

Localized corrosion propagation of carbon steel in inhibited environment: a potentiostatic approach

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ABSTRACT

The initiation of carbon steel localized corrosion is commonly observed in inhibited environments, both in field and laboratory settings, even though the uniform corrosion rate remains low. While many reasons have been reported to explain pit initiation, little research has considered whether these pits will propagate or not. This work focuses on evaluating the tendency of localized corrosion propagation due to galvanic coupling between the inhibited surface and active pit. Complexity in simulating this phenomenon likely influences the paucity of research addressing this mechanism. Given that its main

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driving force is the difference in potential between both surfaces, the potentiostatic technique is an interesting methodology to simulate this corrosion mechanism. This work was done considering a primarily imidazolinium-based corrosion inhibitor under produced water conditions (5 wt.% NaCl, pH 4.5, CO₂) at 55 and 80°C. Linear polarization resistance (LPR) and potentiodynamic polarization were used to obtain baseline results and characterize the inhibitor performance. The baseline anodic potentiodynamic sweeps indicated that, at certain critical anodic potential/current conditions, the inhibitor is fully desorbed from the surface. Several potentiostatic experiments were conducted, maintaining the electrode potential in between the open circuit potential and this critical desorption potential – this was meant to simulate, albeit very artificially, different levels of galvanic couple that could exist in case of active localized corrosion and to investigate why active corrosion could still persist inside a pit even though the corrosion inhibitor was still present in the bulk solution. It is acknowledged that this methodology makes this work quite exploratory and that the results should be viewed as preliminary. The potentiostatic experiments indicated that, at certain anodic potentials, the injection of inhibitor did not decrease the current measured to the same levels expected from the baseline potentiodynamic sweeps. Increased inhibitor dosage proved to be necessary at certain conditions to significantly decrease the current. However, at high current levels, further injections were insufficient, indicating that substrate dissolution might undermine the adsorption of the inhibitor.

Key words: Corrosion inhibition, Localized corrosion propagation, Inhibition efficiency, Imidazoline, High temperature, Potentiostatic.

INTRODUCTION

Localized corrosion is known as the most dangerous and unpredictable corrosion mechanisms found in hydrocarbon production and transmission systems. This mode of corrosion has the potential to cause serious financial loss, environmental damage, production interruption, and even loss of life. Over the years, corrosion engineers have made significant improvements on prediction and mitigation techniques to extend the lifespan of carbon steel pipelines, such as using of corrosion inhibitors; injection of such chemicals has proven to be effective and economic, making them a first choice over other alternatives. However, long-term use of organic corrosion inhibitors in the oil and gas industry has shown a high potential for occurrence of localized attack. This might take place when the inhibitor is not appropriate to the operating conditions or when the inhibitor dosage is too low, in the presence of corrosion product layers or sand, or when the pipeline surface is exposed to extreme shear stress^{1,2}. Although pit initiation has been widely reported in the presence of inhibitors^{1,3,4}, discussion of propagation has been limited.

The propagation process is typically driven by the local galvanic coupling established between the area covered by the corrosion products or corrosion inhibitors and the bare steel surface area of the pit. Galvanic current drives the propagation of the pit causing severe damage to exposed metal surfaces. Some authors⁵⁻⁷ attempted to simulate this mechanism using cells composed of two electrodes – a cathode and an anode – in which they had their surface properly prepared to act as such and then were connected via a zero-resistance ammeter (ZRA) to monitor the galvanic current. The separation between the electrodes giving rise to ohmic resistance was one of the challenges faced by the authors⁷. The poor understanding of the involved phenomena stems from the complex system that does not lend itself to artificial simulation. Thus, it is important to develop methodologies that aim to simulate the mechanisms involved.

While the ZRA setup mentioned above is the “gold standard” when investigating galvanic coupling, other, less complicated, techniques can be used to give some insights on the phenomena. The potentiostatic methodology emerges as an interesting rapid and easy alternative to simulate artificially such phenomenon using only one working electrode in a conventional three-electrode electrochemical cell. Once a potential is applied to the working electrode, a current will be induced. One should be able to apply different ranges of potential to the artificial anode simulating the propagation of localized corrosion might take place following the aforementioned model. Therefore, if the inhibitor is efficient, one should observe a decrease on the current flowing through the sample when injecting the corrosion inhibitor into

the solution. The methodology would also allow a better understanding of the electrochemical parameters that govern the adsorption/desorption mechanisms of the inhibitors as well as improving the existing models⁸ for this matter. Consequently, the objective of this work is to utilize the potentiostatic methodology to further understand the role of inhibitor and important factors in stifle the propagation of localized corrosion of carbon steel. The next step of this work will be to design a proper ZRA setup and repeat this study.

EXPERIMENTAL PROCEDURE

Carbon steel C1018 (UNS G10180⁽¹⁾) was machined into flat specimens and mounted in epoxy for the electrochemical experiments. The chemical composition of the material used is listed in Table 1. The ferritic and pearlitic microstructure contained 2.28 wt.% of cementite phase (Fe_3C) according to the lever rule. The surface was grinded with #180, and #400 grit silicon carbide abrasive paper with water flow, finished with #600 grit SiC abrasive paper with isopropanol flow, cleaned in an ultrasonic isopropanol bath and air-dried prior to each experiment.

Table 1: Composition (wt.%) of flat C1018 carbon steel specimens.

Element	C	Al	Cu	Mn	Mo	Ni	S	Si	Fe
Composition	0.16	0.007	0.088	0.65	0.019	0.055	0.010	0.25	Balance

All experiments were performed using a 2 L glass cell. The electrolyte was an aqueous solution with 5 wt.% NaCl, CO_2 as sparging gas, 1 bar total pressure and pH 4.5. Temperatures of 55°C and 80°C were assessed. Prior to each experiment, the electrolyte was sparged with CO_2 for at least 2 hours to deoxygenate; sparging was continuous during each experiment to avoid any oxygen ingress and maintain CO_2 saturation. The pH of the solution was maintained at 4.5 ± 0.1 by adding hydrochloric acid (HCl) and sodium bicarbonate (NaHCO_3). The corrosion inhibitor used in this study is an imidazolinium-based commercial inhibitor in the concentration of 50 ppm. This dosage is the recommended by the manufacturer and it is above the surface saturation concentration (SSC) for both temperatures.

A three-electrode electrochemical cell was used having a Pt-coated mesh as counter electrode, a KCl saturated Ag/AgCl reference electrode (connected to the glass cell via a salt bridge and a Luggin capillary), and the C1018 as the working electrode. The electrochemical measurements were conducted using a potentiostat. Open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) measurements were taken. The EIS data was collected at OCP from 5 kHz to 1 Hz with a perturbation amplitude of 10 mV rms. The LPR measurements were conducted using a range from -5 mV to +5 mV vs. OCP, with a scan rate of 0.125 mV/s using a B value of 26 mV for corrosion rates calculations. At the conclusion of each experiment, a cathodic potentiodynamic sweep was conducted. The anodic potentiodynamic sweep was conducted after the OCP returned to the original value before the cathodic sweep.

Baseline experiments

Establishing baselines of uninhibited and fully inhibited bare steel prior to the potentiostatic experiments is essential to understand the potential and current densities ranges in which the material will respond whenever a potential is applied. In this step, the corrosion rates were monitored using LPR for 5 hours

⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

under the inhibited and uninhibited conditions. For the inhibited environment, the inhibitor was injected into the solution after 20 minutes of pre-corrosion. For both conditions, after assessing the corrosion rate evolution, potentiodynamic sweeps took place cathodically and anodically.

Potentiostatic experiments

At this stage, before applying any potential to the sample, the sample stayed in the solution for OCP stabilization for 20 minutes. The working electrode was then polarized to 4 different positive fixed potentials over the OCP of the bare steel ($\text{mV}_{\text{OCP, bare steel}}$), simulating possible scenarios:

- $+25 \text{ mV}_{\text{OCP, bare steel}}$ – to simulate the localized corrosion propagation when there is a galvanic coupling established between a surface covered with iron carbonate (FeCO_3) and the active surface of the pit (bare surface) ⁶.
- $+70 \text{ mV}_{\text{OCP, bare steel}}$ – to simulate the localized corrosion propagation when there is a more severe galvanic coupling established between the surface covered with corrosion inhibitors and the active surface of the pit.
- $+100 \text{ mV}_{\text{OCP, bare steel}}$ – to simulate a more extreme condition in which the difference in potential is higher than the OCP difference between the area covered and the area uncovered with inhibitor.
- $+150 \text{ mV}_{\text{OCP, bare steel}}$ – to apply an overpotential in the sample close to the desorption potential ⁹ observed in the baseline tests.

For all potentiostatic tests, the potential was applied to the sample in an uninhibited environment (5 wt.% NaCl, pH 4.5, CO_2) for 300 seconds (5 minutes), and then 50 ppm of the corrosion inhibitor was injected into the solution. The induced current was monitored throughout the experiment, and additional dosage of the inhibitor was added when necessary.

RESULTS

Baseline experiments

The corrosion rate (from LPR) changes over time for both inhibited (CI) and uninhibited (bare steel) environments at 55°C and 80°C are depicted in Figure 1. For the bare steel conditions the rates did not appreciably change, although the condition at 80°C was slightly more aggressive with corrosion rates of around 3 mm/year after 5 hours. As expected, with injection of the corrosion inhibitor the corrosion rates dropped significantly for both temperatures, with the 55°C condition yielding values as low as 0.1 mm/year after 5 hours. Even so, it must be highlighted that at 80°C there was a residual corrosion rate above 0.1 mm/y after 5 hours of experiment.

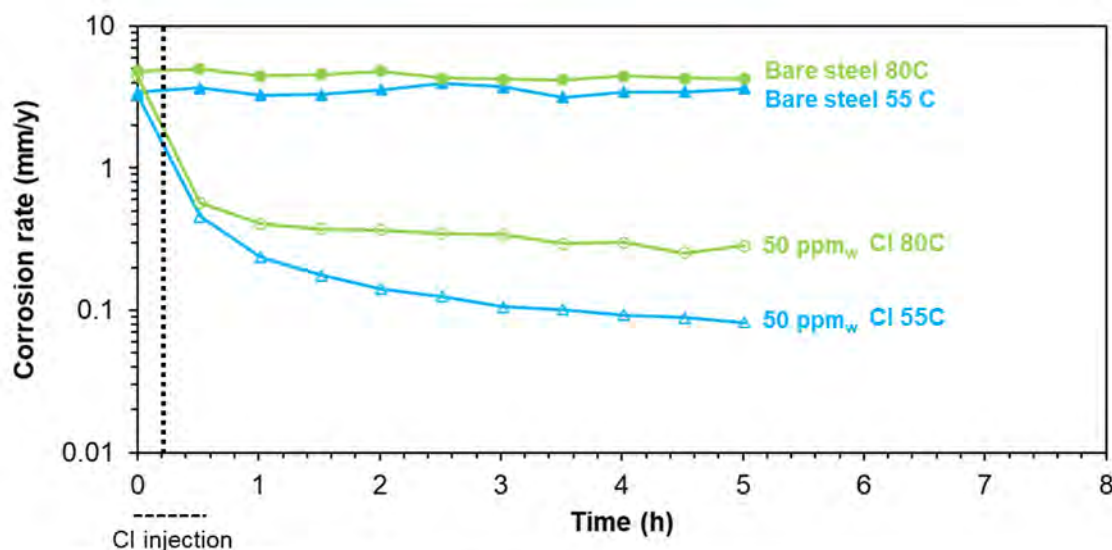


Figure 1: LPR corrosion rates over time for inhibited and uninhibited condition at 55 and 80°C.

The main purpose of this section is to document the anodic current one should expect during the potentiostatic tests. The anodic potentiodynamic sweeps were performed in all four conditions (55°C and 80°C and with/without inhibitor), and the curves are shown in Figure 2.

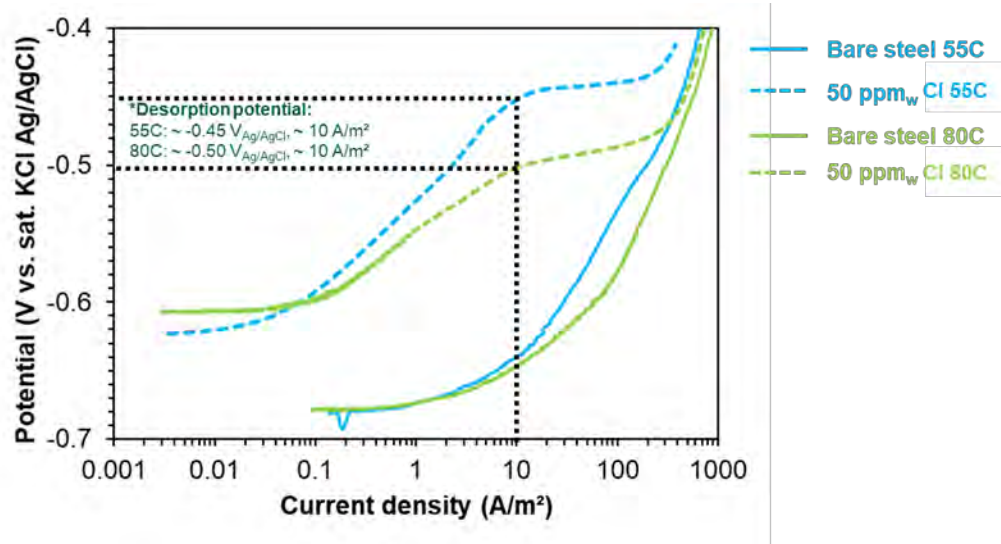


Figure 2: Baseline anodic sweeps for the inhibited and non-inhibited condition at 55 and 80°C.

In the uninhibited environment, the anodic sweeps obtained at both temperatures behaved similarly, with the one at 55°C being slightly retarded in comparison to the one at 80°C. Temperature also played a negative role in the inhibited environment as the curve associated to 80°C was slightly accelerated in relation to that observed at 55°C. Another important observation relates to the so-called “desorption potential”^{9–11} for the anodic sweep in the inhibited condition. According to the literature, it is assumed that the inhibitor adsorbed on the steel surface would be fully or partially desorbed when the potential is applied above a certain critical anodic potential. The main reason for this behavior is linked to a phenomenon called electrochemical desorption¹², associated to the Langmuir isothermal model⁸, that states that applying an anodic potential generates an electrostatic repulsion between the surface and the inhibitor that weakens the adsorption bond. At this point the current increases rapidly and the material starts to behave like bare steel again, evidenced by the overlapping of the curves in both environments