

Corrosion Behavior of API 5L X65 Carbon Steel Under Supercritical and Liquid Carbon Dioxide Phases in the Presence of Water and Sulfur Dioxide

F. Farelas,^{‡,*} Y.S. Choi,^{*} and S. Nešić^{*}

ABSTRACT

Depending on the capture process, liquid or supercritical carbon dioxide (CO₂) can contain impurities like water (H₂O) and sulfur dioxide (SO₂), increasing the likelihood of corrosion of carbon steel pipelines even if there is no free water in the system. To understand the corrosion risk for such pipelines, the present study focused on the effects of CO₂ phase change, water, and SO₂. Different CO₂ phases (liquid and supercritical) and concentrations of SO₂ (<1%) were simulated in an autoclave-based study. The corrosion rate of steel samples was determined with weight-loss (WL) measurements. The surface morphology and the composition of the corrosion product layers were analyzed using surface analytical techniques (scanning electron microscopy [SEM], energy-dispersive spectroscopy [EDS], and infinite focus microscopy [IFM]). Results showed that the corrosion rate decreased with decreasing SO₂ content in the supercritical CO₂ phase containing 650 ppmv of water with no localized attack. In contrast, in high-pressure liquid CO₂, significant localized corrosion was observed.

KEY WORDS: carbon capture and storage, carbon dioxide corrosion, carbon dioxide transport, corrosion, liquid and supercritical carbon dioxide, sulfur dioxide

INTRODUCTION

It has been acknowledged that green house gas (GHG) emissions caused by human activities, such as car-

bon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), are one of the principal reasons for climate change. Among them, CO₂ has been given much attention because CO₂ emissions from fossil fuel combustion have been increasing at an average annual rate of 0.4% from 1990 to 2009, representing 79% of the total emissions in 2009.¹ Coal, natural gas, and oil-fired power plants are together the largest CO₂ emitter. A way to reduce CO₂ emissions to the atmosphere is through carbon capture and storage (CCS). This method consists of capturing CO₂ at the source, transporting it to a suitable storage site, and sequestering it in geological formations such as oil and gas reservoirs, deep saline aquifers, and coal beds.²

One of the forms for transporting CO₂ from the point sources to storage sites is through pipelines manufactured from high-strength steels X65 and X70, which has been established as the most economical approaches of transporting CO₂ to sequestration sites.³⁻⁴ Before the CO₂ is injected in the pipeline, it is dried sufficiently with the purpose of avoiding the presence of free water and then compressed to a dense state (liquid or supercritical phase). From an economical point of view, large volumes of CO₂ can be transported in the dense state because it has a liquid-like density but behaves as a gas, allowing the use of smaller pipeline diameters and larger flow rates.⁵

Some studies have reported that dried supercritical CO₂ is not corrosive.⁶⁻⁸ This noncorrosive property of dry supercritical CO₂ can be ascribed to its low conductivity (3×10⁻⁵ S/m), two orders of magnitude lower than supercritical CO₂ saturated with water (7×10⁻³ S/m).⁶ However, depending on the captured

Submitted for publication: May 15, 2012. Revised and accepted: August 3, 2012. Preprint available online: October 17, 2012, <http://dx.doi.org/10.5006/0739>.

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process, CO₂ could contain impurities like water, oxygen, and sulfur dioxide (SO₂), among others. Such impurities could be the source of corrosion problems for the carbon steel pipelines.^{3,7,9-11}

Several researches have been conducted on corrosion of materials in liquid and supercritical CO₂ contaminated by water, O₂, and SO₂. Recently, it was claimed that water mist saturated with supercritical CO₂ was corrosive for C-steels and responsible of localized attack when water mist droplets, saturated with supercritical CO₂, touched the carbon steel surface.⁹ In addition, no corrosion was observed for 13Cr or Cr-Ni steels even up to 130°C.

Corrosion experiments conducted on X70 steel and iron in water-saturated supercritical CO₂ mixed with SO₂ showed that the corrosion rate of X70 steel increased as the SO₂ concentration increased.³ The corrosion products found by x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) were mainly hydrates of iron(II) sulfate (FeSO₄) and iron sulfite (FeSO₃). It was stated that the presence of SO₂ intensifies the corrosiveness of the water-saturated supercritical CO₂, and the corrosion caused by SO₂ is much more intense than that caused by CO₂.

Dugstad, et al.,⁹ showed that dense phase (liquid) CO₂ with water content significantly lower than the solubility limit is non-corrosive. However, corrosion can take place in dense phase CO₂ at a water content of 200 ppmv (wt) when SO₂ and O₂ are present. In contrast, corrosion rates of approximately 1 mm/y have been reported in pure CO₂ with just 100 ppmv of water.¹⁰

Choi and Nešić¹¹ studied the effect of water content on the corrosion of carbon steel in supercritical CO₂/O₂ phase. It was found that as long as the water content is kept below its solubility limit in CO₂ (3,300 ppmv at 8 MPa and 50°C), no significant attack will take place. However, it was also reported that the addition of 1% SO₂ in the gas phase dramatically increased the corrosion rate of carbon steel to 3.5 mm/y with only 650 ppmv of water, concentration, which is significantly below the solubility limit in CO₂ and the current unofficial industry standard: the so-called Kinder Morgan specification for transporting CO₂ in pipelines.¹²

Considering the real situations for CO₂ transport pipelines, effects of CO₂ phase and SO₂ concentration should be qualified further to establish a clear understanding of the corrosion risk for such pipelines. Therefore, the goal of the present study was to study the corrosion behavior of carbon steel exposed to liquid and supercritical CO₂ with impurities such as water (below the solubility limit: 650 ppmv) and SO₂ (small amounts: <1%). To achieve these goals,

corrosion tests were performed in an autoclave. Corrosion rate of samples were determined by weight-loss measurements. The morphology and compositions of corrosion products were analyzed using scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). To measure the pit depth when localized corrosion was observed, infinite focus microscopy (IFM) was used.

EXPERIMENTAL PROCEDURES

Corrosion tests were performed in a 1,000 mL Type 316 (UNS S31600)⁽¹⁾ stainless steel autoclave. A schematic drawing of the pressurized system is shown in Figure 1. Test samples were machined from API 5L⁽²⁾ X65 pipeline steel with a 10.7 cm² exposed area. At one end of the samples, a 1 mm diameter hole was made to hang them inside the autoclave. Table 1 shows the chemical composition of the pipeline steel used for the corrosion tests.

Before each experiment, the samples were ground with 600 grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol (C₃H₈O) in an ultrasonic bath, dried, and weighed using a balance with a precision of 0.1 mg. Two samples were placed inside the autoclave and 650 ppmv of deionized (DI) water was added at the bottom of the system. The amount of water was chosen taking into account the drying requirement for CO₂ pipelines used for enhanced oil recovery (EOR) in the United States, which is 650 ppmv maximum.¹² Once sealed, the autoclave temperature was adjusted. Then, a technical-grade SO₂ was injected directly into the autoclave to the desired pressure. Finally, high-pressure CO₂ was added to the autoclave with a gas booster pump to the desired working pressure. Details of the experimental matrix are given in Table 2.

Figure 2 shows the phase diagram for pure CO₂ and in the presence of different SO₂ amounts. Values for the critical points for pure CO₂ and CO₂/SO₂ mixtures are reported in Table 2.¹³ At pressures and temperatures above the critical point, the CO₂ is present in a supercritical state. At pressures above and temperatures below the critical point, the CO₂ exists as a liquid. Usually, the presence of impurities causes the formation of a two-phase gas-liquid region;¹⁴ however, as shown in Figure 2 and Table 3, the presence of SO₂ does not have a big influence on the formation of a two-phase region nor on the critical points.

The weight-loss method was used to calculate the average corrosion rate for two samples, which were exposed simultaneously to the aggressive environment for 24 h. After surface analysis, the samples were cleaned using the Clarke's solution,¹⁵ rinsed in DI water, dried, and weighed. Equation (1) was used to calculate the average corrosion rate:

$$CR = \frac{8.76 \times 10^4 (\text{mm} \cdot \text{hour} / \text{cm} \cdot \text{year}) \times \text{weight loss (g)}}{\text{area (cm}^2\text{)} \times \text{density (g/cm}^3\text{)} \times \text{time (hour)}} \quad (1)$$

⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

⁽²⁾ American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.

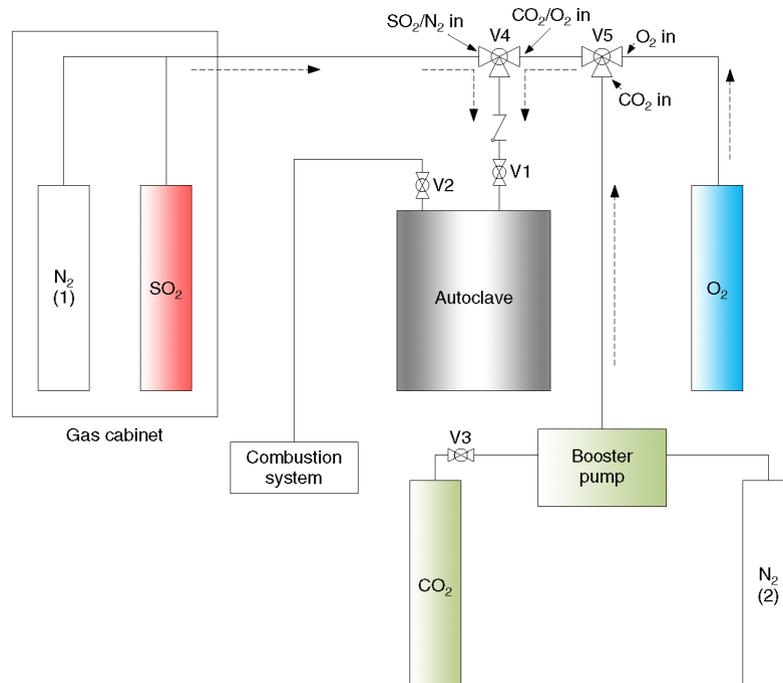


FIGURE 1. Schematic drawing of the CO_2/SO_2 pressurized system used for the corrosion tests.

TABLE 1

Elemental Analysis for the API 5L X65 Carbon Steel (wt%)

C	Mn	Si	P	S	Cr	Cu	Ni	Mo	Al	Fe
0.065	1.54	0.25	0.013	0.001	0.05	0.04	0.04	0.007	0.041	Balance

TABLE 2

Experimental Matrix for the Corrosion Tests

Parameter	Description
Material	API 5L X65
Solution	DI water (650 ppm)
Temperature ($^{\circ}\text{C}$)	25, 50
CO_2 partial pressure (MPa)	8
SO_2 partial pressure (bar)	0.08, 0.04 (0.1 and 0.05% in gas phase)
CO_2 phase	Liquid
	Supercritical
Test methods	WL, SEM, EDS, IFM
Test period (h)	24

The morphology and compositions of corrosion products were analyzed using SEM and EDS. To measure the pit depths when localized corrosion was observed, IFM was used.

RESULTS AND DISCUSSION

Corrosion Tests in Supercritical CO_2 with Impurities

In the absence of SO_2 and when the water is kept below its solubility limit in supercritical CO_2 , no cor-

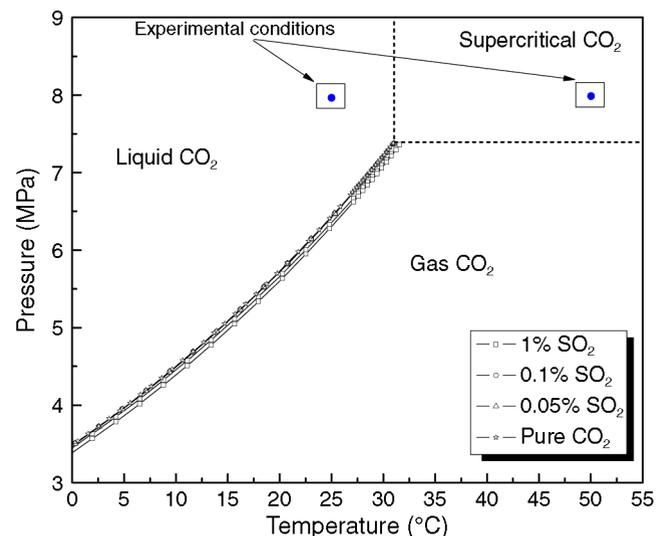


FIGURE 2. Phase diagram for CO_2 with different SO_2 amounts.¹³

rosion has been observed.¹¹ However, the presence of SO_2 in the system can increase the corrosion rate. The effect of SO_2 concentration on the corrosion rate of an API 5L X65 steel exposed to supercritical CO_2/SO_2 phase is shown in Figure 3. Corrosion rate at 1% SO_2 (0.08 MPa) was reported in a previous study and it is

TABLE 3
Critical Point Conditions for Pure CO₂
and in the Presence of SO₂¹³

Component	Critical Pressure (MPa)	Critical Temperature (°C)
CO ₂	7.37	30.97
CO ₂ + 0.05% SO ₂	7.37	31.00
CO ₂ + 0.1% SO ₂	7.37	31.03
CO ₂ + 1.0% SO ₂	7.35	31.55

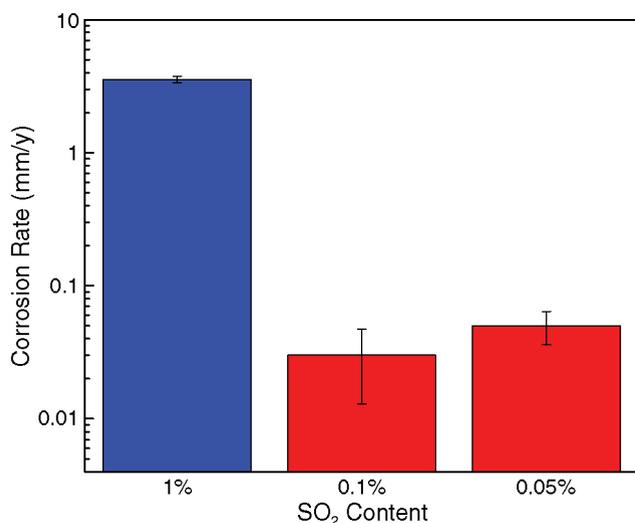
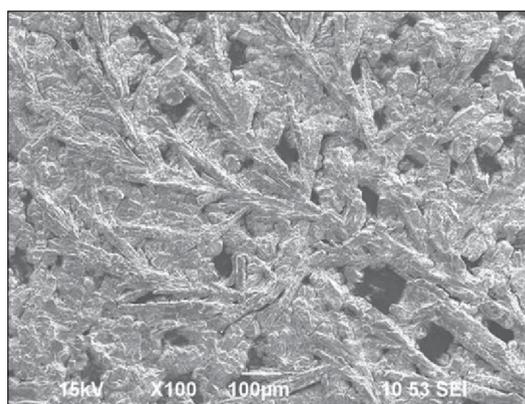
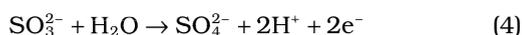
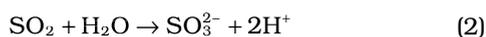


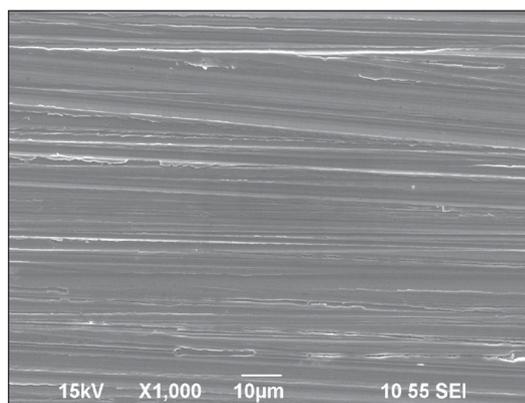
FIGURE 3. Effect of SO₂ concentration on the corrosion rate of carbon steel exposed in the supercritical CO₂ phase for 24 h, at a CO₂ partial pressure of 8 MPa, 50°C, with 650 ppmv water.

reproduced here as a reference point.¹¹ It can be observed that the corrosion rate decreased sharply when SO₂ concentration was reduced from 1% (0.08 MPa) to 0.1% (0.008 MPa). A further decrease in SO₂ content did not show any effect in the corrosion rate and no significant difference between 0.1% and 0.05% (0.004 MPa) was observed.

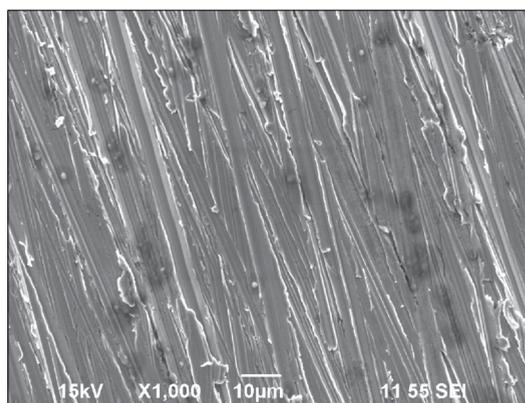
Figure 4 shows the surface morphology of the corroded weight-loss (WL) coupons at different SO₂ concentrations exposed for 24 h in the supercritical CO₂/SO₂ phase with 650 ppmv of water. Figure 4(a) was already reported in a previous publication and it is shown here as a comparison point for the other experimental conditions. Figure 4(a) shows a surface covered by a dendritic corrosion product. According to Choi and Nešić,¹¹ the corrosion product was a mixture of hydrated FeSO₃ and FeSO₄. The formation of FeSO₃ and FeSO₄ in the presence of SO₂ and water can be explained by the following reactions:¹⁶



(a)



(b)



(c)

FIGURE 4. SEM pictures of WL coupon surfaces after being exposed for 24 h in supercritical CO₂ phase, at a CO₂ partial pressure of 8 MPa, 50°C, with 650 ppmv water: (a) 1.0% SO₂, (b) 0.1% SO₂, (c) 0.05% SO₂.



The surface of the samples for 0.1% and 0.05% SO₂ are shown in Figures 4(b) and 3(c), respectively. No visible signs of corrosion were observed for both conditions even at high magnification, i.e., the steel surfaces showed polishing marks and an absence of any corrosion products, which is in qualitative agreement with the low corrosion rate obtained by WL.

Corrosion Tests in Liquid CO₂ with Impurities

Tests in supercritical CO₂/SO₂ phase described above revealed that corrosion of carbon steel can take place even if the concentration of water (650 ppmv) is below its solubility limit. However, corrosion rate was negligible when SO₂ concentration was below 0.1%. On the other hand, during the transport of CO₂ in pipelines, CO₂ can be either in the liquid or supercritical phase. Therefore, it is also important to study the behavior of carbon steels when exposed to liquid CO₂ with impurities such as water and SO₂.

Figure 5 shows the corrosion rates of carbon steel exposed to a liquid CO₂ phase (8 MPa CO₂, 25°C) with different SO₂ contents. Although the general corrosion rates were low in the liquid CO₂ phase with 0.1% SO₂ (≈ 0.1 mm/y), the corrosion rates measured in the liquid CO₂ phase showed higher values than were measured in the supercritical CO₂ phase (≈ 0.03 mm/y). However, in liquid CO₂ with only 0.05% SO₂, there was no measurable specimen weight change (less than 0.1 mg/cm²) after 24 h, indicating an insignificant corrosion rate.

Observation of the corrosion surface of the sample exposed to the liquid CO₂/SO₂ phase with 0.1% SO₂ revealed the presence of heterogeneous, globular corrosion products in an otherwise uniformly cracked layer (Figure 6). According to the chemical analysis performed by EDS (Table 4), the globular corrosion product consisted mainly of iron, oxygen, and sulfur. The cracked layer indicated the same chemical elements by the EDS analysis. In a previous research

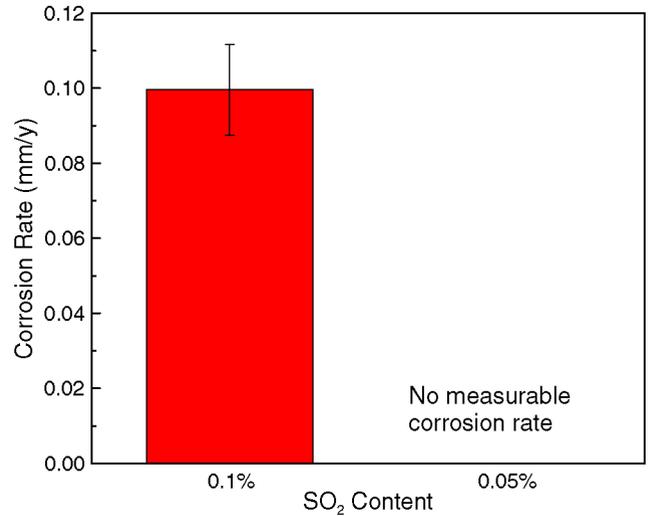


FIGURE 5. Effect of SO₂ content on the corrosion rate of carbon steel exposed in the liquid CO₂ phase for 24 h, at a CO₂ partial pressure of 8 MPa, 25°C, with 650 ppmv water.

TABLE 4
Results from the Energy-Dispersive Spectroscopy
Chemical Analysis

Element	Figure 6(a)		Figure 6(b)		Figure 7	
	wt%	at%	wt%	at%	wt%	at%
O	7.77	20.41	8.85	21.13	12.00	29.46
S	18.31	23.98	32.64	38.87	1.35	1.65
Fe	73.92	55.61	58.51	40.00	83.56	58.78
C					3.09	10.11

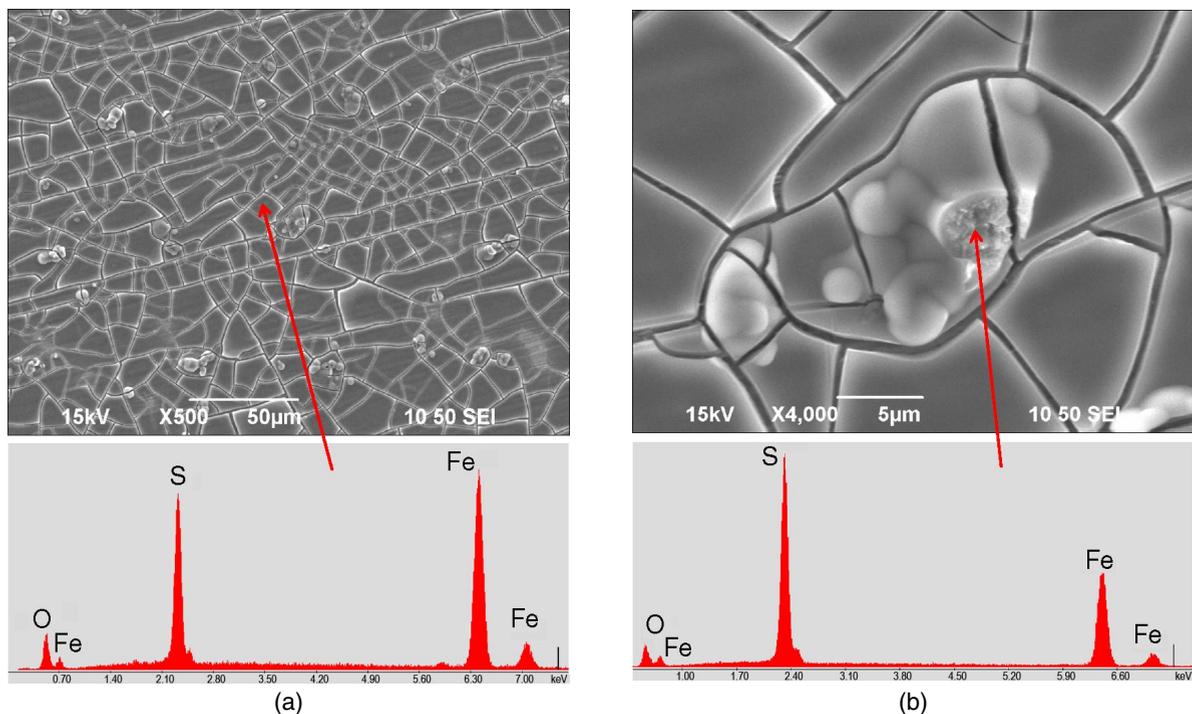


FIGURE 6. SEM images at different magnifications and EDS analysis of the corresponding area of the corroded surface of the coupon exposed to the liquid CO₂ for 24 h, at a CO₂ partial pressure of 8 MPa, 25°C, with 0.1% SO₂.

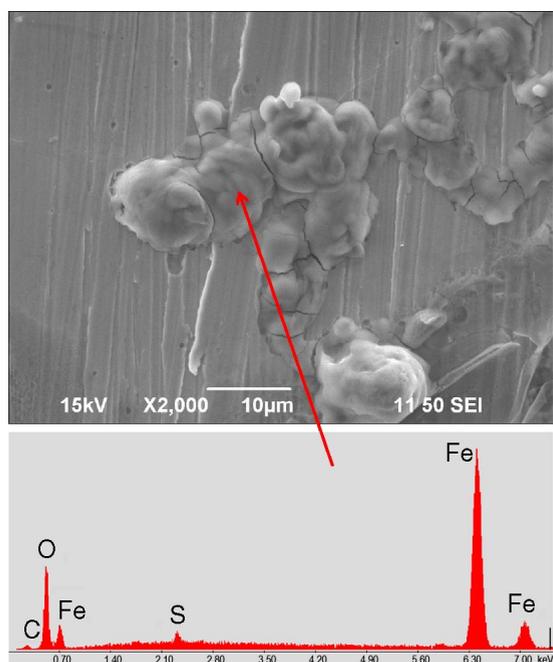


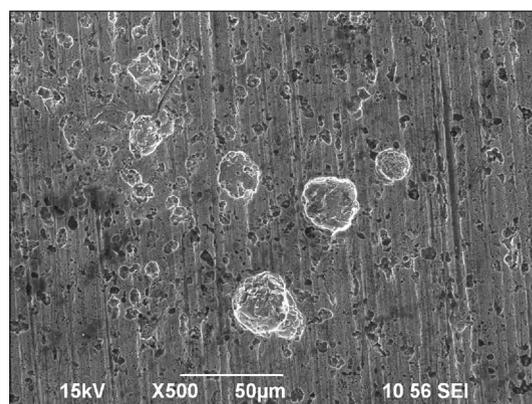
FIGURE 7. SEM image and EDS spectra of the corroded surface of the sample exposed to the liquid CO_2 for 24 h, at a CO_2 partial pressure of 8 MPa, 25°C , with 0.05% SO_2 .

study, this corrosion product was reported to be hydrated FeSO_3 and FeSO_4 .¹¹

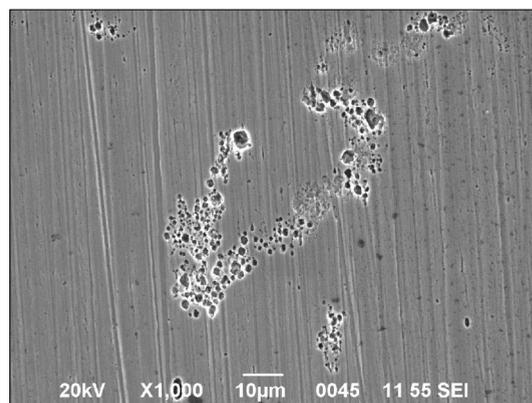
Figure 7 shows the corroded surface and the EDS analysis of the metal sample after being exposed to a liquid CO_2 phase with 0.05% SO_2 . Although no significant corrosion rate was measured, a globular corrosion product was found on the metal surface. EDS analysis (Table 4) revealed the presence of iron, oxygen, and sulfur. Comparing Figure 7 with Figure 6, a less-intense sulfur peak is observed that can be ascribed to the decrease in SO_2 content.

Figure 8 shows the surface morphologies of the two samples after cleaning with Clarke's solution. The polishing marks were still visible and localized attack was observed for both conditions, being more severe with 0.1% SO_2 than 0.05% SO_2 . This suggests that localized corrosion could be accelerated by increasing SO_2 concentration. Furthermore, it implies that even though uniform corrosion rate from the weight-loss measurement was low, localized corrosion can be initiated in the liquid CO_2 phase with SO_2 .

Figures 9 and 10 present the results of IFM analysis of several pits observed on the cleaned sample exposed to the liquid CO_2 for 24 h, at a CO_2 partial pressure of 8 MPa, 25°C . According to the depth of the deepest pits measured using IFM, the maximum localized corrosion rates were measured to be 6.8 mm/y for the samples exposed to 0.1% SO_2 and 2.4 mm/y for the samples exposed to 0.05% SO_2 . Table 5 shows a comparison of the uniform and pitting corrosion rates observed under both experimental conditions. It is important to mention that the pitting corrosion rate



(a)



(b)

FIGURE 8. SEM images of the corroded surface of the samples exposed to the liquid CO_2 for 24 h, at a CO_2 partial pressure of 8 MPa, 25°C , after cleaning: (a) 0.1% SO_2 , (b) 0.05% SO_2 .

of 6.8 mm/y observed in liquid CO_2 phase with 0.1% SO_2 was even higher than the general corrosion rate reported by Choi and Nešić¹¹ in supercritical CO_2 with 1% SO_2 and 650 ppmv of water.

Dugstad and Halseid¹⁷ suggested that the solubility of sulfurous/sulfuric acid ($\text{H}_2\text{SO}_3/\text{H}_2\text{SO}_4$) formed when water and SO_2 are present in the system seems to be low. This statement was confirmed in the present study by the presence of corrosion products formed in liquid CO_2 phase when the water concentration (Figures 6 and 7) is below its solubility limit. Localized corrosion took place when acid droplets are deposited on the metal surface as it was observed by SEM and IFM analyses. However, no data has been found about the solubility limit of sulfurous/sulfuric acid in supercritical and liquid CO_2 phases.

CONCLUSIONS

❖ Corrosion rates measured in liquid and supercritical CO_2 with impurities like H_2O and SO_2 are still limited in the literature. This research contributes to CCS by showing experimental data that revealed potential corrosion problems during the transport of dense CO_2 under such conditions.

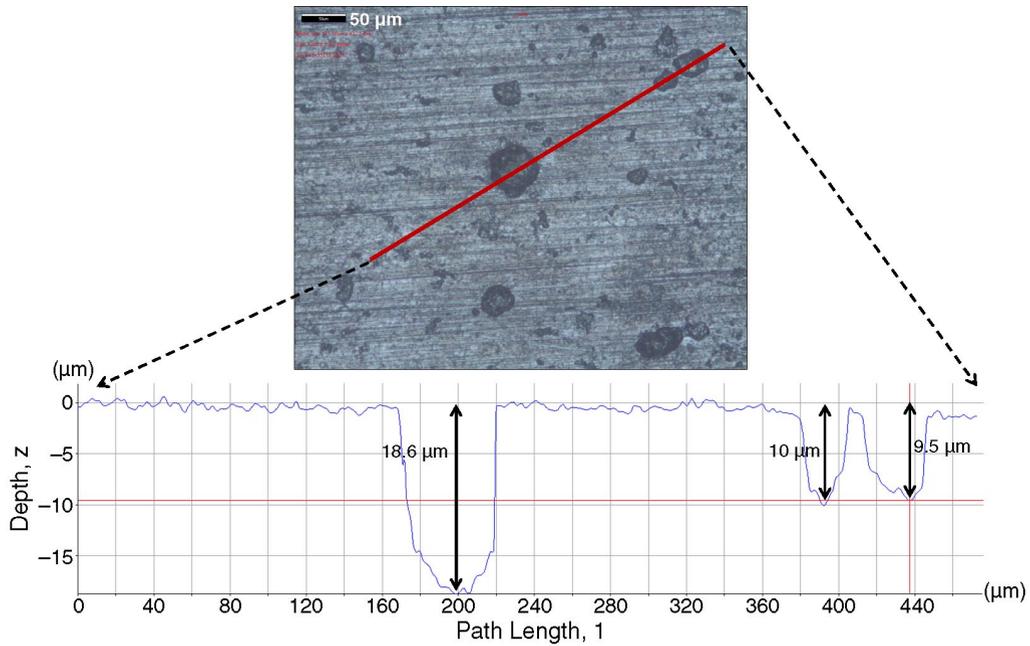


FIGURE 9. IFM analysis of the pits on the sample exposed to liquid CO_2 with 0.1% SO_2 for 24 h, at a CO_2 partial pressure of 8 MPa, 25°C, after cleaning.

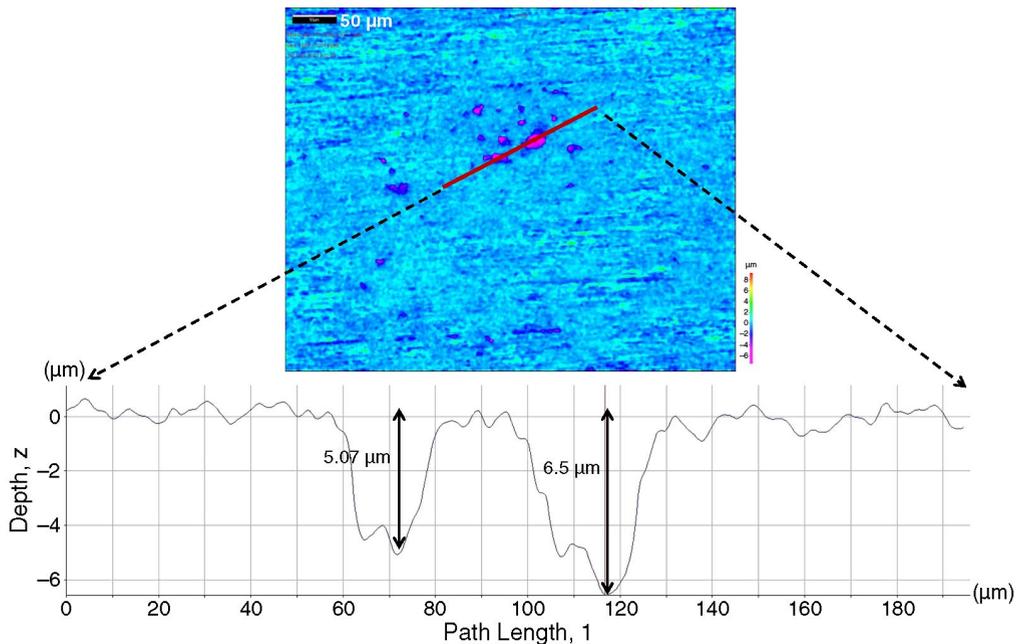


FIGURE 10. IFM analysis of the pits on the sample exposed to liquid CO_2 with 0.05% SO_2 for 24 h, at a CO_2 partial pressure of 8 MPa, 25°C, after cleaning.

- ❖ In high-pressure supercritical CO_2 systems containing 650 ppmv water, the concentration of SO_2 less than 0.1% did not lead to significant corrosion of carbon steel (0.03 mm/y) in short-term experiments.
- ❖ In the high-pressure liquid CO_2 conditions with 650 ppmv of water, localized attack was seen with a rate of 6.8 mm/y (0.1% SO_2) and 2.4 mm/y (0.05% SO_2) in short-term experiments. These results showed

that small amounts of SO_2 are potentially harmful in liquid CO_2 phase even in the presence of limited free water.

ACKNOWLEDGMENTS

The authors would like to thank the financial support from Ohio Coal Development Office (OCDO)

TABLE 5

Comparison of Corrosion Rates Obtained from Weight-Loss Measurements and Infinite Focus Microscopy Analysis of Pit Penetration Depth for Samples Exposed to Liquid CO₂ for 24 h, at a CO₂ Partial Pressure of 8 MPa, 25°C and 50°C, After Cleaning at Different SO₂ Contents in the Liquid and Supercritical CO₂ Phases

CO ₂ Phase	SO ₂ Content (%)	Corrosion Rate from Weight Loss (mm/y)	Error (mm/y)	Maximum Pit Depth from IFM (μm)	Localized Corrosion Rate (mm/y)
Liquid	0.1	0.1	0.01	18.6	6.8
Liquid	0.05	≈0	≈0	6.5	2.4
Supercritical	1.0	3.5	0.21	—	—
Supercritical	0.1	0.03	0.02	—	—
Supercritical	0.05	0.05	0.01	—	—

given to the Institute for Corrosion and Multiphase Technology at Ohio University.

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