

Methodology of Batch Inhibition Applied for Top and Bottom of the Line Corrosion Mitigation

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ABSTRACT

Quaternary ammonium compounds that exist as a waxy solid at low temperatures typically exhibit excellent persistency when applied in batch corrosion inhibitors (BCI), which are one of the mainstays of corrosion protection for many integrity management strategies worldwide. The performance of these type of corrosion inhibitor is often evaluated in laboratory conditions, prior to field application. The most common laboratory method to characterize BCI involves the filming procedure called the dip and drip method, where the steel specimen is immersed in neat BCI for a few seconds before testing. However, this dip and drip method carries several drawbacks, one of them being the likely oxygen (O_2) contamination what is sure to impact the results. In addition, extrapolation of laboratory measurements to field conditions are often performed without rigorous modeling, and application parameters are consequently suboptimal; this results in inefficient or, at worst, ineffective protection being provided to the steel in the corrosive environment. In this research, a BCI testing procedure was developed for bottom of the line corrosion (BLC) that can maintain stable water chemistry and avoid O_2 contamination, with the potential to be adapted for top-of-the-line corrosion (TLC) environments. The pre-filming procedure of BCI and corrosion testing can be done in the same glass cell which eliminates O_2 contamination and have capabilities to remove residual inhibitors after the pre-filming process. The linear polarization resistance (LPR) method was utilized to measure in situ corrosion rates. UV-vis spectroscopy was applied to monitor corrosion inhibitor concentrations, which showed repeatable results and demonstrated the accuracy and efficiency of this methodology of batch inhibition applied for BLC and TLC mitigation.

Key words: Batch inhibition, mild steel, TLC mitigation, inhibitor concentration

INTRODUCTION

Corrosion leads to economic costs equivalent to 4-5% of gross national product (GNP), environmental contamination, infrastructure degradation, safety risks, reputational damage, and litigation ¹. However, 35% of the cost of corrosion can be reduced by adoption of appropriate mitigation measures ². In the industry of transportation of oil and gas, much effort has been made to understand the role of CO_2 in internal corrosion of pipelines, due to the ubiquitous presence of the corrosive gas in wells and geologic formations ³⁻⁸. Main mitigation strategies include use of coatings, cathodic protection, corrosion resistant alloys, and organic corrosion inhibitors. The use of corrosion inhibitor presents many advantages for internal corrosion. First, inhibitors can be directly injected in the flow without affecting

production and their use are relatively versatile as injection rates can be adjusted easily ⁹. Secondly and most importantly, its associated costs are low compared to other mitigation techniques ⁹.

Batch corrosion inhibitors are among common methods of protection against bottom-of-the-line corrosion (BLC) and top-of-the-line corrosion (TLC). These inhibitors are usually high molecular-weight and oil-soluble molecules. Such materials are tenacious, sticking well to pipe surfaces ¹⁰. However, mature oil and gas wells generate large amounts of water. Consequently, water dispersible inhibitors are applied in such production environments. The difference in most batch corrosion inhibitors usually is their formulation, i.e., which molecular species are present therein.

The standard filming procedure for inhibitor evaluation is called the dip and drip method. In this method, mild steel specimens are first polished to a certain (600 or 800 grit) finish. They are then dipped into an inhibitor solution for a specified period at room temperature. During this process, the contact time varies and might affect the persistency ¹¹. The specimen is then drip dried (25 minutes to 1 hour) ¹¹. Excess inhibitor might be wiped from the specimens ¹¹. In addition, there may be a “rinse step” with a model brine ¹². In each step of the procedure, it is likely that O₂ contamination will impact the results.

So far, accurate modeling of batch corrosion inhibitor application for BLC and TLC has not been performed. Moreover, application parameters have not been optimized, which results in inefficient, or ineffective, corrosion protection.

Considering this gap in knowledge and practice, this research aimed to improve the testing/treatment protocol for BCI and its applicability to BLC and TLC scenarios.

EXPERIMENTAL PROCEDURE

Tested Inhibitor in BLC and TLC Experiments

BCI formulations used in industry are typically a proprietary cocktail of several molecules, some acting as the actual corrosion inhibitors and others to aid dispersion. However, for a mechanistic study, it is better to study one single compound. The choice of this model compound is somehow arbitrary, as long as 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 ¹³. The efficiency of batch corrosion inhibitors is typically related to the alkyl tail length ¹³. For this study, the model compound benzyldimethylhexadecyl ammonium (C16-BDA) (Figure 1) was chosen as the inhibitor to investigate the application of BCI to BLC and TLC. While the head group is quaternary ammonium-type, the choice of the tail length (C16-BDA) was made based on preliminary data that showed superior performances ¹³. The surface saturation concentration of C16-BDA was set at 50ppm_w in 1 wt.% NaCl solution¹³. C16-BDA is synthesized in-house as a waxy solid and needs to be solubilized in isopropanol before injection. To simulate batch treatment, 1 mL of a deoxygenated isopropanol solution with 15 wt% inhibitor was sprayed on the API 5L X65 mild steel specimen surface. Assuming full dissolution in the testing electrolyte, the corresponding inhibitor concentration should be 75 ppm_w.

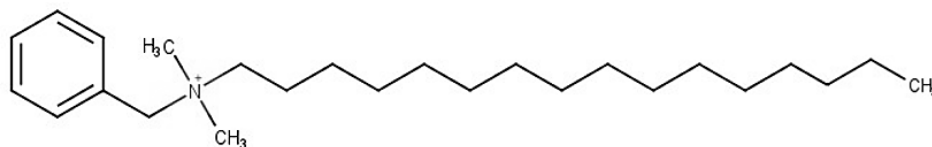


Figure 1 Benzyldimethylhexadecyl ammonium (C16-BDA) molecule

Batch Treatment Testing Protocol for BLC

Experiments were conducted using the “controlled water chemistry” glass cell setup as shown in Figure 2.

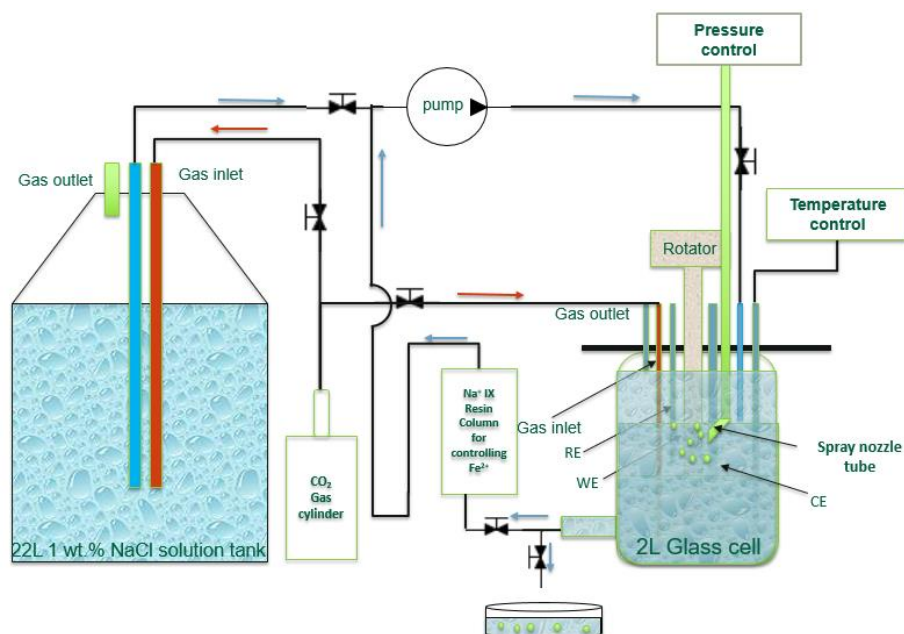


Figure 2 Schematic representation of the experimental setup for batch treatment testing

Four steps were required to begin the corrosion testing. It started with the inhibitor solution formulation and deoxygenation. A 15 wt% C16-BDA solution was prepared by dissolving the inhibitor in isopropanol. The inhibitor solution was then deoxygenated with nitrogen (N_2) for 2 hours. Then 22 L of 1 wt% sodium chloride (NaCl) electrolyte was purged with carbon dioxide (CO_2) for 6 hours to assure that all the dissolved oxygen was removed, and the solution was saturated with CO_2 . A magnetic stirrer was used to ensure that the solution was always well mixed. A Na^+ -form ion exchange resin (Amberlite, IR120, Acros Organics) was used to control Fe^{2+} concentration ($[Fe^{2+}]$). The electrolyte pH was controlled manually controlled at around pH 4 using dilute hydrochloric acid (HCl) or sodium bicarbonate ($NaHCO_3$) solutions. The resins were added into the columns and purged with CO_2 for 2 hours.

The steel specimens used in this part of the study were standard rotating cylinders electrode (RCE). The specimens were sequentially polished with silicon carbide paper of 150, 400, 600 grit. They were then sonicated in isopropanol to remove any residual particles or contamination and dried with N_2 . The surface area of each specimen was measured.

After these initial steps were completed, the glass cell was assembled as shown in Figure 2. The working electrode was then installed, and the glass cell was purged with CO_2 for 2 hours. As for the final step, the glass cell and the purged columns with ion-exchange resins were put together with continuous CO_2 purging until the start of solution transfer.

When the system was properly purged, the desired volume (1mL) of the deoxygenated inhibitor was injected into the tubing connected to the nozzle. The tubing was then pressurized with CO_2 ($pCO_2 \sim 30$ psi). At this point, the rotation of the cylinder was started at a 200rpm rate and the valve connected to the inhibitor injection nozzle was opened to create a mist that was applied to the entire surface of the

specimen. After 30 seconds of inhibitor spraying, the pre-purged electrolyte was pumped into the glass cell at the rate of 2000 mL/min. The pumping was stopped after the solution volume in the glass cell reached 2 L, ensuring that the specimen was fully immersed in the electrolyte. This procedure was repeated 7 times. It is noteworthy that foaming occurred during this procedure but that the amount of foam at the water/air interface decreased after each rinse, suggesting that less inhibitor remained in the test solution.

After the rinsing step was completed, the loop with Na⁺-exchanged resins was opened to circulate the solution. Linear polarization resistance measurements were conducted using a traditional three electrode set up and a Gamry potentiostat. The Stern Geary equation was used to convert the polarization resistance into a corrosion rate, using a B value 26mv/dec¹⁴. A saturated silver/silver chloride Ag/AgCl (KCl sat) reference electrode and a platinum counter electrode were used for the electrochemical experiments. Table 1 shows the experimental matrix that was followed to examine the corrosion persistency of the batch inhibitor.

Table 1 Test matrix for the BLC electrochemical experiment

Parameter	Conditions
CO ₂ partial pressure	0.96 bar
Solution	1 wt.% deoxygenated NaCl solution
Inhibitor solution	15 wt.% C16-BDA
pH	4.00 ± 0.02
Temperature	30.0°C
RCE rotation speed	1000 rpm
Material	API 5L X65 mild steel
Corrosion Rate Measurement	LPR, weight loss

Batch Treatment Testing Protocol for TLC

The schematic of the experimental setup for TLC mitigation experiments is shown in Figure 3. This setup is similar to what was used for the BLC scenario. The main differences lie in the steel samples location (in TLC experiments they are flushed 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 [Fe²⁺] measurement).

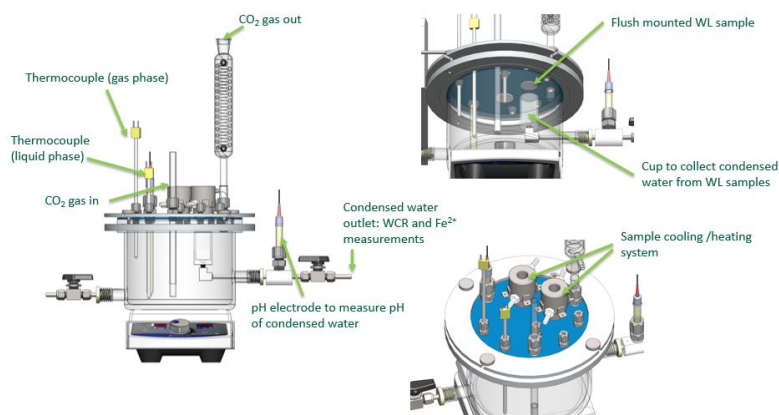


Figure 3 Schematic of the experimental setup for TLC (Image courtesy of Cody Shafer, ICMT)

In these experiments, 1 mL of deoxygenated 15 wt.% C16-BDA (dissolved in isopropanol, 75 ppm_w total) was sprayed on the surface of X65 mild steel specimen using the spray nozzle as shown in Figure 4.



Figure 4 Inhibitor spray nozzle for TLC experiment

Table 2 shows the experimental matrix that was followed to test the persistency of the batch corrosion inhibitor in TLC experiments. A set relatively aggressive conditions were selected, featuring high temperature and water condensation rate, to verify the applicability of batch treatment to TLC and to evaluate the persistency of BCI in condensing environment.

Table 2 Test matrix for the TLC experiment

Parameter	Conditions
CO₂ partial pressure	0.96 bar
Solution	Deionized water
Inhibitor solution	15 wt.% C16-BDA
pH of the bulk electrolyte	4.00 ± 0.02
Steel temperature	35.5 °C
Liquid temperature	75.0 °C
Gas temperature	65.0 °C
Magnetic stirrer rotation speed	200 rpm
Materials	API 5L X65 mild steel, 304 stainless steel
Corrosion Rate Measurements	Ferrous ion concentration measurement Weight loss specimen
Water condensation rate	1.4 mL/(m ² ·s)

RESULTS AND DISCUSSION

Inhibitor Concentration Monitoring

UV-Vis measurements were performed to monitor the concentration of inhibitor in the glass cell solution during the corrosion rate measurements. It was expected that the inhibitor would continuously desorb from the steel sample even after the rinsing steps. A calibration curve of C16-BDA was generated by measuring absorbance at different concentrations. UV-Vis absorbance measurements were performed using an Agilent Cary 60 UV-Vis spectrometer.