

# Adsorption enhancers to improve the retention of scale inhibitors in sandstone rock

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## Abstract

The management of inorganic scales is critical activity in the petroleum industry, as deposits in pipelines and equipment can significantly impact asset productivity. These deposits often result from the mixing of incompatible connate and injection water, with scale inhibitors commonly employed to mitigate such issues. One effective method for delivering these inhibitors is through a squeeze treatment, which involves creating a stock of scale inhibitor in the vicinity of the producer well, within the rock formation. However, the efficacy of this treatment diminishes over time as the stock of inhibitor becomes depleted, prompting ongoing research into novel formulations, including squeeze lifetime enhancer (SLE) chemicals. These SLEs work in combination with scale inhibitors to enhance their retention and release on solid phases. In this study, kinetic and equilibrium experiments were carried out using combinations of SLEs and a specific scale inhibitor, DETPMP, to evaluate their interaction with sandstone rock. The experiments assessed both the retention kinetics and the influence of the inhibitor concentration. The results were promising, indicating that these combinations significantly increased the retention efficiency of the inhibitor.

*Keywords:* Scale inhibitor; adsorption enhancer; polymers.

## 1. Introduction

Inorganic scale deposition is a relevant issue in oil and gas production, usually occurring due to the mixing of incompatible waters such as connate and injection waters. These deposits can lead to a reduced productivity and potential damage to equipments. Scales are particularly challenging in mature fields, prompting the study of new mitigation strategies [1-3].

According to Jordan *et al.* [4], prevention methods with chemical inhibitors are an attractive option to mitigate this problem. These inhibitors may prevent or delay the deposition process, thereby maintaining production at an economically viable level and protecting equipment against salt deposits [5,6].

Several studies have been performed to improve the retention efficiency of inhibitors, where novel products are used to promote higher interaction between the inhibitor and the solid phase [7]. The combined action of inhibitors and polymers has been evaluated to improve the inhibitor adsorption

efficiency. This combination can create a synergetic effect between the solid phase and the scale inhibitor, which may result in increased retention capacity [8,9].

In this context, this study aims to evaluate the interactions between adsorption enhancers, sandstone rock, and a scale inhibitor through immersion experiments. The objective is to assess both the retention kinetics and the influence of inhibitor concentration.

## 2. Materials and methods

### 2.1. Materials

A sample of sandstone rock with particle sizes in the range of 150 to 300  $\mu\text{m}$  was used.

A commercial inhibitor, diethylenetriamine pentamethylene phosphonic acid (DETPMP), was purchased from Sigma-Aldrich (Brazil). As adsorption enhancers, two polyamine solutions (coined as M1 and M2), provided by SNF Water Science (Brazil), and a polyaluminium chloride solution (coined as M3), provided by Chlorum

Solutions (Brazil), were used. Potassium chloride (KCl, >99%) was purchased from Dinâmica (Brazil). Argon (purity >99%) was provided by Messer Gases (Brazil), and standard phosphorus solutions was provided by SpecSol (Brazil).

## 2.2. Rock characterization

The chemical composition of the sandstone rock sample was characterized using X-ray fluorescence (XRF) with Rigaku ZSX Mini II equipment (Japan). For textural characterization, the nitrogen gas adsorption technique at 77 K was used to determine properties such as surface area and total pore volume, measured with an Autosorb-1 MP (Quantachrome, USA). The surface area was calculated using the BET method.

## 2.3. Kinetics experiments

A solution of the pure inhibitor was prepared using 650 ppm (mg/L) of the inhibitor in a solution of KCl (2%wt) in ultrapure water. To simulate the injection real conditions of an oil reservoir, its pH was kept at 4 using NaOH or HCl solutions. The concentrations of the enhancer solutions were: 4,000 ppm of M1 or M2, and 200 ppm of M3. Three experimental conditions were then evaluated: one with only the inhibitor and two with different combinations of enhancers and inhibitor (as shown in equations 1 and 2).

$$C1 = 0.25M1 + 0.5inhibitor + 0.25M3 \quad (1)$$

$$C2 = 0.25M2 + 0.5inhibitor + 0.25M3 \quad (2)$$

These three combinations (only inhibitor, C1 and C2), using a total liquid volume of 0.1 L, were then contacted with the sandstone rock sample (4 g) in a batch system at 70 °C with constant agitation. Immediately after mixing the solutions, samples of the liquid were collected to monitor the concentration of the inhibitor up to 120 minutes.

## 2.4. Equilibrium measurements

The equilibrium experiments were carried out in a batch system using 0.48 g of the rock sample with a liquid volume of 0.012 L. These values were based on the ratio used by Kan *et al.* [10]. The concentrations of the retention enhancers were the same as in the kinetics experiments: 4,000 ppm for M1 and M2, and 200 ppm for M3. For the pure inhibitor, different concentrations were prepared

from 50 to 2,000 ppm. The solutions were mixed following the same proportions and with the same combinations as in the kinetic tests (Equations 1 and 2). The experiments were performed in a thermostatic bath at 70°C for 120 min with constant stirring. The pH of the pure inhibitor solution was also kept at 4.

For each solution with different inhibitor concentrations brought to contact with the rock, the amount of inhibitor retained in the solid phase ( $q^*$ , mg of inhibitor/g) was calculated by mass balance (Equation 3):

$$q^* = \frac{(C_0 - C_f) \times V_{sol}}{m} \quad (3)$$

where  $C$  (ppm) is the inhibitor concentration, with  $C_0$  as the initial concentration and  $C_f$  as the final concentration,  $V_{sol}$  (L) is the solution volume, and  $m$  (g) is the solid weight.

The results of the equilibrium experiments were fitted using the Langmuir equation (Equation 4),

$$\frac{q^*}{q_m} = \frac{bC_{eq}}{1 + bC_{eq}} \quad (4)$$

where:  $q^*$  is the retention capacity of the inhibitor in the solid phase with each final equilibrium concentration ( $C_{eq}$ ) of the inhibitor in the liquid phase,  $b$  is a Langmuir parameter, and  $q_m$  is the maximum retention capacity.

## 2.5. Analytical method

For analysis of the solutions after the immersion experiments, inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer, USA) was used. Standard phosphorus solutions were used to obtain the calibration curve under the conditions required for monitoring the inhibitor concentration.

## 3. Results and discussions

### 3.1. Rock sample characterization

The X-ray fluorescence spectrometry (XRF) is one of the most versatile methods for evaluation of the elements of the rock. The main elements identified in the studied sample are presented in Table 1.

The elements Si and Al stand out in the results, comprising more than 90% of the rock sample. Thus, due to the large dominance of these elements, the inhibitor performance is strongly

related to the surface of the minerals composed of these two elements.

Table 1. FRX analysis of the rock sample.

Chemical elements	% Mass
Silicon (Si)	83.96
Aluminum (Al)	12.28
Iron (Fe)	1.26
Titanium (Ti)	1.02
Calcium (Ca)	0.78
Potassium (K)	0.57
Silver (Ag)	0.14

The profile of the N<sub>2</sub> isotherms of the rock sample is presented in Figure 1. A type II isotherm [11] is observed, with a very low pore volume.

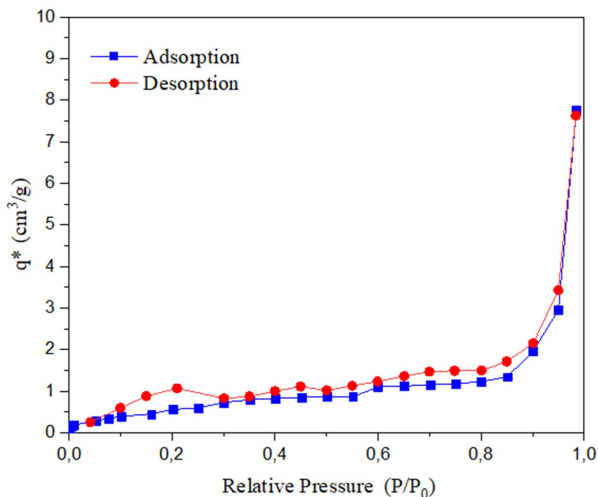


Fig. 1. Nitrogen adsorption and desorption isotherms at 77 K.

The calculated surface area is less than 10 m<sup>2</sup>/g. As expected, the porosity of the consolidated sandstone rocks is around 15% [12]. However, the segregation of the rock sample resulted in particles with low porosity.

### 3.2. Retention experiments

The results of the kinetic experiments are shown in Figure 2. It is possible to observe a steep decline in inhibitor concentration in the liquid during the initial times, which demonstrates how quickly the inhibitor is transferred from the liquid to the solid phase. After 120 min, under the conditions that were studied, the inhibitor concentration in the liquid phase decreased *approx.* 30%, when using

only the pure inhibitor. For both C1 and C2 combinations, the decrease in inhibitor concentrations reached about 50% of the initial concentration in the solution.

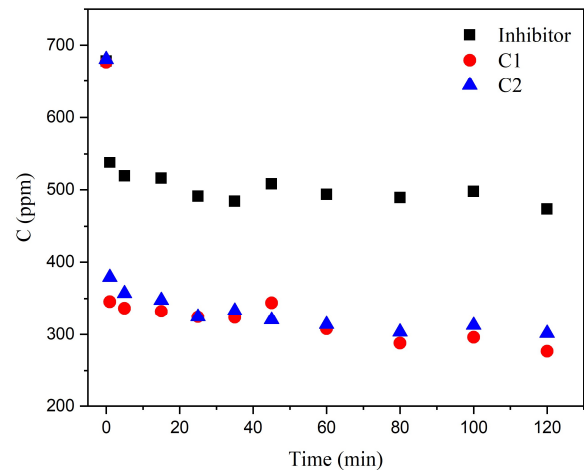


Fig. 2. Decay with time of inhibitor concentrations in solution, at 70 °C.

The results of the equilibrium experiments, fitted using the Langmuir equation (eq. 4), are presented in Figure 3, showing inhibitor retention isotherms for solutions containing only the inhibitor and solutions with the combinations C1 and C2. The maximum retention capacities for each condition are presented in Table 2.

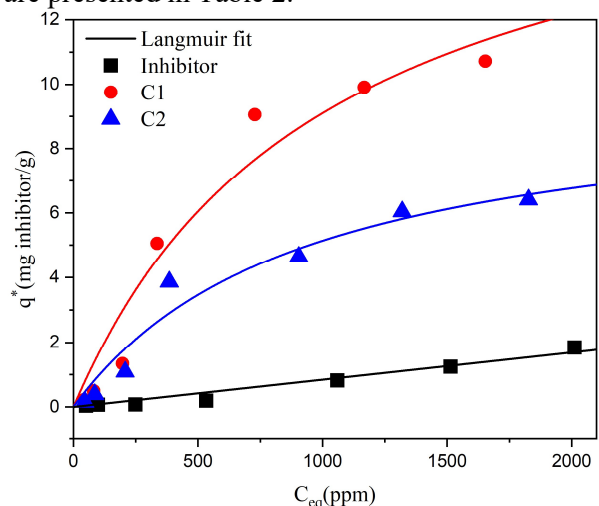


Fig. 3. Equilibrium curves of inhibitor retention at 70 °C.

It may be observed from the equilibrium results that both C1 and C2 mixtures had higher retention

capacities than the pure inhibitor solution at all liquid concentrations.

Table 2. Fitted parameters of the Langmuir equation (eq. 4).

Exp.	b	qm	R2
C1	$9.77 \cdot 10^{-4}$	18.40	0.951
C2	$1.07 \cdot 10^{-3}$	9.92	0.955

From Table 2, it is seen that the maximum retention capacity for C1 is appx. 86% higher than for C2. So, the use of the polymer materials indeed enhanced the retention capacity of the inhibitor for the scale process. Furthermore, the relative capacity enhancements at different concentrations in the liquid phase are presented in Table 3. In general, the use of combinations (C1 and C2) increased from 3-26 times the inhibitor retention, with the C1 combination showing the best results for improving the retention of the inhibitor on the sandstone rock. Similar results, using coreflood tests, were also obtained by Maffra *et al.* [9]. The increased retention is related to the synergetic effect observed between the products (inhibitor + adsorption enhancer) and the rock.

Table 3. Relative retention enhancement for combinations C1 and C2 compared to the pure inhibitor retention.

	Inhibitor concentration (ppm)			
	500	1000	1500	2000
C1	26.1	11.0	7.9	5.8
C2	20.0	5.6	4.8	3.5

## 4. Conclusion

The combined action of polymers and DETPMP to improve the inhibitor's retention efficiency was evaluated. A sample of sandstone rock was prepared, characterized, and utilized in batch experiments employing different combinations of enhancers and DETPMP. Kinetic and equilibrium studies were conducted to understand the timeframe and retention capacity of the inhibitor.

The results using both C1 and C2 combination mixtures showed higher retention capacities than the pure inhibitor solution across all liquid concentrations. Notably, the C1 combination increased inhibitor retention by up to 26 times, indicating that the use of polymer materials can significantly enhance the retention capacity of the scale inhibitor.

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