

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 benzyldimethylammonium (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 reproduceable 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 (benzyl dimethylhexadecyl ammonium), 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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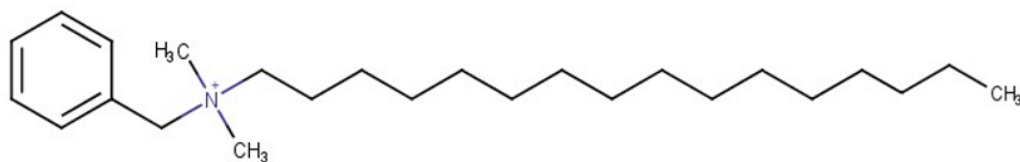


Figure 1. Benzyldimethylhexadecylammonium (BDA-C16)

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.

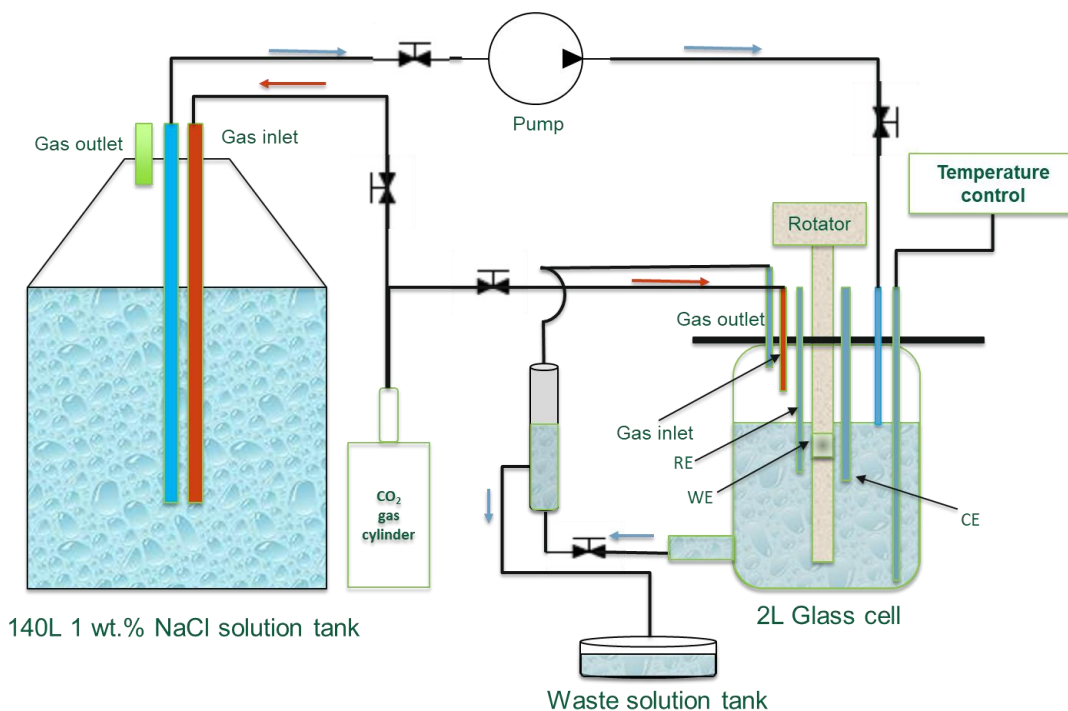


Figure 2. Schematic of the setup used in persistency experiments using continuous dilution.

Table 1. Experimental test matrix for the continuous treatment experiments.

Parameter	Conditions
Working electrode	API 5L X65 (0.05 wt.%C)
Electrolyte	1 wt.% NaCl
Sparge gas	CO ₂
Total pressure	1 bar
Rotational speed	1000 RPM
Temperature	40°C & 30°C ± 1°C
pH	4.0 ± 0.1
Corrosion inhibitor (CI) model compound	Quaternary ammonium type (BDA-C14)
Measurement methods	OCP, LPR, EIS
Contact time (time before dilution)	When stable corrosion rate achieved
Initial inhibitor concentration	50 ppm
Presence of hydrocarbon	None – brine only
Pre-corrosion before CI injection	10 minutes

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 ultra-sonic cleaner. 3 ml isopropanol was injected into the vial containing solid inhibitor and then was fully

[‡] Trade name.