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Effects of Oxygen on Corrosion Inhibition in Sweet Systems

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ABSTRACT

This research investigates the impact of oxygen on a representative corrosion inhibitor's efficacy in oil-water systems, a crucial concern in petroleum engineering. Electrochemical experiments were conducted to explore the relationship between dissolved oxygen and the performance of the inhibitor formulation for various oil-water mixtures. Linear polarization resistance (LPR) and potentiodynamic polarization methods were employed to assess corrosion behavior in the presence and absence of the inhibitor, under both oxygenated and oxygen-free conditions. The findings indicate that oxygen plays a significant role in inhibitor effectiveness, with potential implications for corrosion control strategies. Variations in corrosion rates and polarization characteristics were observed between oxygenated and deoxygenated environments. In the oxygen-containing system, the cathodic polarization curves revealed two distinct limiting currents, attributed to oxygen reduction and hydrogen ion reduction processes. This study offers insights into oxygen-influenced corrosion and inhibition mechanisms in oil-water systems, contributing to the advancement of more effective corrosion prevention approaches in the petroleum sector.

Keywords: Corrosion inhibition; oil-water systems; CO_2; O_2; electrochemical measurements.

INTRODUCTION

Oil and gas production systems use mild steel for the construction of most pipelines. Mild steel pipelines are susceptible to internal corrosion because of the contents flowing through the infrastructure and the conditions inside them. To mitigate the corrosion, corrosion inhibitor chemicals are injected into these systems. The effectiveness of these corrosion inhibitors depends on various factors, including- organic solvents, intermittent wetting, and oxygen contamination, which can all affect their performance. To evaluate the effectiveness of corrosion inhibitors, extensive laboratory evaluation is necessary. These evaluations need to replicate complex field conditions, to demonstrate their real world application efficiency. Laboratory tests not only demonstrate the effectiveness of the corrosion inhibitor, but also how other factors impact its effectiveness. This information plays a key role in effective corrosion mitigation strategies.

As hydrocarbon reservoirs are typically devoid of oxygen[1], it is generally assumed that oil and gas infrastructure is free of any oxygen. However, oxygen contamination is a common occurrence in these systems. Various factors can lead to the ingress of O_2 into the infrastructure, such as leaks, maintenance routines, equipment failures, chemical injections, and improper protocols.[1] Through these ingress mechanisms, the oxygen contamination levels can range from parts per billion (ppb) to parts per million (ppm). This oxygen can get consumed by corrosion process near the point of entry or it may build up in areas with little flow causing localized corrosion.

Gulbrandsen investigated the effect of oxygen contamination on organic, film-forming corrosion inhibitors and their ability to mitigate CO_2 corrosion.[2] Their investigation demonstrated that when the test brine contained less than 1 ppb of dissolved oxygen, the inhibitors successfully mitigated the corrosion rate by two orders of magnitude. Furthermore, changing mass transfer didn't affect these mitigated corrosion rates in absence of oxygen.[2] However, with 100 ppb of oxygen, the corrosion rates were dependent on the mass transfer rates suggesting that diffusion of oxygen through the bulk to the surface affected the corrosion process.[2] Gulbrandsen emphasized the effect of ppb amounts of dissolved oxygen, with concerns for oxygen contamination when testing effectiveness of corrosion inhibitors against CO_2 corrosion. Stricter oxygen protocols could potentially avoid weaker inhibitor performance and misleading flow effects.

Oxygen organic solvents are frequently used to dilute or dissolve corrosion inhibitors for small-scale lab evaluations which can also influence the effectiveness of inhibitors. Wang investigated how isopropanol, a common solvent, affects corrosion inhibition on mild steel in a CO_2 environments using electrochemical test methods.[3] Wang discovered increased currents when the electrode was subjected to cathodic polarization when high amounts of isopropanol was used to dilute the inhibitor, particularly protonated inhibitors like imidazolinium and pyrimidinium.[3] Isopropanol alone did not exhibit such an effect. Wang recommended that the effect of any organic solvents used to dilute inhibitors in small-volume corrosion tests must be evaluated before corrosion inhibitor efficiency testing.[3]

Intermittent wetting due to multiphase flow also has an impact on corrosion inhibition in oil and gas systems. He et al. studied intermittent wetting effects on the corrosion inhibition of mild steel in oil/water systems using a model compound, tetradecyltetrahydropyrimidinium (THP-C14).[4] Their findings revealed that in the presence of CO_2 oil improved corrosion inhibition by promoting the formation of a thicker inhibitor-hydrocarbon film, which created a stronger diffusion barrier and reduced corrosion rates significantly.[4] The researchers stressed the need to develop experimental methods to examine how intermittent wetting influences corrosion inhibition to help predict inhibition performance in oil/water environments.[4]

Oxygen, organic solvents, and intermittent wetting have an impact on the effectiveness of corrosion inhibitors in oil and gas systems. Elucidating the effect of these factors on the performance of corrosion inhibitors is essential to create effective ways to improve inhibition efficiencies and design reliable lab testing methods. This study aims to examine how oxygen affects corrosion inhibition in simulated oil and gas production environments and build mechanistic understanding of the earlier research.[1–4]

BACKGROUND

The oxygen reduction reaction (ORR) goes through a four-electron transfer pathway, Equation (1), with peroxide or superoxide as intermediate species.[5] ORR plays a key role in fuel cells and metal corrosion, where it has an impact on the electrochemistry of the system. Oxygen reduction reaction (ORR) has a high reversible potential,[6] which makes the mass transfer kinetics of oxygen diffusion from the bulk to the steel surface more important than the charge transfer kinetics of the electrochemical reaction. This implies that mass transfer is a dominant factor, not charge transfer kinetics, which controls the corrosion rate. Hence, the limiting currents linked to mass transfer kinetics become key factors when studying how oxygen causes corrosion. This is of great importance in environments with inhibitors, where H^+ reduction might be inhibited because of the presence of these inhibitors. Mathematical implications of these kinetics are discussed further in the paper.

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad E_{rev} = 1.23V\ vs\ SHE\ ^{6} \tag{1}$$

The role of organic solvents in influencing inhibitor performance is another key factor that needs more discussion. Wang et al. studied how corrosion inhibitor model compounds behaved when isopropanol (IPA) was used as a solvent.[3] Imidazolinium, tetrahydropyrimidinium, and phosphate ester compounds were studied as model inhibitor compounds. Without oil present, some inhibitor compounds exhibited two distinct limiting currents in their cathodic polarization curves resembling a double wave appearance.[3]

The present work aims to investigate the effect of oxygen on corrosion inhibition in oil and water systems, building upon the findings of previous studies.[2,3,7] This study aims to shed light on how oxygen, organic solvents, and corrosion inhibitors interact together. This study also hypothesizes that inhibited systems exhibit a double wave pattern when oxygen is introduced, similar to reported literature on organic solvents. However, even with the presence of both oxygen and organic solvents together, it is hypothesized to be the dominant reason for this double wave effect. Evidence of this effect would reinforce the need to primarily consider oxygen contamination in inhibited systems.

EXPERIMENTAL METHODOLOGY

Materials and Chemicals

1018 carbon steel (C1018) specimens with a ferritic-pearlitic microstructure were used for electrochemical measurements. The chemical composition of this carbon steel is shown in Table 1. A commercial inhibitor (Inhibitor A) was used in this study. It was injected at concentrations of 10 ppm and 25 ppm by dilution in isopropanol (IPA) directly into the water phase.

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

Element	**Cr**	**Mo**	**S**	**V**	**Si**	**C**	**Ni**	**Mn**	**P**	**Fe**
Weight %	0.076	0.015	0.026	0.001	0.21	0.15	0.027	0.63	0.011	Balance

Experimental Setup and Procedure

A 5 wt.% NaCl electrolyte was prepared by mixing sodium chloride with deionized water, which was then saturated with CO_2 at 30°C and 1 bar pressure. A three-electrode glass cell setup (Figure 1) was employed to investigate corrosion and the effectiveness of corrosion inhibitors in the presence of hydrocarbons. The working electrode was a rotating cylinder electrode (RCE) made from the C1018 steel. A platinum-coated titanium mesh served as the counter electrode, and a saturated Ag/AgCl electrode was used as the reference electrode.

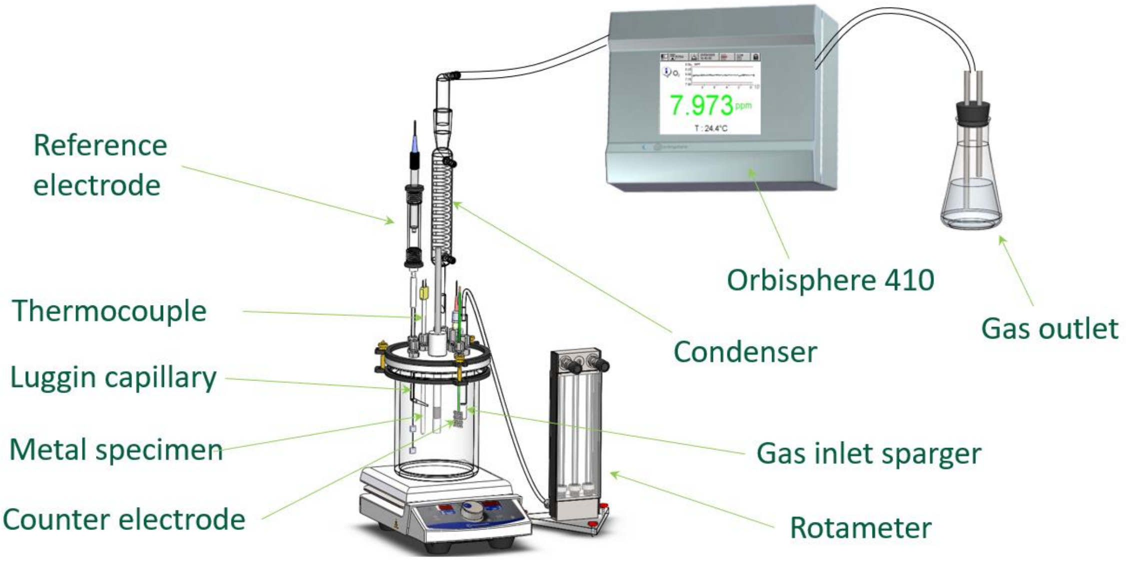

Figure 1. Experimental set up comprised of a 2-liter glass cell (image courtesy of Cody Shafer, Ohio University)

Table 2. Experimental parameters for corrosion inhibition studies.

Parameters	
Temperature	30°C, 80°C
Total pressure	1 bar
pH	4.5
Inhibitor Concentration	10 ppm
Brine and environment	5 wt.% NaCl
Dissolve oxygen concentration	200 ppb
Inhibitor	Commercial corrosion inhibitor
Measurement	LPR and potentiodynamic sweeps
Material	C1018
Rotational Speed (RCE)	1000 rpm (~1m/s pipe flow 0.1m dia.)

Before each experiment, the RCE was polished using progressively finer silicon carbide papers (240, 400, and 600 grit). The sample was then cleaned ultrasonically in isopropanol and left to air dry. The aqueous solution and model oil were sparged with CO_2 for 2 hours to remove dissolved O_2 before introducing the RCE. After placing the RCE in the glass cell, a short pre-corrosion test was performed to check for any contamination from previous experiments. Throughout the experiment, the solution was sparged with CO_2 to prevent O_2 ingress and maintain saturation. Deoxygenated HCl or $NaHCO_3$ was used to adjust the pH to 4.5 ± 0.1 as needed. Controlled oxygen concentrations were maintained in the glass cell by mixing and feeding O_2/CO_2 and CO_2 gases using a rotameter from different gas cylinders. The dissolved oxygen content in the glass cell was monitored on the gas outlet via a connected HACH Orbisphere 410 oxygen analyzer. By adjusting the composition of the gas phase using a rotameter, the oxygen concentration at 200 ppb was maintained during the experiments.

Linear polarization resistance (LPR) was used to measure corrosion rates, scanning from −5 mV to +5 mV vs. OCP at a rate of 0.125 mV/s and using a B value of 26 mV. At the end of each experiment, cathodic and anodic potentiodynamic polarizations were performed to gain insights into the corrosion mechanisms. The cathodic sweep started at OCP and went down to −0.7 V vs. OCP, while the anodic sweep started at OCP and went up to +0.3 V vs. OCP. Both sweeps used a scan rate of 0.125 mV/s and were performed using a Gamry Reference 600 potentiostat for all electrochemical measurements.

The limiting currents for the ORR and H^+ reduction were calculated using mass transfer coefficients for rotating cylinder electrodes (RCE) and corresponding diffusion coefficients. To determine the mass transfer coefficients for the RCE, the Eisenberg correlation was used:[8]

$$Sh = 0.0791\, Re^{0.7} Sc^{0.356} \tag{2}$$

where Sh is the Sherwood number (kd/D), Re is the Reynolds number ($\rho\omega d^2/\mu$), Sc is the Schmidt number ($\mu/\rho D$), k is the mass transfer coefficient, d is the RCE diameter, D is the diffusion coefficient, ρ is the fluid density, ω is the angular velocity, and μ is the dynamic viscosity.

The diffusion coefficient for O_2 in the electrolyte was taken as 2.09×10^{-5} cm^2/s at 20°C, while the diffusion coefficient for H^+ was assumed to be 9.31×10^{-5} cm^2/s at 30°C.[9]

Using these parameters, the limiting currents for the ORR and H^+ reduction were calculated as follows:

$$i_{lim} = nFkC \tag{3}$$

where i_{lim} is the limiting current density, n is the number of electrons transferred (n = 4 for O_2 reduction and n = 2 for H^+ reduction), F is Faraday's constant, k is the mass transfer coefficient, and C is the bulk concentration of the reactant (O_2 or H^+). Contribution from the presence of carbonic acid was also considered, which can be incorporated into H^+ reduction due to an established buffering effect mechanism associated with CO_2 corrosion.[10]

EXPERIMENTAL RESULTS AND DISCUSSION

The polarization curves obtained from the corrosion inhibition experiments were compared in Figure 2. In the presence of CO_2, comparison between the uninhibited and the inhibited (no O_2) test, depicted a significant change in the cathodic and anodic currents. Retarded anodic and cathodic currents were observed, indicating significant retardation of iron oxidation and H^+ reduction kinetics. Upon introduction of 200 ppb of dissolved oxygen, two separate limiting currents in the cathodic region were evident as Figure 2 illustrates. Based on the findings from the literature,[2] the first (lower) limiting current observed at lower overpotentials was linked to the oxygen reduction reaction (ORR). To validate this, expected limiting currents were calculated using the Eisenberg equation for the diffusion-limited oxygen reduction reaction.[10] The measured and calculated values had agreement, suggesting that the first limiting current results from the diffusion-limited reduction of dissolved oxygen in the electrolyte.

The second (higher) limiting current seen at higher overpotentials, was linked to the H^+ reduction reaction. This reaction often occurs at the cathode in acidic environments where H^+ reduction becomes the main cathodic process after the diffusion-limited ORR finishes.[10,11] This was also confirmed by calculating the expected limiting currents and comparing them to the measured values (Figure 2), which suggested that the second limiting current resulted from the diffusion-limited reduction of H^+. The appearance of two separate limiting currents in the cathodic polarization curve demonstrates the importance of considering both the ORR and H^+ reduction when studying the corrosion inhibition works in systems with dissolved oxygen. This is a reoccurring phenomenon as the experiments were repeated twice with the same experimental test conditions.

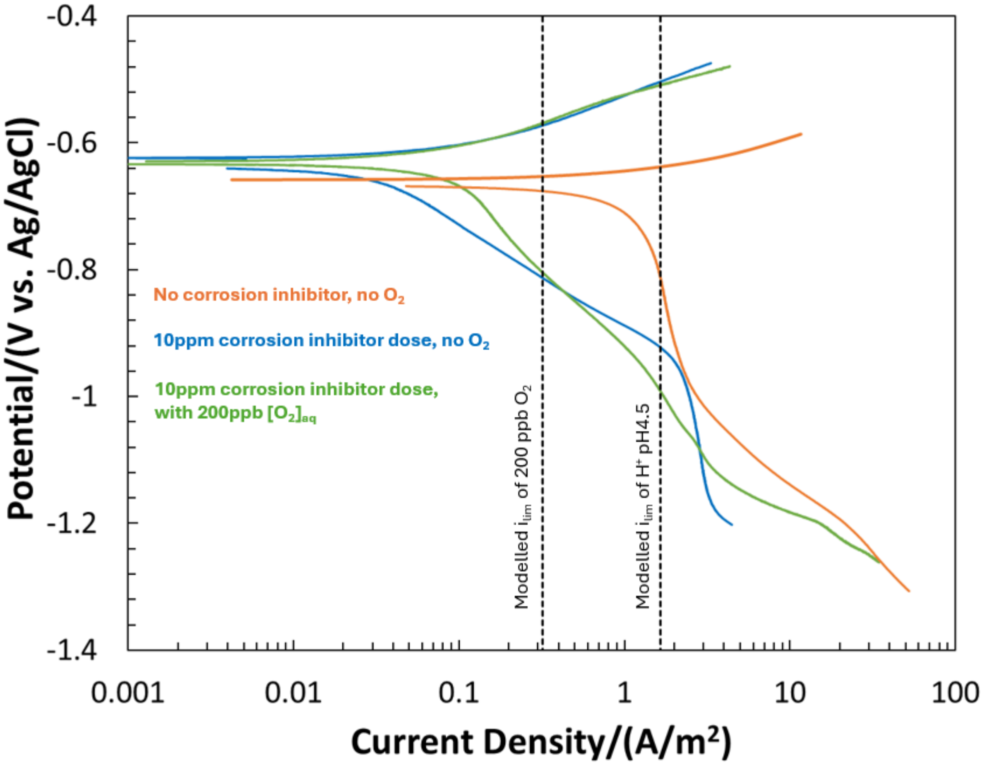

Figure 2. Potentiodynamic polarization curves showing the presence of two limiting currents for the ORR and H^+ reduction. Color legend: orange- blank test without corrosion inhibitor and without oxygen, blue- 10ppm dose of corrosion inhibitor and without oxygen, green- 10ppm dose of corrosion inhibitor with 200ppb dissolved oxygen. (Condition: 30ºC, C1018, 5 wt.% NaCl, CO_2, pH 4.5, 10 ppm inhibitor, 1000rpm RCE, 200 ppb $[O_2]_{aq}$)

Corrosion rate data over time at 30°C and 80°C, both with and without oxygen, is depicted in Figure 3 and Figure 4 respectively. Corrosion rates were initially measured without any corrosion inhibitors, which was the starting baseline. Upon introduction of corrosion inhibitors, the corrosion rates decreased over time and finally reached a steady state value. As seen in Figure 3 and Figure 4, the baseline corrosion rates (before injection of corrosion inhibitors at initial time) were similar for the tests with and without oxygen at both 30°C and 80°C. However, the steady state inhibited corrosion rates in the presence of 200ppb dissolved oxygen were significantly higher than the inhibited corrosion rates without any oxygen. This observation further highlights the impact of dissolved oxygen on the corrosion behavior of the system.

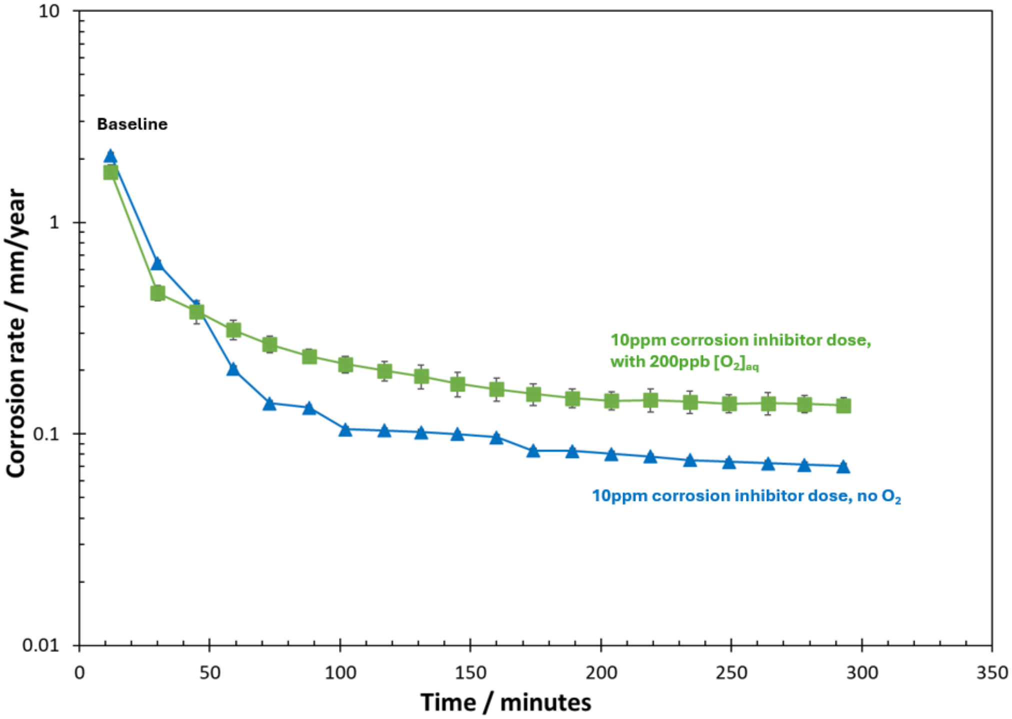

Figure 3: Corrosion rates over time with and without the presence of oxygen. Color legend: blue- 10ppm dose of corrosion inhibitor and without oxygen, green- 10ppm dose of corrosion inhibitor with 200ppb dissolved oxygen. (Condition: 30°C, C1018, 5 wt.% NaCl, CO_2, pH 4.5, 10 ppm inhibitor, 1000rpm RCE, 200 ppb $[O_2]_{aq}$)

This study investigated the oxygen contamination effects on a commercial corrosion inhibitor's performance. Adding 200 ppb of oxygen to a system with 10 ppm of the commercial inhibitor led to higher corrosion rates. Limiting currents for the oxygen reduction reaction were also evident in the cathodic polarization scans. These results corroborate Gulbrandsen's[2] findings when he studied similar effects on three different types of organic, film-forming corrosion inhibitor formulations. Gulbrandsen used three types of inhibitors: one based on imidazoline-based, quaternary ammonium-based, and amine-based.[2] Their study demonstrated that O_2 diffusion had partial or full control. Both studies found consistently higher corrosion rates and limiting currents for oxygen reduction when O_2 was present.

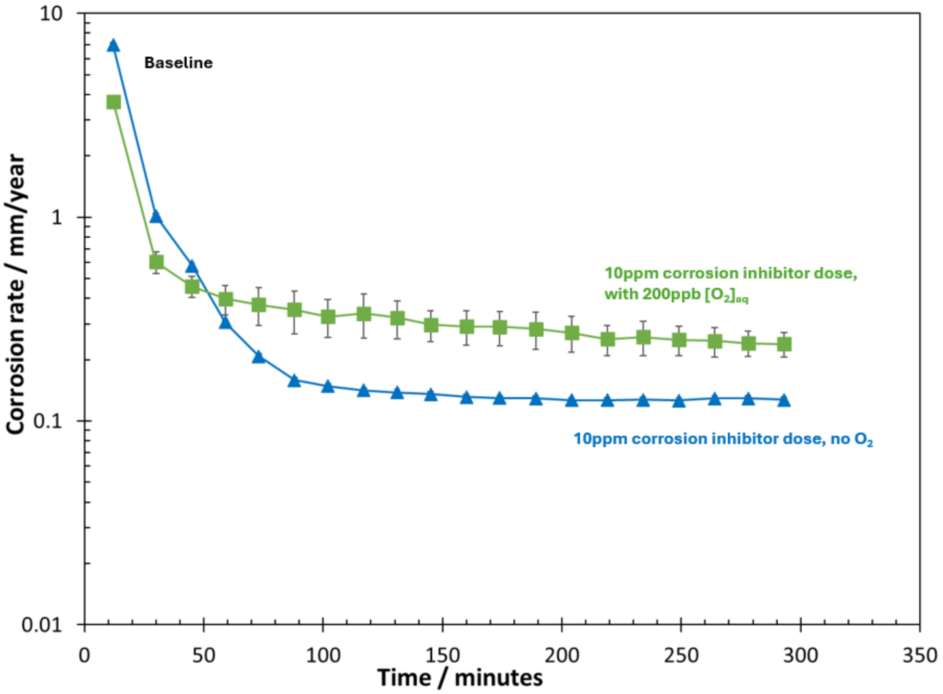

Figure 4: Corrosion rates over time with and without the presence of oxygen. Color legend: blue- 10ppm dose of corrosion inhibitor and without oxygen, green- 10ppm dose of corrosion inhibitor with 200ppb dissolved oxygen. (Condition: 80ºC, C1018, 5 wt.% NaCl, CO_2, pH 4.5, 10 ppm inhibitor, 1000rpm RCE, 200 ppb $[O_2]_{aq}$)

CONCLUSIONS

The effect of oxygen on corrosion inhibition was demonstrated in this paper, the following conclusions can be made:

- The cathodic polarization curves demonstrated two separate limiting currents, which were linked to the oxygen reduction reaction (ORR) and the hydrogen ion (H^+) reduction reaction. The experimental and calculated limiting current values for the ORR and H^+ reduction were in agreement, establishing diffusion-controlled processes.
- In the presence of oxygen, inhibited corrosion rates were significantly higher, suggesting that oxygen interferes with the inhibitor's ability to form a stable protective film on the metal surface.
- Oxygen concentrations in the water phase as low as 200ppb, can impact the protectiveness of corrosion inhibitors.
- Further studies including different inhibitor chemistries, flow conditions are needed to clarify the reasons behind this phenomenon and to investigate its impact on different types of corrosion inhibitors. More experiments need to be performed with lower oxygen concentrations for determining the exact threshold of oxygen that can be tolerated without affecting the inhibitor's performance.

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