

## **Investigation of CO<sub>2</sub> Corrosion Inhibitor Adsorption and Desorption Behavior Using Langmuir Isotherm Model and Effects of Iron Carbide on CI Persistency**

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### **ABSTRACT**

One of the most conventional methods to mitigate CO<sub>2</sub> corrosion of pipelines in the oil and gas industry is to use chemical corrosion inhibitors. Probably the most commonly used inhibition method in the upstream oil and gas industry involves the continuous injection of an appropriate chemical formulation package to maintain a constant concentration of inhibitor in the fluid flowing through the pipeline. Selection of the inhibitor package is typically done through a tedious laboratory testing campaign, which involves the determination of the inhibitor efficiency and persistency in simulated production conditions. Developing laboratory methodologies that can help assessing these properties is of prime importance. This study presents methodologies that could simulate continuous inhibitor treatment (for the determination of efficiency), and also interruption of inhibitor injection (for the assessment of persistency). The study was performed using a model, yet representative, compound benzyldimethylammonium type CO<sub>2</sub> corrosion inhibitor (BDA-C14). Its adsorption/desorption behavior was characterized. Furthermore, the influence of several key aspects of the experimental methodologies, such inhibitor contact and pre-corrosion times were examined using BDA-C14, mostly to investigate the effects of the iron carbide layer on inhibitor persistency. A three-electrode system using a rotating cylinder electrode (RCE) for the working electrode was used in this study with the ability for continuous flow-through dilution. All experiments were divided into three main steps: pre-corrosion, inhibitor addition and corrosion rate stabilization, then inhibitor dilution. The corrosion rate was monitored using linear polarization resistance (LPR) in all experiments. Langmuir isotherm model was used to model inhibitor adsorption and desorption behavior of BDA-C14 inhibitor using calculated kinetic coefficients.

**Keywords:** CO<sub>2</sub> corrosion, corrosion inhibition, inhibitor persistency, continuous treatment, adsorption and desorption, Langmuir model

## INTRODUCTION

CO<sub>2</sub> corrosion of the internal walls of mild steel pipelines has always been a significant problem in the oil and gas industries. Different methods have been implemented to mitigate internal pipeline corrosion. The use of corrosion inhibitors provides advantages compared to other mitigation techniques as inhibitor treatment costs are seen to be lower and can be easily adjusted over time. Thus, chemical inhibitors are widely used as a conventional method to mitigate internal pipeline corrosion. Inhibitors are injected inside producing pipelines using two main methods : continuous corrosion inhibitor (CI) injection and batch inhibitor (BI) treatment.<sup>1-7</sup> In continuous CI treatment (which is of interest in this study), water-soluble inhibitor solutions are injected into the flow stream at a specific volumetric flow rate to obtain the desired concentration, which is typically below 2000 ppm(v). These inhibitors are not expected to form a tenacious film on the pipeline inner surface. The properties on the inhibitor film present on the metal surface are controlled by the inhibitor bulk concentration and the adsorption/desorption equilibrium. Therefore, if an interruption to the continuous injection occurs, the bulk inhibitor concentration in the flow stream decreases rapidly and the inhibitor is expected to desorb from the surface, resulting in a loss of corrosion protection. Adsorption and desorption behaviors of inhibitor molecules depend on several parameters: the physicochemical characteristics of the CI, characteristics of the metal surface, and flow stream conditions (temperature and flow rate).<sup>2-12</sup>

The corrosion inhibitors behavior in continuous treatment is often evaluated in laboratory conditions prior to field application. Different studies have developed experimental procedures to simulate both continuous and batch treatment.<sup>8, 13-16</sup> However, there have always been some difficulties in getting reproducible results due to the lack of consistency and clarity in testing protocols. Nevertheless, a common acceptable experimental procedure for mimicking the ‘failure’ of a continuous treatment program in the laboratory could be found in the literature:<sup>8, 13-16</sup>

1. Prepare deoxygenated solution and metal specimen for a glass cell setup.
2. Measure blank corrosion rate (CR) in a CO<sub>2</sub> saturated solution under specific test conditions without inhibitor (pre-corrosion step).
3. Inject a targeted concentration of inhibitor and measure the stable inhibited corrosion rate (inhibition step) after some time period.
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 over time until it increases back to 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.

Correlations between corrosion inhibition and adsorption/desorption behaviors are typically developed using isotherm models. Several isotherm models can be found in the literature. The most common ones, that are used for interaction between inhibitor molecules and the metal surface, are the Langmuir, Frumkin, Bockris-Swinkels and Virial Parson isotherms. Among these isotherms, the Langmuir isotherm model is the simplest and most widely used in the literature. This model assumes that molecules adsorb on the surface by forming a monolayer and the interaction between the adsorbate molecules is negligible.

In this study, a Langmuir isotherm model was used to calculate the adsorption/desorption kinetics followed by modeling the corrosion rate in both the inhibition and dilution steps.<sup>17-22</sup>

## EXPERIMENTAL PROCEDURE

### Experimental procedure for simulation of (interruption in) continuous treatment

The system set-up described below was used to investigate the effect of continuous dilution of the inhibited solution on inhibitor persistency. All experiments were done in a 3-electrode glass cell apparatus (Figure 1). Experiments investigating the persistency of the inhibitor including the continuous dilution step were performed using an overall larger setup shown in Figure 2. The test matrix for experimental procedures is shown in Table 1.

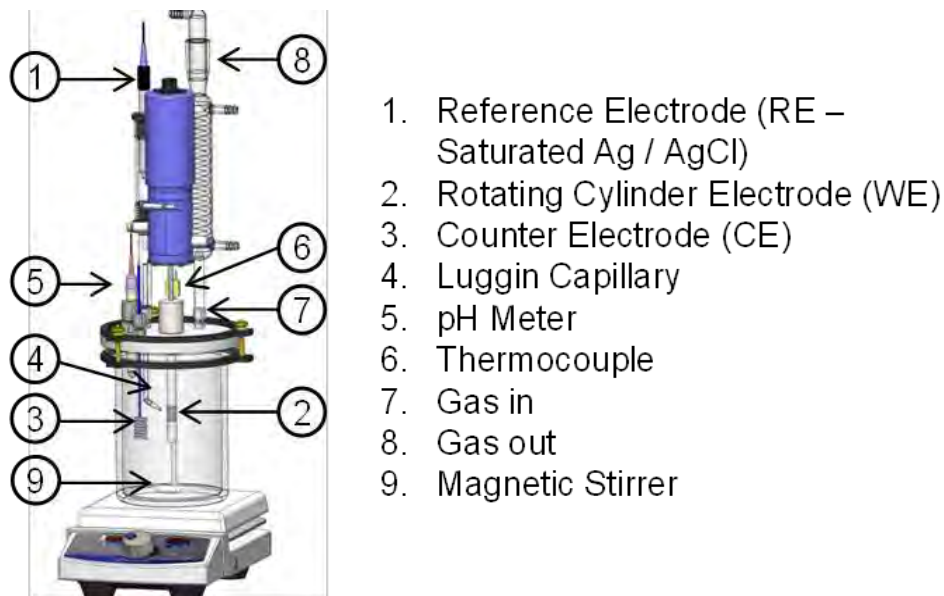


Figure 1: 3-electrode glass cell setup

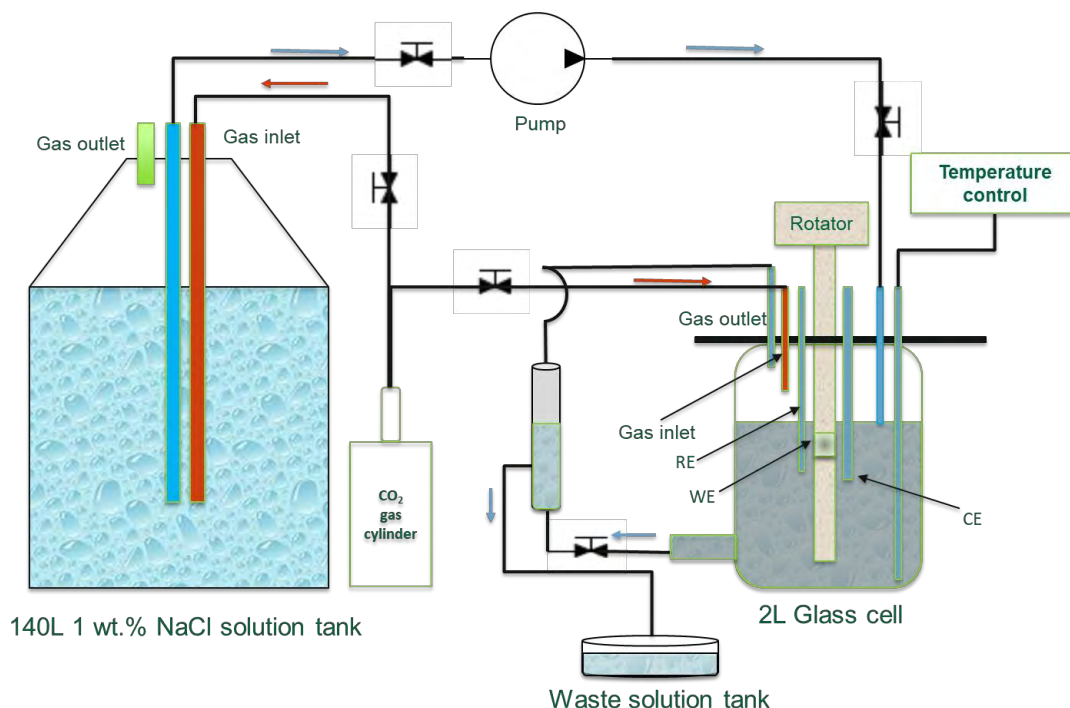


**Figure 2: Schematic of the setup used in persistency experiments which provided continuous dilution.**

**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 <sub>2</sub>                    |
| Total pressure                                         | 1 bar                              |
| Rotational speed                                       | 1000 RPM                           |
| Temperature                                            | 30°C ± 1°C                         |
| pH                                                     | 4.0 ± 0.1                          |
| Corrosion inhibitor (CI) model compound                | Quaternary ammonium type (BDA-C14) |
| Measurement methods                                    | OCP, LPR, EIS                      |
| Initial inhibitor concentration                        | 50 ppm                             |
| Presence of hydrocarbon                                | None – brine only                  |
| Pre-corrosion before CI injection                      | 20 minutes and 2 hours             |
| Contact time with the inhibitor (time before dilution) | 9 hours and 29 hours               |
| CI measurement method                                  | UV-vis spectroscopy                |

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 CO<sub>2</sub> for a minimum of 1 hour to keep the dissolved O<sub>2</sub> content to a few ppb.

3. Insert polished steel specimen in glass cell and 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 (deoxygenated and sparged with CO<sub>2</sub> at the same working temperature) to the working glass cell. An overflow technique is used to continuously drain the solution at the same rate as solution is added while keeping liquid level constant and not allowing oxygen to backflow into the working glass cell.
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 decrease of inhibitor concentration, by taking 10 mL of the solution from the outlet each time.

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

#### Pre-corrosion

1.8 L of 1 wt.% NaCl was purged in a three-electrode glass cell for an hour to ensure deoxygenation and facilitate CO<sub>2</sub> saturation. The concentration of the oxygen was monitored during the experiment via an Orbisphere<sup>†</sup> 410 connected to the gas outlet of the system. The working electrode then was carefully 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 and delivery

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 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 attain 50 ppm<sub>w</sub> 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 at a rate of approximately 80±10 mL/min. This would “fully exchange” the solution in the glass cell every 22 minutes. The fluid renewal was continued until the end of the test. This method should remove all the inhibitor residuals from the solution, which is a key factor in simulating field condition in continuous treatment. With this dilution method, the change in bulk inhibitor concentration with regards to time can be calculated as follows:

$$C_{inh}(t) = C_{inhibitor0} e^{-\frac{Q}{V}t} \quad (1)$$

where  $C_{inhibitor0}$ ,  $Q$ ,  $V$ , and  $t$  are initial inhibitor concentration (ppm), dilution flowrate (L/min), solution volume (L), and time after dilution (min) respectively.

#### CI concentration measurement using UV-vis spectroscopy

The initial and residual inhibitor concentrations were measured during the experiments. Liquid samples were taken directly from the working glass cell at different times of the experiment and their absorbance

<sup>†</sup> Trade name.