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Full Length Article

Performance evaluation of hybrid polymer-phosphonate scale inhibitors in oilfield water flooding operations

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ABSTRACT

The formation of inorganic scales such as calcium sulfate and barium sulfate during water injection in oilfields can severely impair productivity by clogging pores and reducing rock permeability. This study evaluates the performance of two industrial scale inhibitors—diethylenetriaminepenta (methylene phosphonic acid) (DTPMP) and polyphosphinocarboxylic acid (PPCA)—and their hybrid blends in mitigating scale formation under laboratory and simulated reservoir conditions. Laboratory assessments included scale prediction modeling, static bottle tests, dynamic tube blocking, turbidity, and coreflooding experiments to determine inhibition efficiency, retention behavior, and formation damage potential. Thermodynamic modeling using OLI Studio predicted the maximum scaling tendency at a mixture of 70% injection water and 30% formation water, which was used as the baseline brine for testing. The 50:50 PPCA:DTPMP blend achieved the highest inhibition efficiency (>90%) for both calcium and barium sulfate scales at only 50 ppm, outperforming individual inhibitors. Under dynamic tube blocking conditions, the hybrid system maintained stable pressure profiles, effectively delaying scale nucleation and reducing pressure buildup. Turbidity analyses showed lower light transmittance values (5.6%–6.1%) for the blend, confirming its superior resistance to particle formation and growth. Coreflooding experiments further revealed that the hybrid inhibitor minimized permeability loss to only 5%, compared with 72% in the blank and 9–13% for the single-inhibitor cases. Adsorption/desorption experiments confirmed rapid adsorption (equilibrium in <2 pore volumes) and sustained desorption over 20 pore volumes, indicating strong and prolonged retention. These results demonstrate a positive synergistic effect between the nucleation inhibition mechanism of PPCA and the crystal growth suppression mechanism of DTPMP. The 50:50 hybrid formulation offers a practical, efficient, and economically viable solution for long-term scale management under reservoir conditions.

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1. Introduction

Water injection into oil reservoirs is a widely used secondary technique of pressure maintenance and oil displacement to the production wells. One of the most serious issues during waterflooding is the deposition of various salts, which usually occurs when water is injected into the reservoir and two incompatible waters mix (Gruszka and Nagy, 2023; Hajirezaie et al., 2017; Zhang et al., 2024). Formation of salt nuclei occurs during induction period, which is strongly a function of solution supersaturation. Supersaturation is the primary cause of scale formation and occurs when the concentrations of dissolved components (ions) in a solution are higher than their equilibrium concentrations (Olajire, 2015). In addition to the mixing of formation and injection waters, a solution can also become supersaturated due to changes in conditions such as temperature, pressure, and pH (Hamza et al., 2021; Olajire, 2015). Scale precipitation in production equipment and the near-wellbore region leads to expensive capital and unscheduled routine repairs of wells and significantly reduces their productivity (Khormali et al., 2023). In addition, the rock permeability and porosity are decreased due to blockage of the pores as a result the fluid flow in the reservoirs is restricted and the pressure drop is increased (Khormali et al., 2015; Zolfagharroshan and

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Khamehchi, 2024).

Predicting the scale formation under reservoir conditions is one of the most important stages of its control in the production system (Hamid et al., 2016; Olajire, 2015). Thus, prediction of the intensity and potential for inorganic salt deposition during oil production is a fundamental part of the evaluation conducted to control scaling (Khormali et al., 2025a,b). For this purpose, conducting an analysis of the composition of waters, which determines their tendency to form and deposit salt deposits, is the first stage of monitoring the deposition of inorganic salts (Bijani and Khamehchi, 2019; Kan and Tomson, 2012). There are various methods and software packages for the prediction of scale formation. All methods are based on knowledge of the ionic information of waters and the well and near wellbore conditions (Haghtalab et al., 2014; Tayyebi et al., 2025).

In addition to adsorption, precipitation is another key mechanism of scale inhibitor retention. In this process, inhibitors form sparingly soluble complexes with divalent cations (e.g., Ca^{2+} or Ba^{2+}), leading to the precipitation of inorganic–organic compounds within pore spaces or on rock surfaces. This mechanism is often triggered by changes in pH or temperature during squeeze treatment and is time-dependent. The precipitated inhibitor can gradually redissolve or desorb under varying reservoir conditions (such as ionic strength, pressure, or pH fluctuations), releasing active species back into the aqueous phase. This slow release maintains a protective concentration of inhibitor near the wellbore and within production tubing, thereby providing sustained control of scale nucleation and deposition.

Scale management strategies are generally categorized into removal and prevention methods. Among these, prevention is preferred due to its lower operational cost and higher efficiency in maintaining well productivity (Fernandes et al., 2020; Kamal et al., 2018; Khormali and Ahmadi, 2024). Chemical inhibition using scale inhibitors is the most effective and widely applied preventive approach across various industries (Husna et al., 2022). These inhibitors mitigate the risk of salt formation and precipitation arising from the mixing of formation and injection waters by interfering with the growth and stability of scale nuclei (Kumar et al., 2018; Li et al., 2017). The effectiveness of scale inhibitors is influenced by both physical and chemical conditions of the oilfield environment (Ahmadi et al., 2025; Khormali et al., 2025a,b). Key chemical parameters include the composition and ionic strength of the produced fluids, while important physical parameters comprise temperature, pressure, pH, and flow rate. Additionally, the type of scale strongly affects inhibitor performance, as inhibitors exhibit varying efficiencies toward different salts (Ardakani et al., 2024; Mady et al., 2021). For instance, an inhibitor that performs well against carbonate scales may be less effective for sulfate scales. During squeeze treatments, scale inhibitors prevent scale deposition primarily through adsorption and desorption processes. A higher adsorption capacity and slower desorption rate (or greater inhibitor retention) on the rock surface ensure prolonged protection of the production well (Hoang, 2022; Mpelwa and Tang, 2019). The extent of adsorption and desorption is governed by factors such as the inhibitor's chemical structure, rock mineralogy, reservoir pressure and temperature, pH, and flow conditions (Xu et al., 2022). In addition to adsorption, precipitation is another key mechanism of scale inhibitor retention. In this process, inhibitors form sparingly soluble complexes with divalent cations (e.g., Ca^{2+} or Mg^{2+}), leading to the precipitation of inorganic–organic compounds within pore spaces or on rock surfaces. This mechanism is often triggered by changes in pH or temperature during squeeze treatment and is time-dependent (Jarrahian et al., 2020; Kahrwad et al., 2009). The precipitated inhibitor can gradually redissolve or desorb under varying reservoir conditions (such as ionic strength, pressure, or pH fluctuations), releasing active species back into the aqueous phase. This slow release maintains a protective concentration of inhibitor near the wellbore and within production tubing, thereby providing sustained control of scale nucleation and deposition (Sorbie, 2010; Yan et al., 2015).

Although chemical inhibitors are widely used, non-chemical (or minimally chemical) methods may also offer more alternatives for in-situ scale control. One promising approach is the use of engineered surfaces or coatings that resist crystal adhesion, causing nascent scale to dislodge naturally. Another is ultrasound or mechanical vibration applied to pipelines or wells, which disturbs precipitate nucleation and prevents crystal growth on surfaces. Electrokinetic methods — applying electric fields along the flow path — can influence ion migration and suppress scale formation without added chemicals. In addition, microbial or biologically mediated inhibition is emerging: certain microbes or their metabolites can interfere with crystal nucleation or change local supersaturation conditions, thus reducing scale propensity (Mahmoodi et al., 2023; Mahmoodi and Nick, 2022).

Various inhibitors prevent scale formation through distinct mechanisms. In general, scale inhibitors act either by delaying nucleation or by retarding crystal growth (Huang et al., 2024; Wu et al., 2025). Polymeric inhibitors such as PPCA primarily act as nucleation inhibitors by adsorbing onto active crystal growth sites and dispersing early nuclei, while phosphonate-based inhibitors like DTPMP suppress crystal growth by forming stable complexes with scale-forming cations and modifying crystal morphology (Bisatto et al., 2022; Jarrahian et al., 2020; Liu and Zhang, 2022; Mady et al., 2021; Wang et al., 2022). Previous studies have reported the effectiveness of DTPMP and PPCA under high-temperature and high-salinity conditions, highlighting their thermal stability, adsorption potential, and prolonged retention on reservoir rocks (Ghorbani et al., 2017; Li et al., 2022; Sanni et al., 2019; Wang et al., 2013; Zhang et al., 2018). Combining inhibitors with these complementary mechanisms can therefore provide simultaneous control of nucleation and crystal growth, leading to enhanced scale inhibition performance under variable reservoir conditions. Building on this concept, the present study investigates, for the first time, the synergistic performance of PPCA and DTPMP blends for mitigating calcium and barium sulfate scales under both static and dynamic conditions.

One strategy to enhance scale inhibition is by combining two different types of inhibitors to achieve a synergistic effect. Talebi et al. (2022) investigated mixtures of polymeric and organophosphorus (PBTC) scale inhibitors to prevent barium, calcium, and strontium sulfate scales using static and dynamic experiments. They found that the synergistic effect depended on the mixing ratio and inhibitor concentration, resulting in higher inhibition efficiency and lower required concentrations compared to individual inhibitors. Furthermore, the mixture minimized permeability reduction due to scaling. Similarly, Shaw and Sorbie studied blends of polymeric and phosphonate inhibitors under static conditions for barium sulfate prevention (Shaw and Sorbie, 2015). They reported both positive and negative synergistic effects depending on the inhibitor types and noted that phosphonates primarily inhibit crystal growth, while polymeric inhibitors act predominantly through nucleation prevention. They concluded that combining inhibitors with different mechanisms enhances overall performance and recommended dynamic testing to confirm synergistic effects. Fang et al. (2024) examined ternary polymeric inhibitor mixtures with optimized molar ratios for $CaCO_3$ and $CaSO_4$ prevention. The mixture achieved more than 99% inhibition at low concentrations, with molecular dynamics simulations confirming strong adsorption on surfaces. The authors

highlighted that the occurrence of multiple inhibition mechanisms contributes to the superior performance of blended inhibitors. Zeino et al. (2018) reported that a 1:1 mixture of ATMP and DTPMP effectively inhibited calcium sulfate formation and prolonged the induction period, demonstrating a synergistic effect. Khormali et al. (2021) studied a ternary phosphonate mixture (DTPMP, PBTC, ATMP) for calcium and strontium sulfate inhibition under oilfield conditions. They observed a significant improvement in inhibition performance, with the optimal mixture (40% DTPMP, 20% PBTC, 40% ATMP) extending the induction period of strontium sulfate formation by 400% and increasing the coreflooding protection period by at least 34.6% compared to individual inhibitors.

Phosphonate and polymeric scale inhibitors are widely used in oilfield applications, and their hybrid use can provide enhanced scale prevention by simultaneously targeting nucleation and crystal growth mechanisms. However, the blend of PPCA and DTPMP has not been reported for calcium and barium sulfate inhibition. The primary objective of this study is to evaluate the performance of this blended inhibitor and investigate potential synergistic effects. The study also compares the mixture with individual inhibitors under various operational conditions. A combination of laboratory and modeling approaches is employed. Scale prediction modeling is performed using OLI Studio software to assess saturation indices and precipitation potential for key mineral scales, providing insight into scaling risks for different formation and injection water mixtures. Static bottle tests are conducted to screen inhibitor efficiency, while dynamic tube-blocking tests assess performance under flow conditions. Turbidity measurements monitor the onset and intensity of precipitation, and coreflooding experiments evaluate inhibitor behavior in porous media, including adsorption and retention characteristics. Together, these methods enable a comprehensive assessment of the blended inhibitor's effectiveness under both static and dynamic conditions.

2. Material and methods

2.1. The synthetic formation and injection waters

To simulate operating conditions typical of oilfield systems, synthetic formation and injection waters with the ionic composition of real samples were prepared for testing. The formation water originates from an Iranian oil field (south of Iran), while the injection water used for waterflooding operations in this field is seawater. The ionic compositions of both formation and injection waters were measured experimentally by the authors prior to conducting scale tests. The analyses were performed using standard ion chromatography and titration methods. The measured ionic compositions were similar to those reported in our previous studies (Khormali et al., 2016, 2018, 2022). The synthetic formation water primarily contained high concentrations of calcium (Ca^{2+}) and barium (Ba^{2+}) ions, while the injection water was rich in sulfate (SO_4^{2-}) ions. These solutions were formulated by dissolving analytical-grade salts in deionized water. The ionic strength and pH of each solution were adjusted to match field conditions. The interaction between the two water types during mixing was used to induce scaling tendencies, particularly calcium sulfate and barium sulfate precipitation, which were used to assess the efficiency of the scale inhibitor. The ion contents of these waters are shown in Table 1.

Table 1
The ionic composition of synthetic formation and injection waters.

Ion type	Ion concentration (ppm)	
	Formation water	Injection water
Na^+	32,487	13,280
Ca^{2+}	3548	424
K^+	385	48
Ba^{2+}	407	0
Mg^{2+}	716	1545
Cl^-	71,544	28,965
SO_4^{2-}	112	3418
TDS (ppm)	109,199	47,680

2.2. The scale inhibitors

In this study, two well-known industrial scale inhibitors were used: DTPMP (methylene phosphonic acid) and PPCA (polyphosphino carboxyllic acid). DTPMP is a phosphonate scale inhibitor, while PPCA is a polymeric scale inhibitor. The main idea of this study is the application of these reagents for scale prevention in an optimum mixing ratio by providing both inhibition mechanisms of nucleation and crystal growth. The inhibitors were used at various concentrations in different tests to evaluate the required amount of reagent for an effective scale control. The chemical structure of these inhibitors is shown in Fig. 1.

The scale inhibitor pills were prepared individually for DTPMP, PPCA, and their blends. The carrier brine used in all cases was a mixture of injection and formation waters in a ratio of 70:30, having a pH of approximately 7.05. This mixture provided representative ionic strength and compatibility with the formation conditions. For each inhibitor, the required amount was dissolved in the carrier brine to obtain the target concentration, and the solution was gently stirred at ambient temperature to ensure complete homogeneity. The prepared solutions were degassed to remove air bubbles prior to injection to prevent flow disturbances during coreflooding. Moreover, the pills were prepared by dissolving the desired concentrations of the inhibitors in the mixed brine without any additional pH adjustment. The average pH of the prepared pills after dissolving the scale inhibitors was approximately 4. During the coreflooding experiments, the effluent pH gradually increased toward near-neutral values, primarily due to carbonate dissolution and buffering reactions that occurred at the rock–brine interface.

2.3. Rock samples

The coreflooding tests were conducted for prevention of scale precipitation under dynamic conditions. For this purpose, the carbonate core samples were used (diameter of 2.5 cm, and length of 4 cm). The carbonate core samples used in the experiments were composed predominantly of calcite (limestone) (approximately 86%), representing the main mineral phase, with a minor proportion of dolomite (around 8%). Trace amounts of quartz, clay minerals, and pyrite (together about 6%) were also detected. Prior to use, the cores were cleaned using a Soxhlet extraction process with a mixture of toluene and methanol to remove any residual hydrocarbons and salts. They were then dried in an oven at 65 °C until a constant weight was achieved. The porosity and permeability of each core were measured using helium porosity and gas permeability, respectively, to ensure uniformity among samples.

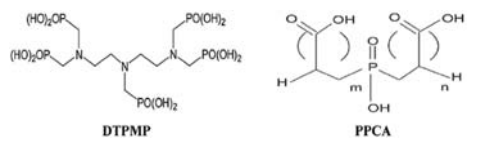


Fig. 1. The chemical structure of DTPMP and PPCA used as scale inhibitors.

The average porosity and permeability of the rock samples before salt precipitation were 19% and 27 mD. These core samples were employed in dynamic flow tests to evaluate the performance and retention of the scale inhibitor under simulated reservoir conditions.

2.4. The method of scale predication

Scale formation potential was evaluated using the OLI Studio software, a thermodynamic modeling tool widely applied for predicting scaling tendencies in oilfield systems. The software calculates the saturation index of various mineral scales based on input parameters such as water chemistry, temperature, and pressure. In this study, reservoir conditions of 10 MPa and 70 °C were used to simulate realistic scaling environments. The saturation indices of calcium sulfate ($CaSO_4$) and barium sulfate ($BaSO_4$) were calculated according to equations (1) and (2). A positive saturation index value indicates a supersaturated state and potential for precipitation, whereas a negative value suggests undersaturation and no scale formation (Kan and Tomson, 2012).

$$\text{For } CaSO_4 : \text{Saturation index} = \log\left(\frac{\left[Ca^{2+}\right] \times \left[SO_4^{2-}\right]}{K_{SP}}\right) \quad (1)$$

$$\text{For } BaSO_4 : \text{Saturation index} = \log\left(\frac{\left[Ba^{2+}\right] \times \left[SO_4^{2-}\right]}{K_{SP}}\right) \quad (2)$$

where K_{sp} is the solubility product, $[Ca^{2+}]$, $[SO_4^{2-}]$, and $[Ba^{2+}]$ represent the concentrations of calcium, sulfate, and barium ions in the solution (ppm).

To assess the influence of water mixing on scale formation, different mixing ratios of formation and injection waters were modeled, ranging from 0% to 100% injection water content. This approach allowed identification of the worst-case scaling conditions for calcium and barium sulfate. For each mixing scenario, the software provided both the saturation index and the predicted amount of scale precipitation (in ppm). These results were analyzed to determine the conditions most prone to scale formation. The identified worst-case scenario was subsequently used as the basis for laboratory-scale static and dynamic tests, ensuring that experimental evaluations reflected the most critical scaling environment predicted by the model.

2.5. Static bottle test for scale inhibitor efficiency

The efficiency of the scale inhibitors was evaluated using the static bottle test method, a well-established laboratory procedure for simulating scale formation under controlled conditions. This method provides a reliable and reproducible means of assessing an inhibitor's ability to prevent scale precipitation in static environments. In this work, synthetic brine solutions containing scaling ions were prepared based on the ionic compositions of the formation and injection waters. The brines were mixed at a 70:30 ratio of injection to formation water, representing the expected reservoir mixing condition. Separate tests were conducted for calcium sulfate and barium sulfate scaling systems. The tested inhibitors included PPCA, DTPMP, and their mixtures at different volume ratios: 30% PPCA: 70% DTPMP, 50% PPCA: 50% DTPMP, and 70% PPCA: 30% DTPMP, to determine the most effective blend. For each system, the scale inhibitors were added to the prepared working solution in a concentration range from 0 ppm (blank) to 80 ppm. The solutions were then transferred into sealed glass bottles and placed in a thermostatic water bath maintained at 70 °C (representative reservoir temperature) for 24 h without agitation. After incubation, the solutions were filtered or carefully decanted to separate any precipitated solids. The residual concentration of scaling cations—Ca^{2+} for calcium sulfate and $Ba2^{+}$ for barium sulfate—was determined using ethylenediaminetetraacetic acid (EDTA) complexometric titration. The scale inhibition efficiency (%) was then calculated by comparing the residual calcium or barium ion concentrations in the presence and absence of the inhibitor, according to the standard formulas:

$$\text{For } CaSO_4 : \textit{Scale inhibition efficiency} = \frac{\left[Ca^{2+}\right]_{inhibited} - \left[Ca^{2+}\right]_{blank}}{\left[Ca^{2+}\right]_{initial} - \left[Ca^{2+}\right]_{blank}} \times 100 \quad (3)$$

$$\text{For } BaSO_4 : \textit{Scale inhibition efficiency} = \frac{\left[Ba^{2+}\right]_{inhibited} - \left[Ba^{2+}\right]_{blank}}{\left[Ba^{2+}\right]_{initial} - \left[Ba^{2+}\right]_{blank}} \times 100 \quad (4)$$

where $[Ca^{2+}]_{inhibited}$, $[Ca^{2+}]_{blank}$, and $[Ca^{2+}]_{initial}$ denote the calcium ion concentrations in the presence of inhibitor, without inhibitor (blank test), and before the test begins (initial condition), respectively. The same notation applies to barium ion concentrations.

Prior to and after the tests, the pH of all solutions was measured to ensure consistent experimental conditions. The results from these static bottle tests were used to identify the effective concentration of each inhibitor and the optimal mixing ratio of PPCA and DTPMP that provided the highest inhibition efficiency for both calcium and barium sulfate scales.

2.6. Dynamic tube blocking test

The dynamic tube blocking test was conducted to evaluate the performance of the scale inhibitors under dynamic flow conditions simulating field operations. This test provides a reliable means of assessing the inhibitor's ability to delay or prevent scale deposition and blockage within production tubing, and it is also used to determine the minimum inhibitor concentration (MIC)—the lowest concentration at which no significant pressure increase is observed over the test duration.

A stainless-steel capillary coil with an internal diameter of 1 mm and length of 1 m was used as the test section. Synthetic brine solutions, representing formation and injection waters, were prepared and mixed in a ratio of 70:30 (injection/formation water) to replicate field conditions. The mixed brine was continuously pumped through the coil using a high-pressure pump system. The flow rate was maintained at 5 mL/min, and the temperature was fixed at 70 °C. Tests were performed separately for PPCA, DTPMP, and their 50:50 PPCA:DTPMP blend at concentrations of 0, 20, 40, and 60 ppm. The pressure drop across the coil was continuously monitored using a precision differential pressure transducer. The onset and rate of pressure increase indicated the initiation and progression of scale deposition. When the pressure drop reached a critical high value, signifying near-complete blockage of the coil, the injection was stopped. The blocking time, defined as the time required to reach the critical pressure drop, was recorded for each test. The MIC was identified as the lowest inhibitor concentration at which the pressure drop remained stable (constant) throughout the entire 90-min test period, indicating complete suppression of scale formation under dynamic conditions. Longer blocking times or constant pressure profiles signify higher inhibition performance. To ensure reproducibility, each test was repeated three

times, and the average pressure was reported. Between tests, the coil was thoroughly cleaned by acid flushing followed by deionized water rinsing to remove any residual scale or inhibitor and restore baseline flow conditions.

2.7. Turbidity test

The turbidity test was conducted to evaluate the efficiency of scale inhibitors in preventing salt precipitation under static conditions. Turbidity, an indicator of water clarity and the extent of suspended particulate matter, directly reflects the degree of scale formation in the solution. Measurements were performed using the nephelometric method with a HACH 2100P turbidity meter, which detects the intensity of light scattered at a 90° angle by suspended particles in the brine samples. The tests were carried out using a mixture of 70% injection water and 30% formation water, corresponding to the worst-case scaling condition predicted by OLI Studio modeling. Three inhibitors were evaluated: PPCA, DTPMP, and their 50:50 PPCA:DTPMP blend, at concentrations of 60 ppm, 60 ppm, and 40 ppm, respectively. These concentrations were selected based on the results of the static bottle tests and dynamic tube blocking experiments, which identified the most effective dosage for each inhibitor.

For each test, the synthetic brine solutions were prepared under identical ionic compositions and maintained at a constant temperature of 70 °C. The inhibitors were added to the brine immediately before testing, and the solutions were gently mixed to ensure homogeneity. The total test duration was 60 min. During this period, samples were collected at predetermined time intervals and analyzed for turbidity to monitor the onset and progression of scale precipitation. Prior to measurement, the turbidity meter was calibrated using standard reference solutions, and all samples were handled in clean glass cuvettes to minimize interference from fingerprints or air bubbles. Turbidity values were expressed as light transmittance. Each measurement was conducted in triplicate to ensure accuracy and reproducibility, and the average values were reported. Higher turbidity (or lower transmittance) indicated greater inhibition efficiency and lower scale formation tendency.

2.8. Coreflooding tests

2.8.1. Permeability tests

Coreflooding experiments were conducted to evaluate the extent of formation damage caused by scale deposition and to assess the effectiveness of scale inhibitors in mitigating permeability reduction under dynamic flow conditions representative of near-wellbore environments. Cylindrical carbonate core samples (2.5 cm diameter, 4 cm length, average porosity 19%) were first cleaned using solvent extraction to remove residual hydrocarbons, then dried in an oven at 60 °C until constant weight. The pore volume (PV) of each sample was calculated to be approximately 3.7 mL ($PV = \pi \times 1.25^2 \times 4 \times 0.19 = 3.7$ mL). The cores were then saturated with synthetic formation water under vacuum to eliminate trapped air and simulate in-situ reservoir conditions. The coreflooding apparatus was equipped with a high-pressure pump, a core holder, and differential pressure transducers connected to a data acquisition system for real-time monitoring. The baseline permeability of each core was first determined by injecting synthetic brine at a constant flow rate of 5 mL/min, corresponding to near-wellbore flow conditions. The permeability was calculated using Darcy's law based on the measured differential pressure. After establishing the baseline, a mixture of 70% injection water and 30% formation water was injected to induce scale precipitation within the core. Separate runs were performed with and without scale inhibitor to assess its performance. Three scale inhibitors were evaluated: PPCA, DTPMP, and their 50:50 PPCA:DTPMP blend, applied at concentrations corresponding to their minimum inhibitor concentration (MIC) values determined from the dynamic tube blocking tests—namely, 60 ppm, 60 ppm, and 40 ppm, respectively. The pressure drop across the core was continuously recorded during injection, and permeability after scaling was again determined from Darcy's equation. The tests were carried out at a constant temperature of 70 °C and an injection rate of 5 mL/min. A total of five pore volumes (5 PV) were injected during each test, corresponding to a total injected volume of 18.5 mL (5 × 3.7 mL) and an injection duration of approximately 3.7 min. The extent of formation damage was quantified by calculating the ratio of the damaged permeability after scaling to the initial permeability before scale formation. A smaller reduction in permeability indicated higher inhibition efficiency and better formation protection. After each run, the system was flushed with deionized water to remove residual brine and inhibitor before the next experiment. The coreflooding procedure enabled a quantitative assessment of the scale inhibitor's ability to preserve permeability, control scale deposition, and minimize formation damage under realistic flow and temperature conditions.

2.8.2. Adsorption/desorption tests

Squeeze treatment is a widely used method for placing scale inhibitors into the near-wellbore region to provide long-term protection against scale formation (Vazquez et al., 2016). To simulate this process under controlled laboratory conditions, coreflooding experiments were performed using reservoir-representative carbonate core samples. These tests enabled a quantitative evaluation of the adsorption and desorption behavior of scale inhibitors during dynamic flow, serving as a model for field-scale squeeze performance. The cleaned and oven-dried cores were first saturated with synthetic formation water to establish baseline flow characteristics. Subsequently, the inhibitor solution (the mixture of 70% injection water and 30% formation water with scale inhibitor) was injected at a constant flow rate of 5 mL/min under controlled differential pressure to mimic field squeeze operations. The adsorption stage was conducted over five pore volumes (5 PV), corresponding to a total injected volume of 18.5 mL, consistent with the formation damage tests described earlier. Following inhibitor injection, a shut-in period of 24 h was maintained to allow adequate contact time for inhibitor adsorption onto the rock surface. This step facilitates the formation of a stable adsorbed layer capable of slowly releasing inhibitor molecules during subsequent production. During the adsorption stage, PPCA, DTPMP, and their 50:50 blend were tested at concentrations of 60, 60, and 40 ppm, respectively—values selected based on the optimal concentrations identified from the bottle test and dynamic tube blocking experiments. During the desorption stage, only injection water was injected (a total of 20 PV, equivalent to 74 mL at a constant rate of 5 mL/min) without adding formation water or inhibitor, allowing the study of inhibitor release kinetics.

Effluent samples were collected at the outlet of the core holder throughout both adsorption and desorption stages. The inhibitor concentrations were quantified using analytical techniques specific to the inhibitor type: Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) for phosphorus-based DTPMP and Total Organic Carbon (TOC) analysis for polymeric PPCA. These measurements provided real-time data on inhibitor breakthrough and retention. The adsorption capacity was determined from the difference between the injected and recovered inhibitor concentrations. The variation of C/C_i (ratio of effluent concentration to initial injected concentration) with injected pore volumes was plotted for both adsorption and desorption stages. These profiles

were used to evaluate the retention efficiency, return concentration, and to predict the effective squeeze lifetime of each inhibitor system. This method provided a robust assessment of inhibitor-rock interactions, revealing the ability of each formulation (PPCA, DTPMP, and their blend) to adsorb effectively and maintain controlled desorption for prolonged scale protection under simulated reservoir conditions.

In addition, the amount of adsorbed scale inhibitor per mass of core samples was examined during adsorption stage. For this purpose, a material balance calculation was performed to quantify adsorption, as described below (applied for a constant initial concentration).

$$V = PV \times 3.7/1000 \tag{5}$$

$$C_{\text{adsorbed}} = C_t - C \tag{6}$$

The combination of equations (5) and (6) gives the next formula, which was used for determination of inhibitor adsorption per mass of rock samples:

$$\frac{m_{adsorbed}}{mass\ rock} = \frac{C_{\text{adsorbed}} \times V}{m_{rock}} = \frac{(C_t - C) \times \frac{(PV \times 3.7)}{1000}}{m_{rock}} \tag{7}$$

where is V the total volume of injected solution (L); 3.7 represents the volume of one pore volume (PV, mL); 1000 is the conversion factor from mL to L; $C_{adsorbed}$ is the concentration of the adsorbed scale inhibitor (ppm); C_t is the total injected inhibitor concentration (ppm); C is the total inhibitor concentration that has left the system through effluent (ppm); $m_{adsorbed}$ is the mass of the adsorbed inhibitor (mg); and m_{rock} is the dry mass of the core sample (42 g).

3. Results and discussion

3.1. Selection of best mixing ratio of injection and formation water

Fig. 2a and b illustrate the effect of varying the percentage of injection water mixed with formation water on the saturation index and salt precipitation of $CaSO_4$ and $BaSO_4$ scales at a constant temperature of 70 °C and pressure of 10 MPa. The x-axis in both graphs represents the proportion of injection water in the water mixture, ranging from 0% to 100%.

The saturation index (Fig. 2a) and salt precipitation values (Fig. 2b) were calculated using scale prediction software to assess scaling tendency. In Fig. 2a, the saturation index of both $CaSO_4$ and $BaSO_4$ increases with increasing injection water up to a critical point, followed by a gradual decline. The maximum saturation index for $CaSO_4$ is approximately 2.9, occurring at around 70% injection water. $BaSO_4$ scale shows a peak saturation index of approximately 2.0 at about also 70% injection water content. These results suggest that scale formation tendency intensifies as the mixing ratio of injection to formation water approaches 70% for both salts. Fig. 2b presents the predicted salt precipitation in ppm for both scales as a function of injection water percentage. $CaSO_4$ precipitation increases sharply with injection water, reaching a peak near 860 ppm at 70% injection water before declining. $BaSO_4$ precipitation follows a similar trend, with a maximum of about 520 ppm observed at 70% injection water. These findings are consistent with the trends observed in saturation indices, confirming the predictive accuracy of the software. Thus, the brine, which is used for the scale inhibition analysis is the mixture of 70% injection water and 30% formation water. This ion content and TDS of this brine is shown Table 2. It should be noted this ionic composition of working brine was calculated using ion concentration of formation (30%) and injection (70%) waters in Table 1. It should be noted that he measured pH was 7.65 for the injection water, 6.45 for the formation water, and 7.05 for the mixed brine (70% injection water and 30% formation water) used in both the static and dynamic experiments.

It is important to note that the minor precipitation predicted for the pure formation and injection waters (at 0% and 100% injection water) in Fig. 2b does not indicate that these fluids were unstable in isolation. Rather, this arises from the equilibrium assumptions used in the OLI Studio simulation, where slight supersaturation is predicted under reservoir conditions (70 °C and

Table 2
The ionic composition of mixture brine (70% injection water with 30% formation water).

Ion type	Ion concentration (ppm)
Na^+	19402.1
Ca^{2+}	1361.2
K^+	149.1
Ba^{2+}	122.1
Mg^{2+}	1296.3
Cl^-	41738.7
SO_4^{2-}	2426.2
TDS (ppm)	66135.7

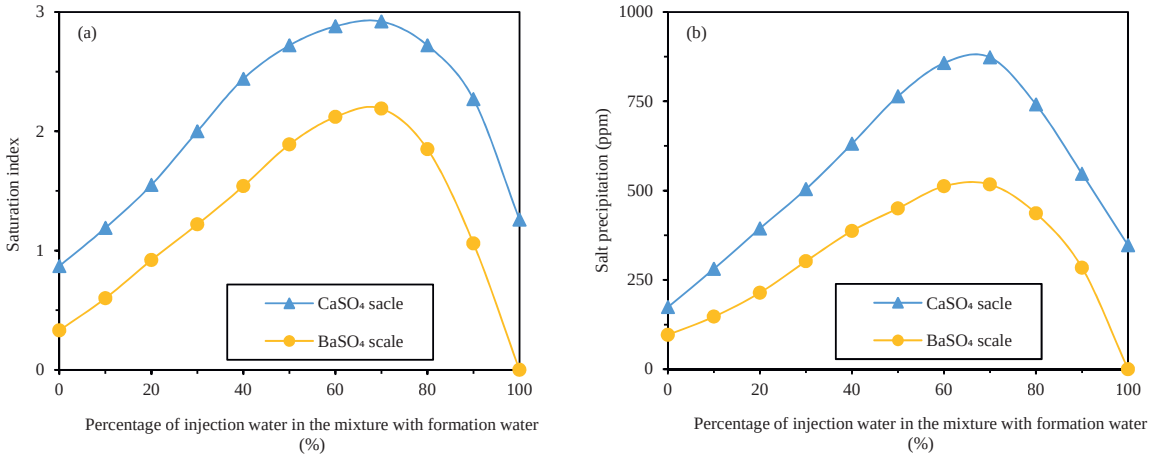


Fig. 2. Saturation index (a) and predicted salt precipitation (b) of $CaSO_4$ and $BaSO_4$ scales as a function of injection water proportion in mixed brine systems.

10 MPa). In particular, both the injection and formation waters contain significant concentrations of calcium and sulfate ions, which under these temperature and pressure conditions can lead to limited CaSO4 precipitation even without blending. In experimental practice, both waters are considered individually stable and close to equilibrium prior to mixing. Therefore, the observed precipitation in the simulation represents the potential for scale formation under thermodynamic constraints rather than actual scaling expected in single-brine systems.

The decrease in scale precipitation beyond the peak values suggests solubility effects or ionic strength adjustments in the solution mixture. At 100% injection water, both $CaSO_4$ and $BaSO_4$ precipitations drop significantly, nearing 300 ppm and 0 ppm respectively. The sharp decline in $BaSO_4$ precipitation at high injection water ratios reflects the absence of barium ions typically present in formation water. The curves highlight that the co-mixing of injection and formation waters introduces favorable conditions for sulfate scale formation. The interaction between calcium or barium from formation water and sulfate from injection water is likely responsible for the observed scale profiles. These results emphasize the importance of water compatibility assessments during waterflooding operations. Understanding the scaling potential at various injection ratios is crucial for selecting appropriate scale mitigation strategies.

3.2. Bottle test

Fig. 3 illustrates the inhibition efficiency of calcium sulfate and barium sulfate scale formation using individual and blended inhibitors, measured by the static bottle test method at a constant temperature of 70 °C. The performance of two widely used inhibitors—diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and polyphosphinocarboxylic acid (PPCA)—was evaluated across a concentration range of 10–80 ppm, along with their mixtures in three different weight ratios: 30% PPCA:70% DTPMP, 50% PPCA:50% DTPMP, and 70% PPCA:30% DTPMP.

In this study, the scale inhibitor pill was prepared using a mixture of formation (30%) and injection (70%) waters to simulate the near-wellbore environment, where these fluids typically interact during squeeze operations. This approach provides a more realistic representation of the chemical conditions encountered in the reservoir during inhibitor placement and release. The mixed brine composition reproduces the potential ion-exchange and precipitation effects (particularly involving Ca^{2+}, Ba^{2+}, and SO_4^{2-} ions) that influence inhibitor performance.

As shown in Fig. 3a for calcium sulfate scale inhibition, both DTPMP and PPCA demonstrated increasing inhibition efficiency with increasing concentration, reaching about 88% and 86% inhibition, respectively, at 80 ppm. In this case, the optimum concentration of individual inhibitors is 60 ppm, and there are no significant changes in the inhibition efficiency with further increase in the dosage. Moreover, the mixed formulations displayed superior performance at lower concentrations due to synergistic interactions between the phosphonate and polymeric functional groups (Jafar Mazumder, 2020). The mixture containing 50% PPCA and 50% DTPMP exhibited the highest inhibition efficiency, achieving more than 90% inhibition at just 50 ppm, which surpasses the performance of the individual components at the same concentration. This enhanced efficiency may be attributed to a synergistic mechanism, where DTPMP acts primarily through threshold inhibition and crystal distortion mechanisms, while PPCA interferes with nucleation by adsorbing onto active crystal

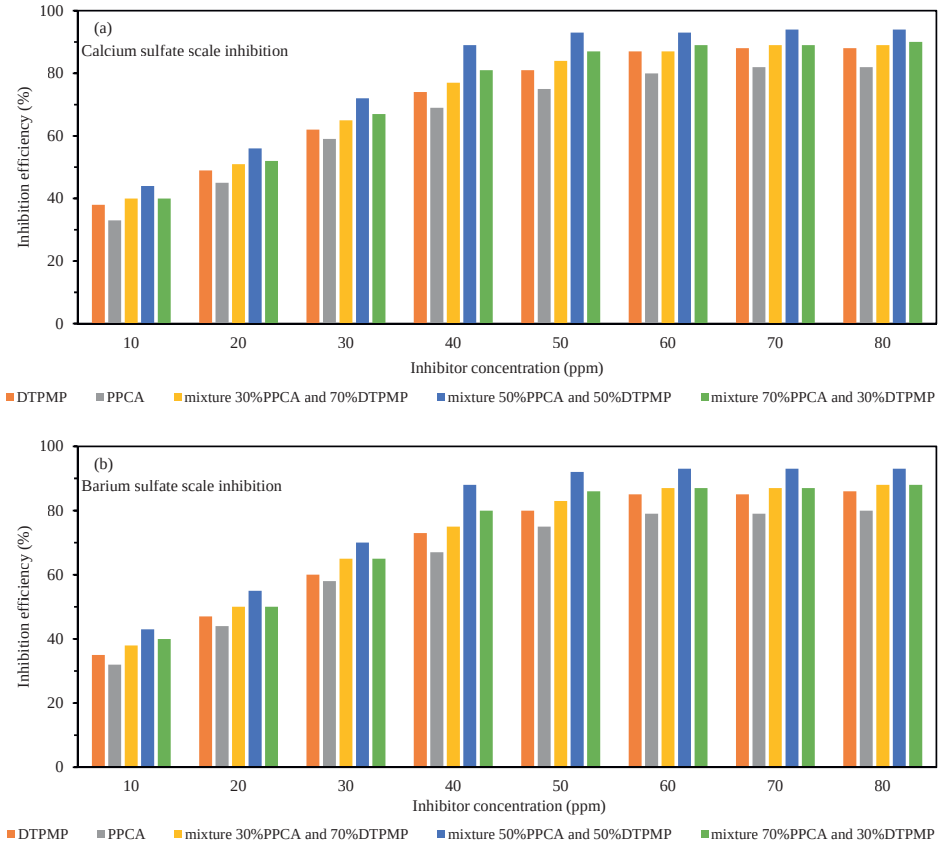


Fig. 3. Scale inhibition efficiency of $CaSO_4$ (a) and $BaSO_4$ (b) using individual inhibitors (PPCA and DTPMP) and their mixtures at different concentrations.

sites. When combined, these mechanisms complement each other, leading to stronger prevention of scale formation (Mpelwa and Tang, 2019).

For barium sulfate scale inhibition, shown in Fig. 3b, a similar trend was observed, though inhibition values were slightly lower compared to calcium sulfate at equivalent concentrations. DTPMP outperformed PPCA at all concentrations due to its stronger complexation with divalent barium ions and higher efficiency in distorting barite crystals. The mixture containing 50% PPCA and 50% DTPMP again outperformed both individual inhibitors, especially at intermediate concentration of 50 ppm, where inhibition efficiencies reached approximately 93%, respectively. The 70:30 mixture also demonstrated good performance but slightly below the 50:50 blend, while the 70% PPCA:30% DTPMP mixture was less effective than other blends but still more efficient than PPCA alone. The observed synergistic behavior likely stems from the complementary inhibition pathways of the two inhibitors: while DTPMP complexes with scale-forming cations and modifies crystal lattice structures, PPCA contributes by dispersing fine particles and stabilizing them in suspension (Razman Shah et al., 2023).

The optimum concentration for effective inhibition was found to be 50 ppm for the 50% PPCA:50% DTPMP mixture, as it consistently provided over 90% inhibition efficiency for both calcium and barium sulfate scales. Beyond this concentration, the efficiency gains were marginal, suggesting that higher doses may not be economically justified. Overall, the 30:70 mixture demonstrated the best inhibition performance and cost-effectiveness, making it the most suitable blend among the tested formulations for high-temperature applications in scale control. This mixing ratio of PPCA and DTPMP is used in the further experiments such as dynamin tube blocking test, turbidity and coreflooding analysis at 50 ppm.

3.3. Dynamic tube blocking test

Fig. 4 presents the results of the Dynamic Tube Blocking Test (DTBT) conducted over a 90-min period to assess the inhibition performance of PPCA, DTPMP, and their 50:50 mixture against calcium sulfate and barium sulfate scale formation. These tests underscore the importance of inhibitor selection and formulation, especially in complex brine systems where multiple scaling ions are present. The tests were performed under constant brine flow conditions, and pressure drop (kPa) was monitored as an indicator of scale deposition within the tube. In all three graphs, the pressure drop for each inhibitor was plotted over time at four different concentrations: 0, 20, 40, and 60 ppm.

In the absence of any inhibitor (0 ppm), the pressure drop increased sharply in all cases after approximately 30–40 min, indicating rapid scale formation and blockage within the tube. When 20 ppm of each inhibitor was introduced, the onset of pressure increase was delayed by about 10–15 min, but scale formation still progressed, evidenced by the eventual rise in pressure toward the end of the test. For 40 ppm, both PPCA and DTPMP showed improved performance, with a further delay in pressure increase and significantly reduced maximum pressure drop compared to the uninhibited case. Notably, the pressure rise was less steep, suggesting slower scale accumulation. At 60 ppm, all three systems demonstrated excellent scale inhibition, with the pressure drop remaining almost flat throughout the 90-min test duration, indicating effective suppression of scale precipitation and deposition under dynamic flow. Among the three, the 50:50 PPCA:DTPMP blend exhibited the most consistent and stable behavior at both 40 and 60 ppm, with virtually no pressure build-up over time. This suggests a possible synergistic effect between the two inhibitors when used in combination, leading to enhanced scale control performance beyond their individual contributions (Zhang et al., 2019).

The mixture's superior performance may be attributed to the complementary inhibition mechanisms of PPCA and DTPMP: PPCA primarily acts by dispersing crystal nuclei and interfering with crystal growth, while DTPMP, a phosphonate-based inhibitor, strongly chelates scale-forming cations such as Ca^{2+} and Ba^{2+}, effectively preventing nucleation (Alsaif and Abdel-Azeim, 2025). This synergy likely extends the protection coverage within the dynamic system, ensuring more uniform inhibition. Moreover, the combination may mitigate individual weaknesses, such as PPCA's reduced efficiency in high ionic strength or DTPMP's potential precipitation under certain pH conditions. From these observations, the minimum inhibitor concentration (MIC) required to prevent scale formation under dynamic conditions is determined to be 40 ppm for PPCA and DTPMP, and 40 ppm for their mixture. In addition, the blended system achieves this with greater reliability and a flatter pressure profile, indicating not just inhibition but also long-term stabilization of the brine system against scaling. Therefore, the use of PPCA: DTPMP in equal proportions offers a promising strategy for mitigating mixed sulfate scale formation in dynamic environments, such as injection and production lines in oilfield operations.

3.4. Results of turbidity test

The light transmittance approach can provide a sensitive and real-time indication of scale inhibition effectiveness. It also allows for continuous monitoring without disturbing the system, making it a valuable method for evaluating scaling behaviors. Furthermore, the dynamic turbidity test aims to assess the degree of clarity in the solution, which correlates inversely with the formation of scale particles: lower light transmittance indicates higher turbidity and, therefore, more effective scale inhibition (Tantayakom et al., 2005).

Fig. 5 illustrates the results of the turbidity test conducted through light transmittance measurements over a 60-min period to evaluate the performance of three scale inhibitors—PPCA, DTPMP, and a 50:50 mixture of both—in ion-rich brine solution. In the turbidity tests, a mixed brine (70% injection water and 30% formation water) was used; its ionic composition is presented in Table 2. Furthermore, he concentrations of the scale inhibitors were 60 ppm for PPCA, 60 ppm for DTPMP, and 40 ppm for the 50:50 PPCA–DTPMP mixture.

As seen in the figure, PPCA consistently demonstrated the highest light transmittance values, starting from around 6.9% and gradually increasing to approximately 7.6% by the end of the 60-min duration. DTPMP followed with intermediate light transmittance values, starting near 6.2% and rising to about 6.7%, suggesting a moderate ability to prevent scale particle formation and maintain brine clarity. Interestingly, the 50:50 mixture of PPCA and DTPMP showed the lowest light transmittance values throughout the test period, ranging from about 5.6% to 6.1%, which indicates higher turbidity and therefore more effective scale inhibition compared to the individual inhibitors. This outcome suggests that the combined use of PPCA and DTPMP at equal ratios resulted in a synergistic effect under these conditions. The differences in transmittance among the three systems highlight the distinct mechanisms of inhibition employed by each additive. The mixture may have introduced steric or chemical interference that hindered the optimal performance of both inhibitors. The relatively stable trend of each curve implies that the precipitation reactions and corresponding turbidity levels reached a steady state within the 60-min timeframe. Notably, none of the inhibitors exhibited a significant drop in transmittance, which would have

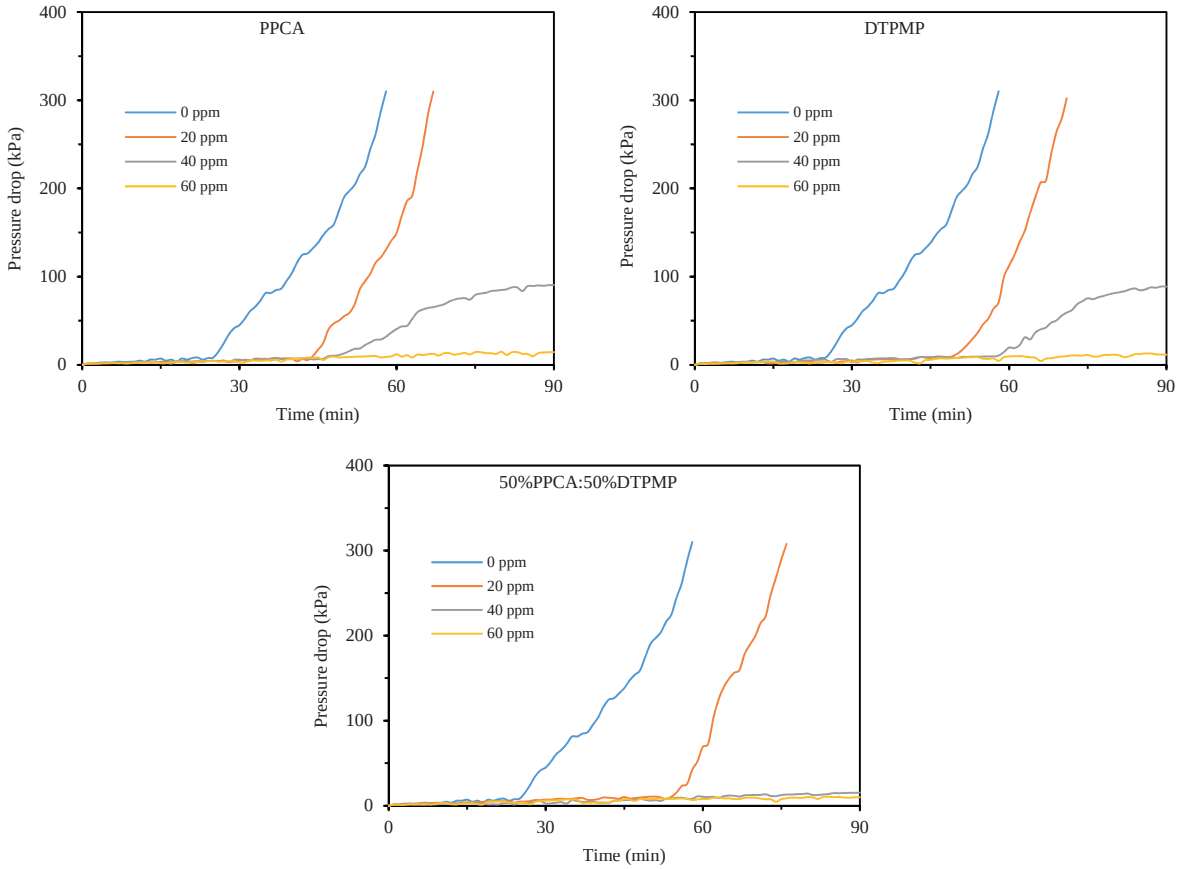


Fig. 4. Pressure-drop profiles during Dynamic Tube Blocking Tests for PPCA, DTPMP, and their 50:50 mixture at varying concentrations.

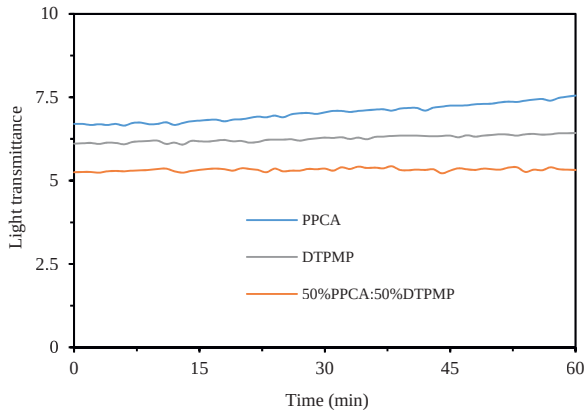


Fig. 5. Light transmittance trends from turbidity tests assessing inhibitor effectiveness.

indicated scale prevention at high levels. The higher performance of the mixed system emphasizes the importance of compatibility and formulation balance when combining inhibitors. These results also reinforce the need for experimental validation when proposing blended inhibitor systems.

The test conditions, such as ion concentration, temperature, and pH, remained constant, ensuring that the observed effects are attributable to the inhibitors themselves. Overall, the data suggest that under the given test conditions, the suggested mixture outperforms both DTPMP and PPCA in preventing scale-induced turbidity. The clear performance hierarchy—PPCA < DTPMP <50:50 mixture—demonstrates the necessity of selecting appropriate inhibitors for specific brine chemistries.

3.5. Formation damage evaluation in the presence and absence of scale inhibitors

Fig. 6 presents the coreflooding results that evaluate formation damage through the reduction in rock permeability due to scale precipitation in porous core samples. The experiments were carried out at a constant temperature of 70 °C to simulate reservoir conditions conducive to scale formation. The figure illustrates the relationship between the reduction in permeability (%) and the volume of fluid injected, expressed in pore volumes (PV), across four test conditions: a blank test (no scale inhibitor), and the use of three scale inhibitors—PPCA, DTPMP, and their 50:50 mixture.

The pH of the produced water after coreflooding remained close to that of the mixed injection/formation brine, with minor variations depending on the inhibitor type: approximately 6.92 for DTPMP, 6.80 for PPCA, and 6.88 for the 50:50 blend. These small differences reflect slight acidification from partially protonated inhibitor species, while the overall salinity and ionic composition of the effluent remained largely unchanged.

The reduction in permeability reflects the extent of scale deposition and associated pore blockage, with a lower reduction indicating better inhibitor performance and less formation damage (Hussein et al., 2024). As shown in the figure, in the blank test, a continuous and pronounced increase in permeability reduction was observed as brine was injected into the core, eventually reaching about 72% reduction at 5 PV. The blank test exhibited

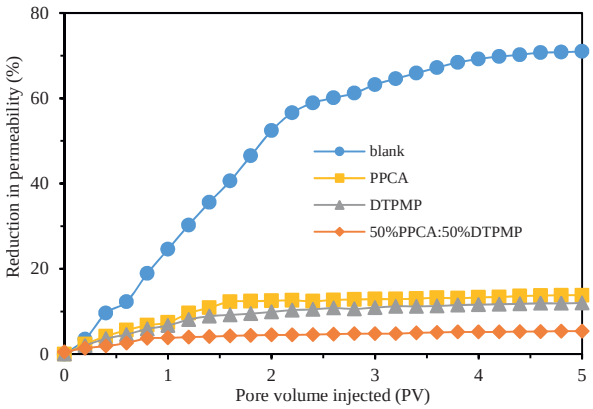


Fig. 6. Permeability reduction in coreflooding tests for blank and inhibited systems using PPCA, DTPMP, and their 50:50 mixture.

continuous degradation, suggesting ongoing scale accumulation without any inhibition barrier. This substantial permeability loss confirms severe scale deposition in the absence of any chemical treatment, highlighting the necessity of effective scale control measures in high-temperature brine systems. The rate of permeability loss accelerated quickly within the first 1.5 PV, followed by a more gradual increase, suggesting a rapid onset of scale nucleation and growth during the early stages of injection. In contrast, the introduction of scale inhibitors significantly improved the permeability preservation. The permeability profiles of all inhibitor-treated cores reached a stable plateau after approximately 2 PVs of injection, indicating that the inhibition mechanisms were effective throughout the majority of the test duration. The reduced formation damage in the presence of inhibitors underscores their value in preserving reservoir rock properties, particularly under harsh conditions such as elevated temperatures.

DTPMP alone exhibited good inhibition performance, maintaining the permeability reduction at about 9–10% throughout the experiment. Its phosphonate-based structure enables strong complexation with scale-forming cations, thereby preventing their precipitation. PPCA showed slightly higher permeability impairment than DTPMP, with a final reduction around 12–13%. This suggests that while PPCA alone is effective in delaying scale formation, it may not be as efficient in preventing long-term deposition compared to DTPMP or the combined formulation. Among the three inhibitor conditions, the 50:50 mixture of PPCA and DTPMP demonstrated the best performance, with a minimal reduction in permeability of approximately 5% after 5 PV of injection. This result indicates strong inhibition of scale formation and minimal pore blockage, reflecting a synergistic effect between the two inhibitors when used in combination. The superior performance of the mixture may result from the complementary mechanisms of PPCA and DTPMP. Together, they likely interfere more effectively with nucleation and crystal growth processes. Interestingly, the 50:50 mixture not only achieved the lowest permeability damage but also demonstrated the fastest stabilization in permeability, reaching steady-state much earlier than the other treatments. This early and persistent inhibition reflects rapid and effective adsorption of the mixed inhibitor onto the rock surface, providing robust protection against scale nucleation. The enhanced inhibition performance may also result from broader spectrum activity against multiple scaling species or crystal phases present in the brine. These findings are consistent with synergistic effects of combined scale inhibitors in the above tests, wherein different chemical functionalities enhance each other's activity.

Moreover, the mixture's ability to outperform the individual inhibitors suggests a potential for reduced chemical dosage in field applications, offering economic and operational advantages. The moderate performance of DTPMP and PPCA individually highlights their limitations under the test conditions, emphasizing the importance of formulation design and compatibility between inhibitors. The low and stable permeability reduction in the mixture test implies that the core remains highly conductive, which is critical for maintaining reservoir productivity during water injection or production operations (Ardakani et al., 2024).

The results also suggest that PPCA and DTPMP, while useful on their own, may benefit significantly from co-application. Such combinations may offer a balance between rapid adsorption, strong complexation, and long-term stability. The application of a properly optimized inhibitor mixture could extend the interval between squeeze treatments and reduce the frequency of remediation efforts.

3.6. The analysis of inhibitor adsorption and desorption on the rock surface

Fig. 7 depicts the results of adsorption and desorption coreflooding experiments for three scale inhibitors—PPCA, DTPMP, and their 50:50 mixture—conducted at a constant temperature of 70 °C. Fig. 7a illustrates the adsorption process, where the y-axis denotes the inhibitor concentration ratio (C/C_i) at the outlet of the core, and the x-axis indicates the cumulative pore volume of inhibitor solution injected. In the context of adsorption, an efficient inhibitor is expected to reach a C/C_i ratio of 1 more quickly, signifying that the rock surface becomes saturated and adsorption is complete. Among the three inhibitors, the 50:50 PPCA-DTPMP mixture exhibited the fastest increase in C/C_i, reaching equilibrium concentration ($C/Ci \approx 1$) before 2 PVs. This indicates that the mixture rapidly saturates the adsorption sites within the core, suggesting a favorable interaction between the mixed inhibitors and the rock surface. PPCA also demonstrated a relatively fast adsorption profile, though it lagged slightly behind the mixture, reaching full saturation slightly after 2.7 PVs. DTPMP, on the other hand, displayed the slowest adsorption behavior, requiring close to 3 PVs to reach a C/Ci ratio near unity. This slower progression implies that DTPMP has a lower tendency to adsorb onto the core material and hence requires more volume to saturate the adsorption sites.

The differences in adsorption behavior can be attributed to the molecular structures and chemical functionalities of the inhibitors. DTPMP, being a phosphonate-based compound with multiple binding sites, likely interacts more rapidly and uniformly with the rock surface. The synergistic behavior of the mixture may stem from complementary adsorption mechanisms, where PPCA modifies surface properties while DTPMP forms stable surface complexes. The fast saturation of the adsorption sites by the mixture indicates efficient utilization of both polymeric and phosphonate components, which could be beneficial in ensuring prompt inhibitor placement during squeeze treatment operations (Mohamed et al., 2022).

The earlier attainment of maximum adsorption observed for the 50:50 PPCA–DTPMP mixture, despite no chemical interaction between the inhibitors, can be explained by several physical and adsorption-related factors. Firstly, the two inhibitors compete for a finite number of adsorption sites on the rock surface, leading to faster occupation of available sites and consequently an earlier apparent saturation (competitive adsorption effect). Secondly, mixed adsorption layers of different molecular structures may exhibit less efficient surface packing, reducing total adsorption

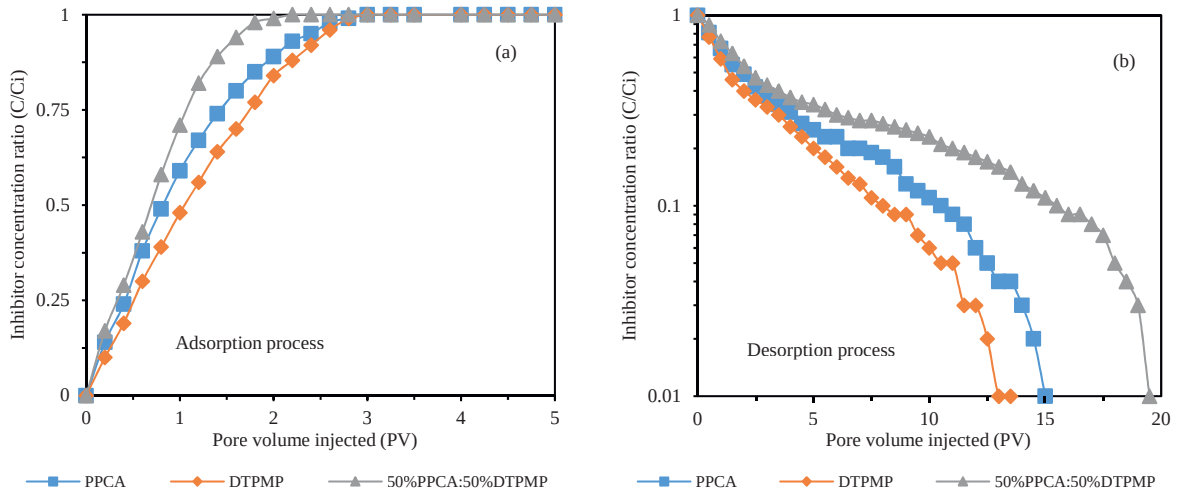


Fig. 7. Adsorption (a) and desorption (b) behaviors of PPCA, DTPMP, and their 50:50 mixture in core samples.

capacity. Thirdly, kinetic differences between the two inhibitors play a role—PPCA may adsorb more rapidly but with lower capacity, while DTPMP adsorbs more slowly but strongly; when combined, the rapid adsorption of PPCA dominates the initial breakthrough behavior. Fourthly, displacement and exchange between the two inhibitors can occur, where one species temporarily adsorbs and is subsequently replaced by the other, contributing to a faster rise in effluent concentration. Lastly, the coexistence of both inhibitors can alter local solution chemistry, such as ionic strength or interfacial pH, slightly reducing adsorption affinity without requiring chemical interaction. Together, these factors explain why the blended inhibitor system reaches apparent adsorption equilibrium sooner than the individual components.

Fig. 7b illustrates the desorption process, where brine injection displaces the previously adsorbed inhibitors. Here, a good inhibitor should exhibit slow desorption, indicated by a gradual decrease in the C/C_i ratio over increasing pore volumes. The 50:50 mixture again exhibited superior performance, maintaining a higher concentration ratio throughout the entire 20 PV desorption process. This suggests strong and stable adsorption of the mixed inhibitor formulation on the rock surface, which is ideal for prolonged scale protection. DTPMP showed the fastest desorption, with the C/C_i ratio declining sharply within the first few PVs and continuing to drop rapidly, indicating weaker retention on the rock surface. PPCA, while showing intermediate desorption behavior, maintained a slightly higher C/C_i ratio than DTPMP during the early stages of the desorption phase. However, it was still less effective than the mixture in providing long-lasting retention. The extended-release profile observed for the mixture reflects an optimal balance between adsorption strength and desorption resistance, critical for achieving long-term inhibitor performance. The sustained release over 20 PVs implies that the mixture could maintain inhibitory concentrations in the produced fluids for extended periods after the initial treatment. This behavior also suggests potential cost-effectiveness by reducing the frequency of squeeze treatments in field applications. The contrast between the rapid saturation during adsorption and the slow release during desorption for the mixture highlights its favorable kinetic profile. These characteristics make the 50:50 PPCA-DTPMP blend a promising candidate for squeeze treatments in scale-prone reservoirs.

The concentrations of Ca^{2+} and Mg^{2+} in the effluents were monitored during both adsorption and desorption stages to assess possible mineral–fluid interactions. The results showed that the concentrations of these divalent cations remained nearly constant within experimental uncertainty (±3–5%), suggesting that any dissolution or precipitation of carbonate minerals was minimal and effectively balanced under the test conditions. In carbonate formations, minor dissolution of the rock matrix can initially increase Ca^{2+} and Mg^{2+} concentrations, while re-precipitation reactions may subsequently counterbalance this effect. Thus, the observed near-constant concentrations indicate that the system reached a quasi-equilibrium state rather than the complete absence of mineral reactivity. Overall, these findings suggest that carbonate dissolution–precipitation effects were minor and did not significantly influence the scale inhibitor transport, which was primarily governed by adsorption onto the rock surface.

Fig. 8 shows the adsorption behavior of three scale inhibitors—PPCA, DTPMP, and their 50:50 blended formulation—on carbonate rock during coreflooding experiments. The adsorption is expressed as the mass of inhibitor retained per gram of rock (mg SI/g rock) versus the effluent concentration of the scale inhibitor at the outlet of the core holder. As shown in Fig. 8, among the tested inhibitors, 50:50 PPCA-DTPMP blend exhibited the highest adsorption capacity. This behavior reflects a desirable property for near-wellbore squeeze treatments, where rapid adsorption helps

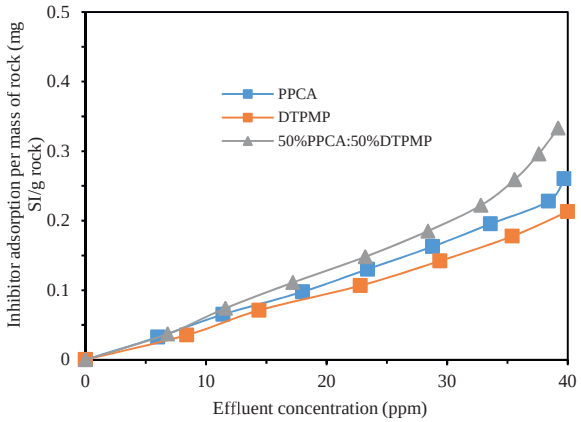


Fig. 8. Inhibitor adsorption per mass of rock versus injected pore volume for PPCA, DTPMP, and 50:50 PPCA–DTPMP mixture.

Table 3
The average ionic composition of production water.

Ion type	Ion concentration (ppm)
Na^+	19,603
Ca^{2+}	1230
K^+	150
Ba^{2+}	124
Mg^{2+}	1112
Cl^-	42,011
SO_4^{2-}	2327
TDS (ppm)	66,557

ensure efficient inhibitor placement and enhanced retention within the formation.

The production water collected during the adsorption and desorption experiments originated from the outlet of the core-flooding system after contact between the injected brine and the rock. Therefore, its composition was not identical to that of the injected water, as ion exchange and limited mineral dissolution/precipitation occurred during flow through the core. The produced water exhibited slightly lower Ca^{2+} and Mg^{2+} concentrations and marginally higher Na^+ and Cl^- levels, mainly due to cation exchange and rock–fluid interactions, while the total salinity and ionic dominance remained nearly constant. The average values of ion concertation of production water are shown in Table 3:

These minor differences confirm that the production water was largely comparable to the injected brine in overall composition, ensuring that observed variations in inhibitor concentration were mainly due to adsorption and desorption mechanisms rather than major chemical alterations of the aqueous phase.

Overall, the results indicate that while individual inhibitors PPCA and DTPMP each have merits in adsorption or desorption, their combination outperforms both in terms of speed of adsorption and duration of desorption. The synergy between the inhibitors not only enhances adsorption kinetics but also reinforces the binding strength, leading to prolonged retention. This dual benefit is essential for maintaining effective scale inhibition during production and extending the treatment lifetime. The observed trends confirm that evaluating both adsorption and desorption behaviors is essential for a comprehensive assessment of inhibitor efficiency. Moreover, the results underscore the importance of optimizing inhibitor formulations rather than relying solely on individual chemistries. At 70 °C, where reaction kinetics and surface interactions are intensified, the superior performance of the mixture becomes even more significant. The ability of the mixture to maintain a slow and consistent desorption profile supports its suitability for high-temperature applications. Thus, from both operational and chemical perspectives, the mixture presents a more robust and sustainable solution for scale management in subsurface environments.

4. Conclusions

This study demonstrates the significant benefits of blending two chemically distinct scale inhibitors—DTPMP and PPCA—for the mitigation of calcium sulfate and barium sulfate scale formation under oilfield waterflooding conditions. The synergistic combination of these inhibitors was evaluated through static, dynamic, and core-scale methods, providing insight into their comparative and combined performance in preventing scale deposition and minimizing formation damage. Key findings from the study include:

(1) Scale prediction modeling using OLI Studio confirmed that the highest scale formation risk occurs at a 70:30 injection-to-formation water mixing ratio. This mixture was selected for all subsequent tests and reflected a realistic brine environment representative of many field conditions.
(2) Static bottle tests revealed that the 50:50 PPCA:DTPMP blend achieved inhibition efficiencies exceeding 90% for both $CaSO_4$ and $BaSO_4$ scales at just 50 ppm concentration. In contrast, individual inhibitors required higher concentrations (60–80 ppm) to reach comparable performance, with DTPMP slightly outperforming PPCA individually.
(3) dynamic tube blocking tests supported these findings under flow conditions. The hybrid inhibitor at 60 ppm maintained a near-zero pressure rise across the test coil for 90 min, whereas the blank test showed a sharp pressure increase due to scale blockage within 30–40 min. The minimum inhibitor concentration (MIC) for reliable inhibition under dynamic conditions was determined to be 40 ppm for the mixture and 60 ppm for DTPMP and PPCA.
(4) Turbidity analysis further confirmed superior inhibition behavior of the 50:50 mixture, showing the lowest light transmittance (5.6%–6.1%) and highest turbidity, implying robust dispersion and suppression of nucleation events.
(5) Coreflooding experiments demonstrated that scale formation without inhibition caused a severe 72% reduction in rock permeability. The PPCA:DTPMP blend preserved 95% of the core's initial permeability (only 5% reduction), outperforming PPCA (13%) and DTPMP (10%) individually. This indicates effective pore protection and minimized formation damage.
(6) Adsorption/desorption tests illustrated that the hybrid inhibitor adsorbed more rapidly (equilibrium reached before 2 PVs) and desorbed more slowly (sustained release over 20 PVs), indicating stronger and longer-lasting retention. DTPMP desorbed the fastest and had the weakest retention profile.
(7) Collectively, these results confirm the existence of a positive synergistic effect in the 50:50 PPCA:DTPMP blend. The combination leverages the strengths of both inhibitors—nucleation inhibition by PPCA and crystal growth suppression by DTPMP—resulting in improved efficiency, lower required dosage, reduced permeability damage, and extended squeeze lifetimes. The formulation shows promise for field-scale deployment in high-temperature reservoirs, where robust, long-term scale management is essential.

Future studies should explore the performance of PPCA-DTPMP blends under a wider range of reservoir conditions, including high pressure, elevated salinity, and complex multi-scale environments. Integrating advanced predictive modeling and data-driven optimization techniques will enable more accurate identification of critical factors influencing inhibition performance. Additionally, assessing long-term field deployment, environmental impact, chemical compatibility, and interactions with different reservoir rock types will enhance the reliability, sustainability, and scalability of hybrid inhibitor formulations for real-world oilfield applications.

CRediT authorship contribution statement

Azizollah Khormali: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Soroush Ahmadi:** Writing – review & editing, Writing – original draft, Validation, Software, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Yousef Kazemzadeh:** Writing – review & editing, Writing –

original draft, Validation, Methodology, Investigation, Formal analysis.

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

Ahmadi, S., Khormali, A., Kazemzadeh, Y., 2025. A critical review of the phenomenon of inhibiting asphaltene precipitation in the petroleum industry. Processes 13 (1).

Alsaif, B., Abdel-Azeim, S., 2025. Molecular insights into scale inhibition: a molecular dynamics study of phosphonate-based inhibitors on a calcite surface. Langmuir 41 (16), 10271–10281.

Ardakani, S.F.G., Hosseini, S.T., Kazemzadeh, Y., 2024. A review of scale inhibitor methods during modified smart water injection. Can. J. Chem. Eng. 102 (11), 3922–3952.

Bijani, M., Khamehchi, E., 2019. Optimization and treatment of wastewater of crude oil desalting unit and prediction of scale formation. Environ. Sci. Pollut. Res. 26, 25621–25640.

Bisatto, R., Picoli, V.M., Petzhold, C.L., 2022. Evaluation of different polymeric scale inhibitors for oilfield application. J. Pet. Sci. Eng. 213, 110331.

Fang, J., Ye, Z., Dou, Z., Zhang, Y., Wu, W., Hu, Y., Wang, B., Li, H., 2024. Design of molecular scale inhibitors for high temperature industrial cooling water systems based on group synergistic effects. Chem. Eng. J. 494, 153164.

Fernandes, R.S., Beserra, N.L., Souza, M.A., Lima, D.F., Castro, B.B., Balaban, R.C., 2020. Experimental and theoretical investigation of a copolymer combined with surfactant for preventing scale formation in oil wells. J. Mol. Liq. 318, 114036.

Ghorbani, N., Wilson, M., Kapur, N., Fleming, N., Tjomsland, T., Neville, A., 2017. Adsorption of polyphosphinocarboxylic acid (PPCA) scale inhibitor on carbon nanotubes (CNTs): a prospective method for enhanced oilfield scale prevention. J. Pet. Sci. Eng. 150, 305–311.

Gruszka, M., Nagy, S., 2023. Precipitation of barium sulphate during the waterflooding process in Polish offshore oilfields—case analysis. Energies 16 (8), 3345.

Haghtalab, A., Kamali, M.J., Shahrabadi, A., 2014. Prediction mineral scale formation in oil reservoirs during water injection. Fluid Ph. Equilib. 373, 43–54.

Hajirezaie, S., Wu, X., Peters, C.A., 2017. Scale formation in porous media and its impact on reservoir performance during water flooding. J. Nat. Gas Eng. 39, 188–202.

Hamid, S., De Jesús, O., Jacinto, C., Izetti, R., Pinto, H., Droguett, E., Edwards, C., Cassidy, J., Zhang, H., Dagenais, P., 2016. A practical method of predicting calcium carbonate scale formation in well completions. SPE Prod. Oper. 31 (1), 1–11.

Hamza, A., Hussein, I.A., Jalab, R., Saad, M., Mahmoud, M., 2021. Review of iron sulfide scale removal and inhibition in oil and gas wells: current status and perspectives. Energy Fuel. 35 (18), 14401–14421.

Hoang, T.A., 2022. Mechanisms of scale formation and inhibition. In: Amjad, Z., Demadis, K.D. (Eds.), Water-Formed Deposits. Elsevier, pp. 13–47.

Huang, B., Hou, S., Hua, Z., Zhang, J., Yang, H., Zhu, Y., Tang, Y., Wang, B., 2024. Comprehensive utilization of formation water scale to prepare controllable size $CaCO_3$ nanoparticles: a new method to improve oil recovery. Nanomaterials 14 (17), 1452.

Husna, U.Z., Elraies, K.A., Shuhili, J.A.B., Elryes, A.A., 2022. A review: the utilization potency of biopolymer as an eco-friendly scale inhibitors. Pet. Explor. Prod. Technol. 12 (4), 1075–1094.

Hussein, M.F., Mubarak, M.F., Al-Sirhani, A.M., Hosny, R., 2024. Examining the factors that impact the formation of barite scale in water injection operations: experimental study and quantification of scale formation. Discov. Appl. Sci. 6 (10), 519.

Jafar Mazumder, M.A., 2020. A review of green scale inhibitors: process, types, mechanism and properties. Coatings 10 (10), 928.

Jarrahian, K., Singleton, M., Boak, L., Sorbie, K.S., 2020. Surface chemistry of phosphonate scale inhibitor retention mechanisms in carbonate reservoirs. Cryst. Growth Des. 20 (8), 5356–5372.

Kahrwad, M., Sorbie, K.S., Boak, L.S., 2009. Coupled adsorption/precipitation of scale inhibitors: experimental results and modeling. SPE Prod. Oper. 24 (3), 481–491.

Kamal, M.S., Hussein, I., Mahmoud, M., Sultan, A.S., Saad, M.A., 2018. Oilfield scale formation and chemical removal: a review. J. Pet. Sci. Eng. 171, 127–139.

Kan, A.T., Tomson, M.B., 2012. Scale prediction for oil and gas production. SPE J. 17 (2), 362–378.

Khormali, A., Ahmadi, S., 2024. Trends in using organic compounds as scale inhibitors: past, present, and future scenarios. In: Yaagoob, I.Y., Verma, C. (Eds.), Industrial Scale Inhibition: Principles, Design, and Applications. Wiley, pp. 188–205.

Khormali, A., Ahmadi, S., Aleksandrov, A.N., 2025a. Analysis of reservoir rock permeability changes due to solid precipitation during waterflooding using artificial neural network. Pet. Explor. Prod. Technol. 15 (1), 17.

Khormali, A., Ahmadi, S., Kazemzadeh, Y., 2022. Inhibition of barium sulfate precipitation during water injection into oil reservoirs using various scale inhibitors. Arabian J. Sci. Eng. 48 (7), 9383–9399.

Khormali, A., Ahmadi, S., Kazemzadeh, Y., Karami, A., 2025b. Evaluating the efficacy of binary benzimidazole derivatives as corrosion inhibitors for carbon steel using multi-modal analysis and optimization techniques. Results Eng. 26, 104671.

Khormali, A., Bahlakeh, G., Struchkov, I., Kazemzadeh, Y., 2021. Increasing inhibition performance of simultaneous precipitation of calcium and strontium sulfate scales using a new inhibitor—Laboratory and field application. J. Pet. Sci. Eng. 202, 108589.

Khormali, A., Koochi, M.R., Varfolomeev, M.A., Ahmadi, S., 2023. Experimental study of the low salinity water injection process in the presence of scale inhibitor and various nanoparticles. Pet. Explor. Prod. Technol. 13 (3), 903–916.

Khormali, A., Petrakov, D.G., Farmanzade, A.R., 2016. Prediction and inhibition of inorganic salt formation under static and dynamic conditions–effect of pressure, temperature, and mixing ratio. Int. J. Technol. 7 (6), 943–951.

Khormali, A., Petrakov, D.G., Lamidi, A.-L.B., Rastegar, R., 2015. Prevention of calcium carbonate precipitation during water injection into high-pressure high-temperature wells. In: SPE European Formation Damage Conference and Exhibition.

Khormali, A., Sharifov, A., Torba, D., 2018. Investigation of barium sulfate precipitation and prevention using different scale inhibitors under reservoir conditions. Int. J. Eng. 31 (10), 1796–1802.

Kumar, S., Naiya, T.K., Kumar, T., 2018. Developments in oilfield scale handling towards green technology-A review. J. Pet. Sci. Eng. 169, 428–444.

Li, A., Zhang, H., Liu, Q., Zeng, H., 2022. Effects of chemical inhibitors on the scaling behaviors of calcite and the associated surface interaction mechanisms. J. Colloid Interface Sci. 618, 507–517.

Li, J., Tang, M., Ye, Z., Chen, L., Zhou, Y., 2017. Scale formation and control in oil and gas fields: a review. J. Dispers. Sci. Technol. 38 (5), 661–670.

Liu, Y., Zhang, P., 2022. Review of phosphorus-based polymers for mineral scale and corrosion control in oilfield. Polymers 14 (13), 2673.

Mady, M.F., Rehman, A., Kelland, M.A., 2021. Synthesis and study of modified polyaspartic acid coupled phosphonate and sulfonate moieties as green oilfield scale inhibitors. Ind. Eng. Chem. Res. 60 (23), 8331–8339.

Mahmoodi, A., Hosseinzadehsadati, S., Kermani, H., Nick, H., 2023. On the benefits of desulfated seawater flooding in mature hydrocarbon fields. Sci. Total Environ. 904, 166732.

Mahmoodi, A., Nick, H., 2022. The interplay between microbial reservoir souring and barite scale formation in hydrocarbon reservoirs. J. Clean. Prod. 377, 134234.

Mohamed, D.F., Hamdi, S.S., Alzanam, A., Mohyaldinn, M.E., Muhsan, A.S., 2022. Carbon-based nanocoating for extended lifetime of conventional scale inhibitor squeeze treatment in sandstone reservoirs. J. Pet. Sci. Eng. 211, 110138.

Mpelwa, M., Tang, S.-F., 2019. State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: a review. Pet. Sci. 16 (4), 830–849.

Olajire, A.A., 2015. A review of oilfield scale management technology for oil and gas production. J. Pet. Sci. Eng. 135, 723–737.

Razman Shah, N.B.B., Sazali, R.A.B., Sorbie, K.S., Khalil, M., Azizi, A., 2023. Nanomaterials for scaling prevention in alkaline–surfactant–polymer flooding: a review. Appl. Nanosci. 13 (6), 3945–3974.

Sanni, O.S., Bukuaghangin, O., Charpentier, T.V., Neville, A., 2019. Evaluation of laboratory techniques for assessing scale inhibition efficiency. J. Pet. Sci. Eng. 182, 106347.

Shaw, S.S., Sorbie, K.S., 2015. Synergistic properties of phosphonate and polymeric scale-inhibitor blends for barium sulfate scale inhibition. SPE Prod. Oper. 30 (1), 16–25.

Sorbie, K.S., 2010. A general coupled kinetic adsorption/precipitation transport model for scale inhibitor retention in porous media: I. Model formulation. In: SPE International Oilfield Scale Conference and Exhibition.

Talebi, S., Riahi, S., Rostami, B., 2022. The effect of blending polymeric and phosphonate scale inhibitors on fluid/fluid and rock/fluid interactions: a comprehensive experimental and theoretical study. SPE J. 27 (6), 3611–3629.

Tantayakom, V., Sreethawong, T., Fogler, H.S., De Moraes, F., Chavadej, S., 2005. Scale inhibition study by turbidity measurement. J. Colloid Interface Sci. 284 (1), 57–65.

Tayyebi, A., Alshami, A., Tayyebi, E., Owoade, A., Talukder, M.J., Ismail, N., Rabiei, Z., Yu, X., Tikeri, G., 2025. Machine learning-based prediction of scale formation in produced water as a tool for environmental monitoring. Results Eng. 26, 105223.

Vazquez, O., Fursov, I., Mackay, E., 2016. Automatic optimization of oilfield scale inhibitor squeeze treatment designs. J. Pet. Sci. Eng. 147, 302–307.

Wang, H., Dong, H., Liu, X., Zhang, P., 2022. Preparation and laboratory testing of polymeric scale inhibitor colloidal materials for oilfield mineral scale control. Polymers 14 (19), 4240.

Wang, W., Kan, A.T., Tomson, M.B., 2013. A novel and comprehensive study of polymeric and traditional phosphonate inhibitors for high-temperature scale control. SPE J. 18 (3), 575–582.
Wu, D., Liu, D., Wang, J., Zhao, H., Dong, Y., Wang, X., 2025. High-performance barium sulfate scale inhibitors: Monomer design and molecular dynamics studies. Processes 13 (3), 660.
Xu, J., Jing, G., Liu, T., Liu, Y., Yanheng, L., Yang, Y., 2022. Research progress of green scale inhibitors: a mini review. Pet. Sci. Technol. 40 (1), 59–72.
Yan, F., Zhang, F., Bhandari, N., Wang, L., Dai, Z., Zhang, Z., Liu, Y., Ruan, G., Kan, A., Tomson, M., 2015. Adsorption and precipitation of scale inhibitors on shale formations. J. Pet. Sci. Eng. 136, 32–40.
Zeino, A., Albakri, M., Khaled, M., Zarzour, M., 2018. Comparative study of the synergistic effect of ATMP and DTPMPA on CaSO4 scale inhibition and evaluation of induction time effect. J. Water Process Eng. 21, 1–8.
Zhang, L., Kim, D., Jun, Y.-S., 2018. The effects of phosphonate-based scale inhibitor on brine–biotite interactions under subsurface conditions. Environ. Sci. Technol. 52 (10), 6042–6049.
Zhang, L., Tariq, S.M., Ali, S.I., Zhang, B., Zhang, X., Li, C., Fu, X., 2024. New strategy for selection of best water chemistry of injected fluid during water flooding to mitigate scaling problem. Arabian J. Sci. Eng. 50 (13), 10317–10326.
Zhang, P., Liu, Y., Kan, A.T., Tomson, M.B., 2019. Laboratory evaluation of synergistic effect of transition metals with mineral scale inhibitor in controlling halite scale deposition. J. Pet. Sci. Eng. 175, 120–128.
Zolfagharroshan, M., Khamehchi, E., 2024. Mineral scaling impact on petrophysical properties of reservoir rock in a geothermal field located in northwestern Iran. SPE J. 29 (2), 1029–1044.