

SCC of Tensile Wires at High CO₂ Partial Pressure in Simulated Annulus Environments of Flexible Pipes

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ABSTRACT

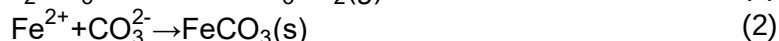
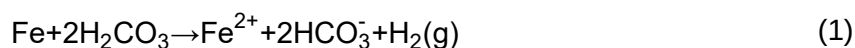
The CO₂-SCC susceptibility of tensile wires of flexible pipes was investigated. Wire specimens were tensioned in four-point bending jigs and exposed to different simulated annulus environments at high CO₂ partial pressure. Unloaded specimens were exposed to the same test environments and corrosion rates were calculated from their mass loss. Artificial sea water solutions at different temperatures were used as electrolyte. Some specimens were pre-corroded in aerated artificial sea water before exposure to the CO₂ environments. The corroded surface of the specimens after removal of corrosion products was analyzed using scanning electron microscopy. Cracks associated with localized attacks were observed in the tensioned specimens exposed to some of the simulated conditions. Temperature and pre-corrosion in aerated sea water influenced cracking susceptibility significantly.

Key words: carbon dioxide, carbon steel, corrosion, flexible pipe, iron carbonate, iron oxy-hydroxide, oxygen, stress corrosion cracking

INTRODUCTION

Unbonded flexible pipes used for transporting process fluids in offshore oil and gas production systems have a complex structure, with alternate polymer and metallic layers. Tensile armors are metallic layers constructed by the helical wrapping of high strength carbon steel wires, and they are responsible for the integrity of the pipe. These armors provide axial strength and torsion resistance to the pipe so that it can sustain its own weight and resist to stresses associated to environmental conditions and vessel motion.^{1,2}

The tensile wires are confined in the annulus of the flexible pipes, which is limited by the inner polymer layer (internal pressure sheath) and the external polymer layer (outer sheath). The annulus is originally dry, but during operation it can be flooded with sea water due to damages to the outer sheath or filled with condensed water following the permeation of H₂O molecules from the bore.^{2,3} When carbon dioxide permeates from the bore through inner polymer layers and arrives at the annulus, it dissolves into water and forms carbonic acid, generating an environment which is corrosive to the steel wires.^{4,5} Corrosion proceeds according to Equation 1 but in the confined annulus environment, because of the low ratio of free volume to steel surface area (V/S), the accumulation of corrosion products is fast, and supersaturation is quickly achieved.⁶ In the absence of oxygen, iron carbonate (siderite, FeCO₃) precipitates according to Equation 2 and forms a film on the steel surface.⁷⁻¹¹ Depending on the conditions in which this film is formed, it will give a varying degree of corrosion protection.^{8,11,12}



Studies have shown that, at temperatures ranging from 25 to 60°C and low CO₂ pressures, protective iron carbonate films can easily form on carbon steels in simulated annulus environments,^{4-6,13} and it was observed that, for the same CO₂ partial pressure, protective iron carbonate films were formed faster at 60°C than at 25°C.^{4,5} Gas injection flexible pipes, however, might experience much higher CO₂ pressures in the annulus during operation,¹⁴ but little is known about the corrosion behavior of tensile wires under these conditions, especially in association with high stress levels, which may result in CO₂ stress corrosion cracking (CO₂-SCC). Due to their structural role, cracking of these wires can compromise the integrity of the entire pipe, shortening its service life.

Another relevant issue which has not been extensively explored is the influence of pre-corrosion in aerated sea water on the subsequent corrosion at high CO₂ partial pressures, even though it is commonly assumed that if a damage to the outer sheath occurs during installation (i.e., before gas injection starts) the wires would initially undergo a period of corrosion in sea water containing dissolved O₂.^{2,15} In this case, iron oxides and oxy-hydroxides would be the first precipitates to be formed on the surface of the corroding steel,¹⁶ while siderite would only form during the subsequent exposure to CO₂ environments.

In this work, tensile wires of flexible pipes were tensioned in four-point bending test jigs and exposed to different simulated annulus conditions to investigate the influence of temperature and pre-corrosion in aerated sea water on their CO₂-SCC susceptibility.

EXPERIMENTAL PROCEDURE

Specimens and Surface Preparation

The material used in this study was a high strength 0.72 wt-% C, 0.76 wt-% Mn steel tensile armor wire with pearlitic microstructure and yield strength of 1085 MPa. Test specimens were sectioned from the wire and divided in the following two groups:

- 4PB: 135 mm x 14 mm x 6 mm specimens used in four-point bending (4PB) stress corrosion cracking tests; these specimens were mounted and tensioned to 90% yield strength (YS) in four-point bending test jigs according to the ASTM⁽¹⁾ Standard G39.¹⁷
- ML/ML_{PC}: 25 mm x 14 mm x 6 mm specimens used as corrosion coupons for average corrosion rate calculations based on gravimetric mass loss (ML); these specimens had a hole drilled through their thickness to facilitate mounting on the specimen holders.

In order to preserve the original cross-sectional geometry of the wire (14 mm x 6 mm), the specimens were not machined, but all surfaces were wet-ground with SiC paper grades P220, P320, P500 and

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

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P1000. After grinding, they were cleaned in acetone, rinsed with isopropyl alcohol, and dried in air flow at room temperature. Subsequently, exposed ends (cross-sections) of all specimens were covered with a protective varnish.

Test Conditions and Experimental Procedure

Four experiments were carried out. Test conditions adopted in the experiments are given in Table 1. Modified ASTM D1141 artificial sea water was used as base solution in all four experiments.¹⁸ The chemical composition of the artificial sea water is given in Table 2.

Table 1
Summary of test conditions.

Experiment	Initial surface condition	σ_{Applied}	Base Solution	Initial Fe ²⁺ (ppm)	pCO ₂ (bar)	Temperature (°C)	Duration (h)
1A	Fresh, wet-ground	90% YS	Sea water*	2000	50	25	2687
1B		90% YS	Sea water*	2000	50	60	2683
2A	Pre-corroded in aerated sea water	90% YS	Sea water*	2000	50	25	1203
2B		90% YS	Sea water*	2000	50	60	1203

* Modified ASTM D1141 artificial sea water, see Table 2.

Table 2
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

During experiments 1A and 1B, the specimens were exposed with a freshly ground surface to high CO₂ pressure environments, while the specimens tested in experiments 2A and 2B were exposed to high CO₂ pressure environments following a two-week period of pre-corrosion in aerated sea water, therefore with their surface already covered with iron oxides/oxy-hydroxides. The conditions used during pre-corrosion are given in Table 3. The 4PB specimens were already tensioned to 90% yield strength during pre-corrosion.

Three 4PB specimens and three ML specimens were used in each experiment. Four additional ML specimens (ML_{PC}) were exposed only during the pre-corrosion step prior to experiments 2A and 2B. Two of these additional specimens were exposed in autoclave A, and the other two, in autoclave B, but they were retrieved from the autoclaves as the aerated solution was drained and, therefore, were not exposed to the high CO₂ pressure environments. Table 4 summarizes the immersion of the specimens during pre-corrosion and experiments 2A and 2B.

Table 3
Summary of pre-corrosion conditions.

Experiment	Initial surface condition	σ_{Applied}	Base Solution	pO ₂ (bar)	Temperature (°C)	Duration (h)
2A	Fresh, wet-ground	90% YS	Sea water*	1	25	330
2B		90% YS	Sea water*	1	25	330

* Modified ASTM D1141 artificial sea water, see Table 2.

Experiments 2A and 2B allowed assessing how corrosion rates, corrosion morphology and CO₂-SCC susceptibility of the material were affected by the pre-corrosion in aerated sea water when the results obtained from these experiments were compared with those from experiments 1A and 1B.

Table 4
Immersion of specimens during pre-corrosion and experiments 2A and 2B.

Specimens	Pre-corrosion in	Experiment 2A
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	aerated sea water	Experiment 2B
ML _{PC}	X	-
ML	X	X
4PB	X	X

X = immersion

The influence of temperature on corrosion rates, corrosion morphology and CO₂-SCC susceptibility of the material was also verified by carrying out experiments at 25 °C (1A and 2A) and at 60 °C (1B and 2B).

The experiments simulated annulus conditions which are characterized by deaerated sea water supersaturated with FeCO₃. Therefore, to ensure an initially high saturation ratio of iron carbonate (SR_{FeCO₃}), high Fe²⁺ concentration was necessary at the beginning of the exposure. To achieve this, the test solution was pre-conditioned in the iron generator, a 3 L jacketed glass cell containing one stainless steel compartment filled with steel wool (Figure 1a). The modified ASTM D1141 solution was deaerated with N₂ gas and then transferred into the cell, where it was sparged with 1 bar CO₂. Upon corrosion in the CO₂-acidified water solution, the steel wool functioned as a source of Fe²⁺ and CO₃²⁻ ions. To retard precipitation of FeCO₃ and ensure a sufficiently high Fe²⁺ concentration in the liquid for a longer time, the temperature in the generator cell was set at 10 °C, controlled by an external cooling bath. 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. When the desired Fe²⁺ concentration was achieved, the solution was transferred to the autoclaves (Figure 1b), where ML and 4PB specimens were placed (Figure 1c).

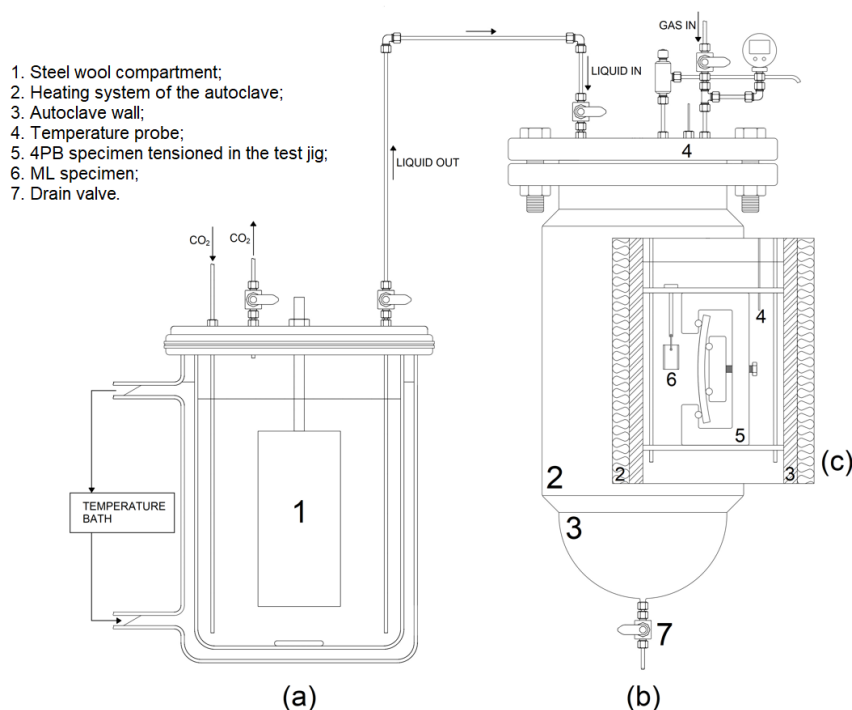


Figure 1: Schematic drawing of the experimental setup: (a) iron generator cell; (b) autoclave; (c) sectional view of the autoclave.

To avoid moving the specimens, which could possibly damage the corrosion products formed on their surface during exposure to aerated sea water, pre-corrosion of specimens to be used in experiments 2A and 2B was also carried out in the autoclaves. Before transference of the test solution, which was deaerated and supersaturated with FeCO₃, the solution used during the pre-corrosion was drained and the autoclave was flushed with CO₂ to remove oxygen from the gas phase.