

The Influence of Oxygen on Protective Iron Carbonate Scales Formed on Carbon Steel in CO₂ Environments at Near-Neutral pH

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ABSTRACT

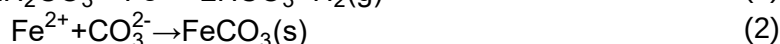
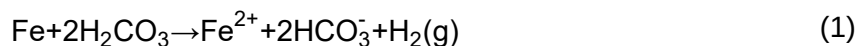
The influence of oxygen on the morphology and protectiveness of iron carbonate scales formed on carbon steel in CO₂ environments at near-neutral pH was investigated. Specimens were tensioned in four-point bending jigs for stress corrosion cracking tests, and unloaded specimens were used for electrochemical tests. All specimens were exposed to CO₂ aqueous solutions with and without dissolved oxygen, and corrosion rates were monitored by linear polarization resistance technique. Corrosion scales were characterized by scanning electron microscopy and X-ray diffraction, while the analysis of the corroded surface of the specimens after scale removal was carried out using scanning electron microscopy and optical profilometry. The iron carbonate scales were destabilized and became less protective in the presence of oxygen, which resulted in localized attacks, but no cracks were observed.

Key words: carbon dioxide, carbon steel, corrosion, flexible pipes, iron carbonate, iron oxy-hydroxide, near-neutral pH, oxygen, stress corrosion cracking

INTRODUCTION

High strength carbon steel tensile wires confined in the annulus of flexible pipes might experience corrosion when the annulus is flooded with water, either due to outer sheath breaches or to condensation of water molecules permeating from the bore through the inner sheath.¹⁻³ Carbon dioxide (CO₂) molecules may also permeate from the bore and reach the annulus,^{1,2,4,5} where it dissolves into water to form carbonic acid (H₂CO₃).

Carbon steel corrodes in carbonic acid according to Equation 1, producing ferrous ions (Fe^{2+}), an equivalent amount of bicarbonate (HCO_3^-) and hydrogen gas (H_2). In deaerated aqueous CO_2 environments, iron carbonate (siderite, FeCO_3) is the typical corrosion product formed.^{4,6,9} It precipitates on the steel surface according to Equation 2, forming a scale which gives a varying degree of protection, depending on the conditions in which it is formed, and may reduce corrosion rates.^{6,7}



Protective FeCO_3 scales cannot be formed, however, when oxygen is dissolved in the solution. Oxygen reacts with Fe^{2+} to form Fe^{3+} , from which iron oxides and oxy-hydroxides are formed.^{8,9} In aerated aqueous CO_2 solutions, the Fe^{2+} concentration is therefore reduced and the formation of FeCO_3 is hindered, limited to occur in regions of the scale which are depleted of oxygen,⁸⁻¹⁰ while previously formed FeCO_3 scales are destabilized and dissolve where the Fe^{2+} concentration is lower than the solubility limit of FeCO_3 .^{8,11,12}

When the outer sheath of a flexible pipe is damaged, the annulus may become flooded with sea water, which contains dissolved oxygen.^{1,2} In this case, protective FeCO_3 scales which are already formed on the armor wires can be destabilized, and localized corrosion may take place. But whenever a breach is identified, the outer sheath can be repaired to restore the barrier between annulus and external environment.¹ These actions, however, are often carried out with the pipe still submerged, therefore sea water is frequently trapped inside the annulus. With time, as oxygen is consumed, the water trapped in the annulus becomes deaerated and iron carbonate scales can be formed again. Nevertheless, it might be that corrosion will still occur. Some studies showed that FeCO_3 scales formed on carbon steels following corrosion in aerated aqueous environments are not always as protective as they would have been if they had formed before exposure to aerated environments,^{3,8,10} which can also result in localized corrosion.

Localized corrosion can be particularly harmful to tensile armor wires, especially under loading, as it might contribute to increase stress corrosion cracking (SCC) susceptibility by generating sites from which cracks could nucleate.¹³ Depending on service conditions, low CO_2 partial pressures and relatively low temperatures ($< 30^\circ\text{C}$) are expected in the annulus of a flexible pipe. These conditions combined with a water-filled annulus containing high concentrations of dissolved corrosion products is favorable to the development of near-neutral pH environments.¹⁴ Corrosion pits caused by dissolved oxygen reportedly increased crack initiation susceptibility of near neutral pH stress corrosion cracking (NNpH-SCC) of steel inland pipes following coating disbondment.¹⁵ Crack nucleation due to hydrogen embrittlement at the bottom of the pits was pointed as one of the explanations for the phenomenon.¹⁶

The effect of dissolved oxygen on the corrosion of steel wires of flexible pipes has already been investigated,^{3,8,10} but its influence on SCC susceptibility have not yet been widely explored. The study described in this paper addressed the influence of oxygen on the CO_2 corrosion of a high strength steel wire in simulated annulus environments of flexible pipes. Focus was given to the morphology of corrosion scales and their correlation with the occurrence of uniform and localized corrosion. Four-point bending (4PB) tests were carried out in similar conditions to verify the susceptibility of these wires to SCC at near-neutral pH.

EXPERIMENTAL PROCEDURE

Specimens and Surface Preparation

The test specimens used in this study were sectioned from a high strength steel tensile wire containing 0.72 wt-% C and 0.76 wt-% Mn (similar to UNS G10700), with pearlitic microstructure and yield strength of 1085 MPa. These specimens were divided in the following two groups:

- LPR: specimens used as electrodes for linear polarization resistance (LPR) tests; electrical wires were connected to each of these specimens to allow them to be used as working electrodes. These specimens were used in Experiment 1.
- 4PB: specimens used in stress corrosion cracking tests; these specimens were mounted and tensioned to 90% yield strength in 4PB test jigs according to the ASTM⁽¹⁾ Standard G39.¹⁷ These specimens were used in Experiments 2 and 3.

All surfaces of the test specimens were wet-ground with SiC paper grades P220, P320, P500 and P1000. After grinding, they were cleaned in acetone, rinsed with isopropyl alcohol, and dried in air flow at room temperature. Subsequently, exposed ends of all specimens were covered with a protective varnish.

Test Conditions and Experimental Procedure

Experiment 1 (Combined Effect of O₂ and CO₂ on Corrosion Rate and Corrosion Morphology)

The experiment followed a three-step procedure, in which each step simulated a different annulus condition:

- step A: annulus containing deaerated sea water.
- step B: annulus flooded with aerated sea water after an outer sheath breach.
- step C: annulus containing deaerated sea water after outer sheath repair.

Modified ASTM D1141¹⁸ artificial sea water (Table 1) was used as base solution in all three steps. Test conditions adopted during these steps are given in Table 2. The solution in the test cell was replaced between the steps in order to achieve the desired test conditions.

Table 1
Chemical composition of the modified ASTM D1141 artificial sea water (g L⁻¹).

NaCl	MgCl ₂	NaSO ₄	CaCl ₂	KCl	NaHCO ₃	H ₃ BO ₃	SrCl ₂
24.530	5.200	4.090	1.160	0.695	0.201	0.027	0.025

Table 2
Summary of test conditions used in Experiment 1.

Step	Base Solution	Initial Fe ²⁺ (ppm)	pCO ₂ (bar)	pO ₂ (bar)	pN ₂ (bar)	Temperature (°C)	Time frame (h)
A	Sea water*	1800	0.1	-	0.9	25	0 - 841
B	Sea water*	<10	0.1	0.2	0.7	25	841 - 1544
C	Sea water*	2200	0.1	-	0.9	25	1544 - 2648

* Modified ASTM D1141 artificial sea water.

Steps A and C simulated annulus conditions characterized by deaerated sea water supersaturated with FeCO₃, therefore high Fe²⁺ concentration was necessary at the beginning of these two steps to ensure an initially high saturation ratio of iron carbonate (SR_{FeCO₃}). To achieve this, the test solution was pre-conditioned in a 3 L jacketed glass cell (hereafter denoted “iron generator”). The modified ASTM D1141 solution was deaerated with N₂ gas and transferred into the iron generator, where it was continuously stirred and purged with 1 bar CO₂. The iron generator contained one stainless steel compartment filled with steel wool (Figure 1a), which functioned as a source of Fe²⁺ ions. To ensure that a sufficiently high Fe²⁺ concentration would be achieved, precipitation of FeCO₃ was slowed down by controlling the temperature in the iron generator using an external cooling bath set at 10 °C. At this temperature and given the composition of the modified sea water, it was expected that some calcium carbonate (CaCO₃) would precipitate in the iron generator cell, consuming part of the alkalinity produced, which shifts the pH towards lower values and reduces the Ca²⁺ concentration. The Fe²⁺ concentration was systematically

⁽¹⁾ ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

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measured and once the desired value was achieved, the solution was transferred to another 3 L jacketed glass cell (hereafter referred to as “test cell”), where the LPR specimens were placed (Figure 1b).

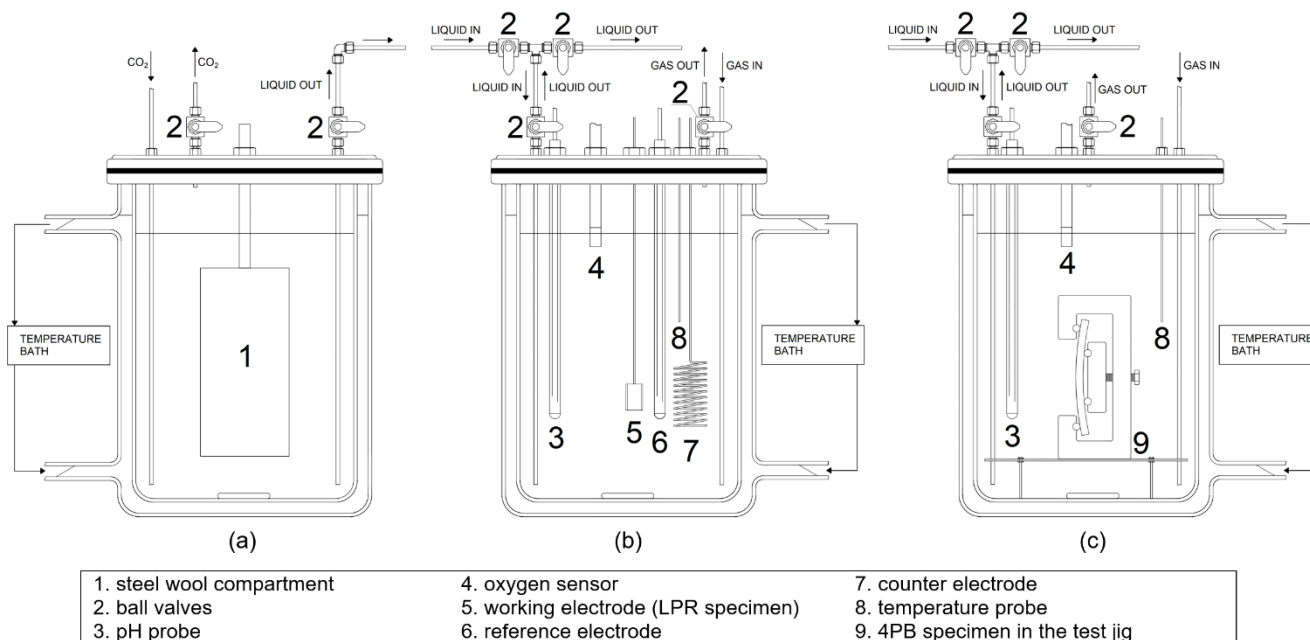


Figure 1: Schematic drawing of the experimental setup: (a) iron generator cell; (b) test cell for Experiment 1; and (c) test cell for Experiments 2 and 3.

The test solution used during step B did not need to be pre-conditioned in the iron generator, since it was used in the simulation of the annulus flooded with aerated sea water.

In the test cell, the temperature was controlled by an external cooling bath set at 25 °C. Ports in the lid of the test cell were used for inserting pH probe, temperature probe, gas and liquid feeding lines, dissolved oxygen sensor, and electrodes for the electrochemical tests: LPR specimens as working electrodes (WE), a titanium spiral as counter electrode (CE), and an additional Ag/AgCl pH electrode as reference electrode (RE). The pH and the concentration of dissolved oxygen and Fe^{2+} were monitored during both experiments.

Three LPR specimens were used in this experiment, and they were labelled according to the steps during which they were exposed in the test cell, i.e. A, AB, and ABC, as shown in Table 3.

Table 3
Sequence of steps during which the specimens were exposed in the test cell throughout Experiment 1.

Specimens	Step A	Step B	Step C
A_{LPR}	X	-	-
AB_{LPR}	X	X	-
ABC_{LPR}	X	X	X

X = immersion

The LPR measurements were carried out every thirty minutes in the test cell using the standard three-electrodes configuration shown in Figure 1b. Potentials were scanned between -5 and +5 mV vs. the open circuit potential (OCP) with a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. For each LPR specimen, corrosion current density (i_{corr}) was calculated from the obtained polarization resistance (R_p) according to Equation 3, where A is the exposed area of the specimen, and B is the Stern-Geary constant, which was calibrated for each specimen so that the integral mass loss obtained from the LPR tests fitted the mass loss obtained

experimentally. The B-values ranged from 10 to 30 mV, and the LPR corrosion rates were calculated in mm y⁻¹ using Equation 4.

$$i_{\text{corr}} = \frac{B}{R_p \cdot A} \quad (3)$$

$$\text{CR} = 1.16 \cdot i_{\text{corr}} \quad (4)$$

Experiments 2 and 3 (NNpH-SCC Susceptibility and Influence of O₂ Ingress)

Experiments 2 and 3 also followed a three-step procedure. Experiment 2 simulated the evolution of the annulus without oxygen ingress, while Experiment 3 reproduced the same conditions previously simulated in Experiment 1, i.e. with oxygen ingress. This allowed assessing how oxygen affected the corrosion morphology of the tensioned wire (4PB specimens) and if it had any influence on cracking susceptibility.

- Experiment 2:
 - steps A, B and C: annulus containing deaerated sea water.
- Experiment 3:
 - step A: annulus containing deaerated sea water.
 - step B: annulus flooded with aerated sea water after an outer sheath breach.
 - step C: annulus containing deaerated sea water after outer sheath repair.

Modified artificial sea water (Table 1) was also used as base solution in the three steps of both experiments, and the test solution in the test cells was replaced between the steps. Test conditions used in Experiments 2 and 3 are given in Table 4.

Table 4
Summary of test conditions used in Experiments 2 and 3.

Step	Base Solution	Initial Fe ²⁺ (ppm)	pCO ₂ (bar)	pO ₂ (bar)	pN ₂ (bar)	Temperature (°C)	Time frame (h)
Experiment 2							
A	Sea water*	2500	0.1	-	0.9	25	0 - 763
B	Sea water*	1700	0.1	-	0.9	25	763 - 1266
C	Sea water*	1960	0.1	-	0.9	25	1266 - 2255
Experiment 3							
A	Sea water*	2170	0.1	-	0.9	25	0 - 759
B	Sea water*	<10	0.1	0.2	0.7	25	759 - 1669
C	Sea water*	2460	0.1	-	0.9	25	1669 - 2631

* Modified ASTM D1141 artificial sea water.

In Experiment 2, all steps simulated annulus conditions characterized by deaerated sea water supersaturated with FeCO₃, therefore the test solution used in each step was pre-conditioned in the iron generator before transference to the test cell. In Experiment 3, the same procedure was followed to prepare the test solution before steps A and C, while the test solution used during step B did not need to be pre-conditioned in the iron generator, since it simulated the annulus flooded with aerated sea water.

As in Experiment 1, the temperature in the test cell in Experiments 2 and 3 was controlled by an external cooling bath set at 25 °C. Ports in the lid of the test cells were used for inserting pH probe, gas and liquid feeding lines, dissolved oxygen sensor and temperature probe. The 4PB specimens were positioned vertically in the cells (Figure 1c). The pH and the concentration of dissolved oxygen and Fe²⁺ were monitored during both experiments.