Insights into the Performance and Mechanism of Scale Inhibitors based on Classic Dynamic Tube-Blocking Tests and Online Real-Time Analysis Techniques

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Abstract

This study investigated the performance of two scale inhibitors, a phosphonate and a polymeric, in a classic dynamic scale loop (DSL) system coupled online with a viewing cell and in a batch system with inline analysis. The DSL determined the scaling time and the minimum inhibitory concentration (MIC) while the viewing cell allowed the evaluation of the precipitation process in flowing conditions through RGB image analysis. The batch system with inline analysis evaluated the precipitation process through Focused Beam Reflectance Measurement (FBRM) and Fourier Transform Infrared Spectroscopy (FTIR). The experimental conditions were a synthetic formation brine containing mostly calcium chloride and sodium bicarbonate, pH 7.8, 63 °C, and varying concentrations of the scale inhibitors. The phosphonate MIC was determined as 50 mg L^{-1} whereas that of the polymeric was 200 mg L^{-1}. RGB image analysis showed that the scale mechanism was probably due to secondary nucleation, which suggested that both inhibitors may act on the crystal growth and agglomeration rather than inhibiting nucleation. On the batch crystallization experiments, FTIR revealed that both inhibitors favored the formation of calcite while SEM analysis showed that the polymeric induced structural damage on calcite. The findings of this study highlight the importance of investigating scale inhibitors from multiple perspectives that help to understand their mechanisms of action and how experimental parameters influence their performance.

Keywords
Dynamic scale loop, RGB image analysis, Inline analysis.

Introduction

Scale is a significant flow assurance challenge in petroleum production. Inorganic salts such as calcium carbonate and barium and strontium sulfates in production water can precipitate and form deposits within pipelines and other production equipment. Changes in pressure that release carbon dioxide from the production water favor the precipitation of calcium carbonate while mixing incompatible waters such as injection seawater with formation water leads to the precipitation of sulfates. Other parameters such as pH, temperature, and ionic strength also influence the scale formation [1].

Chemical products like phosphonates and polymers are currently used to address scale. They are known as scale inhibitors and prevent or retard scale formation through various mechanisms such as metals sequestering, nucleation inhibition, crystal growth and agglomeration retardation, and crystal size and shape distortion [2]. The standard method to evaluate the performance of the scale inhibitors is the tube-blocking test conducted in a DSL system, which determines the scaling time and the minimum inhibitory concentration (MIC).

The DSL system operates by pumping aqueous solutions of precipitant ions through a test coil, controlling temperature, flow rate, and pressure. The scaling time is the time in which an increase greater than 0.5 psi in the differential pressure between the inlet and outlet of the test coil is detected. The MIC is the lowest scale inhibitor concentration at which the scaling time is longer than 3-fold the scaling time of the control test (without inhibitor) or 60 min, whichever is the longest [3].

The DSL does not provide information about the precipitation process that occurs before the scale formation. Therefore, a recent study introduced a novel approach to investigate the scale formation and performance of scale inhibitors based on RGB image analysis that allows the evaluation of the precipitation process in flowing conditions. This is conducted by coupling a viewing cell to the output of the DSL system. The RGB average signal is related to the amount of solid precipitated that flows through the viewing cell. This feature provides insights into possible scale inhibition mechanisms [4].

This study investigates the performance of two commercial scale inhibitors using the cited novel approach. The precipitation process was also evaluated in a batch system with inline analysis. The results obtained from real-time sensors such as FBRM and FTIR probes and the analysis of the precipitated solids by SEM complement the results provided by the DSL with RGB image analysis. FBRM examines the particles' chord size and particle counting [5] while FTIR analyzes crystalline phases of calcium carbonate [6]. This approach with multiple techniques allows for a comprehensive evaluation of the performance of the scale inhibitors, their mechanisms of action, and the parameters that influence them.

Methodology
Materials
The composition of the synthetic brine used in this work is presented in Table 1. The inorganic salts were purchased from Sigma-Aldrich (St. Louis, USA) and used as received. The aqueous solutions were prepared with ultrapure water.

Table 1. Brine composition

Compound	Concentration (mg L^{-1})
Anion-rich aqueous solution	
Sodium chloride	13787
Magnesium chloride	536
Calcium chloride	3036
Barium chloride	36
Strontium chloride	222
Cation-rich aqueous solution	
Potassium bromide	270
Sodium sulfate	232
Sodium bicarbonate	6904

Carbon dioxide used to adjust the pH was supplied by Air Products (Rio de Janeiro, Brazil). Sodium hydroxide, hydrochloric acid, acetic acid, and EDTA used to adjust the pH and to clean the DSL system were purchased from Isofar (Rio de Janeiro, Brazil). The two commercial scale inhibitors, a phosphonate and a polymeric, were provided by Petrobras (Rio de Janeiro, Brazil)

Tube-blocking tests
The tube-blocking tests were conducted following the novel approach proposed by Venancio et al. (2023), which uses a DSL system coupled to a viewing cell [4]. The performance of the scale inhibitors was evaluated at 63 ºC, pH 7.8 and 10 bar. The anion-rich (containing the inhibitor) and cation-rich solutions were pumped to mix into the coil test placed inside an oven at 5 mL min^{-1} each. The differential pressure and the RGB average signal were monitored throughout the experiment. An increase in the differential pressure indicates scale formation while an increase in the RGB signal indicates a flow of suspended solids through the viewing cell. The system was cleaned after each experiment using acetic acid 10% for 10 min followed by distilled water for 10 min, EDTA 10%

(pH 9.5) for 10 minutes and distilled water again for 10 min.

Precipitation experiments with inline analysis
The precipitation experiments were conducted in an EasyMax® 102 Workstation (Mettler Toledo), an automated platform equipped with two glass reactor vessels of 100 mL that facilitate precise control of temperature and stirring. One vessel contained 50 mL of the anion-rich solution with or without scale inhibitor and the other 50 mL of the cation-rich solution. These solutions were mixed and then the precipitation process was analyzed in real-time by the inline sensors, FBRM and FTIR probes (Mettler Toledo). The FBRM was conducted over a size range of 0.5–1000 mm in 90 channels every 2 s. The FTIR was conducted using a ReactIR 45m spectrometer (Mettler Toledo) with a 9.5 mm × 1.5 m silver halide fiber probe interface with data collection every 10 s.

SEM analysis
The solids produced in the precipitation experiments were vacuum filtered, washed with ethanol, and dried at 60 ºC for 1 h. These solids were analyzed by SEM using a ZEISS EVO10 microscope (Oberkoshen, Germany). Each sample was placed on a conducting carbon pad (Plano GmbH) and the beam scan mapping was performed at a 15 kV acceleration voltage.

Results and Discussion
Figure 1 presents the results of the tube-blocking tests conducted in the DSL system with image analysis for the phosphonate inhibitor.
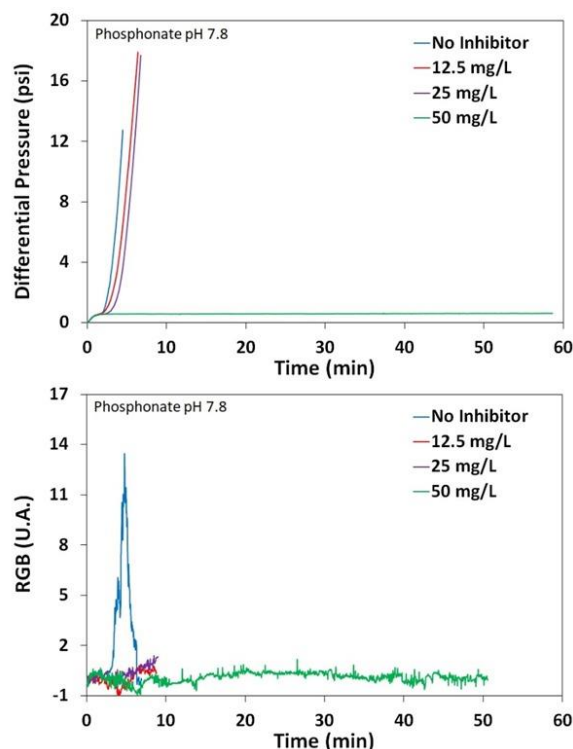

Figure 1. Tube-blocking tests and image analysis results for the phosphonate inhibitor

The MIC for the phosphonate at these experimental conditions was 50 mg L^{-1}, which indicated its good performance. The RGB image analysis showed the absence of solids flowing through the viewing cell at all phosphonate concentrations tested. This would suggest that the phosphonate inhibited the nucleation; however, as observed by the DSL results, the scale formation still occurred at concentrations lower than 50 mg L^{-1}. That is, the precipitation indeed occurred, but the solids immediately deposited inside the test coil. This suggested a fouling mechanism via secondary nucleation directly in the coil surface.

Figure 2 displays the results of the tube-blocking tests conducted in the DSL system with image analysis for the polymeric inhibitor. The MIC of the polymeric inhibitor at these experimental conditions was 200 mg L^{-1}, which was a higher value compared to the phosphonate, indicating an inferior performance. Indeed, the RGB image analysis showed that at a concentration of 50 mg L^{-1} of the polymeric inhibitor, the precipitated solids are so stable that as they flow through the viewing cell also deposit inside the test coil. However, at concentrations between 100 and 150 mg L^{-1}, the solids only deposited. This suggested that, although the polymeric inhibitor affected the precipitation in concentrations higher than 100 mg L^{-1}, it did not prevent the scaling via nucleation inside the coil.
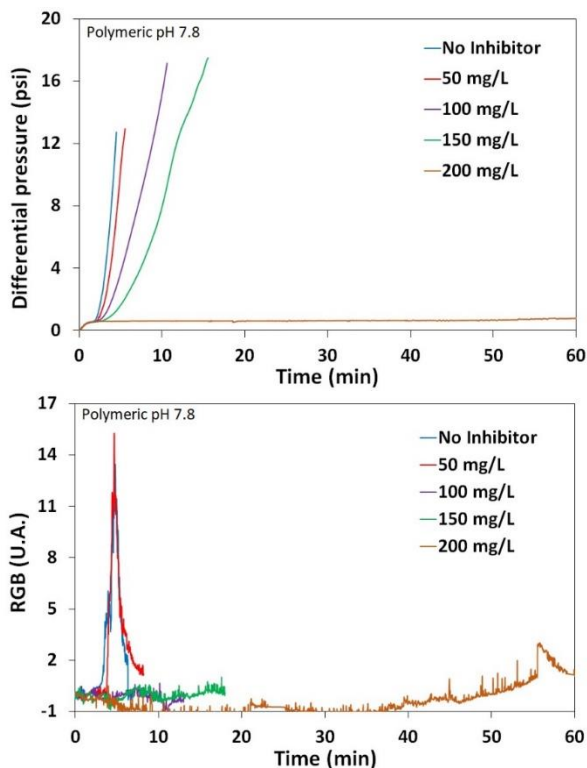

Figure 2. Tube-blocking tests and image analysis results for the polymeric inhibitor

The precipitation process was evaluated in the batch system with inline analysis in three scenarios: without inhibitor, with inhibitor at MIC, and with inhibitor at half of the MIC. Fig. 3 provides the particle count results for the phosphonate in two size ranges: less than 10 μm and between 10 and 50 μm. These results indicate that the phosphonate did not significantly influence the induction time and the particle growth. A similar result was observed for the polymeric inhibitor.
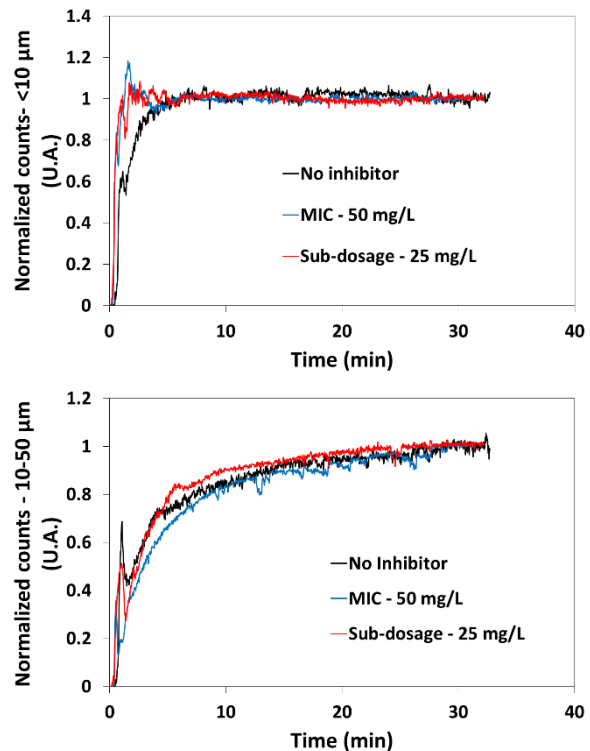

Fig. 3. Particles count provided by the FBRM probe for the phosphate inhibitor.

Figure 4 shows the FTIR results for both inhibitors. The band at 713 cm^{-1} is typical of both calcite and aragonite and the band at 873 cm^{-1} is typical of calcite [6].
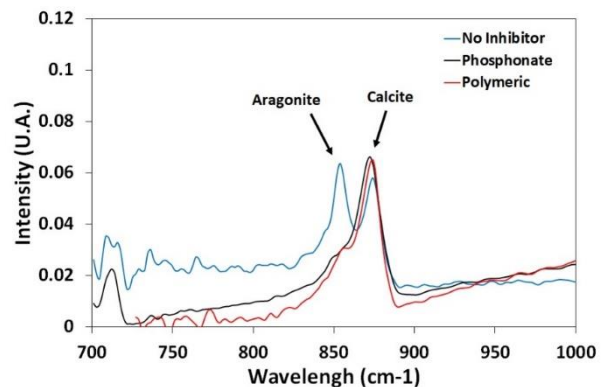

Fig. 4. FTIR spectra of the system without inhibitor and with both inhibitors, indicating characteristic bands of aragonite and calcite

The spectrum of the control experiment shows both bands, indicating that at the experimental conditions of 63 °C and pH 7.8, the stable crystalline phases of calcium carbonate were both aragonite and calcite. Conversely, the spectra in the presence of both inhibitors showed only the

band at 873 cm^{-1}, which indicated that the inhibitors only promoted the formation of calcite. Therefore, although the inhibitors seemed not to inhibit the nucleation nor affect its kinetics, they did influence the stability of the crystalline phase formed. This suggested that the mechanism of crystal shape distortion may play a role in the inhibition of scale at concentrations higher than 50 mg L^{-1} of the phosphonate inhibitor and 200 mg L^{-1} of the polymeric one.

Figure 5 shows the SEM images of the precipitated solids with and without inhibitors at different concentrations. The control experiment (Fig. 5a) exhibited three calcium carbonate polymorphs: aragonite, calcite, and vaterite. The presence of phosphonate destabilized vaterite and favored calcite (Fig. 5b and 5c). The presence of the polymeric also favored calcite despite still observing aragonite (Fig. 5d and 5e). Increasing the concentration of the polymeric inhibitor induces structural damage to the calcite, although occasional cubic structures and other polymorphs were still observed.
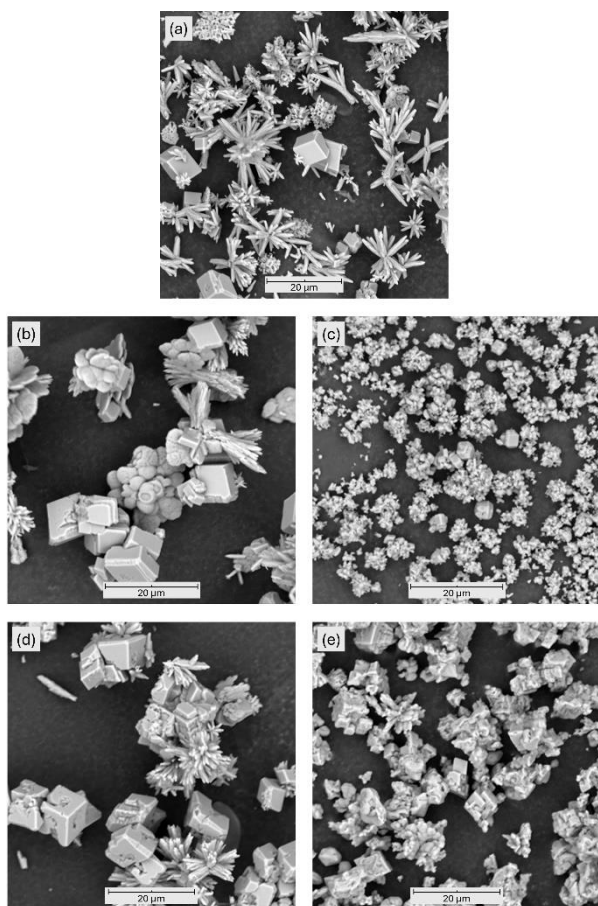

Figure 5. SEM images of the precipitated solids. (a) Control experiment, (b) phosphonate at MIC, (d) phosphonate at half of the MIC, (d) polymeric at MIC, and (e) polymeric at half of the MIC.

Conclusions
The commercial inhibitors evaluated in this study were effective in preventing scale formation, however, the phosphonate MIC was considerably lower than that of the polymeric, indicating its better performance. The approach presented here used multiple analytical techniques, including differential pressure and RGB image analysis in the dynamic system and FBRM and FTIR in the batch system. The results of these analytical techniques, along with the solids characterization by SEM, provided valuable insights into the performance and mechanism of the scale inhibitors. Both inhibitors not only reduced the overall amount of scale but also influenced the precipitation process, particularly promoting the formation of calcite. Therefore, the most likely mechanism of action of these inhibitors was the distortion of the size and shape of precipitated solids rather than the nucleation inhibition or retardation. The findings of this study highlight the importance of investigating scale inhibitors from multiple perspectives that help to understand their mechanisms of action and how experimental parameters influence their performance.

Acknowledgments

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