen surfactant micelles/microemulsion droplets transporting detached oil; (9) aqueous divalent-ion-surfactant complexes; (10, 11) hydrophobic and electrostatic SP association; (12) divalent-ion-polymer complexes.

(MIE) and the release of acidic oil components from positively charged surface sites (2). In addition, local carbonate dissolution may expose fresher, more water-wet mineral surfaces and release previously anchored polar species (3). Alongside these effects, adsorption of the injected chemicals on the carbonate surface may further alter surface properties: cationic surfactant can adsorb on negatively charged surface sites (4), while anionic polymer can adsorb on remaining positively charged sites (5). Surfactant molecules may also associate with the oil phase through hydrophobic interactions and ion pairing with acidic oil groups (6 and 7, respectively), thereby facilitating oil-film disruption and detachment into oil-swollen micelles (8). In the aqueous phase, divalent-ion-surfactant complexes (9), hydrophobic and electrostatic SP associations (10 and 11, respectively), and divalent-ion-polymer complexes (12) further influence the structure, stability, and viscosity of the SP solution. Overall, the figure provides a pore-scale illustration of the different processes that may accompany SP flooding in carbonate rocks and influence oil detachment and displacement.

Although chemical flooding in carbonate reservoirs has been widely studied, most published work has focused on formulation development, interfacial and wettability performance, slug design, and incremental oil recovery rather than on the geochemical evolution that accompanies chemical transport through the rock (Khan et al., 2009; Tavassoli et al., 2016; Ahmed et al., 2023). Effluent-ion analysis has been included in only a limited number of investigations, and these do not represent the harsh carbonate surfactant or SP systems considered here. For example, Alagic et al. (2011) studied low-salinity surfactant floods in Berea sandstone without polymer and under comparatively mild conditions. Carbonate-focused mechanistic studies have linked surfactant transport to calcite dissolution, ion exchange, and divalent-ion complexation, but they were also conducted at lower salinity and at temperatures around 40–50 °C rather than under harsh reservoir-relevant conditions (Ghosh et al., 2019; Groenendijk and van Wunnik, 2021). Experimental studies that track chemical propagation, along together with detailed effluent-ion evolution in carbonate surfactant or SP floods under these conditions, remain limited.

To address this gap, the present work investigates surfactant-only and SP systems in Indiana limestone at 90 °C using formulations prepared directly in seawater (~58,000 mg/L) and its ten-times diluted counterpart. This design allows us to address harsh-temperature carbonate conditions while also examining, within a seawater-based injection framework, how salinity reduction influences chemical propagation and loss, carbonate geochemistry, and divalent-ion redistribution. The study focuses on a zwitterionic carboxybetaine surfactant (OPAC) and an ATBS-based polymer, both of which show strong potential for application in harsh carbonate conditions. The thermal and salt tolerance of OPAC under such conditions has been established by Hussain et al. (2019), who kept 10 wt% OPAC solutions in both seawater and formation water at 90 °C for 90 days and observed no precipitation or phase separation. This stability profile compares favorably with several HTHS surfactant systems reported in the literature. Puerto et al. (2011) showed that alkoxyglycidylether sulfonates (AGESs) can undergo cloud-point phase separation at elevated temperatures and that transparent single-phase solutions at 90 °C were obtained only for selected blends with internal olefin sulfonate (IOS). Zulkifli et al. (2020) reported that at 106 °C in seawater, sulfate-based surfactants suffered hydrolysis, sulfonate-based surfactants precipitated in the presence of divalent ions, and single-surfactant alkyl ether carboxylate (AEC) remained prone to cloudiness, whereas a 50:50 blend of AEC with alkyl polyglucoside (APG) showed better compatibility during long-term aging. Panthi

and Mohanty (2024) further found that for a 100 °C offshore carbonate reservoir previously flooded with seawater, seawater-stable Type III behavior was achieved only after using formulations that combined a carboxylate surfactant, lauryl betaine, IOS, and a co-solvent. Therefore, OPAC offers a simpler and more robust formulation option under harsh conditions, remaining single-phase in both seawater and formation water at 90 °C without precipitation or phase separation, whereas several reported conventional surfactant systems required blending or additional components to maintain compatibility. Moreover, beyond its demonstrated thermal and salt stability, OPAC also showed promising formulation performance in an earlier screening study (Zeynalli et al., 2025), including pronounced wettability alteration, moderate IFT reduction, and compatibility with the ATBS-based polymer. The ATBS-based polymer itself was selected for its established tolerance to salinity, hardness, and temperature, as well as its ability to provide effective mobility control (Sandengen et al., 2018; Sebastian et al., 2024).

The floods were deliberately designed as single-phase, oil-free experiments. This choice was essential to establish a reference state for the carbonate-brine-chemical system, so that changes in surfactant and polymer breakthrough, dynamic retention, mobility response, and effluent-ion composition could be interpreted without the added complexity of oil solubilization, emulsion/microemulsion formation, saturation changes, and wettability evolution during two-phase flow. Such a reference is particularly important in surfactant and SP studies, where a reduction in produced chemical concentration during two-phase flooding may reflect either true retention on the rock or redistribution into oil-containing phases. The single-phase flooding, therefore, provides a clear basis for determining whether the response observed later in two-phase floods will mainly reflect intrinsic carbonate geochemistry or additional effects introduced by the displacement process.

The novelty of this study lies in treating surfactant and polymer transport and carbonate geochemistry as a single coupled problem under harsh conditions. This allows us to examine how salinity reduction and polymer coinjection influence not only chemical propagation but also the accompanying divalent-ion redistribution and the geochemical environment that governs chemical transport and retention. To the best of our knowledge, such an integrated experimental analysis has not previously been reported for a practical zwitterionic surfactant-polymer system in carbonate rock under harsh conditions.

2. Materials and methods

2.1. Materials

Indiana limestone core samples were used in all flooding experiments. The main petrophysical properties of the cores are summarized in Table 1. Sister samples showed closely comparable petrophysical properties, making them suitable for comparing flooding performance across the different experiments. Moreover, synthetic formation water (FW) and seawater (SW), representative of Middle Eastern reservoir conditions, were prepared from laboratory-grade salts: sodium hydrogen carbonate (NaHCO_3), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), all supplied by Aldrich. In addition, a ten-fold diluted seawater was prepared to examine the influence of dilution on the performance of the polymers and surfactants. All brines were filtered through 0.45 μm filter paper to remove undissolved or unwanted solid particles before use. The compositions and basic properties of the prepared brines are given in Table 2.

Table 1

Characteristics of the rock samples used in this study (saturation porosities and absolute permeabilities were measured at room temperature).

Sample number	Diameter, cm	Length, cm	Pore volume, cm ³	Saturation porosity, %	Absolute permeability, mD
Sample #1	3.76	7.44	13.69	16.57	257.32
Sample #2	3.76	7.44	14.17	17.15	250.19
Sample #3	3.77	7.41	13.66	16.51	221.91

Table 2

Composition and properties of the brines used in the experiments.

Ions	Ion concentration, ppm		
	10dSW	SW	FW
Na ⁺	1830	18,300	59,500
Ca ²⁺	65	650	19,100
Mg ²⁺	211	2110	2500
Cl [−]	3229	32,290	132,313
SO ₄ ^{2−}	429	4290	400
HCO ₃ [−]	12	120	400
TDS, ppm	5776	57,760	214,213
Ionic strength, mol/L	0.115	1.150	4.331
Density at 25/90 °C, g/cm ³	1.001/0.976	1.039/1.012	1.142/1.109
Viscosity at 25/90 °C, cP	0.903/0.445	0.997/0.508	1.809/0.818

The surfactant used in this work was the betaine-type zwitter-ionic surfactant oleyl polyoxyethylene amidopropyl carboxybetaine (OPAC). The surfactant was prepared in-house and supplied by King Fahd University of Petroleum and Minerals (KFUPM). The molecular weight of OPAC is 842 g/mol, and its critical micelle concentration (CMC) in seawater at room temperature is around 290 ppm (Hussain et al., 2019). This relatively low CMC is economically advantageous because effective interfacial activity can be achieved at low surfactant dosages. For the present study, surfactant solutions were prepared on a mass basis and stirred overnight using a magnetic stirrer to ensure complete dissolution and compositional uniformity. Furthermore, the suitability of OPAC for harsh reservoir conditions is supported by Hussain et al. (2019), who reported no precipitation or phase separation in 10 wt% OPAC solutions prepared in both SW and FW after aging at 90 °C for 90 days. Thermogravimetric analysis further showed that the onset of thermal decomposition occurs well above 300 °C, far exceeding the 90 °C reservoir temperature considered here.

The polymer employed in this study was the ATBS-based SAV10 polymer, supplied by SNF Floerger in the form of a white granular powder. Its molecular weight is in the range of 4.3–6.8 million Da (Sebastian et al., 2024). A 4000-ppm stock solution was first prepared by adding the required amount of polymer powder to brine under high-speed stirring. After complete hydration, sodium thiourea was added at 200 ppm as an oxygen scavenger to limit oxidative degradation during the high-temperature experiments (Sebastian et al., 2025). Working solutions at the desired concentrations were then prepared by diluting the stock solution. Moreover, the long-term stability of ATBS-based polymers under harsh reservoir conditions has been extensively demonstrated in the literature. Sandengen et al. (2018) reported that ATBS copolymers retain viscosity with only minor degradation over extended periods in high-salinity, high-hardness brines at elevated temperatures. This was further corroborated by Alfazazi et al. (2018), who confirmed that SAV10-type sulfonated polymers maintain rheological performance and acceptable retention levels in carbonate cores under Middle Eastern HTHS conditions. Similarly, Masalmeh et al. (2019) validated the suitability of ATBS-based formulations for high-temperature carbonate reservoirs

through both laboratory and field-oriented studies. Overall, these investigations establish the long-term chemical stability of the SAV10 polymer used here and support its selection for the present application.

Furthermore, SP solutions were prepared by first making separate concentrated stock solutions of surfactant and polymer, each at twice the intended final concentration, in the corresponding brine. The two stock solutions were then mixed in a 1:1 volume ratio to obtain the target SP formulation. Before injection, the SP solutions were filtered to minimize the risk of possible injectivity problems during coreflooding. Filtration was carried out by passing the solutions through a 1.2 µm filter paper under a controlled pressure of 1 bar supplied by a nitrogen gas cylinder. Following preparation, the stability and compatibility of the SP formulations under conditions relevant to the present work were evaluated based on both the earlier screening study and additional aging tests. The compatibility of OPAC-SAV10 SP formulations over a range of salinities was evaluated in earlier screening experiments (Zeynalli et al., 2025), with solutions aged for 30 days at 90 °C in sealed vials exhibiting no precipitation or phase separation. The moderate viscosity reduction they observed in the aged SP solutions was primarily attributed to thermal effects on the polymer, with only a minor contribution from SP interactions. In addition, to assess the stability and compatibility of the SP formulations over an extended aging period, the two formulations selected for coreflooding, containing 0.5 wt% surfactant and 2000 ppm polymer in SW and 10dSW, were aged in sealed vials at 90 °C for 90 days. Both formulations, likewise, remained visually clear, with no evidence of precipitation or phase separation.

2.2. Experimental methods

2.2.1. Polymer and SP bulk rheology measurements

Bulk rheology tests were carried out to characterize the viscosity of the polymer and SP solutions. An Anton Paar rheometer equipped with a concentric-cylinder geometry was used during the experiments (Fig. 2(a)). Measurements were performed in seawater (SW) and ten-times diluted seawater (10dSW) over a shear-rate range of 0.1–1000 s^{−1} and at temperatures between 25 and 70 °C. Polymer solutions were prepared at several concentrations up to 4000 ppm. These measurements were used to quantify how viscosity changes with shear rate, temperature, salinity, and polymer concentration. Moreover, several SP solutions were also prepared by combining surfactants and polymers. Polymer-only and corresponding SP samples were tested under the same experimental conditions and at the same polymer concentrations to compare their viscosities and to evaluate the effect of SP associations on solution viscosity.

Rheology tests were also used to measure effluent polymer concentration and assess mechanical degradation during coreflooding tests. Samples were taken from a bypass line carrying the injected solution directly from the accumulator in the oven, and from the effluent line downstream of the core and back-pressure regulator after many pore volumes of SP solution had been injected. These samples were then measured in a rheometer at 25 °C and a shear rate of 10 s^{−1}. Comparing the viscosities of bypass and effluent samples provided an estimate of mechanical degradation along the flow paths. Additionally, to convert effluent viscosities into effluent polymer concentrations, we initially built a calibration curve by diluting the injected SP solution of known polymer concentration (collected from a bypass line) and measuring the viscosity of each dilution at 25 °C and a shear rate of 10 s^{−1} (Fig. 2(b)). It is worth noting that although these calibration samples were measured at 25 °C in a rheometer, the injected solutions had previously resided in the oven-heated accumulator during coreflooding, so their viscosities already reflected this

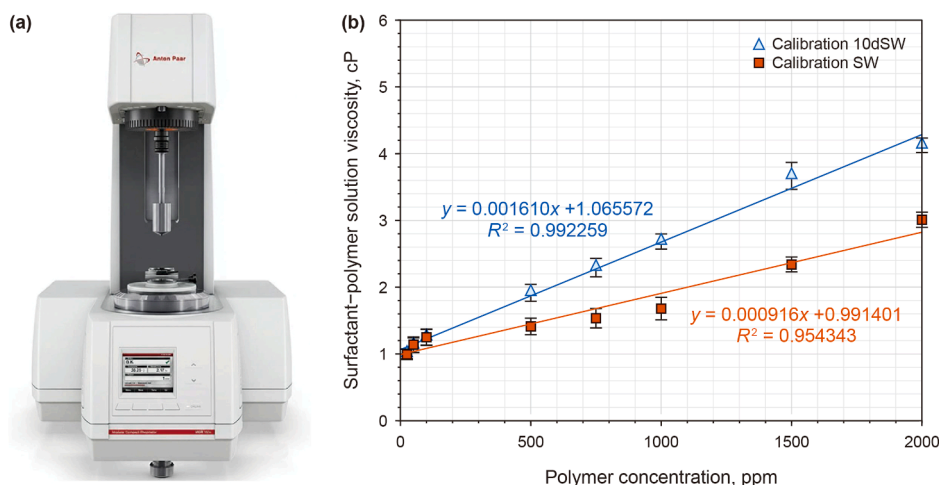


Fig. 2. (a) Anton Paar rheometer used for viscosity measurements; (b) calibration curves relating SP-solution viscosity to polymer concentration, obtained by measuring dilutions of the injected polymer solutions collected from the bypass line at 25 °C and a shear rate of 10 s^{-1} . Separate curves are shown for SP solutions prepared in SW and in 10dSW. For each concentration, three dilutions were prepared from independently collected bypass “mother” samples, and their viscosities were averaged; error bars denote one standard deviation of these three measurements.

thermal exposure and were lower than those of fresh, unheated make-up solutions at the same testing temperature of 25 °C. Thereafter, we tested the viscosity of effluent samples under the same conditions, applied the previously estimated mechanical degradation factor, and fit a linear relation between viscosity and polymer concentration to determine the effluent polymer concentration.

Furthermore, because the floods were conducted in carbonate rock, there is a possibility of additional changes in viscosity due to calcite dissolution and the associated release of Ca^{2+} . Dissolution rates decrease as ionic strength increases, and previous atomic-force-microscopy work shows more active dissolution features at lower NaCl salinity (Finneran and Morse, 2009). In our experiments, this means that some Ca^{2+} release is more likely in 10dSW than in SW. In principle, any additional Ca^{2+} released in this way could reduce polymer viscosity through divalent-ion complexation. Such viscosity losses have been clearly documented for HPAM-based polymers during low-salinity polymer floods, where cation exchange may significantly increase brine hardness (Unsal et al., 2018). The ATBS-based copolymer used here is, however, specifically designed for high-salinity, high-hardness conditions. Long-term aging tests in seawater demonstrate that its hydrolysis rate is essentially insensitive to hardness, and that viscosity losses associated with $\text{Ca}^{2+}/\text{Mg}^{2+}$ complexation, while measurable, remain modest over a wide range of divalent-ion concentrations (Sandengen et al., 2018). In our corefloods, the additional Ca^{2+} released from the rock is small compared with the background seawater hardness and remains well within the range where published ATBS rheology data show only moderate changes in viscosity. For these reasons, we did not attempt to introduce a separate correction for evolving hardness. Any contribution from calcite dissolution and associated Ca^{2+} release to the measured viscosities is expected to be minor relative to the uncertainties in viscosity–concentration calibration and the estimated mechanical-degradation factor and is assumed not to affect the inferred polymer concentrations.

2.2.2. Rock sample preparation and coreflooding experiments

All three sister Indiana limestone core plugs were first cleaned in a Soxhlet extractor at 60 °C for 72 h using alternating methanol (polar) and toluene (nonpolar) cycles. After cleaning and drying, the cores were evacuated for 3 h and saturated with FW at 2000 psi

for 48 h. After saturation, absolute permeability was measured on the coreflooding rig at room temperature, using a confining pressure of 1200 psi and a back-pressure of 200 psi. A schematic of the setup is shown in Fig. 3. The system includes dual injection pumps, a Hastelloy core holder, separate pumps for confining and back-pressure, a back-pressure regulator, fluid accumulators, and an oven. The equipment was supplied by GRACE Instrument Company.

All three cores were then used for single-phase chemical flooding. These tests were run at 90 °C, with the same confining pressure (1200 psi) and back-pressure (200 psi). A constant injection rate of $0.5 \text{ cm}^3/\text{min}$ was used for the brine preflush, main chemical slug, and brine postflush. This rate, which is higher than typical reservoir velocities, was chosen to shorten the time needed to reach retention equilibrium, as the main objective was to quantify dynamic retention and evaluate geochemical interactions. The overall flooding sequence for each core is summarized in Fig. 4. The salinity conditions and chemical formulations used in the corefloods were selected based on prior surfactant and polymer screening, as discussed further in Sections 3.1 and 3.2. The first two corefloods used only surfactant solutions. For Sample #1, the OPAC concentration was 0.5 wt%, and for Sample #2, it was 0.1 wt%. These tests were designed to isolate the effect of surfactant concentration on transport and dynamic retention. The critical micelle concentration (CMC) of OPAC in seawater is about 0.029 wt%, so both injected concentrations are above CMC. Concentrations below 0.1 wt% can result in poor performance during flooding, whereas much higher concentrations increase chemical costs. A level of 0.5 wt% is still considered moderate compared with many reported formulations and does not require co-surfactants or co-solvents to obtain good interfacial behavior (Al-Azani et al., 2023). In both Sample #1 and Sample #2 tests, salinity effects were examined by running two cycles: one at SW salinity and one at 10dSW. In each case, the cycle started with an SW preflush to displace FW and establish the desired aqueous environment for subsequent chemical injection. This was followed by the injection of the surfactant slug prepared in SW and then by an SW postflush to displace the mobile surfactant remaining in the pore space. After this high-salinity cycle, the brine was switched to 10dSW. A 10dSW preflush was injected, followed by the surfactant slug at the diluted salinity and a final 10dSW postflush.

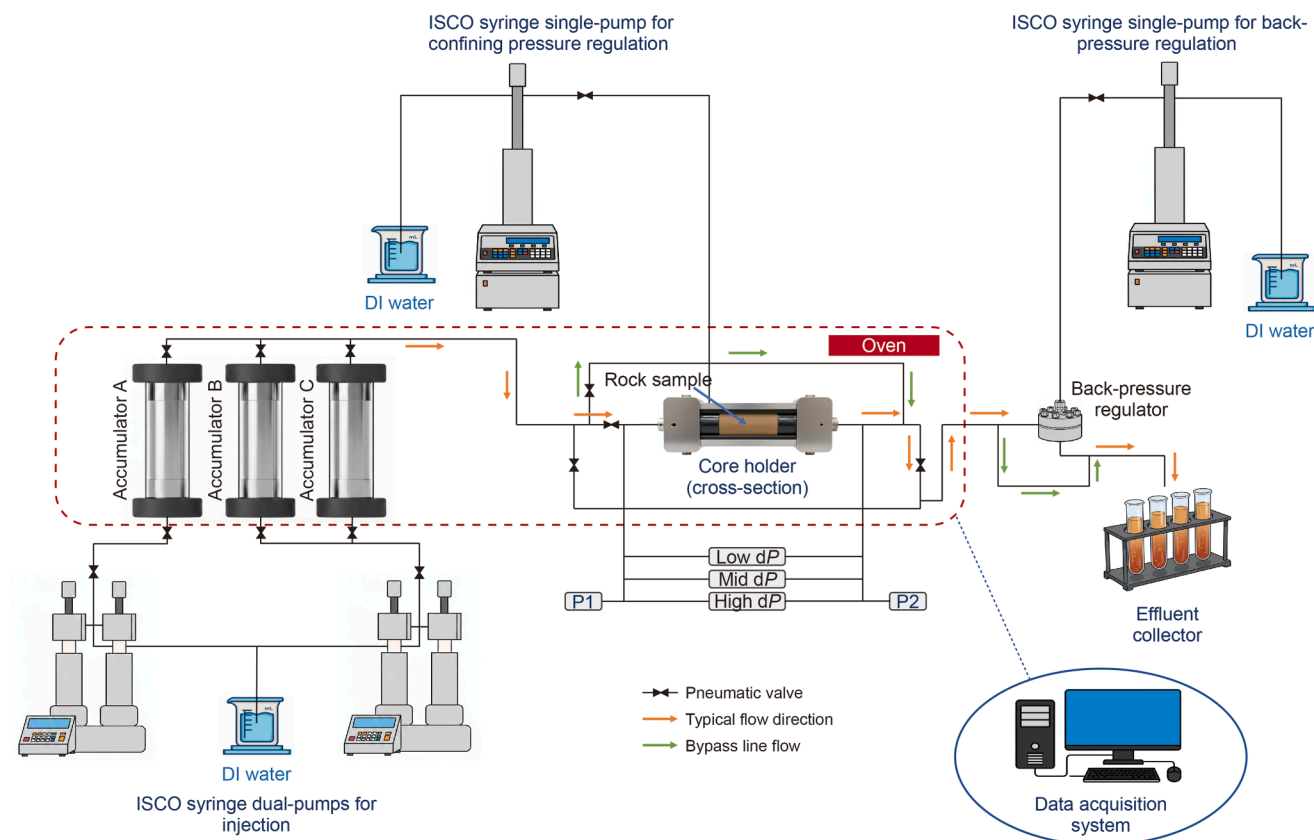


Fig. 3. Schematic of the coreflooding setup by GRACE Instrument.

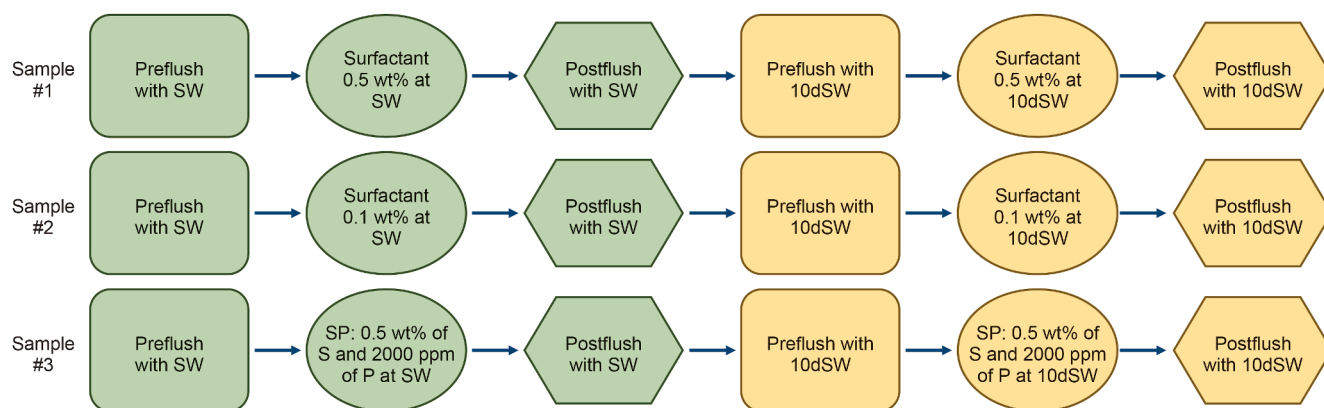


Fig. 4. Coreflood design for the three limestone samples, showing preflush, surfactant or SP slug, and postflush in SW then 10dSW. Sample #1: 0.5 wt% S; Sample #2: 0.1 wt% S; Sample #3: 0.5 wt% S + 2000 ppm P. S = surfactant; P = polymer.

Furthermore, the third test, carried out on Sample #3, used a SP slug to examine the combined effect of surfactant and polymer on fluid–rock interactions and dynamic retention. The SP slug contained 0.5 wt% surfactant and 2000 ppm polymer. The same salinity sequence as in the surfactant-only tests was followed, progressing from FW to SW and then to 10dSW. Using an identical surfactant concentration in Sample #1 (surfactant-only) and Sample #3 (SP) tests allows a direct comparison and helps separate the influence of the polymer from that of the surfactant. Therefore, together, the three corefloods provide a controlled set of conditions to explore how surfactant concentration, salinity, and polymer addition influence retention and geochemical interactions in carbonate rock.

2.2.3. Effluent surfactant concentration measurement

Effluent surfactant concentrations were determined mainly by Ultraviolet–Visible (UV–VIS) spectrophotometry and were cross-checked for selected samples by high-performance liquid chromatography (HPLC). In the UV–VIS method, calibration curves were first built by preparing a series of OPAC standards at known concentrations in each brine. For every concentration, three separate standards were prepared and tested, and the average absorbance was used. It is worth noting that OPAC does not exhibit a single sharp peak at a fixed wavelength, and its spectrum shifts slightly with concentration. Therefore, the calibration was based on the stable plateau region of the spectrum near 265 nm (Fig. 5(a)). On the other hand, our polymer did not exhibit a reliable

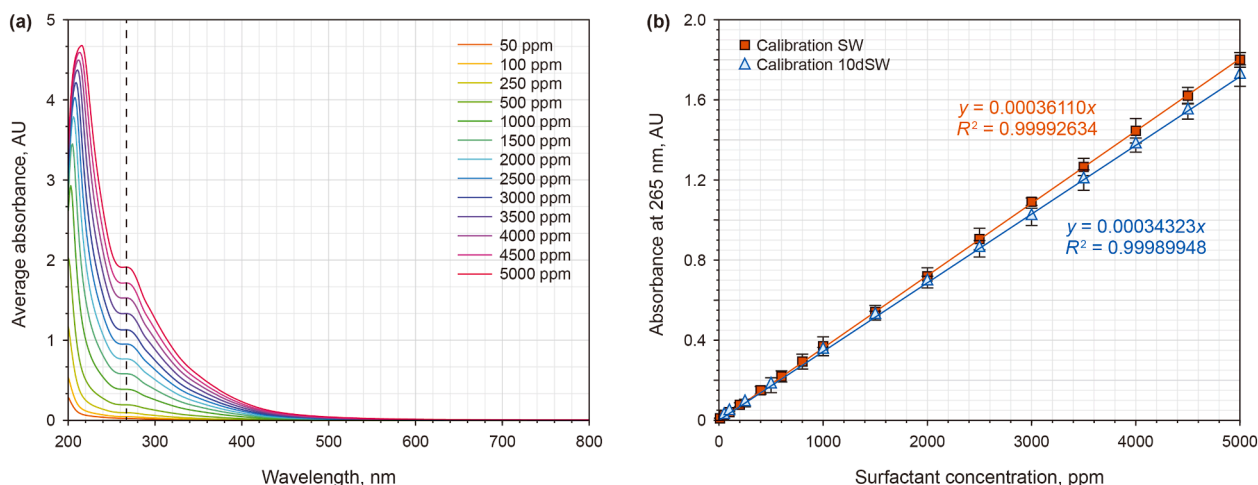


Fig. 5. UV–VIS calibration for OPAC: (a) average absorbance spectra of three OPAC standards (50–5000 ppm) at 10dSW showing the stable plateau near 265 nm used for quantification; (b) linear calibration curves for SW and 10dSW linking absorbance at 265 nm to surfactant concentration. Error bars show the standard deviation of three independently prepared OPAC standards at each concentration.

peak or plateau and was therefore not quantified by UV–VIS; effluent polymer concentrations were instead obtained from rheology, as described later. The resulting relationship between OPAC concentration and absorbance at a plateau wavelength of 265 nm was linear for both SW and 10dSW (Fig. 5(b)). Effluent samples were then measured at this wavelength, and their concentrations were calculated from the corresponding calibration curves.

Furthermore, HPLC measurements were used as an independent check on the UV–VIS method. Effluents were analyzed with a Waters Alliance HPLC system (Fig. 6(a)) equipped with an evaporative light-scattering detector (ELSD) and an Acclaim Surfactant Plus column (3 μ m, 4.6 mm $\times$ 150 mm). Acetonitrile (CH₃CN) was used as mobile phase A, and 0.1 mol/L ammonium formate (NH₄HCOO) adjusted to pH 4.3 with formic acid (HCOOH) was used as mobile phase B. The latter phase was prepared fresh and sonicated before use to remove dissolved gases and ensure complete dissolution. After centrifugation, the surfactant solutions were filtered, transferred into HPLC vials, and loaded onto the autosampler. For each injection, the ELSD peak area was

integrated and converted to concentration using a calibration equation. The calibration was established in advance by analyzing a set of OPAC standards prepared at known surfactant concentrations and relating their ELSD areas to concentration (Fig. 6(b)). The response over this range was clearly non-linear, so a second-order polynomial was fitted to the calibration data and used to back-calculate surfactant concentrations from ELSD peak areas. This behavior is consistent with the general characteristics of ELSD, which is well known to be a non-linear detector (Khan et al., 2022). It is also important to mention that HPLC was applied only to surfactant-only effluents; SP samples were not injected because the polymer can foul the surfactant column and distort the ELSD response.

2.2.4. Dynamic retention of surfactant and polymer

Dynamic retention of both surfactant and polymer was calculated from effluent concentration profiles using a running material balance. For each experiment, the retained mass per unit rock mass, Γ (mg/g-rock), was obtained as follows:

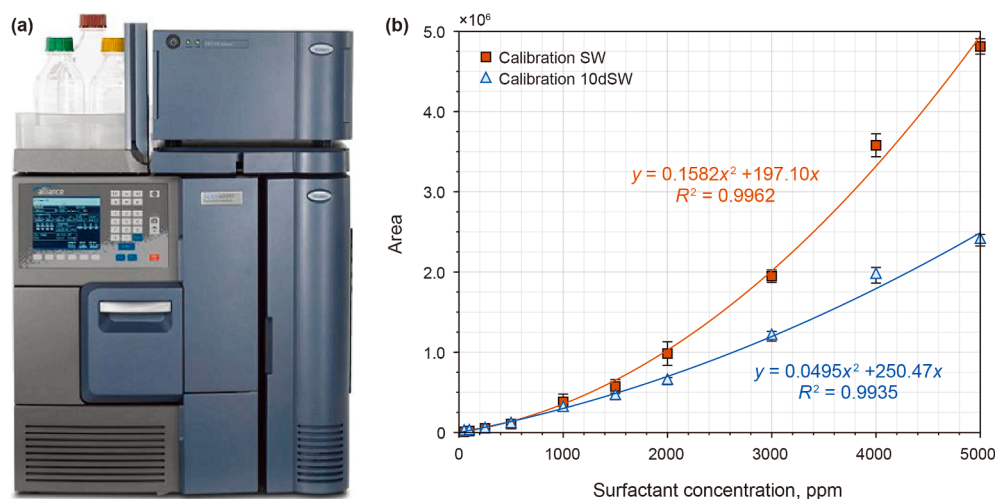


Fig. 6. HPLC method for OPAC: (a) Waters Alliance HPLC system used for measurement of effluent surfactant concentration; (b) HPLC–ELSD calibration curves for OPAC in SW and 10dSW, showing integrated peak area as a function of surfactant concentration. Error bars show the standard deviation of three independently prepared OPAC standards at each concentration.

$$\Gamma = \frac{C_{\text{inj}}V_{\text{inj}} - \sum_{i=1}^N C_i V_i}{m_{\text{rock}}}, \quad (1)$$

where C_{inj} is the injected concentration, mg/L or ppm; V_{inj} is the cumulative volume of injected chemical solution, L; C_i and V_i are the average concentration (mg/L) and volume (L) of effluent collected in sample i ; N is the total number of samples; and m_{rock} is the dry mass of the core sample, g. In practice, the summation term represents the total mass of chemical produced from the core, and the difference from the injected mass is the amount remaining inside the rock sample, expressed per gram of rock. For surfactant, C_i was determined from UV–VIS calibration curves, with HPLC concentrations used as a check in the surfactant-only tests described above. In contrast, the effluent concentrations for the polymer were inferred from the viscosity of SP samples.

2.2.5. Effluent inorganic ion concentration measurements

Effluent cation and anion concentrations were measured using a combination of ion chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP–OES). For the preflush effluents at SW and 10dSW salinities, both cation and anion concentrations were measured with a Dionex ICS-5000 + IC system (Fig. 7(a)). The instrument operates in reagent-free mode with automated eluent generation, so no manual preparation of eluents was required. Calibration curves were prepared for each target ion using certified multi-ion standard solutions. Effluent sample peak areas were then converted to concentrations by comparison with these calibration curves. IC was only used during the preflush stages because surfactant and polymer residues in later stages could damage the IC columns. Each IC sample was diluted in three steps, with a ten-fold dilution at each step (overall 1000-fold dilution). This stepwise dilution was needed because the ionic strengths of FW and SW are above the direct detection range of the IC system, and the staged dilution helps reduce pipetting errors.

On the other hand, during the main surfactant or SP slug and the postflush, cation concentrations were measured by ICP–OES using a Thermo Scientific iCAP 7600 analyzer (Fig. 7(b)). Effluent samples were diluted to bring all ions within the working range of the instrument and to limit matrix effects from the concentrated brines and chemicals. The ICP–OES was calibrated with certified multi-element standard solutions, and the emission intensity at element-specific wavelengths was converted to concentration using these calibration curves. Together, the IC measurements from the preflush and the ICP–OES measurements from the chemical slug and postflush provide a continuous picture of the evolution of inorganic ion composition during the floods and

complement the surfactant and polymer concentration measurements obtained from UV–VIS, HPLC, and rheology.

3. Results and discussion

3.1. Surfactant formulation selection

The surfactant salinities and concentrations used in the present work were selected based on an earlier OPAC screening study under harsh carbonate conditions (Zeynalli et al., 2025). Their results showed that OPAC behaves primarily as a wettability modifier, while still providing a meaningful, though not ultralow, reduction in crude-oil/brine IFT. In contact-angle measurements on oil-aged Indiana limestone, OPAC shifted the carbonate surface from a strongly oil-wet state toward a much more water-wet condition. For example, OPAC induced a pronounced wettability shift, reducing the contact angle from 162° to 32° after the oil-wet rock chips were treated at 90 °C with a 0.5 wt% surfactant solution in SW. Furthermore, OPAC clearly reduced crude-oil/brine IFT, yet the values achieved remained in the low-IFT rather than ultralow regime. For example, 0.5 wt% OPAC lowered the IFT at 23 °C from 13.7 to 2.06 mN/m in SW and from 24.82 to 4.32 mN/m in 10dSW. At 70 °C, the corresponding surfactant-containing systems reached 0.55 mN/m in SW and 1.14 mN/m in 10dSW. At the same time, the additional IFT benefit from increasing OPAC concentration was relatively small, consistent with the fact that these concentrations are already well above the CMC. Therefore, the screening results suggested that OPAC should not be viewed as an ultralow-IFT surfactant, but rather as a formulation whose primary value lies in promoting favorable wettability alteration while still achieving low oil/brine IFT. Moreover, these results indicated that 0.5 wt% OPAC is sufficient to generate a strong interfacial response under practical seawater salinity conditions, without the need for a more concentrated surfactant slug.

Similarly, the selection of SW and 10dSW was guided by the earlier OPAC screening work. SW was selected because SW is one of the practical injection brines in carbonate field operations and, at 0.5 wt% OPAC, produced the strongest wettability alteration. In contrast, 10dSW provided a lower-salinity condition in which OPAC exhibited lower static adsorption and a different interfacial charge response. In that earlier evaluation, OPAC adsorption decreased progressively with seawater dilution, while the calcite/brine interface shifted toward more negative values in the presence of OPAC. On this basis, SW and 10dSW were selected as two contrasting salinity conditions for the present work: SW because it elicited the strongest wettability response at the selected surfactant concentration, and 10dSW since it provided a clear contrast in



Fig. 7. (a) Dionex ICS-5000 + IC system; (b) iCAP 7600 ICP–OES analyzer.

terms of lower adsorption and modified interfacial behavior. Finally, 0.1 wt% was included in the present work as a lower comparison concentration because it is still above the reported OPAC CMC of 290 ppm (Hussain et al., 2019) and therefore allows the influence of surfactant dosage on transport and retention to be examined without falling below the interfacially active regime.

3.2. Rheological evaluation of the polymer formulation

Bulk rheology tests were conducted to determine how polymer viscosity varies with shear rate, salinity, temperature, and polymer concentration. These measurements provide a practical way to screen polymer solutions for injection. As shown in Fig. 8, for a given target viscosity, the required polymer concentration in 10dSW is much lower than in SW. This means that diluting the brine can reduce polymer consumption and lower chemical cost. This is explained by the expected effect of salinity on charged polymers: in the more saline SW, dissolved cations screen the negative charges along the polymer backbone, the coils contract, and the same concentration results in a lower viscosity than in the less saline 10dSW (Turkoz et al., 2018). The figure also shows that higher polymer concentrations increase the viscosifying power and render the solutions more shear-thinning in both SW and 10dSW.

Furthermore, based on Fig. 8, 2000 ppm was selected as the polymer concentration used in the subsequent experiments. Under reservoir-relevant shear conditions of 10 s^{-1} , this concentration yielded adequate viscosity even in SW, the more challenging brine for polymer performance. In comparison, 1000 ppm produced a noticeably lower viscosity in SW and would be further weakened by thermal thinning, whereas 3000–4000 ppm would be unnecessarily high, especially in 10dSW, where the polymer already develops much higher viscosity. This selection is consistent with polymer-flood design practice, which aims to use the minimum polymer dose needed to achieve favorable mobility control while avoiding unnecessary chemical consumption and possible injectivity penalties (Seright and Wang, 2023).

To further evaluate formulation robustness, temperature-sweep tests were conducted at a fixed shear rate of 10 s^{-1} using 2000 ppm polymer (Fig. 9). In both SW and 10dSW, the polymer-only solutions show a smooth decrease in viscosity as the temperature increases from 25 to 70 °C. Over this range, the viscosity drops by roughly one-third in each brine. This type of gradual

decline is consistent with results reported for ATBS-based polymers, in which viscosity decreases steadily with temperature while the polymers retain useful viscosifying power (Jouenne, 2020). The same temperature-sweep protocol was then applied to respective SP solutions in SW and 10dSW. SP solutions contained 0.5 wt% of surfactant and 2000 ppm of polymer. In SW, the polymer and SP curves remained very close, with most differences falling within the experimental scatter. In 10dSW, the SP viscosity was generally slightly lower than the polymer-only viscosity, although the magnitude of the difference varied with temperature. On average, the viscosity reduction caused by OPAC addition was marginal, corresponding to approximately 5.3% in SW and 5.7% in 10dSW over the tested temperature range. This demonstrates that OPAC has only a limited effect on the bulk rheological response of the ATBS-based polymer under experimental conditions. The small viscosity reduction may reflect weak SP interactions, possibly involving the quaternary ammonium center of zwitterionic OPAC and anionic acrylate or ATBS groups along the polymer chain (process 12 in Fig. 18, introduced later). Such interactions could locally reduce the effective charge density of polymer and slightly limit its chain expansion. At the same time, the absence of any strong viscosity enhancement upon adding surfactants may suggest that these interactions do not lead to the network strengthening often reported for hydrophobically associating polymer systems (Ge et al., 2021). Overall, the small separation between the polymer-only and SP curves supports good rheological compatibility and indicates that adding OPAC does not materially impair the viscosifying performance of the polymer.

3.3. Pressure response and mobility control in coreflooding experiments

All coreflooding experiments were carried out at a constant flow rate of $0.5 \text{ cm}^3/\text{min}$, so that differences in pressure response reflect changes in fluid and rock behavior rather than changes in injection rate. In all runs, the pressure drop was low and stabilized quickly, which is consistent with the high permeabilities of the Indiana limestone plugs (Table 1). The chemical slugs and post-flushes were made sufficiently long to ensure thorough propagation of the injected chemicals through the cores and substantial displacement of the mobile chemicals during the subsequent brine postflush. Effluent compositions are discussed in later sections; here, we focus on the pressure trends and what they imply for flow

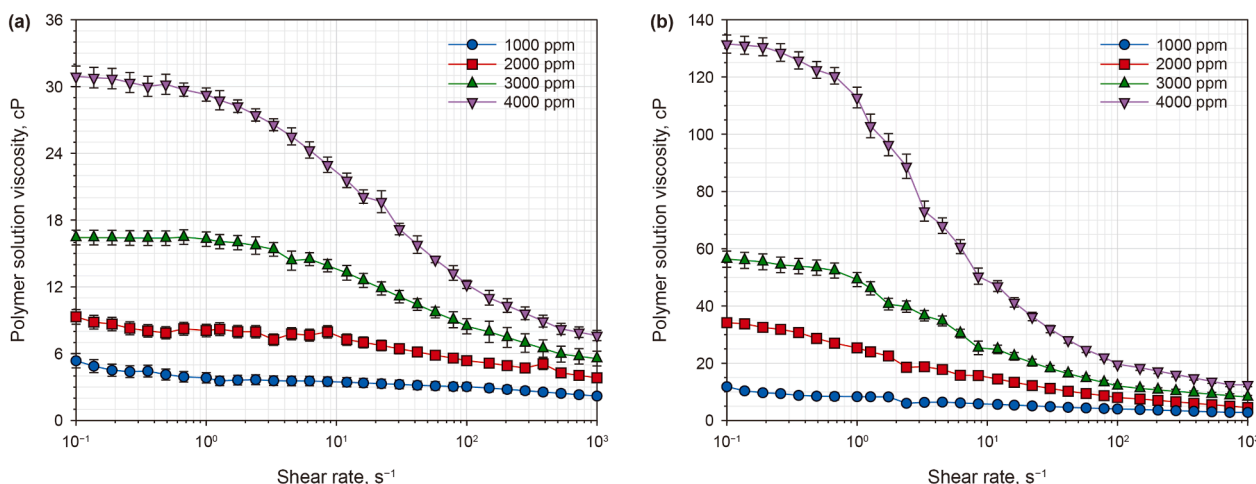


Fig. 8. Freshly-prepared polymer solution viscosity measured at 25 °C as a function of shear rate for different polymer concentrations in SW (a) and 10dSW (b). Error bars show the standard deviation of three independently prepared solutions.

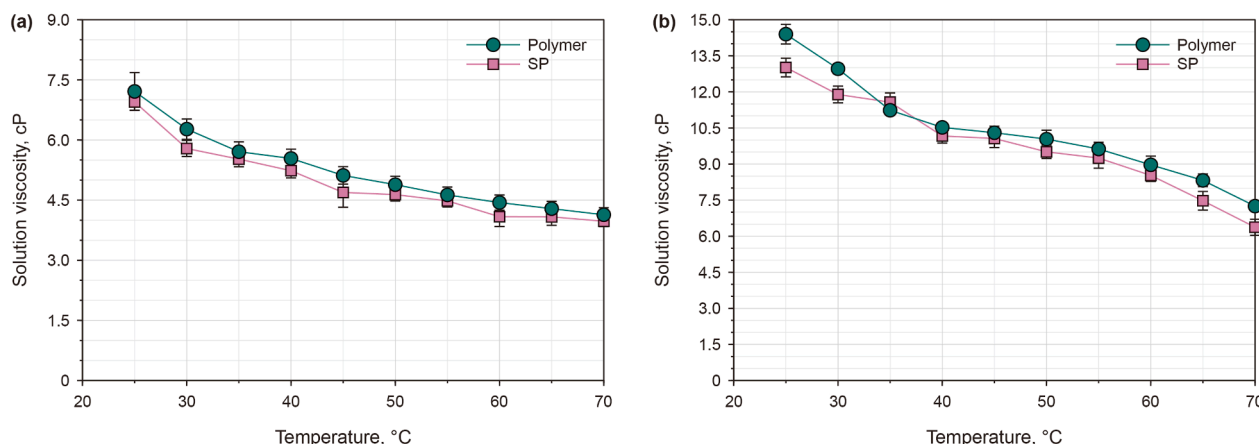


Fig. 9. Temperature-sweep tests at 10 s^{-1} for the freshly-prepared polymer and SP solutions containing 2000 ppm polymer in SW (a) and 10dSW (b). Error bars show the standard deviation of three independently prepared solutions.

resistance and mobility control. The first test used the Sample #1 core plug with a 0.5 wt% OPAC solution. As shown in Fig. 10(a), the sequence started with an SW preflush of 11.3 pore volumes (PVs) to displace FW, followed by a 0.5 wt% OPAC slug in SW for 30.9 PVs and a SW postflush for 39 PVs. The salinity was then reduced: a 10dSW preflush of 10.6 PVs was injected to displace seawater, followed by a 0.5 wt% OPAC slug in 10dSW for 16.8 PVs and a 10dSW postflush for 41.4 PVs. Throughout the entire sequence, the pressure drop remained close to 0.26 psi, indicating that the surfactant solutions did not provide a measurable viscosity increase at 90°C in this high-permeability rock. Furthermore, the second test, on Sample #2, followed the same stage sequence but with a lower surfactant concentration of 0.1 wt%. The SW preflush, surfactant slug, and postflush lasted 14.6, 14.9, and 22.8 PVs, respectively. This was followed by a 10dSW preflush of 17.9 PVs, a 0.1 wt% OPAC slug in 10dSW for 15 PVs, and a 10dSW postflush for 24.8 PVs. As in the first test, the surfactant solutions behaved essentially as brine from a mobility point of view (Fig. 10(b)).

The third test used Sample #3 and an SP formulation containing 0.5 wt% OPAC and 2000 ppm ATBS-based polymer at both salinities. The sequence was again SW preflush (15.6 PVs), SP slug in SW (15.3 PVs), SW postflush (30.7 PVs), 10dSW preflush (14.8 PVs), SP slug in 10dSW (15.3 PVs), and 10dSW postflush (28.3 PVs). In contrast to the surfactant-only floods, the pressure drop rose

sharply during SP injection, reaching about 0.97 psi in SW and about 3.12 psi in 10dSW (Fig. 11). This confirms that the polymer provides substantial mobility control, especially at lower salinity where its viscosifying power is higher. To quantify the polymer's impact, the resistance factor (RF) and residual resistance factor (RRF) were calculated from the test. RF is defined as the ratio of the pressure drop during SP injection to that during the seawater preflush and reflects the increase in flow resistance, mainly due to the higher viscosity. RRF is the ratio of postflush pressure drop to seawater preflush pressure drop and captures any long-lasting permeability reduction due to chemical retention. For SP flooding in SW, the RF was 3.46, and the RRF was 1.36, indicating a more than three-fold increase in resistance during SP injection but only a modest residual permeability loss. At 10dSW, the RF increased to 11.14, consistent with the stronger viscosifying effect of the polymer at lower salinity, while the RRF was 1.29, slightly lower than in SW and suggesting somewhat reduced retention in the diluted brine. These trends agree with reports that polymer retention in carbonates tends to increase with salinity because of stronger electrostatic interactions with the rock surface (Sebastian et al., 2024). In addition, higher salinity promotes a more coiled polymer conformation due to charge shielding, enabling denser packing on carbonate surfaces, whereas at low salinity the expanded chains occupy more surface area and result in lower adsorption

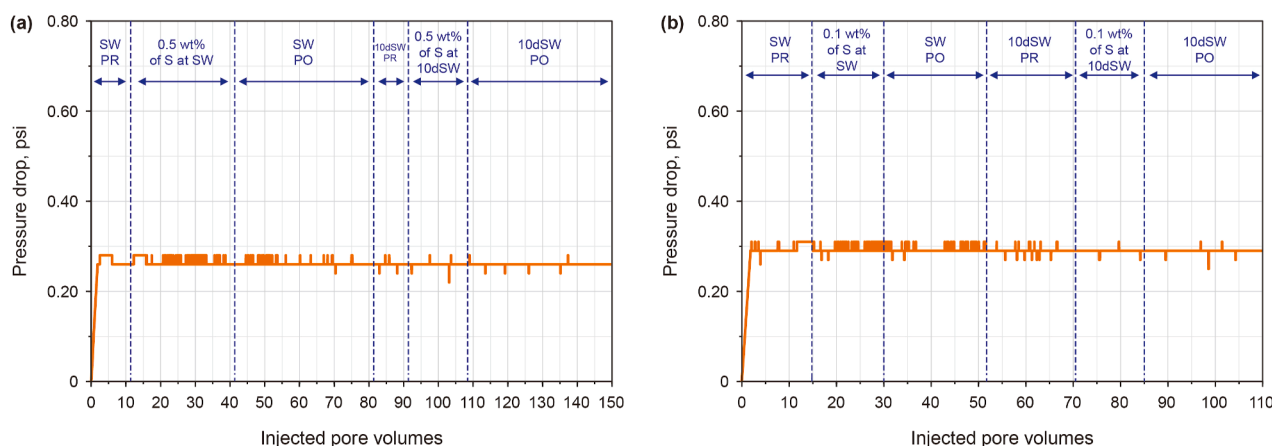


Fig. 10. Pressure drop versus injected pore volumes for single-phase surfactant flooding at 90°C in Sample #1 (a) and Sample #2 (b): SW preflush, OPAC in SW, SW postflush, 10dSW preflush, OPAC in 10dSW, and 10dSW postflush. OPAC concentration was 0.5 wt% in Sample #1 and 0.1 wt% in Sample #2. S refers to the surfactant.

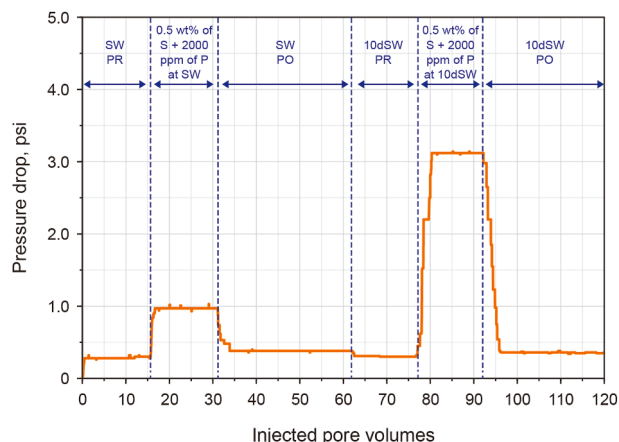


Fig. 11. Pressure drop versus injected pore volumes for single-phase SP flooding in Sample #3 at 90 °C with 0.5 wt% OPAC and 2000 ppm ATBS-based polymer: SW preflush, SP slug in SW, SW postflush, 10dSW preflush, SP slug in 10dSW, and 10dSW postflush. S and P denote surfactant and polymer, respectively.

density (Lee et al., 2019). The effluent concentrations and dynamic retention of polymers and surfactants during our coreflooding experiments are examined in the following subsection.

3.4. Effluent concentration and dynamic retention of surfactants and polymers

Effluent concentrations were measured throughout each core-flood and reported in normalized form, defined as the ratio of effluent concentration to the injected concentration, plotted as a function of injected pore volume. Surfactant concentrations were obtained by UV–VIS spectrophotometry and cross-checked using HPLC in the surfactant-only tests, while polymer concentrations in the SP test were inferred from rheological measurements; the agreement between UV–VIS and HPLC points in the surfactant floods confirms the reliability of the calibration. For the SP floods, the difference between the viscosities of bypass and effluent SP samples provides a single, lumped mechanical-degradation factor for the porous media and back-pressure regulator. By the end of the SW and 10dSW SP slugs, the effluent viscosities were 2.4 and 3.62 cP, respectively, compared with 3.0 and 4.12 cP in the corresponding bypass samples, indicating overall degradation of 20% for SW and 12% for 10dSW. These factors were applied to correct

effluent viscosities before converting them to effluent polymer concentrations using the calibration curves from Fig. 2(b). Because normalization uses a single injected concentration, minor excursions of the plateau slightly above unity fall within analytical uncertainty and are not considered physically significant.

In Sample #1 (0.5 wt% OPAC), the SW cycle in Fig. 12(a) begins with the seawater preflush (SW PR), during which the effluent surfactant concentration remains essentially zero. Once the surfactant slug reaches the outlet, the normalized concentration rises rapidly and reaches a plateau near 1 within about 5–6 PVs, indicating efficient propagation of the surfactant bank through the core with limited spreading. The concentration remains close to unity over most of the slug and then declines during the SW postflush (SW PO) as the remaining mobile surfactant is displaced. The relatively steep decay, similar to the preceding rise, is also consistent with limited spreading. After the brine is switched to 10dSW, the 10dSW preflush (10dSW PR) produces a small but distinct peak, even though no fresh surfactant is injected at that stage. As illustrated schematically in Fig. 1, lowering brine salinity can alter surface and interfacial conditions in carbonate rock through coupled effects such as electrical double-layer expansion, ion exchange, and possible release of previously adsorbed species. These changes may account for the small surfactant peak observed during the 10dSW preflush. Injection of the 0.5 wt% OPAC slug in 10dSW then produces another rapid rise to a plateau near unity, followed by a decline during the 10dSW postflush (10dSW PO). Furthermore, Sample #2, flooded with 0.1 wt% OPAC, shows the same overall pattern (Fig. 12(b)). The effluent remains surfactant-free during the SW preflush, rises quickly to values close to unity when the surfactant slug arrives, and decreases during the SW postflush. After the switch to the 10dSW cycle, the effluent shows a small surfactant peak during the preflush, followed by a rise during the diluted surfactant slug and a decline during the final postflush. Overall, the normalized effluent profiles at 0.5 and 0.1 wt% are similar in shape, with only modest differences in breakthrough sharpness and tailing at the scale of the plots, although the integrated dynamic retention differs with concentration, as discussed below.

On the other hand, in Sample #3, the SP flood containing 0.5 wt% OPAC and 2000 ppm ATBS-based polymer (Fig. 13) shows that the surfactant and polymer propagated through the core together. During the SW slug, both normalized concentrations rose sharply to plateau values near or slightly above unity, remained stable while the bank moved through the core, and then declined during the postflush. The 10dSW cycle showed the same overall

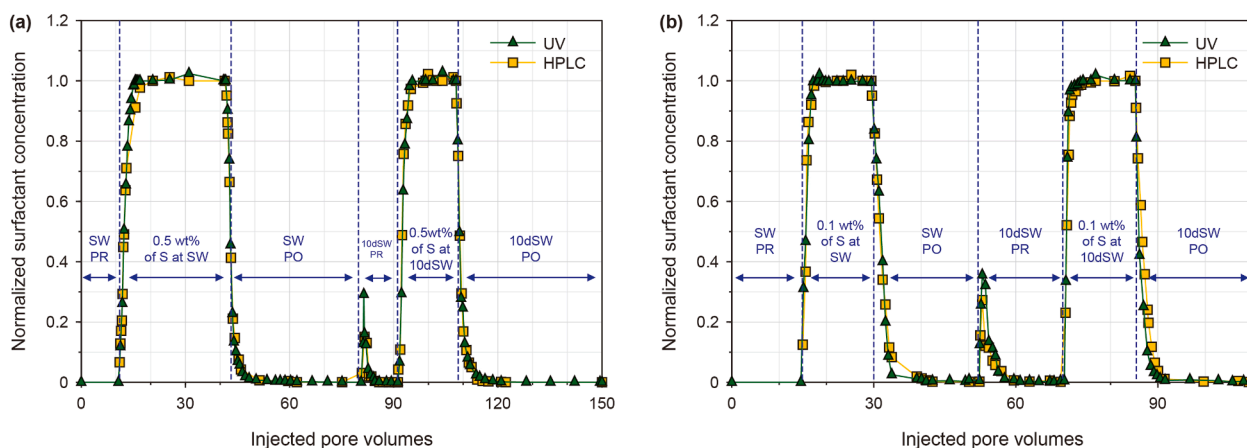


Fig. 12. Normalized effluent surfactant concentration during surfactant flooding in SW and 10dSW: (a) Sample #1 at 0.5 wt% surfactant concentration; (b) Sample #2 at 0.1 wt% surfactant concentration. S denotes surfactant.

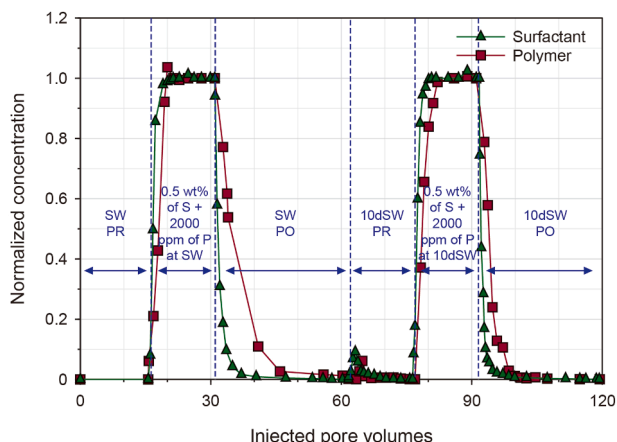


Fig. 13. Normalized effluent surfactant and polymer concentrations for Sample #3 during SP flooding in SW and 10dSW. The SP slug contains 0.5 wt% OPAC surfactant and 2000 ppm ATBS-based polymer. S = surfactant; P = polymer.

pattern, including a small peak during the 10dSW preflush before the main SP bank arrived. The polymer front was somewhat broader, and its tail slightly longer than that of the surfactant, especially in SW, consistent with the larger molecular size of the polymer and the dispersion behavior of macromolecules in porous media (Liu and Masliyah, 2005). Overall, the two chemicals moved as a single bank rather than separating chromatographically, which is desirable for SP flooding.

These effluent histories can be further interpreted in terms of dynamic retention. Dynamic retention of surfactant and polymer was quantified from the effluent histories using the running material balance given in Eq. (1), and the resulting values at the end of each flooding stage are summarized in Table 3. For each sample, the entry under “Chemical slug” corresponds to the calculated retention level at the moment the slug injection is stopped, while the value under the subsequent “Postflush” is the retention after the following brine flush at the same salinity. In the discussion below, the postflush values are taken as the net retention after a given salinity cycle, because they represent the amount of chemical that remains in the core once the bulk of the dissolved chemical has been displaced by brine.

For the 0.5 wt% surfactant flood in Sample #1, the net surfactant retention decreased from 0.284 mg/g-rock after the SW cycle to 0.198 mg/g-rock after the 10dSW cycle, corresponding to an approximately 30% reduction when salinity was lowered. Importantly, before injection of the 10dSW surfactant slug, retention had already declined to 0.177 mg/g-rock during the 10dSW preflush,

Table 3

Dynamic retention of surfactant and polymer for the three corefloods, calculated from effluent histories by running material balance. Values are the stabilized retention at the end of each flooding stage.

Dynamic retention		Chemical slug at SW	Postflush with SW	Preflush with 10dSW	Chemical slug at 10dSW	Postflush with 10dSW
Surfactant, mg/g-rock	Sample #1	0.856	0.284	0.177	0.657	0.198
	Sample #2	0.341	0.191	0.130	0.161	0.084
	Sample #3	0.572	0.202	0.112	0.344	0.086
Polymer, mg/g-rock	Sample #3	0.589	0.063	0.044	0.455	0.044

indicating partial remobilization of surfactant retained during the preceding SW cycle. In contrast, the 0.1 wt% surfactant flood in Sample #2 shows the same overall behavior but at a lower retention level, with net retention decreasing from 0.191 mg/g-rock after the SW postflush to 0.084 mg/g-rock after the 10dSW postflush, corresponding to an approximately 56% reduction upon lowering salinity. Comparison of Samples #1 and #2 also shows that raising the injected OPAC concentration from 0.1 to 0.5 wt% raised net retention from 0.191 to 0.284 mg/g-rock in SW and from 0.084 to 0.198 mg/g-rock in 10dSW, that is, only about 1.5-fold and 2.4-fold, respectively, despite the fivefold increase in bulk concentration.

Furthermore, the SP flood in Sample #3 helps isolate the effect of the polymer on surfactant retention. Particularly, adding 2000 ppm polymer reduced surfactant retention from 0.284 to 0.202 mg/g-rock in SW and from 0.198 to 0.086 mg/g-rock in 10dSW, relative to the 0.5 wt% surfactant-only case (Sample #1). This behavior is consistent with previous SP studies in carbonates, which suggest that anionic polymers can occupy positively charged mineral sites and bind $\text{Ca}^{2+}/\text{Mg}^{2+}$ in solution, thereby reducing the strength and number of adsorption sites available for surfactant headgroups (Groenendijk and van Wunnik, 2021). In this sense, part of the polymer acts sacrificially, helping protect the surfactant from excessive retention. Moreover, the lower value observed already at the end of the 10dSW preflush (0.112 mg/g-rock) also indicates that part of the surfactant retained during the preceding SW cycle was remobilized when the brine was switched to lower salinity. On the other hand, polymer retention itself remains relatively low in the SP flood. The net polymer retention was 0.063 mg/g-rock after the SW cycle and 0.044 mg/g-rock after the 10dSW cycle, corresponding to an approximately 30% reduction at lower salinity. The drop to 0.044 mg/g-rock during the 10dSW preflush further indicates partial remobilization of polymer retained during the preceding SW cycle. A similar trend has been reported in earlier polymer-flooding studies in carbonates, where lower salinity and hardness reduced polymer retention by weakening electrostatic attraction and limiting divalent-polymer complexation (Sebastian et al., 2024). The low net polymer retention is also in line with the moderate residual resistance factors observed in the SP flood, indicating that the ATBS-based polymer provided mobility control without causing excessive irreversible permeability loss.

Overall, the effluent and retention data describe how the injected chemical banks evolve throughout each flood stage. Within a given salinity cycle, the decline in retention from the end of the chemical slug to the end of the corresponding postflush mainly reflects continued production of mobile chemicals that still occupy the pore volume when slug injection stops; for this reason, the postflush value is the more appropriate measure of net retention at that salinity. When the brine is switched from SW to 10dSW, the additional decrease in retention, together with the small preflush peak in normalized effluent concentration, indicates partial remobilization of chemicals retained during the preceding SW cycle. This can be attributed to the lower ionic strength and reduced $\text{Ca}^{2+}/\text{Mg}^{2+}$ content of 10dSW, which weaken the association of surfactant and polymer with the carbonate surface, making the retained fraction easier to displace. Moreover, the reduction in surfactant retention in the SP flood suggests that the polymer competes for positively charged calcium sites and alters divalent-ion-mediated surfactant association with the carbonate surface, thereby reducing surfactant access to available adsorption sites. Collectively, these results show that surfactant retention in this system depends on salinity, surfactant concentration, and polymer presence, and that part of the retained material can be remobilized under the tested brine sequence.

3.5. Effluent inorganic ion concentration

This section examines the evolution of inorganic ions in the effluent during both surfactant-only flooding (Sample #1) and SP flooding (Sample #3) and uses these ion histories as a mechanistic probe of the underlying carbonate–brine–chemical interactions. By comparing the responses of Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , and SO_4^{2-} across SW and 10dSW conditions, the following subsections show how divalent-ion redistribution, ion exchange, and aqueous complexation with the zwitterionic surfactant and polymer jointly influence chemical transport through the carbonate core. This analysis is valuable because it links the observed effluent-ion signatures to salinity-dependent chemical loss and polymer-assisted reduction in surfactant retention, while also supporting literature-based mechanistic interpretation of the underlying ion–chemical interactions and possible surface complexation and divalent-ion bridging processes under harsh carbonate conditions.

3.5.1. Surfactant flooding in Sample #1

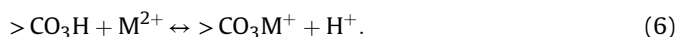
To begin the single-phase surfactant flood, the connate FW in Sample #1 was first displaced by SW during the SW preflush (SW PR), thereby establishing the desired aqueous environment for the subsequent surfactant injection. Effluent compositions were monitored throughout the preflush by ion chromatography (IC), as described in Section 2, in order to follow the evolution of the major aqueous ions. As shown in Fig. 14(a), effluent Na^+ and Cl^- concentrations decreased from their initial FW values and approached the injected SW composition after approximately 2.5 PVs. Because these ions behave nearly conservatively in carbonate systems, they serve here primarily as markers of brine replacement and salinity stabilization. Their convergence toward the SW baseline indicates that the FW-to-SW transition occurred cleanly before surfactant injection. This point is important because it shows that the subsequent deviations observed for Ca^{2+} , Mg^{2+} , and SO_4^{2-} cannot be attributed to incomplete brine replacement but instead reflect reactive carbonate–brine interactions within the core. The mechanistic discussion below, therefore, focuses on these non-conservative ions, since they carry the main evidence for the underlying reactive processes.

In contrast to Na^+ and Cl^- , the divalent cations displayed clearly non-conservative behavior. As illustrated in Fig. 14(a), the effluent Ca^{2+} concentration decreased from FW levels and stabilized at approximately 925 ppm, which is above the 650 ppm Ca^{2+} in the

injected SW. At the same time, Mg^{2+} leveled off at about 1962 ppm, slightly below its injected concentration of 2110 ppm. The contrasting behavior of Ca^{2+} and Mg^{2+} is consistent with established carbonate surface chemistry. In the surface-complexation framework commonly used for calcite (Brady et al., 2012), the hydrated carbonate surface is represented by calcium-type and carbonate-type groups, often written in simplified form as $>\text{CaOH}$ and $>\text{CO}_3\text{H}$, respectively. These groups do not remain in a single fixed state. Rather, they may participate in acid–base and surface-complexation reactions whose extent depends on the surrounding brine chemistry. Calcium-type sites are commonly protonated to form positively charged $>\text{CaOH}_2^+$ species and, in more comprehensive calcite reaction schemes (Bonto et al., 2021; Arellano et al., 2025), may also deprotonate to $>\text{CaO}^-$. Carbonate-type sites, in contrast, may deprotonate to $>\text{CO}_3^-$, as illustrated by the following reaction sets:



The calcite surface in brine should therefore be viewed as a dynamic distribution of neutral, positively charged, and negatively charged species rather than as a single pair of fixed surface sites. In practical terms, the net surface charge is controlled by pH-dependent surface speciation and by the specific adsorption of PDIs. Among the PDIs, Ca^{2+} and Mg^{2+} are particularly important because they specifically associate with carbonate-type surface groups. Depending on the surface-complexation convention, this can be written either as direct binding to deprotonated $>\text{CO}_3^-$ sites (Hiorth et al., 2010) or, equivalently, as proton-release complexation of the protonated form $>\text{CO}_3\text{H}$ (Van Cappellen et al., 1993). In the reactions below, the divalent cations Ca^{2+} and Mg^{2+} are represented generically as M^{2+} :



Changes in the aqueous Ca/Mg ratio, therefore, do not simply alter the composition of the flowing brine; they also shift the distribution of divalent-ion surface complexes on calcite. This

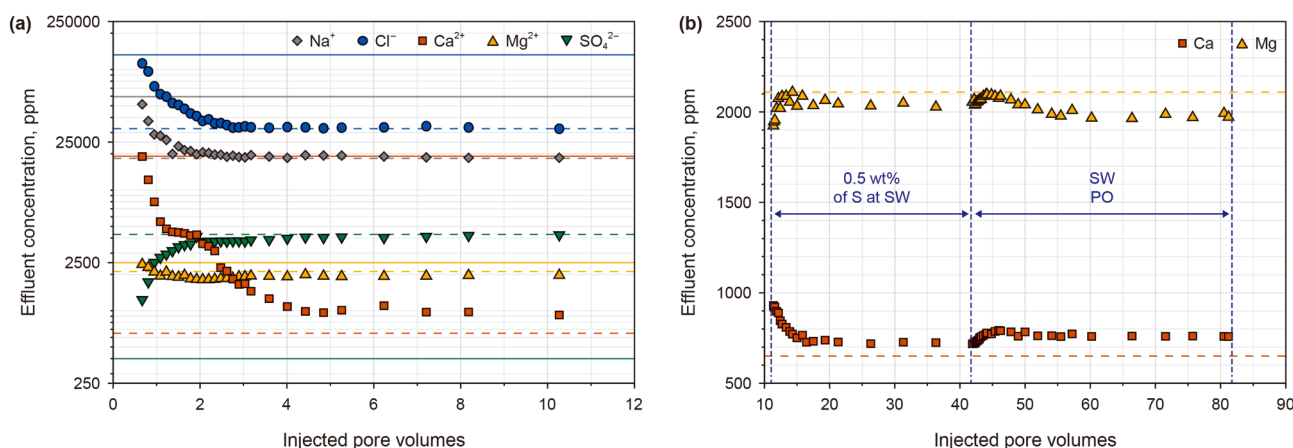
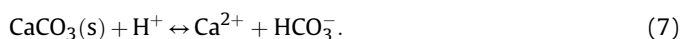


Fig. 14. Effluent inorganic composition for Sample #1 during seawater conditioning and subsequent surfactant flooding: (a) effluent ion concentrations during the seawater preflush (SW PR, measured by IC (Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-}); (b) effluent Ca and Mg concentrations during injection of 0.5 wt% OPAC in SW followed by the SW postflush (SW PO), reported as total dissolved elemental concentrations measured by ICP-OES. Solid horizontal lines show the composition of the initial FW, and dashed horizontal lines show the composition of the injected SW for each species.

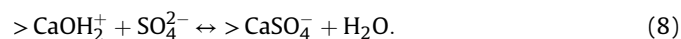
point is directly relevant here. Indiana limestone was initially equilibrated with formation water, a high-salinity brine strongly enriched in Ca^{2+} relative to Mg^{2+} (19,100 vs. 2500 ppm; Table 2). Under these conditions, carbonate-type surface complexes would be expected to favor Ca-bearing species. When seawater was injected, Ca^{2+} in the injected brine dropped sharply to 650 ppm, whereas Mg^{2+} decreased only to 2110 ppm, so the Ca/Mg ratio in the flowing brine was markedly reduced. This shift promoted re-equilibration of the carbonate-type surface complexes, with Mg^{2+} competing more effectively for these sites and progressively replacing part of the previously associated Ca^{2+} . At 90 °C, this redistribution is expected to be more pronounced because Mg participation in calcite surface reactions becomes stronger at an elevated temperature (Zhang et al., 2007).

Additionally, another possible reason behind the observed Ca^{2+} enrichment might be the slight disequilibrium dissolution of calcite when the in-situ brine chemistry is perturbed by SW injection. Calcite dissolution is commonly described by the reaction:



This reaction is governed by the saturation state of the brine with respect to calcite, which depends on pH, dissolved inorganic carbon, ionic strength, and temperature (Hiorth et al., 2010). When seawater replaces formation water, the abrupt reduction in Ca^{2+} concentration and changes in ionic composition can shift the brine toward undersaturation with respect to calcite, providing a thermodynamic driving force for dissolution. In addition, variations in pH and carbonate speciation during mixing may further promote dissolution until a new equilibrium is reached. Such effects have been widely reported in carbonate systems undergoing low-salinity or seawater injection, where transient disequilibrium between the rock and the injected brine can lead to measurable Ca^{2+} release (Shabani and Zivar, 2020). However, without complementary pH and alkalinity measurements, it is not possible to distinguish quantitatively between ion exchange and calcite dissolution. Although IC and ICP-OES provide reliable ionic and elemental concentrations, respectively, they do not resolve carbonate speciation or hydrogen ion activity under reservoir conditions. Because effluent samples were cooled and diluted prior to analysis, the original high-temperature carbonate equilibrium was altered, preventing direct reconstruction of in-situ pH and alkalinity.

Sulfate also exhibited non-conservative behavior during SW PR in Sample #1 (Fig. 14(a)). The SO_4^{2-} concentration in the effluent increased gradually from the resident FW value (~400 ppm) toward the injected SW concentration (~4290 ppm), reaching stabilization only after more than four pore volumes. This delayed approach to the seawater baseline indicates that some of the sulfate introduced with seawater was specifically adsorbed on positively charged calcium surface sites, thereby slowing its transport through the core until the surface approached a new adsorption equilibrium. In this context, SO_4^{2-} can be considered an additional PDI, interacting with surface sites according to reactions such as (Brady et al., 2012):



The eventual agreement between effluent and injected sulfate concentrations, together with the modest Ca^{2+} excess, suggests that anhydrite (CaSO_4) precipitation during the preflush was limited and did not dominate the ion balance (Mosallanezhad and Kalantariasl, 2021). Overall, the SW preflush successfully conditioned the rock-brine system: formation water was effectively removed, the ionic strength and hardness were brought close to SW values, and only moderate, geochemically consistent

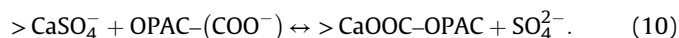
adjustments in divalent-ion concentrations occurred through ion exchange and possibly minor calcite dissolution.

Furthermore, during the main surfactant cycle in Sample #1, a 0.5 wt% OPAC solution in SW was injected at 90 °C after the SW preflush, and the effluent Na, Ca, and Mg were monitored by ICP-OES as a function of injected pore volume and reported as total dissolved elemental concentrations. Although Na is not shown in Fig. 14(b) for visual clarity, its effluent concentration remained close to the 18,300 ppm baseline throughout both the surfactant slug and the subsequent SW postflush, indicating that the seawater background remained stable. With the bulk salinity thus effectively unchanged, the deviations observed in the plotted Ca and Mg curves from their baseline dashed lines can be attributed to specific geochemical interactions among the rock, brine, and OPAC rather than to changes in overall salinity.

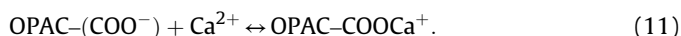
At the start of the surfactant slug, the effluent Ca concentration is roughly 930 ppm, essentially the level reached at the end of the SW preflush and already well above the 650 ppm Ca in SW (Fig. 14(b)). Over the first four to five pore volumes of OPAC injection, Ca drops steeply towards about 740 ppm and then levels off between 730 and 750 ppm for the rest of the slug. OPAC injection thus reduces, but does not remove, the Ca excess that was generated during the FW-to-SW exchange. Magnesium shows the opposite trend. It begins near 1900 ppm, rises modestly in the first few pore volumes to just above 2000 ppm, and then settles into a plateau that remains slightly below the SW value of 2110 ppm. Relative to the preflush, the key new features during the surfactant cycle are therefore a clear relaxation of Ca toward the SW concentration and, for Mg, a small transient increase followed by stabilization at a still mildly depleted level. To interpret these trends, adsorption of OPAC at the seawater-conditioned calcite interface must be considered. At the start of the surfactant slug, the surface had already re-equilibrated with seawater and therefore comprised a distribution of $>\text{CaOH}_2^+$, $>\text{CaOH}$, $>\text{CaO}^-$, $>\text{CO}_3\text{H}$, and $>\text{CO}_3^-$ sites, together with sulfate- and divalent-cation-bearing surface species generated during the preceding SW preflush. Because OPAC is a carboxybetaine containing both a carboxylate moiety and a permanently charged quaternary ammonium center, several adsorption pathways are chemically plausible. Although the adsorption of zwitterionic surfactants on calcite and related carbonate surfaces has been examined experimentally (Durán-Álvarez et al., 2016; Jian et al., 2018; Gbadamosi et al., 2023; Bazaryari et al., 2025), a generally adopted reaction-based surface-complexation description for their adsorption on calcite remains lacking. The reactions below are therefore introduced as mechanistically grounded interfacial representations for interpreting the observed effluent-ion trends. For the carboxylate moiety (COO^-), the most direct precedent is specific interaction with hydrated calcium sites through ligand exchange (Bonto et al., 2022; Claesson et al., 2024; Hosseinzadehsadati et al., 2024). In this representation, the OPAC carboxylate coordinates surface Ca and replaces the hydroxyl ligand of a hydrated calcium site, forming a surface calcium-carboxylate complex:



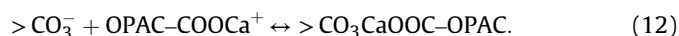
where $\text{OPAC}-(\text{COO}^-)$ denotes the carboxylate moiety of OPAC. A second plausible route involves competitive displacement at sulfate-bearing calcium sites inherited from the SW preflush. Since sulfate adsorption on calcite is commonly represented at hydrated calcium sites, the OPAC carboxylate may also compete for these sites and displace sulfate. Conversely, injection of sulfate-rich brine into porous media containing pre-adsorbed OPAC may, in a more general sense, shift this equilibrium in the reverse direction, leading to partial desorption of OPAC:



However, because sulfate was not monitored during the surfactant slug, the contribution of Eq. (10) cannot be resolved from the available effluent chemistry and should therefore be regarded as a plausible secondary mechanism rather than a verified one. Furthermore, another possible Ca-centered pathway involves complexation of calcium by the OPAC carboxylate in the aqueous or near-surface region. This step is relevant because calcium remained well above the injected SW value at the start of the surfactant slug, indicating that excess Ca inherited from the SW preflush was still available for redistribution. The first step is thus represented as aqueous Ca–carboxylate complex formation, not yet as mineral-surface adsorption:

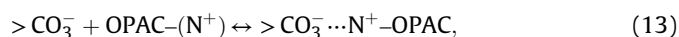


A true cation bridge forms when such Ca-loaded carboxylate associates with a negatively charged carbonate-type surface site (Groenendijk and van Wunnik, 2021). That Ca-mediated attachment can be represented as:



The bridged structure in Eq. (12) is best described as a Ca-mediated specific interfacial complex rather than a purely outer-sphere electrostatic contact. In compact surface-complexation language, the same end state is equivalent to interaction between the carbonate surface complex $>\text{CO}_3\text{Ca}^+$, defined by Eqs. (5) and (6), and $\text{OPAC}-(\text{COO}^-)$. Eqs. (11) and (12) offer a plausible mechanistic basis for the pronounced early decline in Ca during the OPAC slug. Because effluent Ca at the start of surfactant injection remained well above the injected SW concentration, excess calcium was still available for redistribution between the aqueous phase and the developing surfactant-modified interface. Within this framework, part of the excess Ca can first form aqueous or near-surface Ca–carboxylate complexes with OPAC (Eq. (11)), after which a fraction of these Ca-associated species may participate in Ca-mediated attachment to negatively charged carbonate-type surface regions (Eq. (12)). Such redistribution would lower the concentration of freely flowing Ca and is therefore consistent with the decrease in effluent Ca observed during the first four to five pore volumes of the surfactant slug (Fig. 14(b)). The subsequent plateau above the SW baseline suggests that the process does not remove all of the excess Ca but instead establishes a new interfacial partitioning between dissolved Ca and surfactant-associated Ca species.

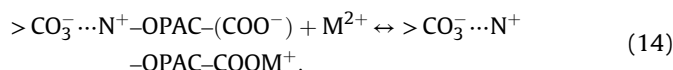
In parallel with these carboxylate-centered routes, the quaternary ammonium center ($-\text{N}^+(\text{CH}_3)_2-$) of OPAC may also associate with negatively charged carbonate-type regions at the calcite surface. For a zwitterionic surfactant, this pathway is more appropriately described as purely electrostatic interfacial association than as direct ligand exchange. In this representation, the permanently charged ammonium center is attracted to negative carbonate-type surface regions. This can be represented schematically as:



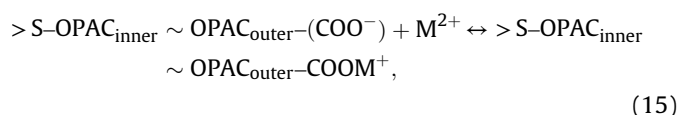
where $\text{OPAC}-(\text{N}^+)$ is the quaternary ammonium center of OPAC. The reaction above is intended only to describe the local electrostatic association between the quaternary ammonium center and a negatively charged carbonate-type surface region. It should not be interpreted as implying the same type of specific

coordination chemistry by which divalent ions interact with carbonate surfaces (Durán-Álvarez et al., 2016; Bazyari et al., 2025). Therefore, adsorption of OPAC through Eq. (13) is not expected to remove Mg from the interface through direct one-for-one replacement. Rather, as the OPAC adsorption layer develops, electrostatic association of the ammonium center near negative carbonate-type regions can perturb the local charge balance and temporarily destabilize part of the pre-existing Mg-bearing carbonate surface population. Accordingly, the small early rise in effluent Mg during the first few pore volumes of the OPAC slug (Fig. 14(b)) is reasonably interpreted as a transient surface re-equilibration effect, in which a limited fraction of interfacial Mg is released to the flowing brine before a new steady state is established. The subsequent mild decline of Mg toward a plateau still slightly below the SW value then suggests that this release is only partial and is followed by renewed partitioning of Mg into surfactant-influenced interfacial environments as surfactant adsorption progresses. Furthermore, in addition to these dominant divalent-cation-mediated and electrostatic pathways, a possible contribution from hydrogen bonding to surfactant adsorption cannot be excluded. Such interactions would most plausibly involve hydrated calcite surface groups and the oxygen-containing moieties of OPAC, particularly the carboxylate group and the ether oxygens of its polyoxyethylene segment, and may therefore provide an additional contribution to adsorption at the calcite interface.

The later-stage redistribution of divalent cations during surfactant flooding in SW is possibly associated with carboxylate-bearing environments created within the developing OPAC adsorption layer. For the fraction of OPAC molecules adsorbed through electrostatic association of the quaternary ammonium center at $>\text{CO}_3^-$ -type regions (Eq. (13)), the carboxylate moiety may remain oriented toward the aqueous phase. Previous studies of carboxybetaine and sulfobetaine surfactants have demonstrated that these anionic groups can form complexes with Ca^{2+} and Mg^{2+} in the interfacial region, modifying both adsorption density and molecular orientation at mineral surfaces (Hu et al., 2010; Gerola et al., 2017). For an individually adsorbed OPAC molecule, subsequent coordination of a divalent cation (M^{2+} , $\text{M} = \text{Ca}$ or Mg) by the outward-facing carboxylate (illustrated in Fig. 18 as process 5) can therefore be represented as:



This step is better interpreted as surfactant-associated interfacial complexation than as a new carbonate surface complex or a second cation-bridge mechanism. Furthermore, as surface coverage increases, isolated adsorbed molecules are unlikely to remain the only interfacial form. Research on zwitterionic surfactants indicates concentration- and salinity-dependent changes in adsorption geometry and packing (Durán-Álvarez et al., 2016; Bazyari et al., 2025); accordingly, the later-stage adsorbed layer may contain more densely packed, aggregate-like interfacial structures (Mushtaq et al., 2023). In such regions, the local abundance of accessible carboxylate groups can increase, providing additional sites for divalent-ion association (depicted in Fig. 18 as process 6). These structures are dynamic surfactant assemblies rather than discrete stoichiometric surface species. Accordingly, the following equation is intended only as a simplified representation of overall divalent-ion retention in these carboxylate-rich interfacial domains, rather than as a unique elementary surface reaction:



where $>S$ denotes a calcite surface site, $\text{OPAC}_{\text{inner}}$ and $\text{OPAC}_{\text{outer}}$ denote surfactant molecules in the inner and outer parts of the interfacial assembly, respectively, and $\sim$ represents the hydrophobic association between their hydrocarbon tails.

These latter pathways complement, rather than replace, the Ca-centered mechanism in Eqs. (11) and (12). The pronounced early decline in Ca during the OPAC slug is more plausibly linked to aqueous or near-surface Ca–carboxylate complexation followed by Ca-mediated attachment to carbonate-type surface regions, as described by Eqs. (11) and (12). Subsequent association of Ca with exposed carboxylate groups on adsorbed or aggregated OPAC may also contribute to sustaining the later plateau that remains above the SW baseline. Magnesium behaves differently. Its small early rise is more consistent with transient release from Mg-bearing carbonate surface complexes as the OPAC layer develops, whereas the subsequent decline toward a plateau still slightly below the SW value is consistent with partial re-association of Mg with OPAC-linked carboxylate environments as surface coverage increases. Overall, OPAC does not simply displace divalent ions from the interface; rather, it redistributes them among pre-existing carbonate surface complexes, surfactant-associated interfacial complexes, and the flowing brine.

Thereafter, the core was flushed with seawater at 90 °C (SW PO stage) while Ca and Mg continued to be monitored (Fig. 14(b)). Both divalent ions exhibited a small initial increase at the onset of postflush, followed by modest relaxation to new steady values, while Ca remained above SW and Mg remained below it throughout. The timing of these Ca and Mg trends coincides with the decline of the OPAC concentration in the effluent: during SW PO, the normalized surfactant concentration decreases from unity to nearly zero, and the dynamic retention drops from 0.856 to 0.284 mg/g-rock. The timing suggests that some of the calcium and magnesium seen during the postflush may come from OPAC-associated interfacial species formed during the surfactant slug. Their release provides a plausible explanation for the small early increase in effluent Ca and Mg at the start of SW PO. Similar co-production of divalent cations with surfactant has been reported

in carbonate coreflows with anionic surfactants, where peaks in Ca^{2+} and Mg^{2+} coincide with surfactant breakthrough and are attributed to surfactant–cation complexes released from the rock surface (Groenendijk and van Wunnik, 2021). As the surfactant concentration in the core then declined further, the interface progressively re-equilibrated with seawater, and both ions relaxed toward new steady levels.

After completing the SW cycle, the brine was switched to 10dSW to set up the low-salinity surfactant flood. During this 10dSW preflush, 10dSW displaced SW at 90 °C, and the effluent Na^{+} , Ca^{2+} , Mg^{2+} , Cl^{-} , and SO_4^{2-} concentrations were monitored by IC (Fig. 15(a)). As expected, Na^{+} and Cl^{-} shifted from their SW levels toward the 10dSW composition, confirming efficient SW displacement. In contrast, the divalent ions again behaved non-conservatively. Calcium decreased from the SW postflush value of around 750 ppm to a plateau of about 85–90 ppm, slightly above the 65 ppm Ca^{2+} in 10dSW. Magnesium fell much more strongly, from 2000 ppm to a stable level near 110–120 ppm, well below its injected concentration of 211 ppm. Sulfate followed a similar pattern, declining from the values slightly above the SW level (≈ 4450 ppm) to a plateau around 340 ppm, lower than the 429 ppm SO_4^{2-} in 10dSW. This combination aligns with geochemical analyses of low-salinity waterflooding in carbonates, in which continued calcite dissolution and ion exchange at higher temperatures release Ca^{2+} while Mg^{2+} and SO_4^{2-} are partly removed from solution by uptake at the carbonate surface (Zhang et al., 2007).

Following the 10dSW preflush, a 0.5 wt% OPAC solution prepared in 10dSW was injected at 90 °C, and the effluent Ca and Mg concentrations are illustrated in Fig. 15(b). At the start of the 10dSW OPAC injection, effluent Ca was about 90 ppm and then declined over a few pore volumes to a plateau around 75 ppm, slightly above the Ca content of 10dSW. Magnesium remained depleted throughout the slug: it started near 100–120 ppm and slowly increased but stayed well below the injected 211 ppm, stabilizing at roughly 160 ppm. Relative to the SW surfactant cycle, the 10dSW surfactant cycle shows the same overall behavior during OPAC injection: Ca declines and then plateaus slightly above the injected-brine value, whereas Mg rises from an initially depleted level but remains below its injected-brine baseline. The main difference is that the absolute deviations are smaller in 10dSW because its divalent-ion concentrations are an order of magnitude lower than in SW.

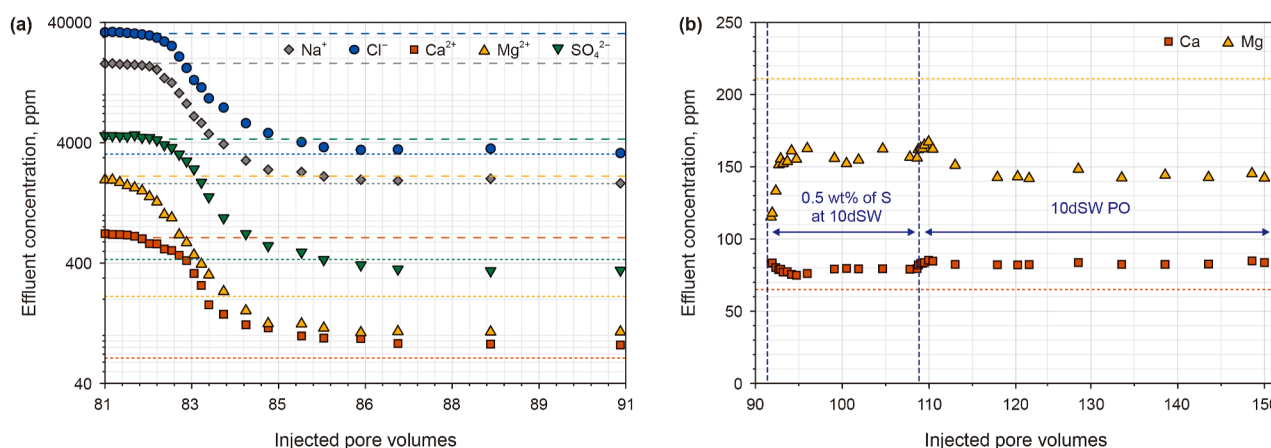


Fig. 15. Effluent inorganic composition for Sample #1 during diluted seawater conditioning and subsequent surfactant flooding: (a) effluent ion concentrations during the diluted seawater preflush (10dSW PR), measured by IC (Na^{+} , Cl^{-} , Ca^{2+} , Mg^{2+} , SO_4^{2-}); (b) effluent Ca and Mg concentrations during injection of 0.5 wt% OPAC in 10dSW followed by the 10dSW postflush (10dSW PO), reported as total dissolved elemental concentrations measured by ICP-OES. Dashed horizontal lines show the composition of the injected 10dSW for each species.

Finally, after the 10dSW surfactant slug, the core was flushed with 10dSW at 90 °C (10dSW PO). At the beginning of 10dSW PO, Ca is around 75–80 ppm, still clearly above the 65 ppm Ca^{2+} in the injected brine. Over the first two to three pore volumes, there is a small but noticeable rise in Ca, after which the concentration slowly drops and settles into a narrow band around 85 ppm. Magnesium exhibits a similar, though even weaker, transient: Mg starts near 160 ppm, shows a slight increase over the first few pore volumes, and then decreases gradually to a new plateau around 145 ppm, remaining below the 211 ppm Mg^{2+} in 10dSW (Fig. 15(b)). So, as in the SW cycle, both ions pass through a small initial bump before relaxing to their final offsets.

Geochemical effluent data for Sample #2 (0.1 wt% OPAC) are not shown here, as the Na, Ca, and Mg trends are very similar to those already described for Sample #1 at both salinities. In the next subsection, we therefore turn to Sample #3 and examine whether adding polymer to the surfactant changes the geochemical response during SP flooding.

3.5.2. SP flooding in Sample #3

The SP coreflood on Sample #3 followed the same sequence of brine and chemical stages as the surfactant-only tests: a seawater preflush (SW PR) to replace formation water, an SP slug prepared in SW, an SW postflush (SW PO), and then the corresponding 10dSW preflush (10dSW PR), 10dSW SP slug, and 10dSW postflush (10dSW PO). Effluent inorganic compositions were monitored throughout by ion chromatography during the preflush stages and by ICP-OES during the SP slugs and postflush cycles. During SW PR (Fig. 16(a)), the effluent concentrations of Na^+ and Cl^- decreased from the formation-water levels ($\approx 59,500$ ppm Na^+ and $\approx 132,000$ ppm Cl^-) toward the SW values of 18,300 and 32,290 ppm after roughly 2–3 PVs. These trends confirm that by the end of SW PR, the overall salinity in the core was effectively reset to seawater. Calcium and magnesium slightly deviated from baseline behavior. Effluent Ca^{2+} fell steeply from its FW value (19,100 ppm) and stabilized around 720–750 ppm, modestly above the 650 ppm Ca^{2+} in SW. Mg^{2+} , in contrast, decreased from about 2500 ppm to a plateau near 1950 ppm, slightly below the SW value of 2110 ppm. Thus, as in Sample #1, the SW preflush produced a persistent Ca^{2+} excess and a mild Mg^{2+} deficit in the effluent, indicative of coupled ion-exchange and possible calcite-dissolution processes.

After SW PR, a surfactant–polymer slug containing 0.5 wt% OPAC and 2000 ppm ATBS-based polymer in SW was injected, followed by an SW postflush (Fig. 16(b)). Because both stages used the same makeup brine, departures from the SW baselines isolate the coupled effect of surfactant, polymer, divalent ions, and calcite surface. At the start of the SW SP slug, magnesium, starting from a mild deficit inherited from SW PR, rises during the first 2–3 PVs of SP injection to about 2150–2200 ppm, briefly overshoots the SW baseline, and then relaxes to a slightly depleted plateau near 2050–2070 ppm. Compared with Sample #1, the Mg overshoot is stronger, suggesting that polymer addition enhances the transient partitioning of Mg between the flowing brine and the near-surface region. Calcium shows the opposite trend. At the start of the SW SP slug, Ca was around 740–760 ppm; during the first 2–3 PVs of SP injection, it declined to about 700–710 ppm and then remained in a narrow band roughly 50–60 ppm above the injected SW value. Relative to the surfactant-only flood in Sample #1, where Ca decreased from about 930 ppm to a plateau of 730–750 ppm, the early Ca decline is clearly smaller.

The most direct explanation is that the SP flood entered the chemical stage with a smaller Ca excess after SW PR, so less excess Ca was available for the Ca-centered redistribution already invoked for OPAC in Section 3.5.1. Polymer coinjection may further moderate this response because the ATBS-based polymer introduces anionic sites that can bind part of this excess Ca in the aqueous or near-surface region before that Ca is incorporated into OPAC-associated interfacial species. In the present system, these sites include the built-in ATBS sulfonate groups (SO_3^-) and any carboxylate groups (COO^-) formed if some acrylamide units hydrolyze to acrylate/carboxylate during thermal exposure. Calcium binding is plausible for both types of sites, but the interaction is expected to be stronger for carboxylate than for sulfonate (Zhao et al., 2018). By analogy with Eqs. (11) and (12) for OPAC, Ca associated with polymer carboxylate groups can follow the same sequence: calcium first binds to a carboxylate site on the polymer chain, and the resulting Ca-loaded carboxylate can then participate in Ca-bridged attachment to a carbonate surface site:

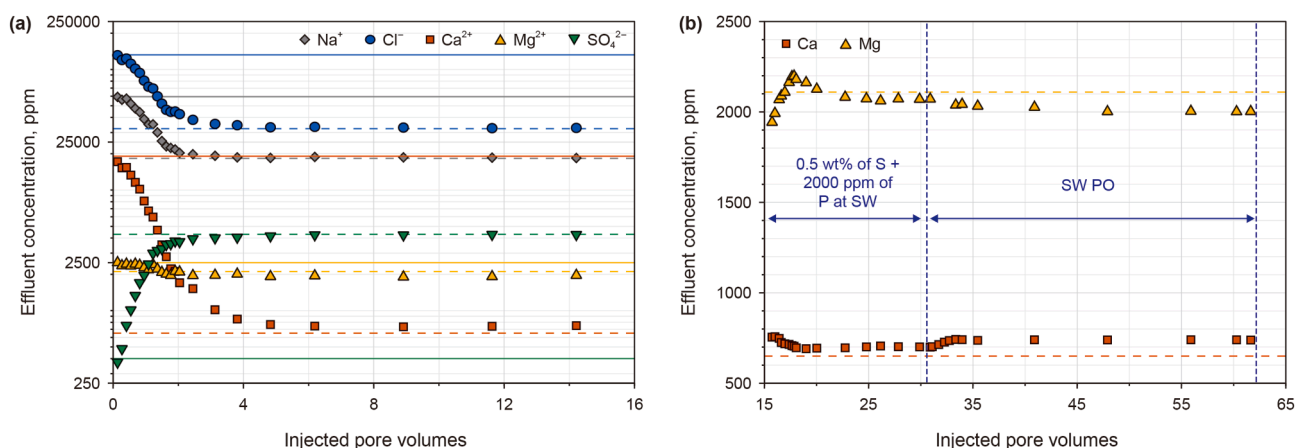
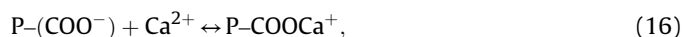


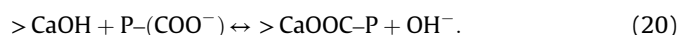
Fig. 16. Effluent inorganic composition for Sample #3 during seawater conditioning and subsequent SP flooding: (a) effluent ion concentrations during the seawater preflush (SW PR), measured by IC (Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-}); (b) effluent Ca and Mg concentrations during injection of 0.5 wt% OPAC and 2000 ppm ATBS-based polymer in SW followed by the SW postflush (SW PO), reported as total dissolved elemental concentrations measured by ICP-OES. Solid horizontal lines show the composition of the initial formation water (FW), and dashed horizontal lines show the composition of the injected SW for each species.



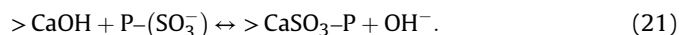
where $\text{P-(COO}^-)$ denotes any hydrolysis-generated carboxylate site on the polymer chain. Together, Eqs. (16) and (17) describe a Ca-centered complexation-and-bridging pathway in which part of the excess dissolved Ca is first captured by a polymer carboxylate site and then incorporated into a Ca-bridged polymer-carbonate interfacial complex. By the same logic, ATBS sulfonate sites can also participate in a parallel Ca-mediated sequence, although this route is expected to be weaker than the carboxylate analog, because Ca binds sulfonate less strongly than carboxylate, and sulfonated polymers generally show lower retention and better tolerance to divalent ions than carboxylate-rich HPAM systems (Rashidi et al., 2011; Zhao et al., 2018):



where $\text{P-(SO}_3^-)$ is the ATBS sulfonate site on the polymer chain. Moreover, beyond the Ca-bridge pathway, carbonate-specific AFM and MD studies also support direct adsorption of anionic polymer sites at positive calcium-type surface sites on calcite (Ekanem et al., 2021; Hue et al., 2023; Lew et al., 2024). Hue et al. (2023) demonstrated that direct polymer–mineral interaction is dominated by short-range oxygen–calcium attraction, with ionized carboxylate groups contributing most strongly at the surface Ca layer. However, Lew et al. (2024) further indicated that, under saline conditions, polymer adsorption on calcite is not governed solely by direct contact between anionic groups and surface Ca sites, but by the combined effect of direct oxygen–calcium attraction and ion-mediated salt bridging. Accordingly, the direct adsorption pathway written below is best regarded as a specific contact contribution that operates alongside, rather than instead of, the Ca-associated bridging routes described earlier. Together with surface-complexation descriptions that place carboxylate adsorption at hydrated calcium sites (Bonto et al., 2022; Hosseinzadehsadati et al., 2024) and the well-established strong affinity of carboxylic acid groups for calcite (Claesson et al., 2024), this supports writing direct polymer carboxylate adsorption in the same ligand-exchange form already adopted for OPAC rather than as a merely diffuse electrostatic interaction:



An analogous direct calcium-site reaction can also be written for ATBS sulfonate groups. Wang et al. (2022) showed by FTIR/XPS that surface Ca^{2+} is the main adsorption site for sulfonic acid groups on calcite, so a direct sulfonate–calcium surface complex is chemically plausible. However, Lew et al. (2024) found that sulfonated PAM adheres less strongly to CaCO_3 than HPAM and attributed this to the bulky ATBS/sulfonate group interfering with efficient surface attachment. The direct sulfonate route is therefore best treated as a weaker analogue of the carboxylate reaction:



Eqs. (16)–(21) also help explain the lower net surfactant retention during polymer coinjection. If polymer carboxylate and sulfonate sites participate in Ca-mediated attachment and direct adsorption at positive calcium sites, then part of the interfacial capacity is occupied by polymer-derived species rather than by OPAC alone. At the same time, polymer binding of dissolved Ca^{2+} can reduce the number of divalent cations available to support OPAC-associated interfacial complexes. In this way, the polymer

may partly act as a sacrificial component by competing for adsorption sites and tying up some divalent ions, thereby reducing surfactant retention. This is consistent with the dynamic-retention results, where net OPAC retention decreases from 0.284 to 0.202 mg/g-rock at SW and from 0.198 to 0.086 mg/g-rock at 10dSW when polymer is present. It is also worth noting that, besides the Ca-mediated and direct calcium-site pathways described above, a secondary contribution from hydrogen bonding is also chemically plausible at the hydrated calcite interface. In particular, amide N–H groups in both acrylamide and ATBS units may donate hydrogen bonds to carbonate-type surface oxygens, whereas amide carbonyl, carboxylate, and sulfonate oxygens may accept hydrogen bonds from proton-bearing surface species such as $>\text{CaOH}$, $>\text{CaOH}_2^+$, and $>\text{CO}_3\text{H}$, and from the structured interfacial water layer. Under aqueous brine conditions, these contacts are best regarded as auxiliary, often water-mediated interactions that can coexist with, but do not replace, the stronger calcium-site complexation and Ca-bridged adsorption routes (Hue et al., 2023).

Furthermore, once SP injection stopped and SW PO began (Fig. 16(b)), calcium started near 700 ppm, increased modestly over the first few pore volumes to about 730–750 ppm, and then fluctuated around that range for the rest of the postflush. Magnesium, in contrast, began near 2030 ppm and remained in a relatively narrow band slightly below the SW value, without the distinct early increase observed during the surfactant-only postflush in Sample #1. Thus, the SW postflush after SP flooding preserved the same overall qualitative signature seen throughout the SW cycle—Ca remaining above SW and Mg remaining below SW—but the magnesium response was clearly more subdued than in the surfactant-only case. In Sample #1, the small early Ca–Mg increase at the onset of SW PO was attributed to the release of OPAC-associated interfacial species as the surfactant bank was displaced and the interface re-equilibrated with seawater. In Sample #3, the absence of a comparable Mg bump suggests that any Mg associated with the SP-conditioned interface was released less abruptly and more progressively during washout. A cautious interpretation is therefore that polymer coinjection did not change the overall direction of divalent-ion redistribution during postflush, but it did dampen the sharpness of the Mg transient and made the SW re-equilibration more gradual than in the surfactant-only flood.

After completing the SW cycle, the brine was switched to 10dSW to establish the low-salinity SP flood. During the 10dSW preflush (Fig. 17(a)), Na^+ and Cl^- shifted from SW to 10dSW values and matched the injected brine after about 4–5 PVs, confirming efficient seawater displacement. Calcium decreased from about 730 ppm to a plateau near 90 ppm, still above the 65 ppm Ca^{2+} in 10dSW. Magnesium declined much more strongly, from about 2000 ppm to roughly 110 ppm, well below the injected 211 ppm. Sulfate decreased from an initial value of about 4830 ppm to a plateau near 346 ppm, below the 429 ppm SO_4^{2-} in 10dSW. Moreover, the initial sulfate level is also noteworthy. During the preceding SW preflush in Sample #3 (Fig. 16(a)), Na^+ and Cl^- shifted cleanly from the FW to the SW values, confirming that the core had been effectively reset to seawater before the SW SP slug began. Additionally, Na^+ remained near the SW level during the SW SP slug and the subsequent SW postflush, confirming that overall salinity was maintained during chemical flooding and the subsequent seawater chase. The sulfate concentration observed at the start of the subsequent 10dSW preflush should therefore be interpreted against that established SW reference state. At the start of Fig. 17(a), the effluent SO_4^{2-} concentration is about 4830 ppm, which is roughly 540 ppm higher than the SW sulfate level of 4290 ppm. This is a clear sulfate excess, indicating that the

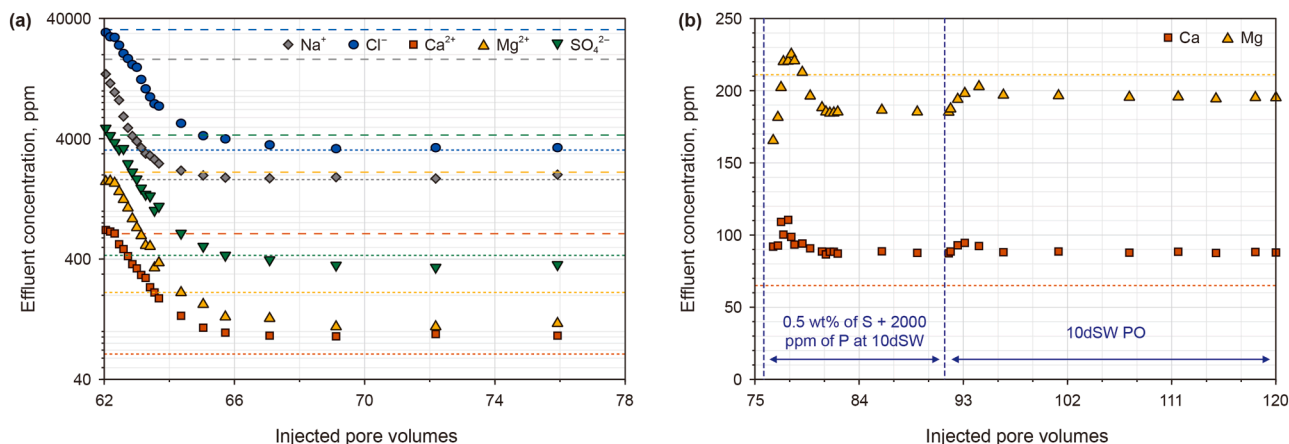
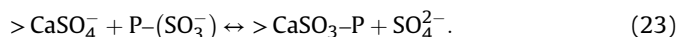


Fig. 17. Effluent inorganic composition for Sample #3 during diluted seawater conditioning and subsequent SP flooding: (a) effluent ion concentrations during the diluted seawater preflush (10dSW PR), measured by IC (Na⁺, Cl⁻, Ca²⁺, Mg²⁺, SO₄²⁻); (b) effluent Ca and Mg concentrations during injection of 0.5 wt% OPAC and 2000 ppm ATBS-based polymer in 10dSW followed by the 10dSW postflush (10dSW PO), reported as total dissolved elemental concentrations measured by ICP-OES. Dashed horizontal lines show the composition of the residing seawater, and dotted horizontal lines show the composition of the injected 10dSW for each species.

resident brine displaced first during the 10dSW PR was not identical to fresh SW but had been chemically modified during the preceding SW SP slug and the SW postflush. This behavior can be understood if sulfate was first adsorbed on calcium-type calcite surface sites during the SW preflush (Eq. (8)) and was then partly displaced during the SW SP stage when OPAC and the polymer contacted the same calcium-bearing interfacial sites. For OPAC, that competition is already represented by Eq. (10). The same type of exchange can also be written for carboxylate sites on the polymer chain:



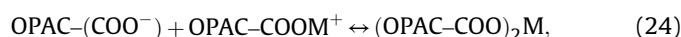
ATBS sulfonate groups can also participate in the same direction of exchange at calcium-type sites:



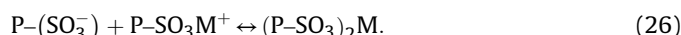
Overall, these exchanges provide a possible explanation for the sulfate excess at the start of the 10dSW preflush. During the SW SP slug and the SW postflush, part of the sulfate inventory associated with calcium-type carbonate surface sites was redistributed into the resident pore brine as OPAC carboxylate, polymer carboxylate, and polymer sulfonate groups competed for those sites. When the brine was switched to 10dSW, the modified resident SW was produced first, giving an initial sulfate level of about 4830 ppm. After this early excess, sulfate declined to a plateau near 346 ppm, below the 429 ppm SO₄²⁻ in injected 10dSW, which is consistent with renewed sulfate uptake as the rock re-equilibrated under the lower-salinity brine. This sulfate deficit developed during the same 10dSW preflush stage in which the normalized effluent and retention data indicate partial remobilization of surfactant and polymer retained during the preceding SW cycle. A cautious interpretation is therefore that lowering salinity may have weakened chemical association with the carbonate surface and, in parallel, may have allowed renewed sulfate uptake at some calcium-type surface sites that became vacated as the interfacial system readjusted to 10dSW.

Furthermore, once the system had been conditioned with 10dSW, the SP slug in 10dSW was injected (Fig. 17(b)). When the SP slug arrives, Ca²⁺ jumps to values around 110 ppm, and Mg²⁺ rises from a strongly depleted state to values close to, and briefly slightly above, the 10dSW Mg level. After this short Ca–Mg “pulse,” both ions relax toward new plateaus: Ca²⁺ declines to a nearly flat level that remains clearly above the 10dSW baseline, while Mg²⁺

drops back to a mild deficit just below the injected concentration. The most likely picture is that, as the low-salinity SP bank arrives, divalent ions are rapidly taken up by the anionic functionalities of the injected chemicals, especially the polymer. For calcium, such aqueous complexation has already been introduced for OPAC in Eq. (11) and for the polymer carboxylate and sulfonate sites in Eqs. (16) and (18), respectively. The same aqueous binding can also occur with Mg²⁺ by direct analogy, so it need not be written out separately here. What matters at this stage is that, once a first 1:1 metal complex has formed, a second anionic site can associate with the same divalent cation, generating a bridged species. For the surfactant, this can be represented as:



where M denotes calcium and magnesium. For the polymer, analogous divalent-ion bridges can form between two carboxylate sites or between two sulfonate sites on the same chain or on neighboring chains:



The divalent-ion bridging given in Eqs. (25) and (26) increases electrostatic screening and reduces the mutual repulsion between anionic polymer groups, promoting a more compact polymer configuration and, consequently, lower solution viscosity (Turkoz et al., 2018). In this context, the comparatively strong resistance of sulfonated polymers to harsh brine conditions is also chemically reasonable, because Ca²⁺ is reported to bind more strongly to carboxylate than to sulfonate groups (Zhao et al., 2018). Consequently, at low salinity, these reactions consume part of the already limited free Ca²⁺ and Mg²⁺ inventory in the injected 10dSW. The resulting decrease in aqueous divalent-ion activity disturbs the equilibrium established during the preceding 10dSW preflush and promotes compensating release of Ca²⁺ and Mg²⁺ from carbonate surface complexes. In the case of calcium, the same perturbation may also favor additional mild calcite dissolution, as already represented by Eq. (7), which further contributes to the transient Ca²⁺ enrichment (Unsal et al., 2018). The observed Ca–Mg pulse at SP arrival can therefore be viewed as the coupled

response of rapid aqueous complexation by surfactant and polymer, followed by compensating desorption and, for Ca^{2+} , possibly some extra mineral release. Once the SP bank is fully established, adsorption of polymer and surfactant on the rock and complexation of divalent ions in the aqueous phase approach a new steady state, and the effluent compositions relax to the elevated-Ca/slightly depleted-Mg pattern characteristic of the low-salinity SP system.

Finally, switching from the SP slug to the 10dSW postflush leads to only modest changes in the divalent profiles (Fig. 17(b)). Sodium stays at the 10dSW level. Calcium starts the postflush around 90–100 ppm and then remains in a narrow band near 90 ppm, consistently above the 65 ppm Ca^{2+} in 10dSW. Magnesium begins slightly below the injected value (≈ 180 –190 ppm), rises over the first few pore volumes to around the 10dSW concentration, and then stays close to 190–200 ppm, generally a bit lower than the 211 ppm Mg^{2+} in the make-up brine.

3.5.3. Mechanistic interpretation of geochemical interactions

Fig. 18 summarizes the interfacial processes that best explain the effluent-ion behavior discussed in Sections 3.5.1 and 3.5.2. The schematics are intended as a conceptual synthesis of the experimental trends developed in the preceding sections rather than as direct molecular-scale proof, and the relative sizes of the species and surface features are not drawn to scale. Fig. 18(a) first separates the main adsorption modes of OPAC on calcite under SW conditions. The most direct route is inner-sphere attachment of the carboxylate moiety to hydrated calcium sites at the surface (callout 1), represented in simplified form by Eq. (9). A second route begins in the aqueous or near-surface region, where Ca^{2+} associates with the OPAC carboxylate (callout 2; Eq. (11)); the resulting Ca-loaded species can then attach to carbonate-type surface sites through a Ca bridge (callout 3; Eq. (12)). In parallel, the quaternary ammonium center of OPAC can associate electrostatically with negatively charged carbonate regions (callout 4; Eq. (13)). This latter pathway is better viewed as interfacial charge association than as a new inner-sphere surface complex, but it can

still alter the local charge environment and trigger ion readjustment near the surface.

After adsorption, OPAC can continue to participate in divalent-ion binding. For molecules attached through the ammonium center, the carboxylate group may remain directed toward the aqueous phase and bind Ca^{2+} or Mg^{2+} at individually adsorbed molecules (callout 5; Eq. (14)). As surface coverage increases, similar ion association can occur within more closely packed OPAC-rich interfacial domains, where accessible carboxylate groups become locally more abundant (callout 6; Eq. (15)). At the same time, development of the OPAC layer can disturb the initial mineral–brine equilibrium. In this way, callout 7 denotes release of Mg^{2+} from previously associated surface complexes as the local interfacial environment is perturbed, whereas callout 8 denotes release of sulfate from calcium-type sites as OPAC carboxylate competes for those sites. These steps are intended as re-equilibration responses rather than strict one-for-one displacement reactions.

Fig. 18(b) extends the scheme to the 10dSW SP flood, where the interfacial chemistry becomes more strongly coupled to polymer-ion interactions. Under these conditions, polymer carboxylate and sulfonate sites provide additional sinks for divalent ions. Callout 9 represents aqueous complexation of Ca^{2+} and Mg^{2+} by anionic sites along the polymer chain; for Ca^{2+} , these interactions are written in Eqs. (16) and (18), while the corresponding Mg^{2+} reactions follow the same logic. Together with the OPAC–divalent association already introduced in callout 2, these polymer reactions consume part of the already limited free divalent-ion inventory in 10dSW. The resulting reduction in aqueous divalent-ion activity shifts the equilibrium established during the preceding low-salinity conditioning step. Callout 10, therefore, represents compensating release of Mg^{2+} from carbonate surface complexes, whereas callout 11 represents calcium release from the rock, including the possibility of additional mild calcite dissolution (Eq. (7)) during re-equilibration.

The low-salinity SP system also introduces direct surfactant–polymer association. In callout 12, the quaternary

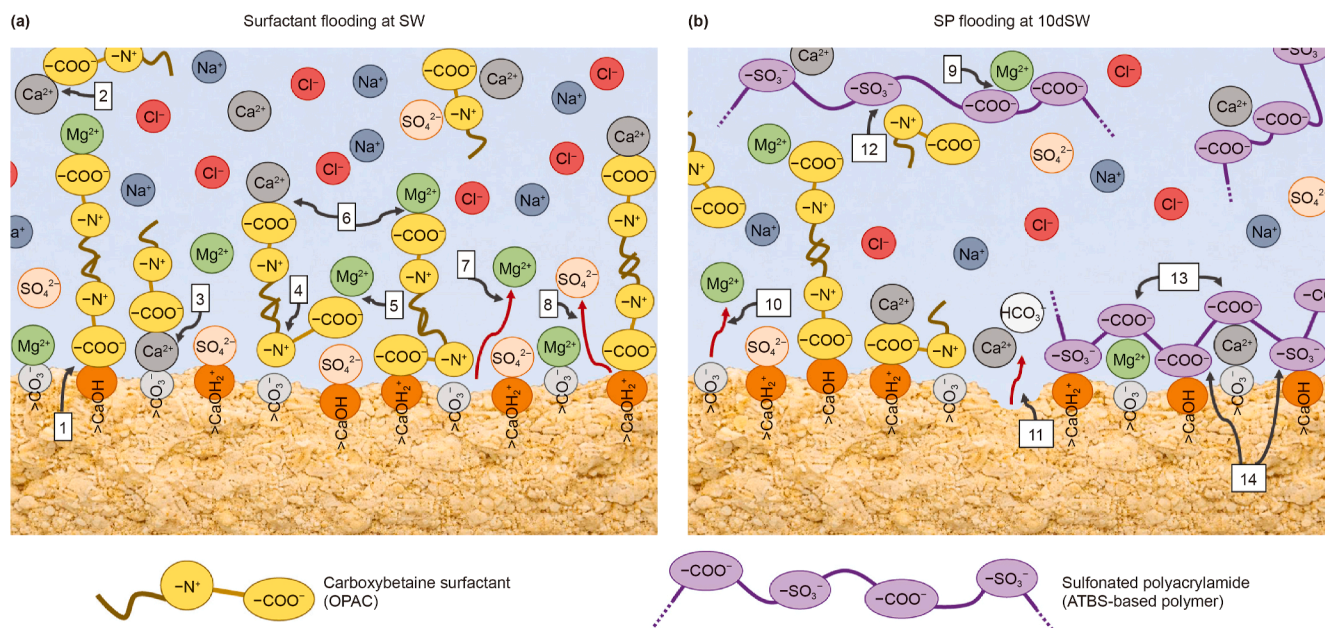


Fig. 18. Proposed mechanisms during surfactant flooding in SW (a) and surfactant–polymer flooding in 10dSW (b) on calcite. The schematic is intended as a conceptual interpretation of the experimental observations rather than a direct molecular-scale depiction, and species and surface features are not to scale. Callouts 1–14 are explained in Section 3.5.3.

ammonium center of OPAC interacts electrostatically with anionic sites on the polymer backbone. This interaction can help explain the slight decrease in viscosity observed for the 10dSW SP solution, as partial charge neutralization can reduce chain expansion and lower the effective hydrodynamic radius of the polymer. The polymer may also compete directly with OPAC for interfacial attachment. Callout 13 denotes adsorption of polymer carboxylate and sulfonate groups at carbonate-type sites through divalent bridges, as represented by Eqs. (17) and (19), respectively. Callout 14 denotes the corresponding direct attachment of these anionic groups at hydrated calcium sites, as described by Eqs. (20) and (21). These polymer pathways occupy calcium-rich adsorption sites and tie up part of the available divalent-ion pool, which helps explain why surfactant retention is lower when polymer is co-injected.

Fig. 18, therefore, describes the system as a continuous redistribution of divalent ions among calcite surface complexes, OPAC-associated interfacial domains, polymer-associated complexes, and the flowing brine. Under SW surfactant flooding, the dominant features are the multiple adsorption modes of OPAC and the ion rearrangement that follows them. After dilution to 10dSW and addition of polymer, the same interface becomes more sensitive to aqueous divalent-ion complexation, surfactant–polymer association, and polymer competition for surface sites, which, in turn, shape the Ca–Mg response and the lower surfactant loss observed during the SP flood.

3.6. Practical implications for chemical-flood design

From a design standpoint, the present results for the zwitterionic carboxybetaine surfactant and the ATBS-based polymer suggest that SW and 10dSW should not be viewed as competing candidates for a single optimal makeup brine, but rather as two stages that can play different roles within a single chemical-flood design. In this system, SW is the more suitable brine for the first active chemical contact, as earlier screening showed that OPAC primarily acts as a wettability modifier and exhibits its strongest interfacial response in SW (Zeynalli et al., 2025). In particular, 0.5 wt% OPAC reduced the contact angle on oil-aged Indiana limestone from 162° to 32° in SW, while also giving lower IFT than in 10dSW. At the same time, our single-phase coreflooding experiments showed that lowering salinity to 10dSW reduced surfactant and polymer retention and, for SP, strengthened mobility control. The practical design question is therefore not whether SW or 10dSW is universally better, but how to balance stronger first-contact wettability conditioning in SW against better chemical propagation and lower retention in 10dSW. In that sense, the present results are consistent with prior literature (Spildo et al., 2014), which shows that chemical flooding design is often a compromise between interfacial performance and retention, rather than a simple preference for a single makeup brine.

This compromise also has a direct implication for flood sequencing. If the process begins with an SW cycle, the first chemical slug at this salinity would mainly weaken oil–rock adhesion in the brine environment, which gives the strongest initial interfacial response. A same-salinity SW postflush could then be applied immediately after the SW chemical slug, before any switch to 10dSW. From a design standpoint, keeping the chase in SW would maintain the ionic environment under which the initial wettability conditioning was established. Such a postflush would be expected to help continue the displacement of oil already mobilized during the preceding SW chemical stage, while also flushing the mobile fraction of surfactant or surfactant–polymer remaining in the pore space under SW conditions. Because the present experiments are single-phase, this should be

understood as a mechanistically reasonable design expectation rather than as a directly demonstrated oil-production outcome of the current study. Consequently, the first SW cycle may be interpreted as the principal wettability-conditioning and first oil-mobilization stage, rather than as the stage that must also minimize chemical loss or retention. This distinction is important for design because it means that the first cycle does not have to satisfy all objectives simultaneously.

If the sequence is then shifted to diluted seawater after completion of the SW cycle, the role of the 10dSW preflush would extend beyond simple brine replacement. The single-phase data show that lowering salinity from SW to 10dSW already weakens part of the chemical association established during the preceding SW stage. In the 0.5 wt% surfactant flood, retained surfactant decreased from 0.284 to 0.177 mg/g-rock during the 10dSW preflush; in the SP flood, retained surfactant decreased from 0.202 to 0.112 mg/g-rock, while retained polymer decreased from 0.063 to 0.044 mg/g-rock over the same stage. This behavior suggests that the diluted-brine preflush can act as both a desorption/remobilization step and a geochemical readjustment stage, releasing part of the material retained under SW and thereby reducing the chemical carryover into the next injected bank. The accompanying $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{SO}_4^{2-}$ response supports this interpretation, indicating that the 10dSW preflush is not merely a hydraulic displacement step, but part of an active carbonate re-equilibration involving ion exchange, divalent-ion redistribution, and possibly mild calcite dissolution. The sulfate trend is particularly informative during this stage. The observed deficit relative to injected 10dSW may reflect renewed sulfate uptake as the interfacial system readjusts to the lower-salinity brine. This, in turn, suggests that some positively charged calcium surface sites become available again while part of the previously retained surfactant and polymer are released.

Furthermore, once this low-salinity readjustment has occurred, the subsequent 10dSW chemical slug can be assigned a more specific design role. For surfactant-only injection, it serves as a lower-retention propagation bank after the first SW stage has already established a stronger initial interfacial condition. For SP, the same logic becomes even more compelling because, relative to SW, the diluted-brine bank provided substantially stronger mobility control ($\text{RF} = 11.14$ vs. 3.46) while the overall cycle ended at lower net retention for both surfactant and polymer. In design terms, this means that a larger fraction of the injected chemicals remains mobile and available for deeper transport through the rock. This has a direct implication for slug sizing. At a fixed injected chemical mass, a 10dSW SP bank would be expected to propagate active surfactant and polymer farther than an equivalent SW bank. Conversely, if the design target is a similar propagated chemical inventory, the diluted-brine slug should require a smaller volume than under SW. The rheology data also support assigning this role to the 10dSW SP bank, because OPAC caused only a slight viscosity reduction and therefore did not materially undermine the viscosifying contribution of the ATBS polymer. In addition, surfactant and polymer propagated through the core as one bank rather than separating chromatographically, which is favorable for maintaining the intended coupled SP action during transport. In practical terms, the 10dSW chemical slug should not be viewed as a weaker repetition of the preceding SW stage, but as the main propagation-oriented bank of the process, introduced after the first cycle has already established the more favorable initial interfacial condition.

The effluent-ion response during low-salinity SP flooding suggests an additional reason why this second chemical stage might still contribute to oil recovery in future two-phase tests,

even though the strongest contact-angle reduction was previously observed in SW. When the 10dSW SP bank arrived, the transient Ca–Mg pulse indicates that the surfactant and especially the polymer rapidly bound part of the already limited free divalent-ion inventory in the diluted brine. This perturbed the equilibrium established during the preceding 10dSW preflush and promoted compensating release of Ca^{2+} and Mg^{2+} from carbonate surface complexes and, for Ca^{2+} , possibly some additional mild calcite dissolution. The latter interpretation should remain cautious because pH and alkalinity were not measured in the present single-phase study. Even so, mineral dissolution may still be regarded as a complementary mechanism rather than one that can be excluded, and it may complement the lower retention and improved mobility control observed during the low-salinity chemical slug. This view is supported by the limestone spontaneous-imbibition study of Karimi et al. (2016), which linked mineral dissolution to a shift toward more water-wet conditions and to higher oil recovery. However, the same released divalent ions can, in principle, compact an anionic polymer by bridging charged sites and reducing intrachain repulsion, that is, by increasing brine hardness, here understood as the $\text{Ca}^{2+}/\text{Mg}^{2+}$ content of the aqueous phase, with the associated risk of some viscosity loss under low-salinity polymer flooding (Unsal et al., 2018). That said, the present formulation uses an ATBS-rich polymer, and sulfonated polymers are generally more resistant to hardness than carboxylate-rich systems because divalent cations bind more strongly to carboxylate than to sulfonate groups (Zhao et al., 2018; Jouenne, 2020). This is consistent with our own observation that the 10dSW SP slug still delivered a strong mobility response in the study. The same logic extends to the 10dSW postflush. In design terms, that chase should not be treated as a neutral displacement step, but as the stage that preserves the lower-retention state created under diluted brine and continues displacement of the mobile chemical bank under the same ionic environment.

Overall, the present results suggest a hierarchy of practical sequencing options. The most complete design emerging from this study is an SW cycle followed by a diluted-brine cycle: the first stage may establish the more favorable initial oil–rock detachment environment, whereas the second stage may still yield additional oil in a two-phase system through improved chemical propagation, stronger SP mobility control, continued low-salinity geochemical re-equilibration, possibly including some supportive mineral readjustment or mild dissolution, and lower net retention. Reversing the order would appear less attractive in this system. If 10dSW was injected first and followed by SW, the later exposure to higher salinity would be expected to reintroduce the brine environment associated with greater surfactant and polymer retention, thereby sacrificing part of the lower-loss advantage of the diluted stage. However, if operational time, facility constraints, or desalination logistics do not allow a full second chemical cycle, a shortened alternative would still begin with the SW sequence but replace at least the early chase after the SW chemical slug with 10dSW, or another project-qualified diluted seawater, so that chemicals retained under SW are mobilized directly while the flood is accelerated. Such a shortened plan would likely retain part of the benefit of salinity switching, but would also give up part of the additional response that a dedicated 10dSW chemical slug could provide. Finally, the selected 2000 ppm polymer concentration appears adequate for the present non-heavy-oil application and was sufficient to place the injected viscosity in a practical range, but it sits near the lower end of that window. For comparatively heavier oils, or where economics support a more aggressive mobility target, testing higher polymer concentrations would remain justified (Seright and Wang, 2023).

3.7. Limitations and future directions

The findings of this research are most directly applicable to the experimental window studied: high-permeability Indiana limestone, the zwitterionic surfactant OPAC, the ATBS-based polymer, and two seawater-based brines, SW and 10dSW, at 90 °C. Within this scope, the data provide a clear mechanistic picture of how salinity reduction and polymer coinjection affect chemical propagation, retention, mobility response, and effluent-ion evolution. Extension of these trends to other carbonate rocks, especially tighter, more heterogeneous, or dolomitic systems, and to other surfactant or polymer families should therefore be made with care. The same applies to brine design. In this work, the brine change was limited to simple seawater dilution. More targeted brine engineering, with independently adjusted Ca^{2+} , Mg^{2+} , and SO_4^{2-} levels, may shift the balance among adsorption, ion exchange, and mineral dissolution.

A central boundary of the present work is that the corefloods were conducted under single-phase, oil-free conditions. This was necessary to establish a controlled geochemical reference state in which surfactant and polymer breakthrough, dynamic retention, pressure response, and effluent-ion evolution could be attributed directly to carbonate–brine–chemical interactions rather than being overprinted by oil solubilization, emulsion/microemulsion behavior, saturation changes, and evolving wettability during multiphase flow. As a result, the observed retention levels and ion-composition responses should be viewed as upper-bound, oil-free benchmarks. In the presence of crude oil, however, competition for surface sites by polar oil components, possible changes in surface charge, and surfactant partitioning between the oil and aqueous phases may alter chemical retention, divalent-ion redistribution, and the observed mobility and pressure behavior (Bergfreund et al., 2021). These effects may either amplify or mitigate trends observed in the present single-phase reference system. Such a limitation directly motivates the next steps. This study builds on earlier formulation-screening work on OPAC and OPAC–polymer solutions under harsh carbonate conditions, in which IFT reduction, wettability alteration, and rheological parameters were systematically evaluated (Zeynalli et al., 2025). The natural next step is therefore two-phase corefloods using the same formulations and salinity sequence, combined with effluent chemical and inorganic analysis, so that the mechanistic expectations established here can be tested against incremental oil recovery and so that the effluent-ion evolution in the two-phase system can be compared with the single-phase reference established in the present study under reservoir-relevant multiphase conditions.

In parallel, the present dataset provides a strong foundation for a staged modeling workflow that connects laboratory insights to field applications. The first step is to history-match the current single-phase corefloods, because these experiments isolate chemical propagation, dynamic retention, mobility response, and effluent-ion evolution without the added complexity of oil. Once the key geochemical parameters are constrained at that level, the same reactive-transport and surface-complexation framework can be extended to the planned two-phase corefloods and refined against oil recovery, phase behavior, pressure response, and effluent chemistry in the presence of crude oil. A reactive-transport model calibrated in this way would then provide a practical tool for field-scale evaluation and SP process design. It could be used to compare injection sequences, optimize slug size and chase design, to test sensitivity to salinity, rock heterogeneity, wettability state, and reservoir flow conditions, and to evaluate how these factors influence oil recovery, chemical efficiency, and overall field performance.

4. Conclusions

This study links bulk rheology, dynamic surfactant–polymer retention, and detailed effluent ion chemistry to build a mechanistic picture of surfactant–polymer (SP) flooding in Indiana limestone under harsh reservoir conditions. The work comprised three sequential single-phase coreflood designs, each progressing through preflush, chemical-slug, and postflush stages; first sequence in seawater (SW) and then in ten-times diluted seawater (10dSW). The first two corefloods used the zwitterionic carboxybetaine surfactant OPAC alone at 0.5 and 0.1 wt%, and in the third coreflood, the combined SP case, OPAC at 0.5 wt% was used together with a 2000 ppm ATBS-based polymer. The main conclusions are as follows:

- (1) At 2000 ppm, the polymer maintained practical viscosifying power in both SW and 10dSW, and adding 0.5 wt% OPAC caused only a slight viscosity penalty (~5% on average). This small reduction may reflect weak electrostatic interactions between the positively charged center of the zwitterionic surfactant and anionic sites along the polymer chain.
- (2) During SP flooding experiments at 90 °C, the formulations preserved their mobility-control function, yielding resistance factor of 3.46 and 11.14 in SW and 10dSW, respectively, while residual resistance factor remained low at 1.29–1.36. This combination indicates effective in-situ propagation with only modest permeability impairment, consistent with low polymer retention in the high-permeability limestone.
- (3) Overall, surfactant retention remained low and operationally favorable, within about 0.08–0.28 mg/g-rock. Retention decreased with reduced salinity, lower surfactant concentration, and the addition of polymer.
- (4) The small surfactant and polymer increases observed during the 10dSW preflush indicate partial remobilization of material retained in SW as the lower ionic strength and lower $\text{Ca}^{2+}/\text{Mg}^{2+}$ content weaken surface associations. The effluent sulfate deficit observed during the same stage suggests sulfate uptake on positively charged calcite sites, which became available as weakly retained surfactant and polymer were released.
- (5) The drop in effluent Ca during chemical injection at seawater salinity may be attributed to the formation of aqueous Ca–surfactant or Ca–polymer complexes, some of which could attach to the carbonate surface through Ca-mediated interactions. The subsequent trends in Ca and Mg also suggest that a portion of the divalent ions associates with carboxylate-rich surfactant domains on the surface, rather than remaining fully mobile.
- (6) The Ca–Mg pulse when the 10dSW chemical bank arrived shows that low-salinity injection perturbs carbonate equilibrium through rapid divalent-ion complexation, compensating release from surface complexes, and possibly mild calcite dissolution. This argues for using hardness-tolerant polymers in low-salinity carbonate floods, since weaker polymers could suffer larger-than-expected viscosity loss after divalent-ion release.
- (7) Based on the earlier screening study together with the present single-phase coreflooding results, the most promising sequence for future two-phase testing and possible SP design in this system is an SW cycle followed by a 10dSW cycle: the SW cycle would establish the more favorable interfacial/wettability condition, whereas the subsequent 10dSW cycle would propagate the chemicals with lower retention and stronger SP mobility control.

CRedit authorship contribution statement

Mursal Zeynalli: Writing – original draft, Investigation, Conceptualization. **Emad W. Al-Shalabi:** Writing – review & editing, Supervision. **Waleed AlAmeri:** Project administration, Funding acquisition. **Ahmed Eleslambouly:** Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Ahmed, M.E., Sultan, A.S., Al-Sofi, A., et al., 2023. Optimization of surfactant–polymer flooding for enhanced oil recovery. *J. Pet. Explor. Prod. Technol.* 13 (10), 2109–2123. <https://doi.org/10.1007/s13202-023-01651-0>.
- Al-Azani, K., Abu-Khamsin, S., Kamal, M.S., et al., 2023. Enhanced oil recovery in carbonate reservoirs using single component synthesized surfactants under harsh reservoir conditions. *Energy Fuels* 37 (15), 11004–11016. <https://doi.org/10.1021/acs.energyfuels.3c01909>.
- Alagic, E., Skauge, A., 2010. Combined low salinity brine injection and surfactant flooding in mixed–wet sandstone cores. *Energy Fuels* 24 (6), 3551–3559. <https://doi.org/10.1021/ef1000908>.
- Alagic, E., Spildo, K., Skauge, A., et al., 2011. Effect of crude oil ageing on low salinity and low salinity surfactant flooding. *J. Pet. Sci. Eng.* 78 (2), 220–227. <https://doi.org/10.1016/j.petrol.2011.06.021>.
- Alfazazi, U., AlAmeri, W., Hashmet, M.R., 2018. Screening of new HPAM base polymers for applications in high temperature and high salinity carbonate reservoirs. In: Abu Dhabi International Petroleum Exhibition & Conference. <https://doi.org/10.2118/192805-MS>.
- Arellano, A.G.T., Al-Shalabi, E.W., Hassan, A.M., et al., 2025. Geochemical modeling of low salinity polymer flooding for carbonate rocks. *SPE J.* 30 (5), 2819–2836. <https://doi.org/10.2118/218842-PA>.
- Bashir, A., Sharifi Haddad, A., Rafati, R., 2022. A review of fluid displacement mechanisms in surfactant-based chemical enhanced oil recovery processes: Analyses of key influencing factors. *Pet. Sci.* 19 (3), 1211–1235. <https://doi.org/10.1016/j.petsci.2021.11.021>.
- Bazyari, A., Hashemi, A., Soulgani, B.S., 2025. Experimental and theoretical investigation of zwitterionic surfactant adsorption on calcite for enhanced oil recovery. *Sci. Rep.* 15 (1), 22730. <https://doi.org/10.1038/s41598-025-05707-5>.
- Bergfreund, J., Siegenthaler, S., Lutz-Bueno, V., et al., 2021. Surfactant adsorption to different fluid interfaces. *Langmuir* 37 (22), 6722–6727. <https://doi.org/10.1021/acs.langmuir.1c00668>.
- Bonto, M., Eftekhari, A.A., Nick, H.M., 2022. Adsorption of carboxylates on calcite: The coupled effect of calcite–brine and brine–oil interactions. *Energy Fuels* 36 (5), 2688–2700. <https://doi.org/10.1021/acs.energyfuels.1c04093>.
- Bonto, M., Nick, H.M., Eftekhari, A.A., 2021. Thermodynamic analysis of the temperature effect on calcite surface reactions in aqueous environments. *Energy Fuels* 35 (20), 16677–16692. <https://doi.org/10.1021/acs.energyfuels.1c01652>.
- Brady, P.V., Krumhansl, J.L., Mariner, P.E., 2012. Surface complexation modeling for improved oil recovery. In: *SPE Improved Oil Recovery Symposium*. <https://doi.org/10.2118/153744-MS>.
- Claesson, P.M., Wojas, N.A., Corkery, R., et al., 2024. The dynamic nature of natural and fatty acid modified calcite surfaces. *Phys. Chem. Chem. Phys.* 26 (4), 2780–2805. <https://doi.org/10.1039/D3CP04432G>.
- Deng, X., Alotaibi, M.B., Fahmi, M., et al., 2024. Locally synthesized zwitterionic surfactants as EOR chemicals in sandstone and carbonate. *ACS Omega* 9 (42), 43081–43092. <https://doi.org/10.1021/acsomega.4c06804>.

- Deng, X., Shahzad Kamal, M., Patil, S., et al., 2021. Wettability alteration of locally synthesized cationic gemini surfactants on carbonate rock. *J. Mol. Liq.* 344, 117817. <https://doi.org/10.1016/j.molliq.2021.117817>.
- Druetta, P., Picchioni, F., 2020. Surfactant-polymer interactions in a combined enhanced oil recovery flooding. *Energies* 13 (24), 6520. <https://doi.org/10.3390/en13246520>.
- Durán-Álvarez, A., Maldonado-Domínguez, M., González-Antonio, O., et al., 2016. Experimental-theoretical approach to the adsorption mechanisms for anionic, cationic, and zwitterionic surfactants at the calcite-water interface. *Langmuir* 32 (11), 2608–2616. <https://doi.org/10.1021/acs.langmuir.5b04151>.
- Ekanem, E.M., Rücker, M., Yesufu-Rufai, S., et al., 2021. Novel adsorption mechanisms identified for polymer retention in carbonate rocks. *JCIS Open* 4, 100026. <https://doi.org/10.1016/j.jciso.2021.100026>.
- Finneran, D.W., Morse, J.W., 2009. Calcite dissolution kinetics in saline waters. *Chem. Geol.* 268 (1), 137–146. <https://doi.org/10.1016/j.chemgeo.2009.08.006>.
- Gbadamosi, A., Hussai, S.M.S., Kamal, M.S., et al., 2023. Evaluating the potential of zwitterionic surfactants for enhanced oil recovery: Effect of headgroups and unsaturation. *Energy Fuels* 37 (7), 5078–5086. <https://doi.org/10.1021/acs.energyfuels.3c00093>.
- Gbadamosi, A.O., Junin, R., Manan, M.A., et al., 2019. An overview of chemical enhanced oil recovery: Recent advances and prospects. *Int. Nano Lett.* 9, 171–202. <https://doi.org/10.1007/s40089-019-0272-8>.
- Ge, J.-J., Zhang, T.-C., Pan, Y.-P., et al., 2021. The effect of betaine surfactants on the association behavior of associating polymer. *Pet. Sci.* 18 (5), 1441–1449. <https://doi.org/10.1016/j.petsci.2021.08.003>.
- Gerola, A.P., Costa, P.F.A., Nome, F., et al., 2017. Micellization and adsorption of zwitterionic surfactants at the air/water interface. *Curr. Opin. Colloid Interface Sci.* 32, 48–56. <https://doi.org/10.1016/j.cocis.2017.09.005>.
- Ghosh, P., Sharma, H., Mohanty, K.K., 2019. ASP flooding in tight carbonate rocks. *Fuel* 241, 653–668. <https://doi.org/10.1016/j.fuel.2018.12.041>.
- Groenendijk, D.J., van Wunnik, J.N.M., 2021. Surfactant adsorption and ion exchange on calcite surfaces. *Energy Fuels* 35 (10), 8763–8772. <https://doi.org/10.1021/acs.energyfuels.1c00670>.
- Hiorth, A., Cathles, L.M., Madland, M.V., 2010. The impact of pore water chemistry on carbonate surface charge and oil wettability. *Transport Porous Media* 85, 1–21. <https://doi.org/10.1007/s11242-010-9543-6>.
- Hosseinzadehsadati, S., Bonto, M., Mokhtari, R., et al., 2024. Modified salinity waterflooding in chalk reservoirs: A journey from rock and fluid interfaces to field scale applications. *Fuel* 356, 129461. <https://doi.org/10.1016/j.fuel.2023.129461>.
- Hu, X., Li, Y., Sun, H., et al., 2010. Effect of divalent cationic ions on the adsorption behavior of zwitterionic surfactant at silica/solution interface. *J. Phys. Chem. B* 114 (27), 8910–8916.
- Hue, K.Y., Lew, J.H., Myo Thant, M.M., et al., 2023. Molecular dynamics simulation of polyacrylamide adsorption on calcite. *Molecules* 28 (17). <https://doi.org/10.3390/molecules28176367>.
- Hussain, S.M.S., Kamal, M.S., Fogang, L.T., 2019. Synthesis and physicochemical investigation of betaine type polyoxyethylene zwitterionic surfactants containing different ionic headgroups. *J. Mol. Struct.* 1178, 83–88. <https://doi.org/10.1016/j.molstruc.2018.09.094>.
- Jadhawar, P., Saeed, M., 2023. Low salinity water and polymer flooding in sandstone reservoirs: Upscaling from nano-to macro-scale using the maximum energy barrier. *J. Pet. Sci. Eng.* 220, 111247. <https://doi.org/10.1016/j.petrol.2022.111247>.
- Jian, G., Puerto, M., Wehowsky, A., et al., 2018. Characterizing adsorption of associating surfactants on carbonates surfaces. *J. Colloid Interface Sci.* 513, 684–692. <https://doi.org/10.1016/j.jcis.2017.11.041>.
- Jouenne, S., 2020. Polymer flooding in high temperature, high salinity conditions: Selection of polymer type and polymer chemistry, thermal stability. *J. Pet. Sci. Eng.* 195, 107545. <https://doi.org/10.1016/j.petrol.2020.107545>.
- Karimi, M., Al-Maamari, R.S., Ayatollahi, S., et al., 2016. Wettability alteration and oil recovery by spontaneous imbibition of low salinity brine into carbonates: Impact of Mg^{2+} , SO_4^{2-} and cationic surfactant. *J. Pet. Sci. Eng.* 147, 560–569. <https://doi.org/10.1016/j.petrol.2016.09.015>.
- Khan, M.Y., Samanta, A., Ojha, K., et al., 2009. Design of alkaline/surfactant/polymer (ASP) slug and its use in enhanced oil recovery. *Pet. Sci. Technol.* 27 (17), 1926–1942. <https://doi.org/10.1080/10916460802662765>.
- Khan, S., Gbadamosi, A., Norrman, K., et al., 2022. Adsorption study of novel gemini cationic surfactant in carbonate reservoir cores—Influence of critical parameters. *Materials* 15 (7), 2527. <https://doi.org/10.3390/ma15072527>.
- Khlaifat, A.L., Fakher, S., Harrison, G.H., 2024. Evaluating factors impacting polymer flooding in hydrocarbon reservoirs: Laboratory and field-scale applications. *Polymers* 16 (1), 75. <https://doi.org/10.3390/polym16010075>.
- Kumar, A., Mandal, A., 2019. Critical investigation of zwitterionic surfactant for enhanced oil recovery from both sandstone and carbonate reservoirs: Adsorption, wettability alteration and imbibition studies. *Chem. Eng. Sci.* 209, 115222. <https://doi.org/10.1016/j.ces.2019.115222>.
- Lee, Y., Lee, W., Jang, Y., et al., 2019. Oil recovery by low-salinity polymer flooding in carbonate oil reservoirs. *J. Pet. Sci. Eng.* 181, 106211. <https://doi.org/10.1016/j.petrol.2019.106211>.
- Lew, J.H., Hue, K.Y., Matar, O.K., et al., 2024. Atomic force microscopy and molecular dynamic simulation of adsorption of polyacrylamide with different chemistries onto calcium carbonate. *Polymers* 16 (4), 494. <https://doi.org/10.3390/polym16040494>.
- Lindman, B., Antunes, F., Aidarova, S., et al., 2014. Polyelectrolyte-surfactant Association—From fundamentals to applications. *Colloid J.* 76 (5), 585–594. <https://doi.org/10.1134/S1061933X14050111>.
- Liu, S., Masliyah, J.H., 2005. Dispersion in porous media. In: *Handbook of Porous Media*. CRC Press, pp. 99–160.
- Masalmeh, S., AlSumaiti, A., Gaillard, N., et al., 2019. Extending polymer flooding towards high-temperature and high-salinity carbonate reservoirs. In: *Abu Dhabi International Petroleum Exhibition & Conference*. <https://doi.org/10.2118/197647-MS>.
- Mishra, S., Bera, A., Mandal, A., 2014. Effect of polymer adsorption on permeability reduction in enhanced oil recovery. *J. Pet. Eng.* 2014, 395857. <https://doi.org/10.1155/2014/395857>.
- Mosallanezhad, A., Kalantariasl, A., 2021. Geochemical simulation of single-phase ion-engineered water interactions with carbonate rocks: Implications for enhanced oil recovery. *J. Mol. Liq.* 341, 117395. <https://doi.org/10.1016/j.molliq.2021.117395>.
- Mushtaq, M., Al-Shalabi, E.W., AlAmeri, W., 2023. A review on retention of surfactants in enhanced oil recovery: A mechanistic insight. *Geoenergy Sci. Eng.* 230, 212243. <https://doi.org/10.1016/j.geoen.2023.212243>.
- Pal, N., Saxena, N., Mandal, A., 2018. Characterization of alkali-surfactant-polymer slugs using synthesized Gemini surfactant for potential application in enhanced oil recovery. *J. Pet. Sci. Eng.* 168, 283–300. <https://doi.org/10.1016/j.petrol.2018.05.026>.
- Pal, N., Vajpayee, M., Mandal, A., 2019. Cationic/nonionic mixed surfactants as enhanced oil recovery fluids: Influence of mixed micellization and polymer association on interfacial, rheological, and rock-wetting characteristics. *Energy Fuels* 33 (7), 6048–6059. <https://doi.org/10.1021/acs.energyfuels.9b00671>.
- Panthi, K., Mohanty, K.K., 2024. Development of surfactant formulation for high-temperature off-shore carbonate reservoirs. *Front. Chem.* 12. <https://doi.org/10.3389/fchem.2024.1408115>.
- Puerto, M., Hirasaki, G.J., Miller, C.A., et al., 2011. Surfactant systems for EOR in high-temperature, high-salinity environments. *SPE J.* 17 (1), 11–19. <https://doi.org/10.2118/129675-PA>.
- Rashidi, M., Blokhus, A.M., Skauge, A., 2011. Viscosity and retention of sulfonated polyacrylamide polymers at high temperature. *J. Appl. Polym. Sci.* 119 (6), 3623–3629. <https://doi.org/10.1002/app.33056>.
- Sandengen, K., Meldahl, M.M., Gjersvold, B., et al., 2018. Long term stability of ATBS type polymers for enhanced oil recovery. *J. Pet. Sci. Eng.* 169, 532–545. <https://doi.org/10.1016/j.petrol.2018.06.001>.
- Sebastian, A., Mushtaq, M., Al-Shalabi, E.W., et al., 2024. Investigating the effect of water softening on polymer adsorption onto carbonates through single-phase and two-phase experiments. *SPE J.* 29 (9), 4988–5001. <https://doi.org/10.2118/211470-PA>.
- Sebastian, A., Mushtaq, M., Al-Shalabi, E.W., et al., 2025. Measurement of acrylamido tertiary butyl sulfonate polymer retention on limestone by three methods under varying temperature and oil presence. *SPE J.* 30 (1), 409–422. <https://doi.org/10.2118/216662-PA>.
- Seright, R.S., Wang, D., 2023. Polymer flooding: Current status and future directions. *Pet. Sci.* 20 (2), 910–921. <https://doi.org/10.1016/j.petsci.2023.02.002>.
- Shabani, A., Zivar, D., 2020. Detailed analysis of the brine-rock interactions during low salinity water injection by a coupled geochemical-transport model. *Chem. Geol.* 537, 119484. <https://doi.org/10.1016/j.chemgeo.2020.119484>.
- Spildo, K., Sun, L., Djurhuus, K., et al., 2014. A strategy for low cost, effective surfactant injection. *J. Pet. Sci. Eng.* 117, 8–14. <https://doi.org/10.1016/j.petrol.2014.03.006>.
- Standnes, D.C., Austad, T., 2000. Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. *J. Pet. Sci. Eng.* 28 (3), 123–143. [https://doi.org/10.1016/S0920-4105\(00\)00084-X](https://doi.org/10.1016/S0920-4105(00)00084-X).
- Tan, F.-Q., Ma, C.-M., Qin, J.-H., et al., 2022. Factors influencing oil recovery by surfactant-polymer flooding in conglomerate reservoirs and its quantitative calculation method. *Pet. Sci.* 19 (3), 1198–1210. <https://doi.org/10.1016/j.petsci.2022.01.001>.
- Tavassoli, S., Korrani, A.K., Pope, G.A., et al., 2016. Low-salinity surfactant flooding—A multimechanistic enhanced-oil-recovery method. *SPE J.* 21 (3), 744–760. <https://doi.org/10.2118/173801-PA>.
- Turkoz, Y., Perazzo, A., Arnold, C.B., et al., 2018. Salt type and concentration affect the viscoelasticity of polyelectrolyte solutions. *Appl. Phys. Lett.* 112 (20), 203701. <https://doi.org/10.1063/1.5026573>.
- Unsal, E., ten Berge, A.B.G.M., Wever, D.A.Z., 2018. Low salinity polymer flooding: Lower polymer retention and improved injectivity. *J. Pet. Sci. Eng.* 163, 671–682. <https://doi.org/10.1016/j.petrol.2017.10.069>.
- Van Cappellen, P., Charlet, L., Stumm, W., et al., 1993. A surface complexation model of the carbonate mineral-aqueous solution interface. *Geochem. Cosmochim. Acta* 57 (15), 3505–3518. [https://doi.org/10.1016/0016-7037\(93\)90135-J](https://doi.org/10.1016/0016-7037(93)90135-J).
- Wang, Y., Pan, G., Chu, H., et al., 2022. Application of a superplasticizer in scheelite selective flotation from calcite. *Minerals* 12 (4), 483. <https://doi.org/10.3390/min12040483>.
- Yue, L., Pu, W., Zhao, S., et al., 2020. Insights into mechanism of low salinity water flooding in sandstone reservoir from interfacial features of oil/brine/rock via intermolecular forces. *J. Mol. Liq.* 313, 113435. <https://doi.org/10.1016/j.molliq.2020.113435>.
- Zeynalli, M., Al-Shalabi, E.W., AlAmeri, W., et al., 2025. Exploring surfactant-polymer flooding in challenging environments: A study in carbonate reservoirs. In: *SPE Western Regional Meeting*, Garden Grove. <https://doi.org/10.2118/224126-MS>.

- Zhang, P., Tweheyo, M.T., Austad, T., 2007. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} . *Colloids Surf. A Physicochem. Eng. Asp.* 301 (1), 199–208. <https://doi.org/10.1016/j.colsurfa.2006.12.058>.
- Zhao, H., Yang, Y., Wang, Y., et al., 2018. Binding of calcium cations with three different types of oxygen-based functional groups of superplasticizers studied by atomistic simulations. *J. Mol. Model.* 24 (11), 321. <https://doi.org/10.1007/s00894-018-3853-y>.
- Zulkifli, N.N., Mahmood, S.M., Akbari, S., et al., 2020. Evaluation of new surfactants for enhanced oil recovery applications in high-temperature reservoirs. *J. Pet. Explor. Prod. Technol.* 10 (2), 283–296. <https://doi.org/10.1007/s13202-019-0713-y>.