

Impact of Fe₃O₄ on the Performance of an Imidazolinium-Based Inhibitor for Mitigation of CO₂ Corrosion of Carbon Steel

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ABSTRACT

Use of corrosion inhibitors to mitigate pipeline corrosion is common in the oil and gas industry. Despite this, few studies focus on how the presence of corrosion products affect their performance. This work aimed to understand the impact of Fe₃O₄ on the performance of a commercial primarily imidazolinium-based corrosion inhibitor formulation. A magnetite layer was formed in an autoclave at a high temperature (1 wt.% NaCl, N₂ sparged, pH 4, 120°C). The performance of the corrosion inhibitor was investigated with and without the presence of Fe₃O₄ (5 wt.% NaCl, CO₂, pH 4.5, 55°C). Linear polarization resistance (LPR) and potentiodynamic polarization were employed to study the effect of Fe₃O₄ on corrosion rate (CR) and inhibition efficiency (IE). Scanning electron microscopy (SEM) and Raman spectroscopy were used to characterize specimen surfaces. The acquired data showed that the presence of magnetite limited inhibitor performance. Dissolution of the magnetite layer over time in the CO₂ environment was also observed. This behavior was expected as the experiments were performed in non-thermodynamically favorable conditions for magnetite formation. Polarization sweeps indicated that the cathodic charge transfer and the limiting current of the H⁺ reduction reaction were significantly accelerated due to the Fe₃O₄ layer. This behavior can be explained by the increase in cathodic reaction area due to the conductive nature of magnetite.

Keywords: Corrosion inhibition, Iron oxide, Magnetite, Inhibition efficiency, Potentiodynamic polarization

INTRODUCTION

Among the techniques disseminated in the industry to protect carbon steel pipelines against internal corrosion, the use of corrosion inhibitors (CIs) is one of the most common. Organic compounds containing nitrogen are commonly employed in the petroleum industry to decrease corrosion rates. The high inhibition efficiency can be attributed to adsorption capacity on the metallic surface, creating a protective film that interferes with the electrochemical reactions involved in the corrosion processes.^{1–3}

The selection of appropriate corrosion inhibitors, however, poses several challenges. Typically, it is done through a lengthy and systematic testing process where the performances of each CI candidate are evaluated in simulated operating conditions. Yet, the corrosion inhibitor performances are commonly determined on carbon steel specimens with freshly polished surfaces – this is done to ensure consistency of the results but omits to consider the actual state of the pipeline internal surface. Under operating conditions, however, the internal pipeline surface is far from being neatly polished, and it may instead be covered by products of corrosion such as iron carbonate, sulfides, oxides (which form by precipitation) and/or carbide (which is the results of the dissolution of the ferrite phase). These layers can affect corrosion inhibition, and it is important to document their role. This study focuses on the role of magnetite in corrosion inhibition. Magnetite is not as commonly encountered in oil and gas production as carbonates or sulfides. However, magnetite can still be present on the steel surface in certain conditions: as a product of the manufacturing process (mill scale),^{4,5} in cases of oxygen ingress⁶ or at high-temperature applications ($>120^{\circ}\text{C}$).^{7,8} When investigating the influence of surface layers on corrosion inhibition, in this case, magnetite, several effects can be expected:

- Magnetite can act as a mass transfer barrier to species diffusing to and away from the metal surface, preventing CI from reaching the surface,
- Inhibitor molecules can adsorb preferentially on magnetite, decreasing the effective concentration of CI in bulk and limiting the CI efficiency, and possibly leading to surface heterogeneity and localized corrosion,
- Magnetite being a moderate electrical conductor, can create galvanic coupling with the surface and enhance the baseline corrosion rate, which in turn can decrease the CI efficiency,
- Since magnetite can be protective, a synergistic effect with CI is possible.

The research described herein focuses on the impact of the presence of Fe_3O_4 on the inhibition behavior in a simulated exploration production environment. A thick and uniform Fe_3O_4 layer was formed at high temperatures in an autoclave, thus providing a consistent method for magnetite formation. The inhibition behavior of an imidazolinium-based corrosion inhibitor was evaluated with and without the presence of Fe_3O_4 through linear polarization resistance (LPR) and potentiodynamic sweeps. Surface analysis techniques, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy, were employed to characterize the specimen surfaces after the magnetite formation and after the experiments at the exploration production environment.

EXPERIMENTAL PROCEDURE

Carbon steel specimens used for electrochemical measurements were machined from UNS G10180* carbon steel (C1018) with a ferritic-pearlitic microstructure with the specified elemental composition provided in Table 1. Before each experiment, the specimens were sequentially polished with 180, 400, and 600-grit silicon carbide abrasive papers, rinsed, and ultrasonically cleaned with isopropanol for two minutes. The specimens were then dried in nitrogen gas and stored in a desiccator.

* 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.

Table 1
Composition (wt.%) of UNS G10180 carbon steel

Element	C	Mn	Si	Ni	Cu	Mo	S	Al	V	Ti	Nb	P	Fe
	0.16	0.65	0.25	0.055	0.088	0.019	0.01	0.007	0.002	0.001	0.002	0.009	balance

Experimental Method and Electrochemical Techniques

The experimental procedure consisted of a two-stage process (Figure 1). The first stage consisted of forming a magnetite layer on the surface of the specimen in a consistent and repeatable manner. To achieve this, the UNS G10180 carbon steel specimens were exposed to a high-temperature aqueous environment in an autoclave (Figure 2-a) to generate the magnetite layer. The specimens were characterized using Raman spectroscopy, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The “magnetite” specimens (i.e., specimen covered with a magnetite layer) were stored under vacuum before being transferred to glass cells (Figure 2-b) and were tested both in the absence and presence of an imidazolinium-based commercial corrosion inhibitor, after which they were again characterized using the same techniques.

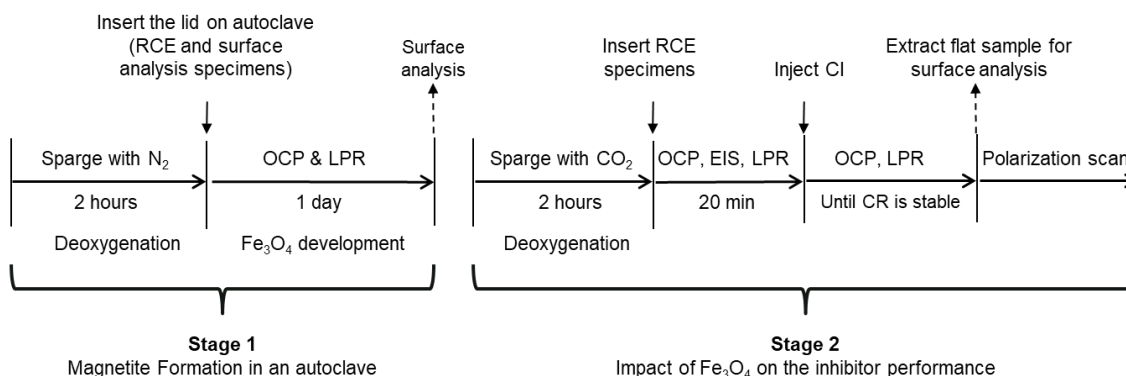


Figure 1: General experimental procedure.

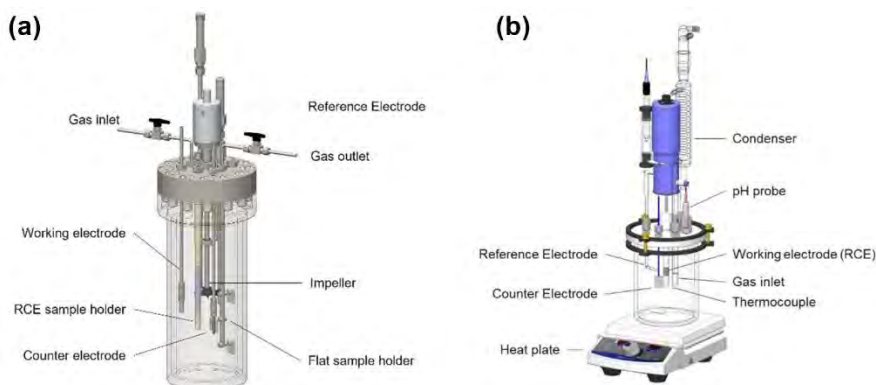


Figure 2: Experimental setup[†]. Note: (a) 4 L stainless steel autoclave setup used in Stage 1 in Figure 1; (b) 2 L glass cell setup used in Stage 2 in Figure 1.

The corrosion rate was assessed by linear polarization resistance (LPR) measurements, with a scan rate of 0.125 mV/s between ± 5 mV vs. OCP, and B value of 26 mV.⁹ Electrochemical impedance spectroscopy

[†] Image courtesy of Cody Shafer, ICMT, Ohio University.

(EIS) data were collected from 5kHz to 1 Hz with 7 points per decade with a perturbation amplitude of 5mV rms. Cathodic potentiodynamic polarization sweeps were conducted at the end of each experiment in the glass cell when the corrosion rates were stable. The anodic potentiodynamic sweeps were taken subsequently when the OCP returned to the original value; they were taken from the OCP up to +0.1 V vs. OCP. The ohmic drop was compensated for in all the presented curves. All electrochemical measurements were carried out via a potentiostat (Gamry Interface 1010[‡]).

Magnetite Formation

Carbon steel with a preformed Fe₃O₄ layer was generated following a methodology presented in the literature: the layers were performed in high-temperature condition and an N₂ environment.⁸ This step was not done in a CO₂ environment in order to create a pure and uniform layer of Fe₃O₄ on the carbon steel surface and to avoid the formation of FeCO₃ (which is a standard corrosion product in the presence of CO₂). Magnetite was formed in a 4L stainless steel autoclave in a deaerated brine solution containing 1 wt.% NaCl in deionized water under anaerobic conditions at 120°C for 24 hours, as summarized in Table 2. A full schematic representation of the autoclave setup is shown in Figure 2-a. The autoclave was filled with 3000 mL of brine solution and purged with N₂ for at least 2 hours. Then the solution pH was adjusted at 80°C according to the water chemistry calculation to achieve pH 4.0 at 120°C. The magnetite formation experimental parameters are provided in Table 2.

Three geometries of UNS G10180 specimens were employed: 1) cylindrical specimens (rotation cylinder electrode, RCE, 1.4 cm in height and 1.2 cm in outer diameter) for inhibition experiments in the glass cell, 2) flat square specimens (1.0 cm x 1.0 cm x 0.2 cm) for weight loss and surface analysis, and 3) cylindrical specimen (2.0 cm in height and 1.0 cm in outer diameter) for electrochemical measurements in the autoclave. Once the specimens were in place, the autoclave was sealed and heated to 120°C. A three-electrode electrochemical cell setup was used: a high-temperature and high-pressure Ag/AgCl reference electrode, a Pt-coated Nb counter electrode, and the working electrode (UNS G10180 carbon steel, Table 1). OCP, EIS, and LPR measurements were performed to ensure that the surface conditions of the steel specimens were consistent among all sets of tests. The pH is monitored using a ZrO₂-based pH probe that can operate in high-temperature and high-pressure environments. A centrally located impeller was used to keep the solution fully mixed during each test. When the experiment was completed, the autoclave was depressurized. The specimens were then rinsed with deionized water and isopropanol and dried in air.

Table 2
Experimental matrix for magnetite formation

Description	Parameters
System	4 L stainless steel autoclave
Aqueous solution	1 wt.% NaCl
Material	UNS G10180
Spurge gas	N ₂
Temperature	120°C
Initial pH	4.0 ± 0.1
Rotational speed of impeller	1000 rpm
Duration	1 day
Measurement Methods	OCP, LPR, weight loss
Surface Characterization	Raman spectroscopy, SEM/EDS

[‡] Trade name

Inhibition Experiments

The magnetite specimens obtained from the autoclave experiments were immediately rinsed, dried, weighted, and stored in a desiccator before being inserted into a glass cell. The inhibition experiments were performed in a 2 L glass cell with a rotating cylinder electrode (Figure 2-b). All experiments were conducted at 55°C in the 5 wt.% NaCl solution saturated with CO₂ at pH 4.5, as summarized in Table 3. The conditions were selected based on a previous study by the authors.^{10,11} and aimed at mimicking an environment typical of exploration & production. The solution was deoxygenated with CO₂ for at least 2 hours before each experiment. Sparging with CO₂ was maintained throughout the test to prevent O₂ ingress. A pH probe was inserted in the glass cell to monitor the pH changes. The electrolyte pH was adjusted throughout experiments to 4.5±0.1 with deoxygenated NaHCO₃ or HCl solutions, as necessary. After the insertion of the RCE specimen, the rotation speed was set at 1000 rpm. An imidazolinium-based commercial corrosion inhibitor package (50ppm_w) was injected into the solution directly using a syringe equipped with a long needle. The inhibitor concentration was above their bare steel surface saturation concentration, where the inhibited uniform corrosion rate would not decrease further if more corrosion inhibitor were added. It is important to mention that, at the time of this experimental series, no method had been developed to measure the Cl concentration in the aqueous phase.

Table 3
Experimental matrix for the experiments in EP environment

Parameter	Condition
System	2 L glass cell with RCE
Aqueous solution	5 wt.% NaCl
Material	UNS G10180
Sparge gas	CO ₂
Total pressure	1 bar
Temperature	55°C
pH	4.5 ± 0.1
Rotational speed of RCE	1000 rpm
Corrosion inhibitor	Imidazolinium-based (50 ppm _w)
Measurement Methods	OCP, LPR, potentiodynamic sweeps
Surface Characterization	Raman spectroscopy, SEM/EDS

A three-electrode electrochemical setup was used in this study, with a Pt-coated mesh as a counter electrode, a KCl saturated Ag/AgCl reference electrode connected to the glass cell via KCl salt bridge and a Luggin capillary, and C1018 RCE samples with and without the magnetite layer as a working electrode. For the uninhibited conditions, the OCP, EIS, and LPR were collected periodically for 5 hours until the LPR stabilized. The corrosion inhibitor was injected directly into the water phase for the inhibited conditions after a 20-minute pre-corrosion period. Subsequently, the OCP, EIS, and LPR were collected for 24 hours. The cathodic and anodic potentiodynamic polarization sweeps were collected at the end of the experiments. Each experiment was repeated twice.

RESULTS

Magnetite Formation

Corrosion rate

Electrochemical measurements were taken every 30 minutes over 24 hours in a deaerated N₂ environment at 120°C. These measurements facilitated real-time monitoring of the corrosion rate during