Corrosion Inhibition of Carbon Steel in Supercritical CO₂/H₂S Environments

Yoon-Seok Choi, Shokrollah Hassani, Thanh Nam Vu, Srdjan Nesic
Institute for Corrosion and Multiphase Technology,
Department of Chemical and Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

Ahmad Zaki B Abas, Azmi Mohammed Nor, Muhammad Firdaus Suhor
Petronas Research SDN. BHD, Selangor Darul Ehsan, Malaysia

ABSTRACT

The effect of small amounts of H₂S on the corrosion behavior and corrosion protection of carbon steel was investigated in high pressure CO₂ environments. The experiments were carried out in a 7.5L autoclave with two combinations of CO₂ partial pressure and temperature (12 MPa/80°C and 8 MPa/25°C) with different H₂S concentrations (0, 100 and 200 ppm). The corrosion behavior of specimens was evaluated using electrochemical measurements and surface analytical techniques. It was found that the addition of small amounts of H₂S reduced the corrosion rate of carbon steel in high pressure CO₂ environments. However, the corrosion rate was still higher than the targeted rate (< 0.1 mm/y). Additional protection was required in order to achieve the target. Utilizing 400 ppm of an imidazoline-type corrosion inhibitor reduced the corrosion rate of carbon steel below 0.1 mm/y in a high pressure CO₂ condition with H₂S. Compared to carbon steel, the corrosion resistance of low Cr steels was lower in the corresponding CO₂ conditions with H₂S.

Key words: Supercritical/liquid CO₂, CO₂ corrosion, carbon steel, low Cr alloy steel, corrosion inhibitor

INTRODUCTION

Numerous studies of corrosion issues in high pressure CO₂ environments relating to carbon capture and storage (CCS), enhanced oil recovery (EOR), and deep water oil and gas production applications have recently been published.¹-⁵ Aqueous corrosion mechanisms in high pressure CO₂ are similar to those in low pressure CO₂ conditions.⁶ However, the corrosion rate of carbon steel in the presence of high pressure CO₂ without formation of protective corrosion product layers is very high (≥ 20 mm/y) due to the presence of significantly high concentrations of corrosive species, such as H⁺ and H₂CO₃.⁷-¹⁴
Controlling corrosion in such cases usually involves use of Corrosion Resistant Alloys (CRAs). Since the use of CRAs is very costly, there is a need to better quantify their performance, as well as that of mild steels, against the risk of corrosion associated with high pressure CO₂ environments. This facilitates identification of production conditions where mild steel may still be used in the construction of pipelines, and related, systems. Furthermore, this has the potential to significantly reduce costs associated with use of CRAs for infrastructure construction.

In previous studies, an attempt was made to control the corrosion of carbon steel in high pressure CO₂ conditions using low Cr alloy steels and corrosion inhibitor (CI). The studies showed that utilizing low Cr alloy steels (1% Cr and 3% Cr) alone was insufficient to decrease the corrosion rate below the targeted value of 0.1 mm/y. Adequate protection was achieved by applying generic “imidazoline+thiosulfate” CI to carbon steel in the high pressure CO₂ environments. Furthermore, the CI performance with carbon steel was better than Cr-containing steels.

It has recently been reported that small amounts of H₂S can be present in high pressure CO₂ streams related to gas field development. Although the effect of H₂S on the aqueous corrosion of carbon steel at low CO₂ partial pressures is well investigated, limited work has been done in high pressure CO₂ environments. In addition, there is no systematic study on corrosion inhibition in high pressure CO₂ environments with H₂S. Thus, the objective of the present study was to identify and quantify the key issues that affect integrity of carbon steel in high pressure CO₂ in the presence of small amounts of H₂S, and to establish potential corrosion mitigation strategies using low Cr alloy steels and corrosion inhibitors.

**EXPERIMENTAL PROCEDURE**

The test specimens were machined from UNS K03014 carbon steel (CS), UNS G41300-1Cr steel (1Cr) and UNS G41300-3Cr steel (3Cr) with two different geometries: cylindrical type with 5 cm² exposed area for electrochemical measurements, and rectangular type with a size of 1.27 cm × 1.27 cm × 0.254 cm for surface analysis. The chemical compositions of the studied alloys are shown in Table 1. The specimens were ground sequentially with 250, 400 then 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol in an ultrasonic bath for 60 seconds, and dried. A 1 wt.% NaCl aqueous electrolyte was prepared using deionized (DI) water.

| Chemical compositions of materials used in the present study (wt.%, balance Fe). |
|--------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| C   | Cr   | Mn   | P      | S      | Si     | Cu      | Ni      | Mo      | Al      |
| CS  | 0.065 | 0.05 | 1.54   | 0.013  | 0.001  | 0.25    | 0.04    | 0.04    | 0.007   | 0.041   |
| 1Cr | 0.3   | 0.85 | 0.91   | 0.015  | 0.008  | 0.29    | ---     | ---     | ---     | ---     |
| 3Cr | 0.08  | 3.43 | 0.54   | 0.006  | 0.003  | 0.3     | 0.16    | 0.06    | 0.32    | ---     |

An ‘imidazoline + thiosulfate’ generic corrosion inhibitor (CI1) and an ‘imidazoline’ generic corrosion inhibitor (CI2) were selected for evaluation under high pCO₂ environments with H₂S. In this instance, ‘imidazoline’ is shorthand for tall oil fatty acid (TOFA)imidazoline-type inhibitor.

The corrosion experiments were conducted in a 7.5-liter autoclave (UNS N10276) with a three-electrode setup, consisting of a working electrode, a high pressure/high temperature Ag/AgCl reference electrode and a platinum coated niobium counter electrode. An impeller was used to stir the solution at a rotation speed of 1000 rpm (corresponding to approximately 1 m/s), stirring was maintained during the test.
Experimental procedure is outlined in Figure 1. Initially, 1 wt.% of NaCl solution was placed in an autoclave and this electrolyte purged with CO₂ for 1 ~ 3 hours in order to remove dissolved O₂. The electrodes and specimens were then placed in the autoclave. After closing the autoclave, temperature was increased to the testing temperature. Once the working temperature was achieved, a mixture of CO₂ and H₂S was injected into the system to achieve the working H₂S partial pressure. High pressure CO₂ was then injected with a booster pump. Corrosion rate and corrosion potential of specimens were evaluated with time by linear polarization resistance (LPR) measurements. The details of LPR measurements are shown in our previous work. After each test, the specimens were removed from the autoclave, rinsed with DI water and isopropyl alcohol, dried with N₂ and stored in a desiccator cabinet in an inert atmosphere until surface analyses could be conducted. For testing with inhibitors, the procedure was the same as shown in Figure 1, except inhibitor was added to the solution before inserting the specimens.

Figure 1: Experimental procedures for evaluating the corrosion behavior of materials in high pCO₂ environments with H₂S.

Table 2 shows the test conditions for the present study. The test conditions were set in order to simulate the inlet and outlet conditions for CO₂ transportation pipeline, where the CO₂ is present in a supercritical state at the ‘inlet’ condition and it exists as a liquid at the ‘outlet’ condition.

Table 2
Test conditions for corrosion testing

<table>
<thead>
<tr>
<th></th>
<th>pCO₂ (MPa)</th>
<th>H₂S (ppm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>12</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>Outlet</td>
<td>8</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>200</td>
<td>25</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Experiments at the inlet condition (12 MPa, 80°C)

Figure 2 shows the variations of corrosion rate and corrosion potential with time under different H₂S concentrations. Without H₂S, the corrosion rate is about 90 mm/y at the beginning of the experiment. Note that the corrosion rate decreased after 15 hours because of the change in solution chemistry within the autoclave caused by release of ferrous ion (Fe²⁺) and the formation of protective iron.
carbonate (FeCO₃), which is an experimental artifact and would not happen in the field conditions. With the presence of 100 ppm of H₂S, the initial corrosion rate was much lower than in the pure CO₂ condition, and the corrosion rate and corrosion potential were constant with time. This indicates that addition of small amount of H₂S reduced the corrosion rate almost 10 times under high pressure conditions. With 200 ppm of H₂S, the corrosion rate also starts out initially with similar values as for the case with 100 ppm H₂S, and then decreased to a low value, in the range of 1 ~ 2 mm/y.

![Graph](image1)

**Figure 2:** LPR data of CS in CO₂ saturated brine containing 0, 100 and 200 ppm H₂S at 12 MPa CO₂ and 80°C: (a) Corrosion rate, (b) Corrosion potential.

Figure 3 shows the surface and cross-section SEM images of the corroded samples after 2 days at 12 MPa CO₂ and 80°C with different H₂S concentrations. In the presence of 200 ppm H₂S, the corrosion product layer is more compact and adherent to the metal surface, providing better corrosion protection. Figure 4 shows the XRD pattern of the corrosion product layer formed at 12 MPa and 80°C with 200 ppm H₂S. The layer formed in this condition showed a combination of FeS and FeCO₃. Therefore, the corrosion rate decrease in this case is because of the formation of a protective corrosion product layer on the surface.
Cross-section Figure 3: SEM surface and cross-sectional analyses of CS after corrosion experiment at 12 MPa CO$_2$ and 80°C with different H$_2$S concentrations.

Figure 4: Result of XRD analysis for CS exposed to 12 MPa CO$_2$ and 80°C with 200 ppm H$_2$S.

Although the addition of H$_2$S provided a certain degree of protection to CS in the high pressure CO$_2$ condition, the corrosion rate was still high and it required additional protection in order to achieve the targeted inhibited corrosion rate (< 0.1 mm/y). Figure 5 shows LPR corrosion data of CS, 1Cr and 3Cr steels in the CO$_2$/H$_2$S system. It is interesting to note that CS shows the lowest corrosion rate in comparison with 1Cr and 3Cr steels. The 1Cr steel shows very active behavior in the CO$_2$/H$_2$S system with high corrosion rate and low corrosion potential. The result suggests that no beneficial effect of Cr is observed at these conditions (12 MPa CO$_2$ and 80°C) with 200 ppm H$_2$S, contrary to the case of pure CO$_2$ system.\textsuperscript{16}
Figure 5: LPR data of different materials in CO$_2$ saturated brine containing 200 ppm H$_2$S at 12 MPa CO$_2$ and 80°C: (a) Corrosion rate, (b) Corrosion potential.

SEM and EDS surface analysis of specimens after corrosion experiments was conducted and the results are shown in Figure 6 and Table 3. CS formed a compact corrosion product layer, which is a combination of FeS and FeCO$_3$, and reduces the corrosion rate. However, 1Cr and 3Cr steels formed a Cr-rich layer on the surface (Table 3), which was identified as Cr(OH)$_3$. It can be hypothesized that this layer reduces the adherence of the FeS layer to the metal surface, and, consequently compromises the corrosion resistance. Adherence of corrosion product layer to the metal surface is a key element in corrosion protectiveness of corrosion product layers. Furthermore, severe localized attack was observed on the surface of 1Cr steel.
Figure 6: SEM surface analysis of different materials after corrosion experiments in NaCl electrolyte at 12 MPa CO$_2$ and 80°C with 200 ppm H$_2$S.

Table 3
EDS surface analysis of materials after corrosion experiment in brine system at 12 MPa CO$_2$ pressure containing 200 ppm H$_2$S and temperature of 80°C.

<table>
<thead>
<tr>
<th>Element</th>
<th>CS (at.%)</th>
<th>1Cr (at.%)</th>
<th>3Cr (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>28</td>
<td>37</td>
<td>20</td>
</tr>
<tr>
<td>O</td>
<td>39</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td>S</td>
<td>6</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>22</td>
<td>53</td>
<td>7</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>36</td>
<td>36</td>
</tr>
</tbody>
</table>

Corrosion inhibitor (CI) were added to reduce the corrosion rate of CS in high pressure CO$_2$ with H$_2$S. Corrosion behavior of CS with different CIs in the CO$_2$/H$_2$S environment (12 MPa, 80°C, 200 ppm H$_2$S) is shown in Figure 7. The concentration of the CIs was fixed at 400 ppm based on the result of previous study in the pure CO$_2$ environments. Although both CIs showed similar inhibition performance at the beginning of the test, only CI2 reduced the corrosion rate to lower than 0.1 mm/y at the end of the test.
Figure 7: LPR data of CS in CO$_2$ saturated brine with and without CIs at 12 MPa CO$_2$ and 80°C (200 ppm H$_2$S): (a) Corrosion rate, (b) Corrosion potential.

According to the surface analysis, Figure 8, a significant amount of corrosion products were found on the sample with CI1 whereas no visible corrosion attack was observed on the surface with CI2. In the presence of CI1, the corrosion products contain high amounts of sulfur (S) (Table 4). This can be postulated to be due to formation of elemental S resulting from the reaction between thiosulfate and H$_2$S, as described by Siu and Jia:

$$S_2O_3^{2-} + 2H_2S + 2H^+ \rightarrow 4S + 3H_2O$$ (1)

This formation of elemental S could be a reason for insufficient inhibition with CI1.

Figure 8: SEM images of the sample surface in CO$_2$ saturated 1 wt.% NaCl solution with the presence of 400 ppm of inhibitors at 12 MPa and 80°C (200 ppm H$_2$S): (a) CI1, (b) CI2.

Table 4

<table>
<thead>
<tr>
<th>Element</th>
<th>CI1 (at.%)</th>
<th>CI2 (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>52</td>
<td>18</td>
</tr>
<tr>
<td>O</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>S</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>20</td>
<td>79</td>
</tr>
</tbody>
</table>

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Experiments at the outlet condition (8 MPa, 25°C)

Corrosion rates and corrosion potentials of CS at 8 MPa and 25°C in CO₂ saturated 1 wt.% NaCl electrolyte with the presence of 0, 100, and 200 ppm of H₂S are shown in Figure 9. Without H₂S, the corrosion rate is constant about 10 mm/y from the beginning to the end of the experiment. With the presence of H₂S, again the corrosion rate was lower than the pure CO₂ condition. Although the corrosion rate with 200 ppm H₂S starts at a lower value than the case with 100 ppm H₂S, the corrosion rates for both conditions show similar values of around 0.3 mm/y after 15 h.

![Graphs showing corrosion rate and potential vs. time for different H₂S concentrations.](image)

**Figure 9:** LPR data of CS in CO₂ saturated brine containing 0, 100 and 200 ppm H₂S at 8 MPa CO₂ and 25°C: (a) Corrosion rate, (b) Corrosion potential.

SEM surface and cross-section analysis for the effect of H₂S at 8 MPa and 25°C is shown in Figure 10. CS is unable to form a FeCO₃ corrosion product layer at 25°C. Therefore, the absence of this FeCO₃ at 25°C means there is no as protective ness due to corrosion product layer formation, as occurred at the inlet condition (12 MPa and 80°C). In the system without H₂S, there was only a small amount of iron carbide (Fe₃C) on the surface; this is a residue of cementite in the steel when corrosion dissolved the ferrite phase. With 200 ppm H₂S, the surface was covered by a thin but more adherent S-containing corrosion product, which provides corrosion protection.

<table>
<thead>
<tr>
<th>H₂S Concentration</th>
<th>Surface</th>
<th>Cross-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm H₂S</td>
<td><img src="image" alt="Surface Image" /></td>
<td><img src="image" alt="Cross-section Image" /></td>
</tr>
<tr>
<td>15kV X500 50μm</td>
<td>11 59 SEI</td>
<td>15kV X1,000 10μm 11 59 SEI</td>
</tr>
</tbody>
</table>
Figure 10: SEM and EDS surface analysis of CS after corrosion experiment at 8 MPa CO₂ and 25°C with different H₂S concentrations.

Figure 11 shows LPR corrosion data of CS and 3Cr steel in the 1 wt.% NaCl electrolyte at 8 MPa CO₂ and 25°C with 200 ppm H₂S. CS showed lower corrosion rate from the very beginning of the experiment, which means that a protective FeS layer immediately formed on the surface. However, 3Cr steel showed a drop in corrosion rate after a few hours then reached a stable corrosion rate similar to CS. The LPR results suggest that at the outlet condition, 3Cr steel shows a comparable corrosion performance with CS in a CO₂/H₂S system.

Figure 12 shows SEM surface analysis of CS and 3Cr steel after removing corrosion product using Clarke’s solution (20 g antimony trioxide, 50 g stannous chloride and hydrochloric acid to make 1,000 mL). In the case of CS, SEM surface analysis shows uniform corrosion attack on the surface. However, it shows localized corrosion of 3Cr steel occurs. High resolution optical profilometry was used to study the depth of the surface features associated with the observed localized corrosion attack.

Figure 13 shows the results of high resolution optical profilometry analysis of several pits observed on the cleaned 3Cr steel exposed to 8MPa CO₂ and 25°C with 200 ppm H₂S. According to the depth of the deepest pits, the maximum localized corrosion rate was measured to be 8 mm/y, which is 26 times higher than the general corrosion rate.
Figure 12: SEM images of CS and 3Cr steel after removing corrosion products.

Figure 13: Surface analysis of 3Cr steel after corrosion experiment in brine system at 80 bar CO$_2$ pressure containing 200 ppm H$_2$S and temperature of 25°C.

The corrosion rate and corrosion potential of CS as a function of time with and without H$_2$S and Cl$_2$ in the outlet condition are shown in Figure 14. The addition of 200 ppm of H$_2$S decreased corrosion rate significantly from about 10 mm/y to about 0.3 mm/y, and the addition of Cl$_2$ in the CO$_2$/H$_2$S environment decreased the corrosion rate to much lower values (less than 0.1 mm/y).
Figure 14: LPR data of CS in CO\textsubscript{2} saturated brine with and without H\textsubscript{2}S and Cl\textsubscript{2} at 8 MPa CO\textsubscript{2} and 25°C: (a) Corrosion rate, (b) Corrosion potential.

SEM surface analysis of the sample surface before and after removing corrosion products once again confirms the superior inhibition performance of Cl\textsubscript{2} in the outlet condition (Figure 15).

![Before removing corrosion product](image1)

![After removing corrosion product](image2)

Figure 15: SEM images of the sample surface in CO\textsubscript{2} saturated 1 wt.% NaCl solution with the presence of 400 ppm of Cl\textsubscript{2} at 8 MPa CO\textsubscript{2} and 25°C with 200 ppm H\textsubscript{2}S.

**CONCLUSIONS**

The corrosion mechanisms and corrosion protection of CS in a CO\textsubscript{2}/H\textsubscript{2}S system at different conditions were investigated by conducting electrochemical measurements and using surface analytical techniques. The following conclusions are drawn:

- The presence of small amounts of H\textsubscript{2}S reduces the corrosion rate of CS in high pressure CO\textsubscript{2} conditions.
- The corrosion resistance of low Cr steels was worse than that of CS in high pressure CO\textsubscript{2} condition with some H\textsubscript{2}S, indicating that applications of low Cr steels are limited to pure CO\textsubscript{2} condition.
- Adding 400 ppm of imidazoline-type corrosion inhibitor can be utilized in order to reduce the corrosion rate of CS below 0.1 mm/y in high pressure CO\textsubscript{2} conditions with some H\textsubscript{2}S.
REFERENCES


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