

## Investigating the Effect of Trace O<sub>2</sub> Concentrations on CO<sub>2</sub> Corrosion Mechanisms

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### ABSTRACT

CO<sub>2</sub> co-produced in brine with crude oil is the governing corrodent in upstream oil and gas systems. A potential additional corrosive species that can be introduced through ingress is O<sub>2</sub>. Consequently, strict guidelines exist within the oil and gas industry to limit O<sub>2</sub> levels in production environments, emphasizing the significance of understanding any associated corrosion risks. These guidelines require O<sub>2</sub> concentrations to be as low as 20 ppb, however, there is little to no experimental evidence to support this limit. The aim of the research described herein was to advance the understanding of how trace O<sub>2</sub> concentrations can influence CO<sub>2</sub> corrosion mechanisms of bare steel at the acidic pH of 4. Elucidating these underlying mechanisms would enable more effective corrosion prediction, thereby enabling development of effective mitigation strategies, as well as establishing validity of the aforementioned “20 ppb” guideline related to O<sub>2</sub> ingress. To accomplish these goals, controlled experiments were performed to test aqueous O<sub>2</sub> concentrations up to 100 ppb on pipeline steel in a CO<sub>2</sub> saturated 1 wt% NaCl brine at 1 bar total pressure. Various electrochemical analytical techniques, including LPR, EIS, and potentiodynamic polarization measurements were employed. The research reported herein is foundational for characterizing the impact of oxygen in CO<sub>2</sub> corrosion environments, an ongoing research activity. This will contribute to the development of more reliable and sustainable corrosion control practices for industries experiencing CO<sub>2</sub> corrosion which can be extendable to carbon capture and transmission systems.

**Keywords:** CO<sub>2</sub> corrosion mechanisms, O<sub>2</sub> ingress, electrochemical techniques

## INTRODUCTION

Corrosion is a major problem in the oil and gas industry and pipeline failures due to corrosion can lead to catastrophic incidents such as explosions, oil spills, significant production loss, and severe safety risks. CO<sub>2</sub> corrosion (sweet corrosion) is the most common type of corrosion encountered in these systems. Carbon dioxide dissolves in water to form carbonic acid, which creates a corrosive environment via the buffering mechanism of carbonic acid corrosion<sup>1</sup>. Limited studies have demonstrated an effect of trace amounts of oxygen on CO<sub>2</sub> corrosion mechanisms<sup>2,3</sup>, reporting significantly higher corrosion rates. This paper further investigates the effect of trace amounts of oxygen on sweet corrosion at conditions relevant to upstream oil and gas production systems.

Oil and gas systems are assumed to be free from any O<sub>2</sub> as this is not present in crude hydrocarbon extracted from geologic reservoirs. However, atmospheric O<sub>2</sub> can find its way into these systems due to various reasons: leaks, maintenance, pumps, pigging, fluid injections, etc. A detailed account of these ingress sources has been discussed extensively by the authors<sup>4</sup>. Moreover, AMPP/NACE has published several standards for relating to the threshold of dissolved oxygen which are as follows<sup>5,6,7</sup>:

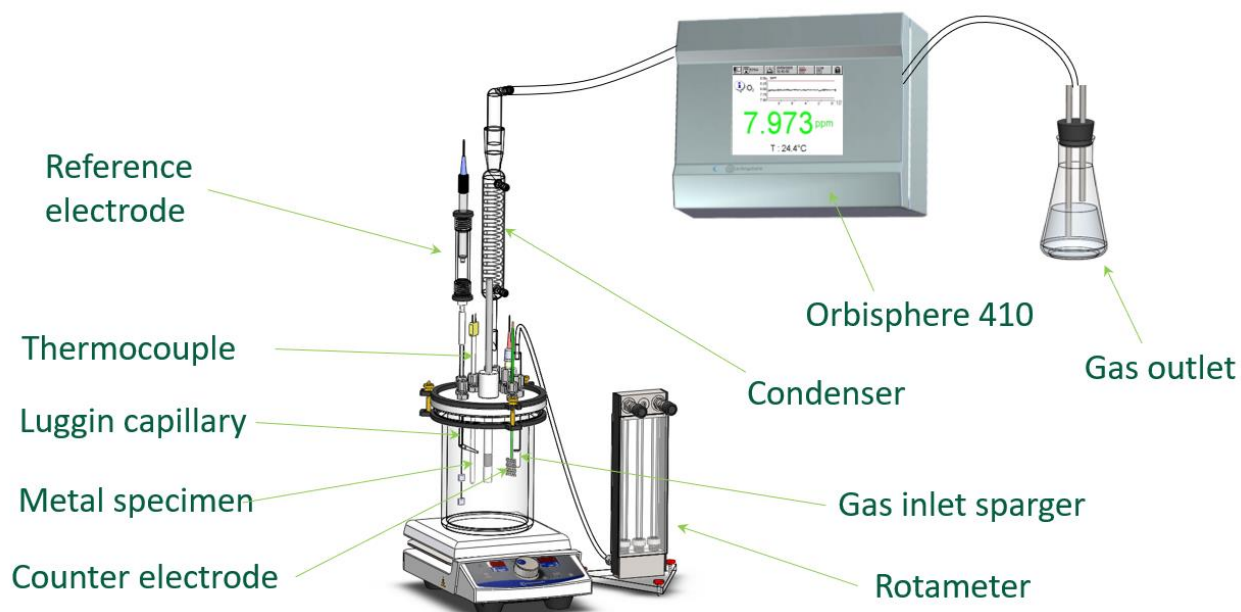
- NACE MR0175/ISO 15156: Petroleum, petrochemical and natural gas industries - Materials for use in H<sub>2</sub>S-containing environments in oil and gas production. Part 2, Section 7.2.6, which addresses the control of corrosion caused by oxygen: "Where oxygen is known or suspected to be present in the environment of the equipment, its concentration should be reduced as far as possible. If the oxygen concentration in water cannot be controlled effectively, then materials resistant to oxygen corrosion should be selected. The maximum acceptable oxygen concentration in the water is 20 ppb."
- NACE SP0490: Control of External Corrosion on Underground or Submerged Metallic Piping Systems. In Section 4.1.3.1, which discusses the requirements for controlling oxygen content in refinery feedwater: "The recommended maximum oxygen concentration for feedwater to the boilers should be 7 ppb (0.007 mg/L) or less. A maximum limit of 20 ppb (0.02 mg/L) is generally used as the acceptable limit for oxygen in water for most refinery services."
- NACE Standard RP0193-2001, which states: "The dissolved oxygen content of the water in contact with the tank bottom shall be controlled to a maximum of 20 ppb to prevent corrosion of the tank bottom."

Limited literature and understanding of the effect of oxygen on sweet systems needs to be investigated, with an emphasis on the trace oxygen amounts which are regulated by guidelines in the industry.

## EXPERIMENTAL PROCEDURE

The experiments were carried out in a 2-liter glass cell with an X65 steel rotating cylinder electrode (RCE) specimen. The composition of the X65 steel can be seen below in Table . The X65 steel specimen was polished up to a 600 grit SiC sandpaper, until no polishing marks were visible. The pH was manually adjusted to pH 4.0, using sodium hydroxide. Different gas

mixes were fed to this glass cell assembly using a rotameter. The gas phase content of O<sub>2</sub> was adjusted using the rotameter in order to attain the desired dissolved oxygen concentration. The oxygen concentration was monitored by analyzing the outlet gas from the glass cell using a HACH<sup>‡</sup> Orbisphere 410. The glass cell was equipped with all the necessary components required for electrochemical corrosion studies: a reference probe, Luggin capillary, counter electrode, thermocouple, hotplate stirrer, and a pH probe. Experimental procedures lasting less than a few hours per test were used to observe the influence of oxygen on CO<sub>2</sub> corrosion of bare steel. This was done to limit the influence of a corrosion product layer on these measurements. This experimental procedure is being used for ongoing research to test higher oxygen concentrations at varying conditions.



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

**Table 1. Experimental test conditions.**

<b>Temperature</b>	30 °C
<b>pH</b>	4.0
<b>Total pressure</b>	1 bar
<b>CO<sub>2</sub> partial pressure</b>	0.97 bar
<b>O<sub>2</sub> concentration in liquid phase</b>	0 ppb, 25 ppb, 50 ppb, 100 ppb
<b>Electrolyte</b>	1 wt.% NaCl
<b>Specimen</b>	X65 Steel
<b>RCE speeds</b>	1000 rpm, 2000 rpm, 4000 rpm, 6000 rpm
<b>Electrochemical tests</b>	LPR, EIS, Potentiodynamic sweeps:

<sup>‡</sup> Trade Name

	Cathodic (OCP to OCP -0.7V), Short Anodic (OCP to OCP +0.025V), Long Anodic (OCP to OCP +0.1V)
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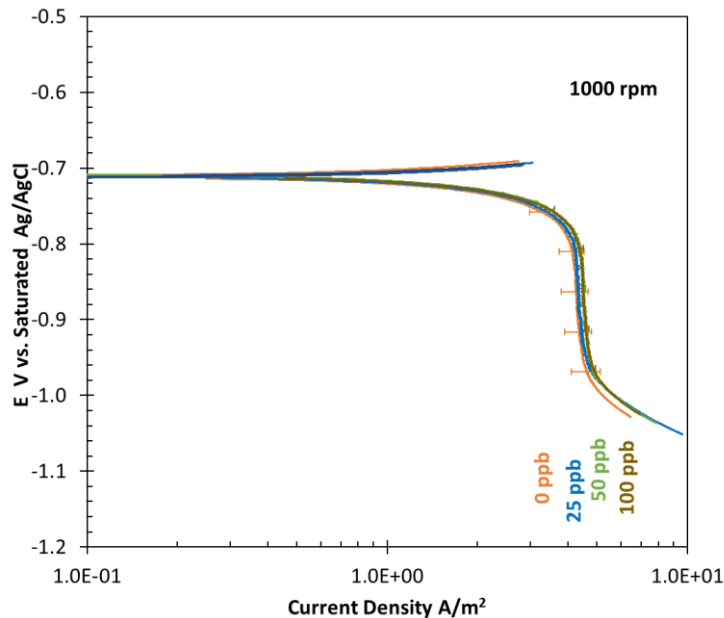
**Table 2. X65 steel composition**

C	Mn	Nb	Si	V	Mo	Cu	Cr	Ni	Fe
0.05%	1.40%	0.04%	0.22%	0.03%	0.07%	0.11%	0.23%	0.24%	balance

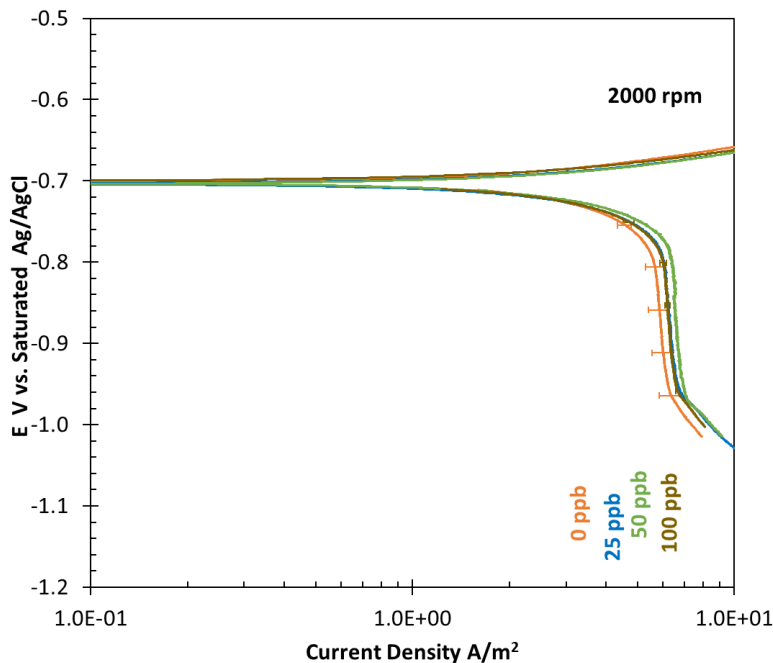
## EXPERIMENTAL RESULTS

Linear polarization resistance (LPR), Electrochemical Impedance Spectroscopy (EIS), cathodic and anodic polarization sweeps were performed for varying trace oxygen concentrations. The potentiodynamic polarization sweeps were corrected for any IR drop due to solution resistance. The solution resistance was calculated via EIS. The polarization sweeps for different concentrations of O<sub>2</sub> obtained from the experiments did not exhibit any distinct separation.

Figure 2 and Figure 3 show the comparison of the potentiodynamic sweeps with error bars for different [O<sub>2</sub>]<sub>aq</sub> concentrations at 1000 rpm and 2000 rpm rotational speeds of the RCE. The curves have a significant overlap and, hence, the numerical limiting current values need to be analyzed separately for better resolution.

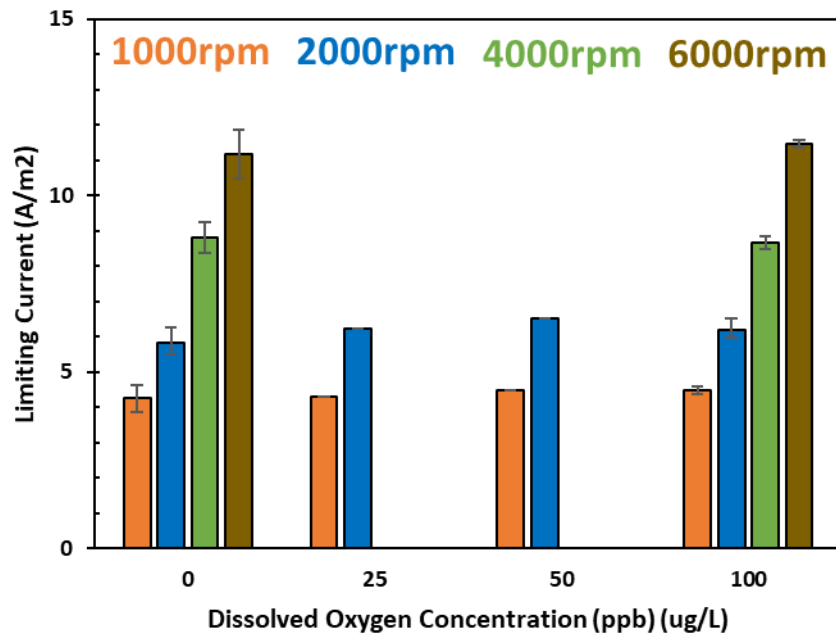


**Figure 2. Comparison of polarization sweeps for different O<sub>2</sub> concentrations at 1000rpm RCE rotation speed (pH 4.0, 30 °C, 1 wt.% NaCl, X65, 1 bar, CO<sub>2</sub> and O<sub>2</sub> system )**



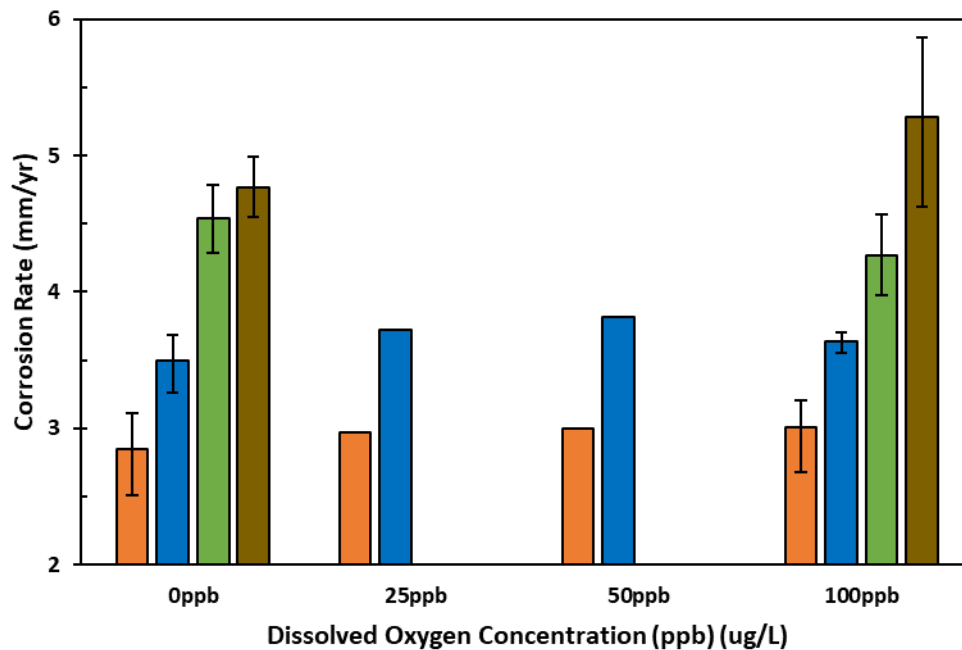
**Figure 3. Comparison of polarization sweeps for different O<sub>2</sub> concentrations at 2000rpm RCE rotation speed (pH 4.0, 30 °C, 1 wt.% NaCl, X65, 1 bar, CO<sub>2</sub> and O<sub>2</sub> system)**

Theoretically, increasing the O<sub>2</sub> concentration increases the limiting current for the O<sub>2</sub> reduction reaction, thus increasing the overall limiting current of the polarization sweep. Hence, an increase in the overall limiting current was expected with an increase in O<sub>2</sub> concentration. The overlap of limiting currents in the polarization curves was difficult to analyze and hence numerical limiting current values were extracted from each experimental condition and plotted on a bar chart with error bars. Figure 4 compares the numerical limiting currents for different [O<sub>2</sub>]<sub>aq</sub> and RCE rotational speeds. Data for dissolved oxygen concentrations of 25 ppb and 50 ppb for 2000 rpm and 6000 rpm RCE rotational speeds was not obtained, as it was not expected to provide any new insights. An increase in limiting currents was observed with an increase in the RCE rotational speed. No distinct change was observed in limiting currents with change in [O<sub>2</sub>]<sub>aq</sub> up to 100 ppb.



**Figure 4. Comparison of limiting currents for different  $[O_2]_{aq}$  and RCE rotational speeds (pH 4.0, 30 °C, 1 wt.% NaCl, X65, 1 bar, CO<sub>2</sub> and O<sub>2</sub> system)**

LPR derived corrosion rates were obtained for different O<sub>2</sub> concentrations and RCE rotational speeds. Figure 5 compares the corrosion rates for different  $[O_2]_{aq}$  and RCE rotational speeds. An increase in corrosion rates was observed with an increase in the RCE rotational speed. No distinct change was observed in limiting currents with change in  $[O_2]_{aq}$  up to 100 ppb.



**Figure 5. Comparison of corrosion rates for different  $[O_2]_{aq}$  and RCE rotational speeds (pH 4.0, 30°C, 1 wt.% NaCl, X65, 1 bar, CO<sub>2</sub> and O<sub>2</sub> system)**

## CONCLUSIONS

Trace amounts of dissolved oxygen up to 100 ppb were tested for an effect on sweet corrosion mechanisms at pH 4.0 without the influence of a corrosion product layer. This study has not reached a definitive conclusion about the mechanisms of the oxygen reduction reaction and further research is ongoing. The following inferences can be drawn from the experimental data reported herein:

- Oxygen did not exhibit an influence on corrosion mechanisms of bare steel for concentrations of up to a 100 ppb  $[O_2]_{aq}$  at pH 4.0, 30 °C, 1 bar, CO<sub>2</sub> and O<sub>2</sub> system, 1 wt.% NaCl, up to 6000 rpm RCE rotational speed during short term experiments without a corrosion product layer.
- At the conditions tested, no effect of O<sub>2</sub> was seen on corrosion rates nor the limiting currents of bare steel corrosion, as the effect of O<sub>2</sub> was masked by H<sup>+</sup> reduction.
- Localized corrosion was not investigated as no pitting was observed visually on the steel specimens.
- Further ongoing research and insights from mechanistic corrosion modelling will prove crucial in understanding the effects of oxygen.
- Higher concentrations of oxygen at varying conditions would be tested in further studies to elucidate the mechanisms of the oxygen reduction reaction and will be reported in future publications.
- Ongoing research would help develop a comprehensive mechanistic model for the effect of oxygen reduction reaction on sweet corrosion mechanisms.

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