

Investigating the Effect of Trace O₂ Concentrations on CO₂ Corrosion Mechanisms

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ABSTRACT

CO₂ 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 O₂. Consequently, strict guidelines exist within the oil and gas industry to limit O₂ levels in production environments, emphasizing the significance of understanding any associated corrosion risks. These guidelines require O₂ 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 O₂ concentrations can influence CO₂ 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 O₂ ingress. To accomplish these goals, controlled experiments were performed to test aqueous O₂ concentrations up to 100 ppb on pipeline steel in a CO₂ 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 CO₂ corrosion environments, an ongoing research activity. This will contribute to the development of more reliable and sustainable corrosion control practices for industries experiencing CO₂ corrosion which can be extendable to carbon capture and transmission systems.

Keywords: CO₂ corrosion mechanisms, O₂ 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. CO₂ 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 corrosion¹. Limited studies have demonstrated an effect of trace amounts of oxygen on CO₂ corrosion mechanisms^{2,3}, 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 O₂ as this is not present in crude hydrocarbon extracted from geologic reservoirs. However, atmospheric O₂ 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 authors⁴. Moreover, AMPP/NACE has published several standards for relating to the threshold of dissolved oxygen which are as follows^{5,6,7}:

- NACE MR0175/ISO 15156: Petroleum, petrochemical and natural gas industries - Materials for use in H₂S-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 O₂ 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[‡] 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 CO₂ 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.

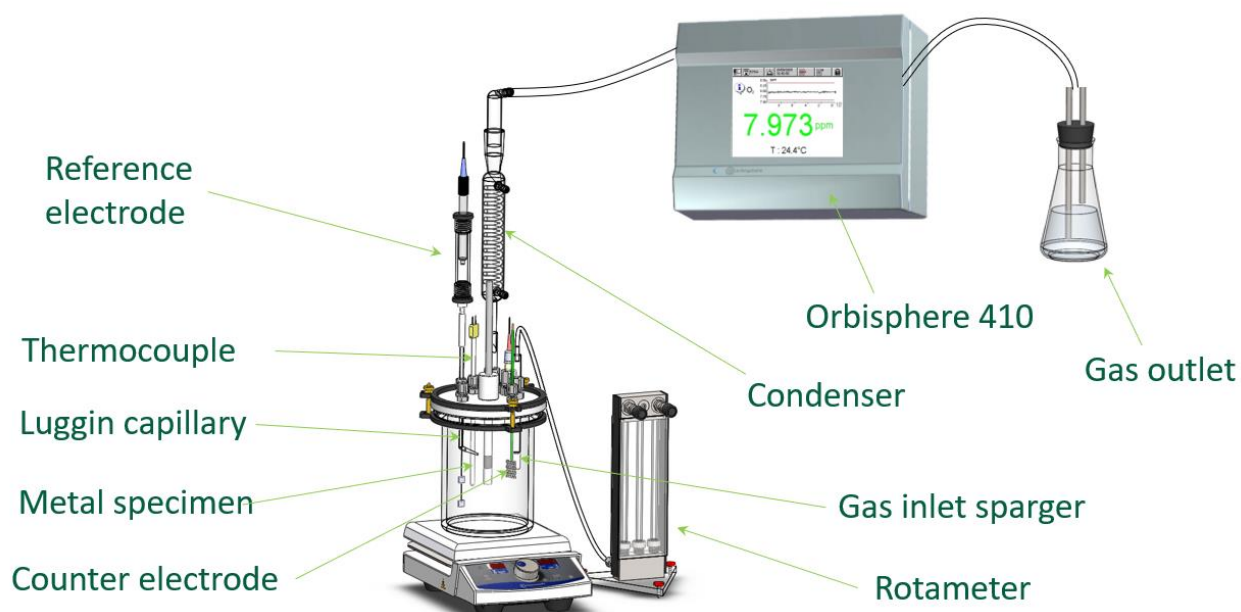


Figure 1. Experimental set up comprised of a 2-liter glass cell (image courtesy of Cody Shafer, Ohio University)

Table 1. Experimental test conditions.

Temperature	30 °C
pH	4.0
Total pressure	1 bar
CO₂ partial pressure	0.97 bar
O₂ concentration in liquid phase	0 ppb, 25 ppb, 50 ppb, 100 ppb
Electrolyte	1 wt.% NaCl
Specimen	X65 Steel
RCE speeds	1000 rpm, 2000 rpm, 4000 rpm, 6000 rpm
Electrochemical tests	LPR, EIS, Potentiodynamic sweeps:

[‡] Trade Name