Development of Methodologies for Continuous and Batch Inhibitor Film Persistency Investigation in the Laboratory

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ABSTRACT

Organic corrosion inhibitors (CIs) are widely used in the oil and gas industry to mitigate corrosion in pipeline transmission systems. Upstream, there are two distinct internal pipeline corrosion mitigation methods using inhibitors: continuous injection and batch inhibition. Each treatment mode has its own challenges, requiring specific knowledge of inhibitor film persistency (i.e., interrupted continuous injection or irregularity in batch inhibitor application frequency). The performance of applied corrosion inhibitors is typically evaluated in laboratory conditions, prior to field application. This study is focused on development of methodologies to investigate inhibitor film persistency using inhibitor model compounds, possessing only one molecular type, in both continuous and batch inhibition. For persistency studies related to continuous treatment, experiments were divided into three main steps: pre-corrosion, inhibitor addition, and inhibitor dilution. For batch inhibition, an inhibitor testing procedure was developed that can maintain stable water chemistry and avoid O₂ contamination, with the potential to be adapted for top-of-the-line corrosion (TLC) environments. Corrosion rates were monitored using linear polarization resistance (LPR) in all experiments (except in TLC conditions). The Langmuir isotherm model was used to calculate adsorption coefficient $k_A$ and desorption coefficient $k_D$ for benzyltrimethylammonium (BDA) inhibitor model compounds, possessing tetradecyl and hexadecyl tails, at different temperatures.

Keywords: corrosion inhibition, inhibitor persistency, batch treatment, continuous injection, top-of-the-line corrosion

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INTRODUCTION

Application of corrosion inhibitors confer many advantages for combatting internal pipeline corrosion in the upstream oil and gas industry. It is known that the associated costs for using corrosion inhibitors are low compared to other mitigation techniques [1]. For continuous injection procedures, water-soluble inhibitors are not expected to form long-lasting films, so they must be continuously injected to maintain their effectiveness. Batch inhibitors are usually higher molecular weight species and oil soluble. They tend to be more tenacious, providing a protective barrier between the water and the metal over a long period of time. For corrosion inhibitors used in the field, the physicochemical characteristics of the inhibitor molecules is of vital importance. These characteristics determine whether the inhibitor is classified as water-soluble or oil-soluble; a major factor relating to effectiveness and the way the inhibitor is applied [2].

The most common inhibition method in the upstream oil and gas industry uses continuous injection of an appropriate chemical formulation package to maintain a constant concentration of inhibitor in the fluid flowing through the pipeline [3-5]. Inhibitors can be directly injected into the flow stream without impacting production (a method called “continuous inhibition”), their use is relatively versatile as injection rates can be readily adjusted. This treatment is preferable to batch treatment because it does not require any interruption of the production and is characterized by a better control of inhibitor concentration [6, 7]. In this method, inhibitor is injected continuously into the flow stream through an injection port connected to the pipeline. This injection system contains a pump and a filter to remove any solid material that can block the injection port and a capillary tube [6]. The design of the injection system is adapted to the application, whether it is developed for transport pipelines or downhole tubulars [6, 8].

Conventional injection methods for delivery of corrosion inhibitors in wet gas pipelines are incapable of providing consistent inhibitor coverage for the entire inside pipe wall if the flow dynamics are not favorable [9]. Continuous inhibitor injection in a stratified flow is very effective to combat bottom of the line corrosion (BLC) but is completely useless in top-of-the-line corrosion (TLC) mitigation. When continuous injection is not an effective mitigation method, batch corrosion inhibitors (BCI) must be used as an alternative. As conventional inhibitor injection fails to mitigate TLC, many innovative technologies have been developed to deliver batch corrosion inhibitors to the top of the pipeline.

In the batch inhibitor treatment method, the corrosion inhibitor is packed between two devices, called "pigs" or “scrapers”, which contact with the entire internal diameter of the pipeline and move with the flow from the launch location to the retrieval location [10,11]. The shortcomings of this method are production interruption (which involves loss of revenue) as well as difficulties meeting the required processing frequency. In addition, many lines are not “pig-able” (they may not be equipped with the pig launcher/receiver assembly or may have sharp bends where the pig could get stuck). This technique involves the formation of a plug of highly concentrated inhibitor solution flowing inside the pipeline between the two pigs. Quaternary ammonium compounds that exist as a waxy solid at low temperatures typically exhibit excellent persistency when applied as a BCI and are one of the mainstays of corrosion protection for many integrity management strategies worldwide [12].

The performance of corrosion inhibitors, either used for continuous treatment or batch inhibition, is often evaluated in laboratory conditions, prior to field application. Experimental procedures related to persistency have been developed, simulating both continuous and batch treatment; however, there is often a lack of consistency and clarity in the testing procedures that leads to difficulties getting reproducible results. In addition, some common procedural steps can introduce experimental artefacts that can also affect the results.

Commonly accepted experimental procedures, from published literature, for conducting a glass cell experiment to mimic a continuous inhibition treatment are as follows [5-8].
1. Prepare solution and specimen in glass cell setup.

2. Measure blank corrosion rate (CR) in a deoxygenated solution without inhibitor (pre-corrosion step).

3. Inject a targeted concentration of inhibitor and measure inhibited corrosion rate (inhibition step).

4. Flush the inhibited solution from the glass cell and replace it with an uninhibited solution or move the working electrode from an inhibited electrolyte to an identical uninhibited environment (dilution step).

5. Measure the corrosion rate continuously until it reaches the blank corrosion rate (CR) to determine CI persistency.

The most important step in the simulated experiment of continuous treatment is the “dilution” step, which should reproduce the sudden decrease in the bulk CI concentration. However, limited studies have been conducted using a procedure that effectively continuously decreases the bulk concentration of the inhibitor to undetectable level.

Experimental procedures for testing a BCI are quite different than those for a continuous injection type inhibitor. The standard filming procedure adopted to conduct laboratory-based research for BCI evaluation is called the dip and drip method. In this method, mild steel specimens are first polished to a certain (600 or 800 grit) surface finish. They are then dipped into an inhibitor solution (typically neat inhibitor) for a specified period at room temperature. The reported contact time varies which might affect the persistency [11]. The specimen is then drip dried (25 minutes to 1 hour). In some reported procedures, excess inhibitor might be physically wiped from the specimens or there may be a “rinse step” with a model brine [10, 11]. In each step of this type of procedure, it is likely that O2 contamination will impact the results. There is no comprehensive filming procedure for simulating BCI application to corrosion environments and the existing ones, described in the literature, are not consistent (different contact times, for example) and carry potential experimental flaws (oxygen contamination) that can hinder the reproducibility of the results.

Extrapolation of laboratory measurements to field conditions are often performed without rigorous modeling, and application parameters are not well defined. In order to improve the current understanding of batch inhibition application, it is essential to develop a simulated setup with multiple capabilities, such as, BCI filming process, temperature control, water chemistry control, and adaptability to TLC environments. The behavior of corrosion inhibitors following the simulated batch treatment procedure can then be characterized to get better understanding on the mechanisms of inhibition by batch treatment.

BCIs used in the oil and gas industry are typically a proprietary cocktail of several chemicals, only a few of which are active corrosion inhibitors themselves whilst others have a secondary purpose (e.g., dispersant). When an understanding of the mechanisms is sought, it is customary to only study one single compound. The choice of this model compound is somewhat arbitrary, if it is representative, and its composition is known. The ICMT† has a long history of synthesizing and characterizing model CIs, especially quaternary ammonium-type chemical products. As reported in the literature [12], the efficiency of batch corrosion inhibitors is typically related to the alkyl tail length. The model compound BDA-C16 (benzylidimethylhexadecylammonium), shown in Figure 1, was chosen as the inhibitor to investigate batch corrosion inhibition; BDA-C16 is synthesized in-house as a waxy solid and needs to be solubilized in isopropanol before injection.

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The shorter tail length inhibitor model compound benzyldimethyltetradecylammonium (BDA-C14) was used in the investigation of interruption in continuous inhibition reported herein.

EXPERIMENTAL PROCEDURE

Experimental procedure for simulation of (interruption in) continuous treatment

The system set-ups described below was used to investigate the effects of continuous dilution of the inhibited solution on inhibitor persistency. All experiments were done in a 3-electrode glass cell apparatus. Experiments investigating the persistency of the inhibitor following a continuous dilution step were performed in the setup shown in Figure 2. The test matrix for both dilution procedures is shown in Table 1.

Figure 1. Benzylidimethylhexadecylammonium (BDA-C16)

Figure 2. Schematic of the setup used in persistency experiments using continuous dilution.
Table 1. Experimental test matrix for the continuous treatment experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>API 5L X65 (0.05 wt.%C)</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1 wt.% NaCl</td>
</tr>
<tr>
<td>Sparge gas</td>
<td>CO₂</td>
</tr>
<tr>
<td>Total pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>1000 RPM</td>
</tr>
<tr>
<td>Temperature</td>
<td>40°C &amp; 30°C ± 1°C</td>
</tr>
<tr>
<td>pH</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>Corrosion inhibitor (CI) model compound</td>
<td>Quaternary ammonium type (BDA-C14)</td>
</tr>
<tr>
<td>Measurement methods</td>
<td>OCP, LPR, EIS</td>
</tr>
<tr>
<td>Contact time (time before dilution)</td>
<td>When stable corrosion rate achieved</td>
</tr>
<tr>
<td>Initial inhibitor concentration</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Presence of hydrocarbon</td>
<td>None – brine only</td>
</tr>
<tr>
<td>Pre-corrosion before CI injection</td>
<td>10 minutes</td>
</tr>
</tbody>
</table>

The general procedure for experiments simulating continuous dilution of the inhibitor is as follows:

1. Fill the system and glass-cell with electrolyte (1 wt.% NaCl).
2. Sparge complete system with CO₂ for a minimum of 1 hour to keep the dissolved O₂ content to a few ppb.
3. Complete pre-corrosion LPR measurements for 10 min.
4. Inject corrosion inhibitor, continue LPR measurements.
5. After a stable inhibited corrosion rate is obtained, dilution is started by pumping fresh brine to the working glass cell and an overflow technique is used to continuously drain the solution at the same time while keeping liquid level constant.
6. LPR measurements are continued at 30-minute intervals until a new stable corrosion rate is obtained.
7. Periodic sampling of the solution was done to confirm the loss of inhibitor concentration.

The following sections provide more details on different steps of the procedures.

Pre-corrosion

1.8 L 1 wt.% NaCl was purged in a three-electrode glass cell for an hour to ensure deoxygenation and facilitate CO₂ saturation. The concentration of the oxygen was monitored during the experiment via an Orbisphere‡ 410 connected to the gas outlet of the system. The working electrode then was mounted on the rotating shaft after polishing to a 600-grit finish. The open circuit potential was monitored for 10 minutes for a stable value and then LPR was measured prior to inhibitor injection.

Inhibitor preparation

136 mg solid BDA-C14 was weighed in a vial which was previously cleaned using isopropanol in an ultrasonic cleaner. 3 ml isopropanol was injected into the vial containing solid inhibitor and then was fully

‡ Trade name.
mixed using the same ultra-sonic device for 20 minutes. 2 ml of this mixed solution was injected into the main solution (1.8L 1 wt.% NaCl) using a long needle into the bulk solution to reach 50 ppm\textsubscript{w} concentration of the inhibitor.

**Dilution procedure**

The dilution step was performed by equalizing input and output flowrate using an overflow technique to transfer brine from a 140 L supply which was able to continue until the end of the test. This method can remove all the inhibitor residuals from the solution which is a key factor in simulating field condition in continuous treatment.

**Cl concentration measurement using UV-vis spectroscopy**

The initial or residual inhibitor concentrations could be measured during the experiments. Liquid samples were taken directly from the working glass cell at different times of the experiment and their absorbance was measured using an Agilent’s Cary 60\textsuperscript{6} UV-vis spectrophotometer. Beer’s law was used to make a calibration curve from pre-mixed known solutions containing BDA-C14, which would be later used to measure its concentration in each experiment. This technique is not valid for every corrosion inhibitor as it requires that the inhibitor displays structural moieties that can be detected via UV-Vis spectroscopy.

\[
A = \epsilon l C
\]  
(1)

\( A = \) Absorbance measured with UV-vis spectroscopy \( \epsilon = \) Absorption coefficient \( C = \) Concentration \( l = \) Path length

The calibration curve was developed by plotting measured absorbances vs. Cl concentration.

The UV-vis calibration curve for BDA-C14 using different liquid samples with known inhibitor concentration is shown in Figure 3. Using this calibration curve, an equation for measuring the inhibitor concentration of the liquid samples taken from the solution during the experiments was derived as follows (2):

\[
CI\ concentration\ (ppm) = \frac{\text{Absorbance}}{0.0332}
\]  
(2)

\textsuperscript{6} Trade name

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Figure 3. BDA-C14 UV-vis calibration curve.

Experimental procedure for simulation of batch corrosion inhibition (BCI)

The glass cell assembled for the experimental setup and procedures developed to simulate BCI is shown in Figure 4. It consists of two main cells: the 2L glass cell where the corrosion inhibition experiment was performed, and a holding tank that contains fresh brine (free of corrosion inhibitor) that was used to flush the 2L glass cell of any inhibitor residuals.

Figure 4. Schematic representation of the experimental setup for batch CI testing.

The following paragraph explains the procedure in detail:

22 L of 1 wt.% NaCl electrolyte was sparged with carbon dioxide (CO₂) for 6 hours in the holding tank to ensure that all the dissolved oxygen was removed, and the solution was saturated with CO₂. A Na⁺-form
ion-exchange resin (Amberlite, IR120, Acros Organics**) was used to control Fe$^{2+}$ concentration ([Fe$^{2+}$]). The resin was added into the columns and purged with CO$_2$ for 2 hours. [Fe$^{2+}$] was controlled using the ion-exchange resin and the acidity of the solution was manually controlled at around pH 4 (or at any pH of interest). The RCE working electrode was installed in the 2L glass cell, and the empty cell was purged with CO$_2$ for 2 hours. At this point, the specimen was hanging in the dry gas phase.

After the system was properly purged, the desired volume (1mL) of the deoxygenated inhibitor was injected into the tubing connected to the nozzle. 1mL inhibitor solution was enough to cover the whole surface of the sample and just enough to fit into the spray tubing. The tubing was then pressurized with CO$_2$ (pCO$_2$~30 psi). At this point, the rotation of the RCE was started at 200 rpm and the valve of the nozzle was opened to create a mist that is applied to the entire surface of the specimen. After 30 seconds the inhibitor injection was completed, and the pre-purged electrolyte was pumped into the 2L glass cell. The pumping was stopped after the solution volume in the glass cell reaches 2 L, ensuring that the specimen was fully immersed in the electrolyte. This glass cell rinsing procedure was repeated 7 times while rotating the RCE to simulate the dilution effect after application of the BCI.

After the rinsing step was completed (after depletion of the 22L of un-inhibited brine), the loop with Na$^+$-exchange resin was opened to circulate the solution. Experimental evidence has shown that the same resin can also be effective in absorbing cationic inhibitors, but this observation is inhibitor-dependent and would need to be verified case by case. LPR measurements were conducted using a traditional three electrode setup and a Gamry†† potentiostat. A saturated silver/silver chloride (Ag/AgCl, KCl saturated) reference electrode and a platinum counter electrode were used for all the electrochemical experiments in this study.

It is important to mention that there is no inherent advantage of using this methodology (flush with 22L un-inhibited brine followed by recirculation with ion-exchange resin) compared to the one proposed in the previous section in Figure 2 (continuous flush with uninhibited brine). Table 2 shows the experimental conditions that were followed to test the corrosion persistency of the batch inhibitor.

**Table 2. Test conditions for the BLC electrochemical experiment**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ partial pressure</td>
<td>0.96 bar</td>
</tr>
<tr>
<td>Solution</td>
<td>1 wt.% deoxygenated NaCl solution</td>
</tr>
<tr>
<td>Inhibitor solution</td>
<td>15 wt.% BDA-C16 in isopropanol</td>
</tr>
<tr>
<td>pH</td>
<td>4.00 ± 0.02</td>
</tr>
<tr>
<td>Temperature</td>
<td>30.0°C</td>
</tr>
<tr>
<td>Rotation speed</td>
<td>1000 rpm</td>
</tr>
<tr>
<td>Material</td>
<td>API 5L X65 mild steel</td>
</tr>
<tr>
<td>Corrosion rate measurement</td>
<td>LPR, Weight loss</td>
</tr>
<tr>
<td>Test duration</td>
<td>1h - 90h</td>
</tr>
</tbody>
</table>

** Trade name
†† Trade name

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Experimental procedure for batch treatment adapted to top of the line corrosion

The schematic of the experimental setup for TLC mitigation experiments is shown in Figure 5. This setup is akin to what was used for the BLC BCI scenario. The main differences lie in the steel sample location (in TLC experiments, they are flush mounted to the top lid and exposed to the vapor phase), the method of CI injection (sprayed in a fine mist on the specimen surface) and the corrosion measurement method (weight loss and ferrous ion [Fe^{2+}] measurement).

Figure 5. Schematic of the experimental setup for TLC (image courtesy of Cody Shafer, ICMT)

In these experiments, 1 mL of deoxygenated 15 wt.% BDA-C16 (dissolved in isopropanol, 75 ppm_{w} total) is sprayed on the surface of the X65 mild steel specimen using the spray nozzle as shown in Figure 6.

Figure 6. Inhibitor spray nozzle for TLC experiment
Table shows the experimental conditions followed to test the persistency of the batch corrosion inhibitor in TLC experiments. A condition having a high condensation rate is chosen to verify the persistency of the BCI.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ partial pressure</td>
<td>0.65 bar</td>
</tr>
<tr>
<td>Solution</td>
<td>Deionized water</td>
</tr>
<tr>
<td>Inhibitor solution</td>
<td>15 wt.% BDA-C16</td>
</tr>
<tr>
<td>pH of the bulk electrolyte</td>
<td>4.00 ± 0.02</td>
</tr>
<tr>
<td>Steel temperature</td>
<td>35.5 °C</td>
</tr>
<tr>
<td>Liquid temperature</td>
<td>75.0 °C</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>65.0 °C</td>
</tr>
<tr>
<td>Magnetic stirrer rotation speed</td>
<td>200 rpm</td>
</tr>
<tr>
<td>Materials</td>
<td>API 5L X65 mild steel</td>
</tr>
<tr>
<td>Corrosion rate measurements</td>
<td>Ferrous ion concentration measurement</td>
</tr>
<tr>
<td>Water condensation rate</td>
<td>1.4 mL/m²·s</td>
</tr>
<tr>
<td>Test duration</td>
<td>1h - 60h</td>
</tr>
</tbody>
</table>

The exposed area of the specimen is 7.786 cm². The microstructure of the specimen shows ferrite grains with cementite precipitates at their boundaries [13].

**RESULTS AND DISCUSSION**

**Validation of the continuous treatment protocol**

**Persistency results with continuous dilution**

The experiments were run at 40°C with a system set up by which the dilution could be done continuously using 140 L uninhibited brine. In all these experiments, a X65 specimen was corroded for 10 minutes and then 50 ppm BDA-C14 was prepared and added using the same previously described procedure. After approximately 5 hours, when the corrosion rate was stable, uninhibited brine was continuously flushed through the glass cell until the final corrosion rate reached the initial uninhibited value. During the dilution process, different samples were taken from the solution for inhibitor concentration evaluation. Figure 7 shows representative results for this type of persistency experiment with continuous dilution. These results suggest that the persistency of BDA-C14 is only a couple hours after which the corrosion rate starts to continuously increase. This period also corresponds to the time needed to remove any residual corrosion inhibitor from the solution. The gradual increase of the corrosion rate is assumed to be governed by the desorption kinetics of the inhibitor, as it is discussed in the next section. As it shown in Figure 7, after a couple of hours the inhibitor concentration is zero until the end of the test which suggests
that a continuous dilution experiment would be successful in simulating a field condition with an interruption in continuous injection of an inhibitor.

The Langmuir isotherm is commonly used to describe inhibitor adsorption/desorption behavior. It is a simple model assuming a mono layer adsorption and no interaction between inhibitor molecules. This model expresses the change in surface coverage with regards to time as shown in Equation (3).

\[
\frac{d\theta}{dt} = k_A C_{inh} (1 - \theta) - K_D \theta
\]  

(3)

By solving for surface coverage (\(\theta\)), and considering \(\theta = 0\) at \(t = 0\), an explicit function of the \(\theta\) with respect to time, expressing the change in surface coverage during the adsorption process, can be obtained:

\[
\theta(t) = \left( \frac{K_{AD} C_{inh}}{1 + K_{AD} C_{inh}} \right) (1 - e^{-(k_A C_{inh} + k_D)t})
\]  

(4)

where \(\theta\) is surface coverage, \(K_{AD}\) is the equilibrium constant (\(M^{-1}\)), \(k_D\) is the desorption constant (\(M^{-1}.s^{-1}\)), \(k_D\) is the desorption constant (\(s^{-1}\)) and \(t\) is time (\(s\)). This equation can be fitted to the experimental data to determine values of kinetic constants (using a least squares regression method). Figure 8 shows the results of Equation (4) fitted to the experimental data at 40\(^\circ\)C for BDA-C14 inhibitor concentrations of 25, 50, and 75 ppm.
Desorption behavior

To calculate change in the corrosion rate for the desorption part, Equation (3) can be used with different assumptions than the adsorption part. After the dilution, change in the CI concentration can be calculated using Equation (5). Thus, Equation (3) can be solved numerically by considering $\theta = 1$ at $t = 0$.

$$C_{\text{inh}}(t) = C_0 e^{-\frac{Q}{v} t}$$  \hspace{1cm} (5)

where $C_{\text{inh}}(t)$, $C_0$, $Q$ and $v$ are CI concentration at time $t$ $(M)$, initial CI concentration in $(M)$, volumetric flowrate $(m^3/s)$ and solution volume $(m^3)$ respectively. Accordingly, changes in corrosion rate with time can be calculated using the below equation:

$$CR_{\theta(t)} = CR_{\theta=0} - \theta(t) \times (CR_{\theta=0} - CR_{\theta=1})$$ \hspace{1cm} (6)

where $CR_{\theta=0}$ is blank corrosion rate and $CR_{\theta=1}$ is stable corrosion rate at maximum coverage.

Calculated values

Using Equation (4) fitted to experimental values, adsorption/desorption kinetic constants were calculated for BDA-C14 as shown in Table 4. Utilizing these calculated values, Equation (3), Equation (5) and Equation (6), change in corrosion rate with time can be plotted for the desorption part of the experiment (Figure 9). Although the calculated corrosion rates are different in the transient part, the general behavior of the corrosion rate after dilution is successfully modeled using the Langmuir isotherm model. The observed deviations from the model in the transient part could be due to the Langmuir model not being adapted to the behavior of the inhibitor at 40°C. In addition, experimental errors in the determination of the surface saturation concentration and of the values of the kinetic constants $k_A$ and $k_D$ could also affect the shape of the corrosion rate curve in the transient part.
Table 4. Calculated values for adsorption/desorption kinetics for BDA-C14.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$k_A (mM^{-1} s^{-1})$</th>
<th>$k_D (s^{-1})$</th>
<th>$K_{AD} (mM^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>135.8</td>
</tr>
</tbody>
</table>

Figure 9. Corrosion rate for the desorption part using Langmuir isotherm model versus experimental data (40°C, 0.97 bar pCO$_2$, X65 RCE, 1000 rpm, BDA-C14 inhibitor).

Validation of the batch treatment protocol

BLC corrosion rate analysis

Figure 10 shows the corrosion rate trends without the inhibitor (blank test) and after exposure to the batch inhibitor, following the procedure outlined earlier. According to Figure 10, in the absence of the batch treatment inhibitor, the corrosion rate remained constant at around 3.5 mm/y during the entire experimental duration. However, with the application of the batch corrosion inhibitor BDA-C16 and its subsequent removal by rinsing, the corrosion rate decreased to around 0.5 mm/y immediately after the rinsing procedure (time 0 hour) and remained constant for approximately 20 hours. The corrosion rate increased progressively to reach a value of around 2.9 mm/year after 60 hours of exposure and remained relatively stable until the 90-hour mark. The BCI showed a relatively long persistency (50 to 60 hours). However, the corrosion resistance started to decrease after 20 hours of exposure. The OCP of the sample shifted to more anodic potential with BCI compared to the blank at the beginning of the experiments, which confirmed that the inhibitor initially was adsorbed on the sample surface. With time, the OCP decreased to reach the same value as the blank. This may be explained by desorption of the BCI as the surface coverage of inhibitor on the sample surface decreased after 20 hours of experiments [12]. The experiment has been repeated and the overall error was less than 6%.

Figure 10. Corrosion rate versus time: (X65 RCE, 30°C, pH 4.0, 1000 rpm, 0.96 bar CO$_2$).
TLC corrosion rate analysis

Additional experiments were performed using the TLC setup. The TLC rate was calculated based on the \( \text{Fe}^{2+} \) concentration measurement in the condensed water.

According to Figure 11, the corrosion rate of the blank specimen without BCI treatment remained at 0.4 mm/y for 55 hours of the experiment (black squares). The corrosion rate of the BCI treated specimen was 0.02 mm/y at the beginning of the experiment and remained at 0.04 mm/y for 30 hours, after which it increased to 0.2 mm/y over the remaining time of the exposure (red dots). The change in inhibitor concentration in the condensed water was modeled and persistency time could be predicted, giving trends qualitatively like what was measured with corrosion results [13].

![Figure 11. TLC rate based on Fe²⁺ concentration measurements in the condensed water. (The experimental condition: T gas 65°C, T specimen 35.5°C, pCO₂ 0.65 bar)](image)

CONCLUSIONS

A new experimental setup was used for mimicking the continuous treatment of a metal surface by a corrosion inhibitor. Continuous dilution was successfully implemented and could ensure minimum residual corrosion inhibitor content in solution. This method for the dilution could be used for corrosion inhibitor persistency measurements because it is more representative of the interruption in continuous treatment by a corrosion inhibitor in the field. BDA-C14 model compound inhibitor showed little persistency when all the inhibitor residuals were removed from the bulk. In addition, Langmuir isotherm model was shown to be a useful technique for modeling the adsorption and desorption of the inhibitor.

A batch corrosion inhibitor testing procedure that can maintain stable water chemistry, avoid \( \text{O}_2 \) contamination, and be adapted for TLC environments was developed. Testing and evaluation of a batch inhibitor for BLC and TLC mitigation was then performed. The pre-filming procedure and corrosion testing was done in the same glass cell. During the corrosion testing process, linear polarization resistance (LPR) is utilized to measure in situ corrosion rates for BLC and \( \text{Fe}^{2+} \) concentration is monitored to measure corrosion rates for TLC. BDA-C16 has a relatively long persistency compared to BDA-C14 applied by continuous injection, but it could leave the TLC specimen’s surface with condensed water droplets, leading to a diminution in corrosion resistance.

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REFERENCES


