

Effect of Flow on the Corrosion Behavior of Pipeline Steels Under Supercritical CO₂ Environments with Impurities

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ABSTRACT

Corrosion is a major concern in transmission pipelines that transport captured CO₂. While dry CO₂ is noncorrosive, significant corrosion has been reported in dense phase CO₂ with trace amounts of water and impurities such as O₂, H₂S, SO_x, and NO_x. The aim of this work is to improve our understanding of the physicochemical aspects on the corrosion of carbon steels in the high-pressure environments associated with CO₂ transmissions pipelines. The effect of flow on the corrosion of X65 carbon steel was investigated in a series of autoclave tests with different combinations of impurity concentrations in supercritical CO₂ condition (8 MPa and 35°C). The corrosion rate of samples was determined by weight loss measurements. The surface morphology and the composition of the corrosion product layers were analyzed by using surface analytical techniques (SEM and EDS). Localized corrosion was measured via surface profilometry after corrosion products were removed. Results showed that no corrosion was observed in the supercritical CO₂ with 650 ppm of water, 50 ppm SO₂, and 100 ppm NO, but corrosion occurred when SO₂ concentration was increased to 4500 ppm and 40,000 ppm of O₂ was added to the system. The presence of flow significantly accelerated the corrosion of carbon steel. Furthermore, localized corrosion was observed in the presence of both O₂ and flow.

Key words: Supercritical Carbon Dioxide, Corrosion, Impurities, Carbon Capture and Storage

INTRODUCTION

It is well known that dry CO₂ does not corrode carbon steels, and negligible corrosion occurred at water-unsaturated conditions (below solubility level) in dense phase CO₂ (liquid and supercritical).¹⁻⁵ However, it has been reported that noticeable, and potentially severe, corrosion occurs at water-unsaturated conditions in dense phase CO₂ with the presence of impurities, such as O₂, H₂S, SO₂, NO₂, etc. due to synergisms between chemical species.⁶⁻¹⁴

Hua, *et al.*,⁸ reported that general corrosion rates ranged from 0 to 0.012 mm/y with water contents varying from 300 ppm to 2800 ppm in the supercritical CO₂ with 1000 ppm O₂. They also found that the general corrosion rates of X65 steel increased from 0.01 mm/y to 0.06 mm/y with water concentration increasing from 300 ppm to 1770 ppm with 100 ppm SO₂ and 20 ppm O₂ at 35°C and 80 bar.⁹ Xu, *et*

al.,¹⁰ reported that the general corrosion rates of X70 steel varied from 0.03 mm/y to 1.78 mm/y at relative humidities ranging from 45% to 100% at 10 MPa CO₂ and 50°C with 2% SO₂ and 1% O₂. Dugstad, *et al.*,¹¹ investigated the corrosion behavior of carbon steel exposed to liquid CO₂ flow for 10 days at 10 MPa and 25°C. The results showed that there was no corrosion in the liquid CO₂ flow with 500 ppm_w H₂O, while adding 500 ppm_w SO₂ induced corrosion at a rate of 0.02 mm/year, and adding 500 ppm_w NO₂ caused severe corrosion with rates reaching 1.6 mm/year. Choi, *et al.*,¹¹ investigated the effect of H₂S on the corrosion behavior of pipeline steels in high pressure CO₂ systems. It was found that the general corrosion rates of the carbon steel and 1Cr steel tested were below 0.01 mm/year with the presence of 100 ppm H₂O and 200 ppm H₂S in the liquid (25°C, 12 MPa) and supercritical (80°C, 12 MPa) CO₂ phases.

Considering that the application of above mentioned studies is the internal corrosion of pipeline related to carbon capture and storage (CCS), enhanced oil recovery (EOR), and deep water oil and gas production, an attempt to evaluate the effect of flow on the corrosion behavior must also be made. Liu *et al.*,¹⁵ investigated the effect of flow rate on steel corrosion in supercritical CO₂ with different water concentrations. The results showed that a higher flow rate significantly enhanced the corrosion rate of carbon steel which is related to a mechanism of water droplet entrainment. However, they investigated only the effect of water without considering other impurities. Sui *et al.*,¹⁶ reported that the wall shear stress formed in the water-saturated supercritical CO₂ system was not enough to damage the formed corrosion product film but affected the morphology of the corrosion product film. The study was conducted in the water-saturated supercritical CO₂ with 1000 ppm H₂S.

There are very limited data on the corrosion behavior in flowing supercritical CO₂ conditions with different impurities. Thus, the objective of the present study was to identify and quantify the effect of flow on the integrity of carbon steel in supercritical CO₂ with different impurities (H₂O, SO₂, O₂ and NO).

EXPERIMENTAL PROCEDURE

The test specimens were machined from UNS K03014 low carbon steel with a size of 12 x 12 x 2.5 mm for the stagnant tests and 25.4 x 12.5 x 3.1 mm for the flowing tests. The specimens were ground with 600 grit silicon carbide paper, cleaned with alcohol in an ultrasonic bath, dried, and weighed using a balance with a precision of 0.1 mg. The solution used in this work corresponded to 650 ppm of DI water in CO₂ phase at the testing pressure and temperature.¹⁷

Experiments were performed in a 7.5L Hastelloy autoclave where the specimens were attached to holders hung from the lid. Pictures of the autoclave corrosion test system used in this study are presented in Figure 1. After the lid was attached, the autoclave was purged by multiple cycles of pressurization with CO₂ and then depressurization. The required volume of N₂-purged deionized water was then added just prior to pressurization with impurities and CO₂. The impurities were added from technical grade (ultra-high purity) sulfur dioxide (SO₂), nitric oxide (NO), and oxygen (O₂) cylinders with a special built gas injection system as shown in Figure 1 (a). For trace quantities of impurity gas, the moles of gas required was obtained by injecting the gas into a cylinder of known volume at known temperature and pressure. The gas was then pushed into the autoclave with CO₂. Gases at higher concentrations were injected directly into the autoclave until the required ΔP was obtained (Figure 1 (b)). The moles of each impurity required to reach the required concentrations was calculated from the Peng-Robinson equation of state.¹⁸ High pressure CO₂ sourced from high-purity bottles was added to the autoclave aided with a gas booster pump to the desired working pressure. An impeller was used to stir the supercritical CO₂ and to generate flow velocities of about 1 m/s (1000 rpm) during the test for the conditions with flow.

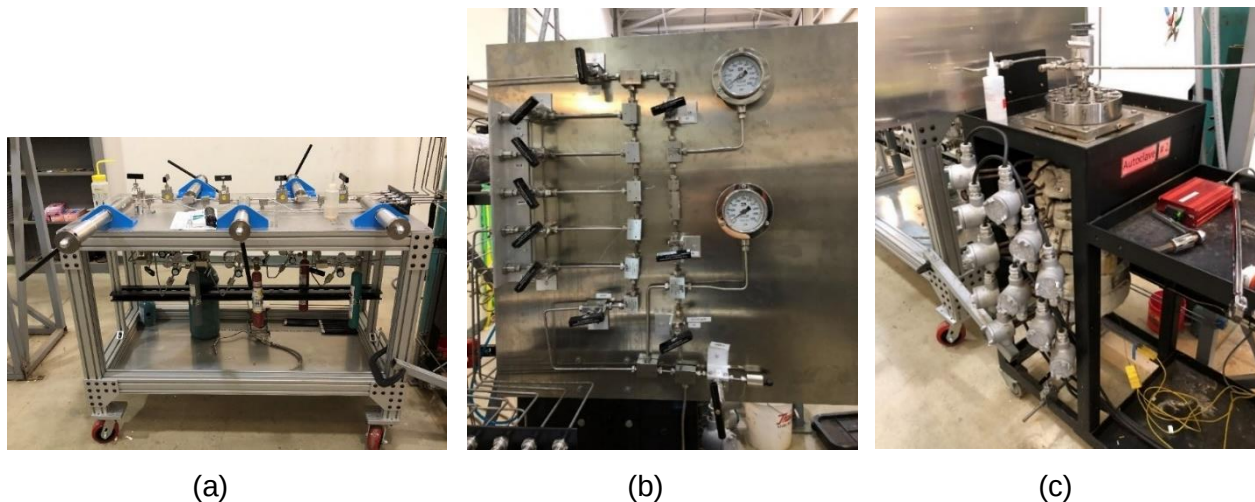


Figure 1: Photographs of the autoclave system used for corrosion testing: (a) impurity injection system, (b) control panel, and (c) autoclave.

The corrosion rates were determined by weight-loss methods at the end of 48 hours exposure. The specimens were removed and cleaned for 5 min in Clarke's solution (20 g antimony trioxide + 50 g stannous chloride and hydrochloric acid to make 1000 ml). The specimens were then rinsed in distilled water, dried and weighed to 0.1 mg. The corrosion rate can be calculated by the following equation:

$$\text{Corrosion rate (mm/y)} = \frac{8.76 \times 10^4 \times \text{weight loss (g)}}{\text{surface area (cm}^2\text{)} \times \text{density Fe (g/cm}^3\text{)} \times \text{exposure time (hour)}}$$

Following extraction, the morphology and compositions of corrosion products were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Localized corrosion was measured via surface profilometry after corrosion products were removed. Table 1 shows the detailed test conditions for the present study. The concentrations of impurities are set upon autoclave closure and left to proceed naturally without further additions. Impurity levels were determined based on CO₂ specifications and field conditions provided by the sponsor.¹⁹⁻²¹

Table 1
Test conditions for corrosion testing. Concentrations are initial values set upon autoclave closure.

Test	Material	pCO ₂ (MPa)	Temp. (°C)	H ₂ O (ppm)	SO ₂ (ppm)	NO (ppm)	O ₂ (ppm)	Flow
1	X65	8	35	650	50	100	0	No
2	X65	8	35	650	4500	100	0	No
3	X65	8	35	650	50	100	40,000	No
4	X65	8	35	650	4500	100	40,000	No
5	X65	8	35	650	4500	100	0	Yes
6	X65	8	35	650	4500	100	20,000	Yes
7	X65	8	35	650	4500	100	40,000	Yes
8	X65	8	35	650	50	100	40,000	Yes

RESULTS AND DISCUSSION

Effect of SO₂ and O₂

Figure 2 shows the corrosion rates of carbon steel in the supercritical CO₂ phase with different concentrations of SO₂ and O₂ under quiescent conditions. There was no measurable sample weight change (less than 0.1 mg/cm²) after the test in the presence of 50 ppm of SO₂ with 650 ppm H₂O and 100 ppm NO, indicating an insignificant corrosion rate. However, a moderate corrosion rate was measured (≈ 0.16 mm/y) when the SO₂ concentration increased to 4500 ppm. This corrosion rate is slightly higher than the previous experiments (≈ 0.1 mm/y) conducted under lower SO₂ concentration (1000 ppm).⁷ It is noteworthy that the corrosion rates increased with the addition of 40,000 ppm O₂ for both low (0 to 0.15 mm/y) and high (0.16 to 0.42 mm/y) SO₂ concentrations. This may be due to the formation of sulfuric acid (H₂SO₄) in the presence of O₂.⁶

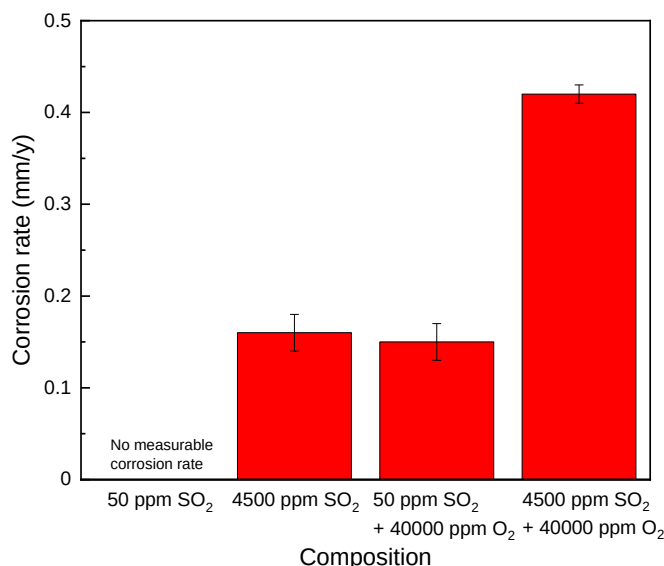


Figure 2: Corrosion rates of X65 carbon steel under supercritical CO₂ with different SO₂ and O₂ concentrations in the absence of flow.

Figure 3 shows pictures of the samples after conducting the corrosion tests in the supercritical CO₂ phase (80 bar and 35°C) with different SO₂ and O₂ concentrations. For the condition with 50 ppm SO₂ (Figure 3 (a)), it can be seen that a majority of the surface was shiny, and no visible signs of corrosion were observed, i.e., the surfaces showed polishing marks. For the condition with 4500 ppm SO₂ (Figure 3 (b)), the formation of scattered corrosion products was observed on the surface of steel. When O₂ was present in the system, the whole surfaces were covered by dark reddish corrosion products (Figure 3 (c), (d)).

Figure 4 shows the SEM image of the surface of the sample after 48 hours exposure in the supercritical CO₂ phase with 650 ppm H₂O, 4500 ppm SO₂, and 100 ppm NO. The surface was covered by corrosion products with cracks, which clearly show the occurrence of corrosion under the testing condition. Table 2 represents EDS analysis of different locations on the sample surface. Location A showed that it was mainly consisted of iron (Fe), oxygen (O) and sulfur (S), suggesting the formation of FeSO₃. Furthermore, areas where no corrosion products were formed were also observed (location B).

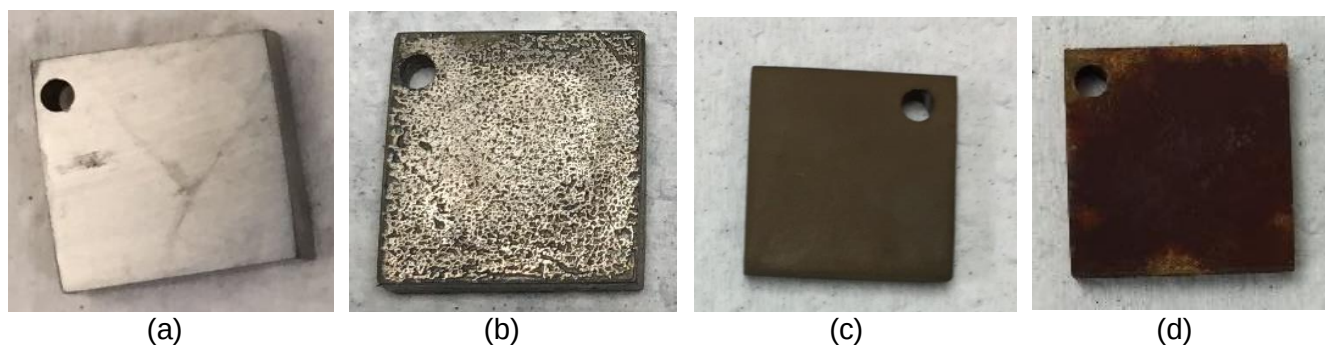


Figure 3: Picture of the surface of the X65 samples after corrosion tests with 650 ppm H₂O and 100 ppm NO at 80 bar and 35°C: (a) Test 1: 50 ppm SO₂, (b) Test 2: 4500 ppm SO₂, (c) Test 3: 50 ppm SO₂ + 40,000 ppm O₂, (d) Test 4: 4500 ppm SO₂ + 40,000 ppm O₂.

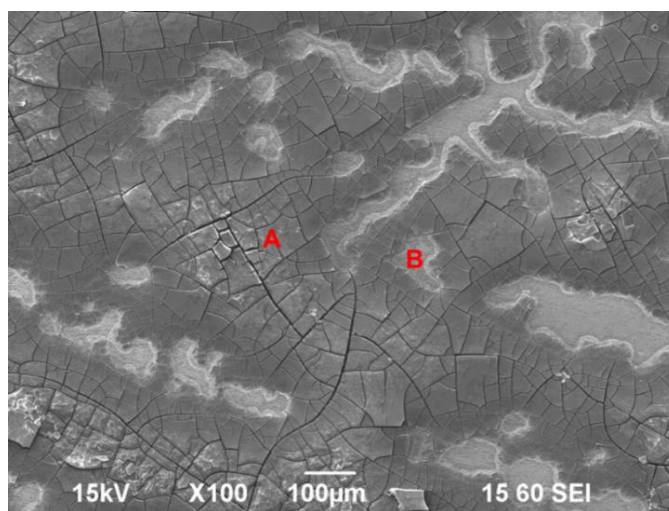


Figure 4: SEM image of the corroded surface of sample exposed to the supercritical CO₂ phase with 650 ppm H₂O, 4500 ppm SO₂ and 100 ppm NO for 48 hours.

Table 2
EDS analysis for different locations of the corroded surface shown in Figure 4.

	Fe (At %)	C (At %)	S (At %)	O (At %)
A	24.05	10.34	29.14	36.47
B	90.56	8.14	1.29	-

Figure 5 shows the SEM image of the surface of the sample after 48 hours exposure in the supercritical CO₂ phase with 650 ppm H₂O, 50 ppm SO₂, 100 ppm NO, and 40000 ppm O₂. The surface was covered by thin corrosion products, which clearly show the occurrence of corrosion under the testing condition. EDS analysis of corrosion products showed that it was mainly consisted of Fe, O and S, indicating the formation of FeSO₄ or Fe₂O₃ (Table 3).