

Corrosion Behavior of Transmission Pipeline Steels in Dense-Phase Carbon Dioxide

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ABSTRACT

Pipeline transportation systems are the most cost-effective method to transport liquid or supercritical CO₂ from points of capture to sites where it will be permanently stored or used for industrial purposes. Many factors complicate designing an efficient CO₂ transmission pipeline and selecting materials. These factors include gas chemistry and impurities (O₂, H₂O, H₂S), pressure, and velocity. The presence of impurities in supercritical CO₂ can promote steel corrosion. The objective of this study was to investigate the corrosion behavior of three pipeline steels (X56, X65, and X100) exposed to dense-phase CO₂ at 100 bar CO₂ partial pressure and 30 °C. The corrosion performance of each steel was evaluated in a CO₂ saturated water phase and dense-phase CO₂ utilizing an immersion autoclave. The weight loss method was used to investigate the corrosion performance of the pipeline steels in dense-phase CO₂. Post-corrosion surface characterization was performed by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy. The data obtained show that each steel's corrosion degradation is more dominant in the CO₂ saturated water phase compared to dense-phase CO₂.

Key words: CO₂ corrosion, transmission pipeline steels, dense-phase CO₂

INTRODUCTION

High-pressure steel pipeline is a common, cost-effective method for transporting CO₂ from its point of capture to storage sites¹. In pipeline transport systems, CO₂ is mostly transported in its liquid or supercritical phase, depending on the operating pressure^{2,3}, which requires compression of CO₂ gas to a pressure above 80 bar (Figure 1) and avoid a two-phase flow regime in the steel pipelines. In the USA, the longest CO₂ pipelines, which transport more than 40 MtCO₂ per year from production point to sites in Texas, where the CO₂ is used for enhanced oil recovery (EOR), operate in the “dense phase” mode and at ambient temperature and high pressure ¹. However, steel pipelines are susceptible to corrosion during the transportation of CO₂, due to the presence of moisture and corrosive impurities such as H₂S and O₂. The type and content of these impurities depends on the CO₂ point source and capture technology⁴.

Table 1 shows recommended limits for CO₂ stream impurities required by the pipeline and EOR application⁵.

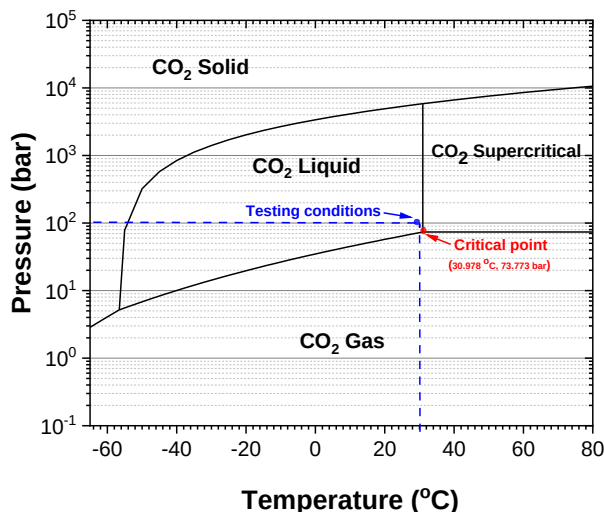


Figure 1. CO₂ pressure-temperature diagram.

Table 1. Recommended Limits for CO₂ Stream Impurities⁵

Constituent	Carbon steel pipeline	EOR
CO ₂	90-99.8 (vol %)	90-99.8 (vol %)
H ₂ O	20-650 (ppm _w)	20-650 (ppm _w)
N ₂	0.01-7 (vol %)	0.02-2 (vol %)
O ₂	0.01-4 (vol %)	0.001-1.3 (vol %)
H ₂ S	0.002-1.3 (vol %)	0.002-1.3 (vol %)
CO	10-5000 (ppm _w)	10-5000 (ppm _w)
SO ₂	10-50000 (ppm _w)	10-50000 (ppm _w)
NO _x	12-2500 (ppm _w)	20-2500 (ppm _w)
NH ₃	0-50 (ppm _w)	0-50 (ppm _w)
Hydrocarbon	< 5 (vol %)	< 5 (vol %)

To reduce the risk of internal corrosion and hydrate formation in CO₂ pipelines, the CO₂ stream is dehydrated up to 30 lbs H₂O/MMscf (650 mg/l) prior to pipeline transport. If free water is present in dense or liquid CO₂, the corrosion rates of steel pipelines could be on the order of mm per year^{6,7}, and localized corrosion could be expected depending on pressure, temperature, and flow rate. The concentration of dissolved water in the dense-phase CO₂ depends on the presence of impurities, such as H₂S, SO₂, CH₄, N₂, and amines. Ahmad *et al.*⁶ studied water solubility in CO₂ mixtures at pipeline operation conditions. The authors observed a drop of water solubility limit of around 200 ppm_w with the presence of 2.5% of any of N₂, O₂ or CH₄ in CO₂⁶. However, in dry supercritical CO₂ where the humidity is less than 60%, or the water concentration less than 60% of the dew point, steel pipelines are less susceptible to corrosion¹. It has been reported that the corrosion rate of a carbon steel pipeline transporting dry supercritical CO₂ is between 0.00025 and 0.0025 mm/y^{8,9}. Therefore, to keep the corrosion rates of steel pipelines low, CO₂ should be dry, or the water should be fully dissolved at all operation conditions.

In general, carbon steels (X60, X65, and X80) are the main commercial materials used in constructing CO₂ transportation pipelines¹⁰. However, upstream of the dehydration unit, the pipes are made of

corrosion-resistant alloys such as 304L¹¹. Several studies related to the corrosion behavior of carbon steel in supercritical CO₂-water environments have been reported^{11,12}. Seiersten *et al.*⁷ investigated the corrosion performance of two types of carbon steel X65 and 0.5 Cr exposed to wet CO₂ at 40 °C and pressure below and above the critical point. The authors found that corrosion rates decreased with the increase of CO₂ fugacity. Teeter *et al.*¹³ investigated the effect of oxygen on corrosion behavior of carbon steel X65 in a simulated supercritical CO₂ heat exchanger environment. The authors reported that the presence of oxygen increases the corrosion rates of steel. Russick *et al.*¹⁴ observed that corrosion occurred only on 1018 carbon steel exposed to supercritical CO₂ containing 3% water. However, no corrosion was observed on 1018 carbon steel exposed to pure supercritical CO₂. Choi *et al.*¹⁵ conducted experimental tests and thermodynamic modeling to understand the corrosion mechanism of carbon steel in water-saturated CO₂, and CO₂-saturated water in the CO₂ pressure range of 40–80 bar at 50 °C. The authors detected FeCO₃ on the steel surface, which lowers the corrosion rate (0.2 mm/y) of carbon steel exposed to the CO₂ saturated water phase under high-pressure conditions. Few experimental studies have been performed to investigate the corrosion behavior of carbon steel (S355J2) in dense-phase CO₂. Morland *et al.*¹⁶ determined the corrosion rates of carbon steel exposed to CO₂ with various concentrations of dissolved water (100 ppmv to the solubility limit) at 95 bar and at a temperature range between 8 and 35 °C. The authors found that if the water content in dense-phase CO₂ is below the solubility limit, the expected corrosion rate of carbon steel will be below 1 µm/y. McGrail *et al.*¹⁷ found that above the threshold water content limit (~600 ppm_w) corrosion of steel exposed to liquid CO₂ (7 MPa, 25 °C) will occur and appear visible.

A major challenge in CO₂ capture and storage processes is removal of the water content below 50 ppm_w to mitigate internal corrosion and ensure that CO₂ transmission pipelines are designed and operated safely and economically. This challenge stems from the properties of the CO₂ travelling through the pipeline and the presence of small amounts of solvent vapor, which could accelerate corrosion in the pipeline steel⁴. In addition, in the pipeline transportation system, the carbon steel microstructure plays an important role in the corrosion process. Therefore, an alternate way to mitigate internal corrosion is by using corrosion-resistant steel pipelines.

Suitable steel alloy candidates for the construction of CO₂ pipeline networks are conventional API grade 5 L steels, due to their mechanical properties, wide availability, and low cost. Very limited studies on the corrosion behavior of X100 carbon steel in the supercritical CO₂-water environment have been performed. To our knowledge, no research studies have been performed on the corrosion performance of X56 carbon steel exposed to dense-phase CO₂. Therefore, the objective of this study was to investigate the corrosion behavior of three pipeline steels (X56, X65, and X100) exposed to dense-phase CO₂ at 100 barg CO₂ pressure and 30 °C. The corrosion performance of each steel was evaluated in two phases: CO₂ saturated water phase and dense-phase CO₂ using an immersion autoclave.

EXPERIMENTAL PROCEDURE

Materials and Chemicals

In this study, three grades of API¹ 5 L steel were tested (X56, X65, and X100). X56 carbon steel specimens were machined from commercial pipe manufactured in 2002 with yield strength of 422 MPa. X65 carbon steel specimens were machined from commercial pipe made by Nippon[†] Steel with yield strength of 491 MPa (in the transverse direction). For the X100 carbon steel, the specimens were machined from an experimental pipe fabricated in the late '90s with a yield strength of 731 MPa (in the longitudinal direction)¹⁸. The chemical composition of the steel pipelines provided by manufacture is

¹ American Petroleum Institute (API), 1220L St, N. W. Washington, D.C. 20005-4070

[†] Trade name

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shown in Table 2. The microstructures of tested steel pipelines were obtained by etching the specimens with Murakami's reagent following the ASTM E407 standard¹⁹.

Figure 2 shows the microstructure of tested steel pipelines. For X56 carbon steel, needle structures of martensite are present. The X65 carbon steel microstructure consists of a ferrite structure with cementite precipitates at the grain boundaries. For X100 carbon steel, the microstructure consists of fine ferrite grains and bainite structure (elongated cementite $[\text{Fe}_3\text{C}]$ particle in α -ferrite matrix)¹⁸.

Table 2. Composition (wt.%) of API¹ 5L Carbon Steels

Elements	C	Mn	Al	Cr	Cu	Mo	Nb	Ni	Si	Ti+P+S	B	Fe
X56	0.056	1.09	0.03	0.04	0.11	0.01	0.02	0.05	0.21	0.022	-	balance
X65	0.08	1.17	-	0.018	0.011	0.001	0.001	0.013	0.2	0.028	-	balance
X100	0.085	1.69	0.029	0.19	0.14	0.17	0.047	0.24	0.26	0.031	<0.0015	balance

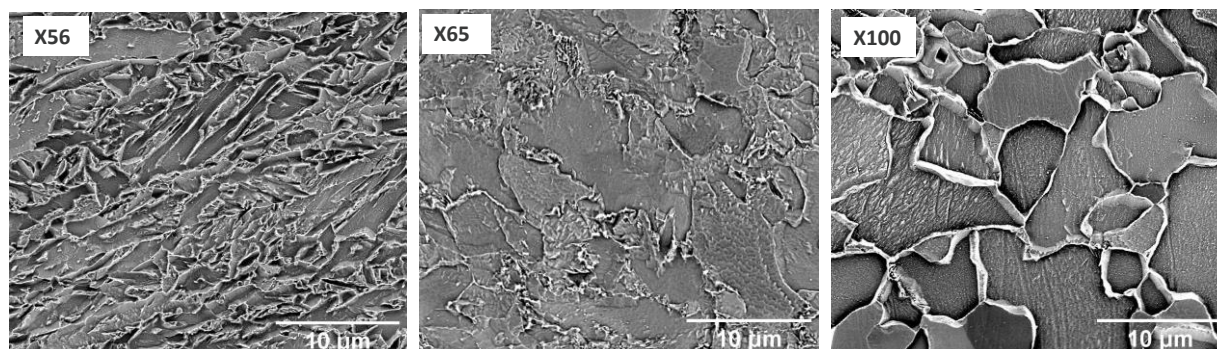


Figure 2. Microstructure of the API 5L carbon steel (X56, X65, and X100).

Corrosion Immersion Test

To investigate the corrosion performance of steel pipelines in simulated CO_2 transmission pipeline conditions, corrosion tests were carried out in a 1.1 L autoclave (UNS N10276). The experimental setup is shown in Figure 3. For each corrosion test two rectangular specimens made of the same pipeline steel (Table 2), each specimen with an exposed area of 16.81 cm^2 , were used for weight loss measurements. One sample was immersed at the bottom in the water phase (CO_2 - saturated H_2O phase) and the second sample at the top in the CO_2 liquid phase (H_2O - saturated CO_2 phase) (Figure 3). Before the immersion test, each specimen was ground using silicon carbide paper (320, 400, and 600 grit), rinsed with isopropanol in an ultrasonic cleaner for 2 to 3 minutes and air dried. A volume (0.3 L) of deionized water was introduced in a TeflonTM liner that was placed inside the autoclave vessel and heated to 30°C . The concentration of water in the autoclave is around 273 g/L. To eliminate dissolved oxygen, the solution was sparged with CO_2 (99.999%) for 3 to 4 hours. After the insertion of the sample, the oxygen in the gas phase was removed by pulling a vacuum and back filling with CO_2 . This procedure was repeated three times to reduce the residual air in the gas phase. The final pressure of CO_2 in the system was

achieved by introducing CO₂ to the liquid phase until pressure became stable (100 barg). Using OLI^{††} software the pH of the pressurized aqueous solution was calculated to be around 3.1 at 30 °C and 100 barg CO₂. The concentration of dissolved iron ions in the aqueous phase was measured by withdrawing a volume of 1.5 mL, every 24-hours during a total exposure time of 96 hours. The weight loss corrosion rate was calculated using the ASTM Standard G1²⁰ as follows:

$$CR = \frac{K \times \Delta m}{A \times t \times \rho} \quad (1)$$

Where *CR* is corrosion rate in mm/y, *K*: conversion factor 7.76×10^4 (24 h/d * 365 d/y * 10 mm/cm). Δm : loss in g. *A*: area in cm². ρ : density of steel, 7.87 g/cm³. *t*: time of exposure in h. To verify the reproducibility of the results, each immersion test was repeated two times. To confirm there was no oxygen contamination in the system, at the end of each experiment the solution was visually analyzed by checking the color of the solution. In all tests, no visible orange color was observed in the solution, indicating that no iron oxide had formed during the test. The test matrix is shown in Table 3.

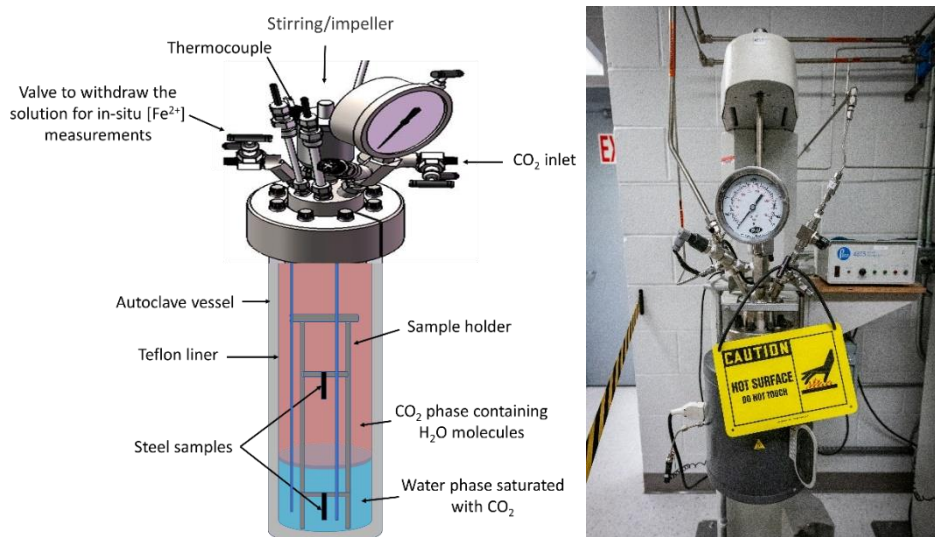


Figure 3. Experimental setup for immersion test in autoclave.

Table 3. Experimental Matrix for Immersion Tests

$p\text{CO}_2$ (barg)	100 ± 2
Solution temperature (°C)	30 ± 0.1
Density of CO ₂ (g/mL)	0.7715
Volume of Di water (mL)	300
Tested steel	X56 X65 X100

^{††}Trade name