Effects of CO₂ Phase Change, SO₂ Content and Flow on the Corrosion of CO₂ Transmission Pipeline Steel

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ABSTRACT

Results from previous studies demonstrated that significant corrosion of carbon steel was observed when 1% SO₂ impurity was contained in a supercritical CO₂ phase in the presence of small amounts of water (650 ppm). Considering real situations for CO₂ transportation pipelines, the effects of CO₂ phase change, impurity concentration and flow were evaluated in the present study in order to establish a clearer understanding of the corrosion risk for such pipelines. Different CO₂ phases (liquid and supercritical), concentrations of SO₂ (< 1%) and flow velocities were used in an autoclave based study. The corrosion rate of steel 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, EDS, and IFM). Results showed that the corrosion rate decreased with decreasing SO₂ content in the supercritical CO₂ phase containing 650 ppm of water. In addition, significant localized corrosion was observed when CO₂ phase was liquid.

Keywords: CO₂ corrosion, CCS, liquid and supercritical CO₂, CO₂ transport, SO₂

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It has been acknowledged that greenhouse gas (GHG) emissions due to human activities such as carbon 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 percent from 1990 to 2009, representing 79 percent of the total emissions in 2009.¹ Coal, natural gas and oil fired power plants are together the largest CO₂ emitter. One 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 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 ways for transporting CO₂ from the point sources to storage sites is through pipelines manufactured from high strength steel X65 and X70.⁴ Due to high pressures, the CO₂ in these pipelines is typically in supercritical or liquid phase. Depending on the source and capture process, the CO₂ can contain impurities.³ Before the CO₂ is injected in the pipeline it is sufficiently dried in order to avoid the presence of free water and therefore reduce the likelihood of corrosion of the carbon steel. In the absence of impurities and with water below its solubility limit, it appears that the high pressure CO₂ is not corrosive to the steel.⁵,⁶ However, the presence of impurities such as SO₂ and O₂ increases the likelihood of corrosion even if there is no free water in the system.⁵⁻⁷

Recently, several researches have been conducted on corrosion of materials in liquid and supercritical CO₂ contaminated by water, O₂, and SO₂. Beck et al.,⁸ developed an experimental system for carrying out in-situ measurements of conductivity and steel corrosion in supercritical CO₂ fluids. Water-saturated supercritical CO₂ had a conductivity near 7×10⁻³ S/m, with dry supercritical CO₂ having a conductivity two orders of magnitude lower. In addition, they found that the passive layer that apparently formed on the metal surface during system pressurization in gaseous CO₂ further degraded over time under supercritical conditions.

Zhang et al.,⁹ claimed that water mist saturated with supercritical CO₂ was corrosive for C-steels, however not for 13Cr or Cr-Ni steels even up to 130°C. In addition, they showed that droplets of water mist, saturated with supercritical CO₂, caused localized attack when touching the carbon steel surface.

Xiang et al.,⁴ conducted corrosion experiments of X70 steel and iron in water-saturated supercritical CO₂ mixed with SO₂. The corrosion rate of X70 steel increased as the SO₂ concentration increased, and the corrosion products were mainly hydrates of FeSO₄ and FeSO₃. They claimed 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.,⁶ 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 ppm (wt) when SO₂ and O₂ are present.

Choi et al.,¹⁰ 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 (3300 ppm at 80 bar 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 ppm 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.¹⁰

Considering the real situations for CO₂ transport pipelines, effects of CO₂ phase and SO₂ concentration should be further qualified in order to establish a clear understanding of the corrosion risk for such pipelines. Therefore, the present study aimed at studying the corrosion behavior of carbon steel exposed to liquid and supercritical CO₂ with impurities such as water (below the solubility limit: 650 ppm) and SO₂ (small amounts: < 1%). In order 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 by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). In order to measure the pit depth when localized was observed an infinite focus microscope (IFM) was used. Some preliminary results about the effect of flow in liquid and supercritical CO₂ are also reported.

**EXPERIMENTAL PROCEDURE**

Corrosion tests were performed in a 1000 mL 316 stainless steel autoclave. A schematic drawing of the pressurized system is shown in Figure 1. Test samples were machined from API 5L X65 pipeline steel with a 10.7 cm² exposed area. At one end of the samples, a 1 mm diameter hole was made in order 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 paper, cleaned with isopropyl alcohol 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 ppm (mole) of 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 ppm (mole) maximum.¹¹ Once sealed, the autoclave temperature was adjusted. Then, a technical grade SO₂ was directly injected 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 2.¹² 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 region¹³, however, as shown in Figure 2 and Table 3, the presence of SO₂ does not have a big influence neither on the formation of a two phase region nor on the critical points.

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¹¹ 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 carbon steel (API 5L X65) used in the corrosion tests (wt. %)

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.065</td>
<td>1.54</td>
<td>0.25</td>
<td>0.013</td>
<td>0.001</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.007</td>
<td>0.041</td>
<td>balance</td>
</tr>
</tbody>
</table>

**TABLE 2**

Experimental matrix for the corrosion tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>API 5L X65</td>
</tr>
<tr>
<td>Solution</td>
<td>DI water (650 ppm)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25, 50</td>
</tr>
<tr>
<td>CO$_2$ partial pressure (bar)</td>
<td>80</td>
</tr>
<tr>
<td>SO$_2$ partial pressure (bar)</td>
<td>0.08, 0.04 (0.1 and 0.05% in gas phase)</td>
</tr>
<tr>
<td>CO$_2$ phase</td>
<td>Liquid, supercritical</td>
</tr>
<tr>
<td>Test methods</td>
<td>WL, SEM, EDS, IFM</td>
</tr>
<tr>
<td>Test period (hr)</td>
<td>24</td>
</tr>
</tbody>
</table>
The weight–loss method was used to calculate the average corrosion rate for two samples which were simultaneously exposed to the aggressive environment for 24 hours. After surface analysis, the samples were cleaned using the Clarke solution, rinsed in DI water, dried and weighed. Equation 1 was used to calculate the average corrosion rate:

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

(1)

The morphology and compositions of corrosion products were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). In order to measure the pit depths when localized was observed, an infinite focus microscope (IFM) was used.

Figure 2: Phase diagram for CO₂ with different SO₂ amounts.  

TABLE 3  
Critical point conditions for pure CO₂ and in the presence of SO₂.  

<table>
<thead>
<tr>
<th>Component</th>
<th>Critical Pressure (bar)</th>
<th>Critical Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>73.77</td>
<td>30.97</td>
</tr>
<tr>
<td>CO₂ + 0.05% SO₂</td>
<td>73.76</td>
<td>31.00</td>
</tr>
<tr>
<td>CO₂ + 0.1% SO₂</td>
<td>73.75</td>
<td>31.03</td>
</tr>
<tr>
<td>CO₂ + 1.0% SO₂</td>
<td>73.57</td>
<td>31.55</td>
</tr>
</tbody>
</table>
RESULTS

Corrosion tests in supercritical CO\textsubscript{2} with impurities

In the absence of SO\textsubscript{2} and when the water is kept below its solubility limit in supercritical CO\textsubscript{2}, no corrosion has been observed.\textsuperscript{5} However, the presence of SO\textsubscript{2} in the system can increase the corrosion rate. The effect of SO\textsubscript{2} concentration on the corrosion rate of an API 5L X65 steel exposed to supercritical CO\textsubscript{2}/SO\textsubscript{2} phase is shown in Figure 3. Corrosion rate at 1\% SO\textsubscript{2} (0.8 bar) was reported in a previous study and it is reproduced here as a reference point.\textsuperscript{10} It can be observed that the corrosion rate decreased sharply when SO\textsubscript{2} concentration was reduced from 1\% (0.8 bar) to 0.1\% (0.08 bar). A further decrease in SO\textsubscript{2} content did not show any effect in the corrosion rate and no significant difference between 0.1\% and 0.05\% (0.04 bar) was observed.

![Figure 3: Effect of SO\textsubscript{2} concentration on the corrosion rate of carbon steel exposed in the supercritical CO\textsubscript{2} phase for 24 h, at a CO\textsubscript{2} partial pressure of 80 bar, 50\textdegree C, with 650 ppm water.](image)

Figure 4 shows the surface morphology of the corroded WL coupons at different SO\textsubscript{2} concentrations exposed for 24 h in the supercritical CO\textsubscript{2}/SO\textsubscript{2} phase with 650 ppm of water. Figure 4(a) was already reported in a previous publication\textsuperscript{10} 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 \textit{et al.},\textsuperscript{10} the corrosion product was a mixture of hydrated FeSO\textsubscript{3} and FeSO\textsubscript{4}. The formation of FeSO\textsubscript{3} and FeSO\textsubscript{4} in the presence of SO\textsubscript{2} and water can be explained by the following reactions:\textsuperscript{10}

\begin{align*}
\text{SO}_2 + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_3 \\
\text{Fe} + \text{H}_2\text{SO}_3 &\rightarrow \text{FeSO}_3 + \text{H}_2
\end{align*}
SO₂ + H₂O → SO₃²⁻ + 2H⁺  \hspace{2cm} (2)
Fe²⁺ + SO₃²⁻ → FeSO₃ \hspace{2cm} (3)
SO₃²⁻ + H₂O → SO₄²⁻ + 2H⁺ + 2e⁻  \hspace{2cm} (4)
Fe²⁺ + SO₄²⁻ → FeSO₄ \hspace{2cm} (5)

The surface of the samples for 0.1% and 0.05% SO₂ are shown in Figure 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, what is in qualitative agreement with the low corrosion rate obtained by WL.

Figure 4: SEM pictures of WL coupons surface after being exposed for 24 h in supercritical CO₂ phase, at a CO₂ partial pressure of 80 bar, 50°C, with 650 ppm water: (a) 1.0% SO₂, (b) 0.1% SO₂, (c) 0.05% SO₂.
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 ppm) 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 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 6 shows the corrosion rates of carbon steel exposed to a liquid CO₂ phase (80 bar 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 hours, indicating an insignificant corrosion rate.

Observation of the corrosion surface of the sample exposed to liquid CO₂/SO₂ phase with 0.1% SO₂ revealed the presence of heterogeneous, globular corrosion products in an otherwise uniformly cracked layer (Figure 6(a)). According to the chemical analysis performed by EDS (Figure 6(b)), the globular corrosion product consisted mainly of iron, oxygen and sulfur. The cracked layer indicated the same chemical elements by the EDS analysis (not...
shown here). In previous research study, this corrosion product was reported to be hydrated FeSO$_3$ and FeSO$_4$.$^{10}$

![Figure 6: SEM image (a) and EDS analysis (b) of the corroded surface of the coupon exposed to the liquid CO$_2$ for 24 h, at a CO$_2$ partial pressure of 80 bar, 50°C, with 0.1% SO$_2$.](image)

Figure 6: SEM image (a) and EDS analysis (b) of the corroded surface of the coupon exposed to the liquid CO$_2$ for 24 h, at a CO$_2$ partial pressure of 80 bar, 50°C, with 0.1% SO$_2$.

Figure 7(a) shows the corroded surface 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 (Figure 7(a)) revealed the presence of iron, oxygen, and sulfur. Comparing Figure 7(b) with Figure 6(b) observed a less intense sulfur peak is observed that can be ascribed to the decrease in SO$_2$ content.

![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 80 bar, 50°C, with 0.05% SO$_2$.](image)

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 80 bar, 50°C, with 0.05% SO$_2$. ©2012 by NACE International. Requests for permission to publish this manuscript in any form, in part or in whole, must be in writing to NACE International, Publications Division, 1440 South Creek Drive, Houston, Texas 77084. The material presented and the views expressed in this paper are solely those of the author(s) and are not necessarily endorsed by the Association.
Figure 8 shows the surface morphologies of the two samples after cleaning with Clarke solution. Localized attack was observed for both conditions, being more severe with 0.1% SO₂ than 0.05% SO₂. This suggests that localized corrosion could be accelerated by increasing SO₂ 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 CO₂ phase with SO₂.

Figure 8: SEM images of the corroded surface of the samples exposed to the liquid CO₂ for 24 h, at a CO₂ partial pressure of 80 bar, 50°C, after cleaning: (a) 0.1% SO₂, (b) 0.05% SO₂.

Figure 9 and Figure 10 present the results of Infinite Focus Microscope (IFM) analysis of several pits observed on the cleaned sample exposed to the liquid CO₂ for 24 h, at a CO₂ partial pressure of 80 bar, 50°C. According to the depth of the deepest pit measured by IFM, the maximum localized corrosion rates were calculated for each condition and shown in Table 3.
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 80 bar, 50°C, after cleaning: (a) optical image of the pits, (b) measured depth of the pits.
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 80 bar, 50°C, after cleaning: (a) optical image of the pits, (b) measured depth of the pits.
TABLE 3

Comparison of corrosion rates obtained from weight loss measurements and IFM analysis of pit penetration depth for samples exposed to liquid CO\textsubscript{2} for 24 h, at a CO\textsubscript{2} partial pressure of 80 bar, 50\textdegree\text{C}, after cleaning at different SO\textsubscript{2} contents in the liquid CO\textsubscript{2} phase.

<table>
<thead>
<tr>
<th>SO\textsubscript{2} Content</th>
<th>Corrosion rate from weight loss (mm/y)</th>
<th>Maximum pit depth from IFM (μm)</th>
<th>Localized corrosion rate (mm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% SO\textsubscript{2}</td>
<td>0.1</td>
<td>18.6</td>
<td>6.8</td>
</tr>
<tr>
<td>0.05% SO\textsubscript{2}</td>
<td>≈ 0</td>
<td>6.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Effect of flow on the corrosion of carbon steel in liquid and supercritical CO\textsubscript{2}/H\textsubscript{2}O/SO\textsubscript{2} environments

In order to investigate the effect of flow on the corrosion behavior of carbon steel, stirred autoclave corrosion experiments were conducted in both supercritical and liquid CO\textsubscript{2} phases with SO\textsubscript{2}. Intense stirring (i.e. 1000 rpm) was achieved using a stainless steel impeller at the bottom of the autoclave.

Figure 11 shows some preliminary results in flowing conditions for the corrosion rates of carbon steel in the supercritical CO\textsubscript{2} (80 bar CO\textsubscript{2}, 0.08 bar SO\textsubscript{2}, 50\textdegree\text{C}) and liquid CO\textsubscript{2} (80 bar CO\textsubscript{2}, 0.08 bar SO\textsubscript{2}, 25\textdegree\text{C}) with 650 ppm water. It is interesting to note that the corrosion rates for both conditions showed lower values than those without flow. Especially, the corrosion rate in the liquid CO\textsubscript{2} phase decreased from 0.1 mm/y (without flow) to 0.013 mm/y (with flow).

![Figure 11: Corrosion rates of carbon steel in supercritical and liquid CO\textsubscript{2} phases with flow, at 80 bar CO\textsubscript{2}, 0.08 bar SO\textsubscript{2}, 50\textdegree\text{C} and 650 ppm of water.](image)
Figure 12 shows the SEM surface images of the samples exposed to the supercritical CO$_2$/SO$_2$ and liquid CO$_2$/SO$_2$ phases with flow. It can be seen that some corrosion product deposits formed on the steel surfaces for both conditions.

Figure 13 shows the surface morphology of the samples after cleaning with Clarke solution. No significant corrosion attack was observed on the sample for the supercritical CO$_2$ condition, i.e., the surfaces showed clear polishing marks and are devoid of localized corrosion. However, some pits were observed on the surface for the liquid CO$_2$ condition, suggesting localized corrosion risk, even if these pits were very small and shallow. Further research is ongoing in order to understand the effect of flow on the corrosion of steel in liquid and supercritical CO$_2$/H$_2$O/SO$_2$ environments.

![Figure 12: SEM images of the corroded surface of the samples exposed to a flowing CO$_2$ at 80 bar CO$_2$, 0.08 bar SO$_2$, and 650 ppm of water: (a) supercritical CO$_2$ and (b) liquid CO$_2$.](image1)

![Figure 13: SEM images of the cleaned corroded surface of the samples exposed to a flowing CO$_2$ at 80 bar CO$_2$, 0.08 bar SO$_2$, and 650 ppm of water: (a) supercritical CO$_2$ and (b) liquid CO$_2$.](image2)
CONCLUSIONS

- In the high pressure supercritical CO₂ systems containing 650 ppm water, the concentration of SO₂ less than 0.1% did not lead to significant corrosion of carbon steel, in short term experiments.
- In high pressure liquid CO₂ conditions with 650 ppm of water and 0.05% SO₂, localized attack was seen with a rate about 2.4 mm/y, in short term experiments.

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