Strategies for Corrosion Inhibition of Carbon Steel Pipelines Under Supercritical CO₂/H₂S Environments

Yoon-Seok Choi, Shokrollah Hassani, Thanh Nam Vu, Srdjan Nešić, Ahmad Zaki B. Abas, Azmi Mohammed Nor, and Muhammad Firdaus Suhoor

The objective of the present study was to identify and quantify the key issues that affect the integrity of carbon steel in high-pressure CO₂ and CO₂/H₂S environments and to establish potential corrosion mitigation strategies using low Cr alloy steels and corrosion inhibitors. The experiments were performed in a 7.5 L autoclave with two combinations of CO₂ partial pressure and temperature (12 MPa/80°C and 8 MPa/25°C) with different H₂S concentrations (0 ppm, 100 ppm, and 200 ppm). The corrosion behavior of specimens was evaluated using electrochemical measurements and surface analytical techniques. Results showed that the addition of corrosion inhibitor decreased corrosion rate significantly from 90 mm/y to below 0.1 mm/y at supercritical CO₂ condition (12 MPa CO₂, 80°C). However, insufficient protection was achieved from low Cr alloy steels. 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: carbon steel, CO₂/H₂S corrosion, corrosion inhibitor, low Cr steel, supercritical CO₂

INTRODUCTION

Numerous studies on corrosion issues in high-pressure CO₂ environments relating to carbon capture and storage, enhanced oil recovery, and deep water oil and gas production applications have recently been published. The published literature primarily addresses topics related to CO₂ sequestration and enhanced oil recovery that usually involve “dry” gases where water is only present at the ppm level. However, due to the direct impact of the presence of formation water and high-pressure CO₂ on the corrosion of pipeline steel, the aqueous corrosion rate of carbon steel at high-CO₂ pressure (liquid and supercritical CO₂) without the formation of protective FeCO₃ corrosion product layers is very high (>20 mm/y). Therefore, sufficient gas "drying" (water removal) upstream of the pipeline is required in order to prevent breakthrough of free water and excessive corrosion rates. However, it can be too costly to dry the gas stream in the field conditions. As the aqueous corrosion mechanisms of carbon steel are similar under both low-CO₂ pressure and high-CO₂ pressure, using corrosion inhibitors (CIs) and/or corrosion resistant alloys (CRAs) could be a promising strategy in order to control corrosion at high-pressure CO₂ conditions.

The performance of various CIs in the CO₂-saturated aqueous solutions has been widely studied. Imidazoline-based inhibitors are the mostly used formulations in the oil and gas field to control CO₂ corrosion. However, the studies were usually conducted under low-CO₂ pressure related to typical conditions seen in oil and gas pipelines. For high-CO₂ pressure conditions, publications that report on efficiencies of corrosion inhibitors in supercritical CO₂ systems are sparse. Classic corrosion inhibitor formulations based on imidazoline, piperazine, alkenylsuccinic acids, and quaternary ammonium compounds were evaluated in supercritical CO₂ systems. Although these chemicals did reduce the corrosion rate, none of them were fully effective. In previous research, an attempt was made to control the corrosion of carbon steel in high-pressure CO₂ conditions (8 MPa CO₂ and 70°C) using imidazoline-based CIs. The study showed that adequate protection was achieved by applying "imidazoline + thiosulfate" CI blend to carbon steel in the high-pressure CO₂ environments. As the use of CRAs remains very expensive, there has been an attempt to use low-Cr alloy steel (0.5% to 3% Cr) in high-pressure and high-temperature CO₂ environments without inhibitor injection. This has the potential to significantly reduce costs associated with the use of CRAs for infrastructure construction.

It has recently been reported that small amounts of H₂S can be present in high-pressure CO₂ streams related to gas field development. Even though the effect of H₂S on the aqueous corrosion of carbon steel at low CO₂ partial pressures is widely investigated, limited work has been done in high-pressure CO₂ environments. In addition, there is no systematic study on corrosion inhibition strategy in high-pressure CO₂ environments with H₂S.

Thus, the objective of the present study was to identify and quantify the key issues that affect the integrity of carbon steel in high-pressure CO₂ and CO₂/H₂S environments and to establish potential corrosion mitigation strategies using low-Cr...
alloy steels and CIs for achieving targeted corrosion rate (<0.1 mm/y).

**EXPERIMENTAL PROCEDURES**

The materials used in this work are as follows:
- UNS K03014\(^{(1)}\) carbon steel, named CS
- UNS G41300-1Cr steel, named 1Cr
- UNS G41300-3Cr steel, named 3Cr

The chemical compositions of the studied alloys analyzed using atomic emission spectroscopy are shown in Table 1. The test specimens were machined with two different geometries: cylindrical type with 5 cm\(^2\) exposed area for electrochemical measurements, and rectangular type with a size of 1.27 cm \(\times\) 1.27 cm \(\times\) 0.254 cm for surface analysis. The specimens were ground sequentially with 250, 400, then 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol in an ultrasonic bath, and dried.

In the present study, “imidazoline + thiosulfate” corrosion inhibitor blend (CI1) and “imidazoline” generic corrosion inhibitor (CI2) were selected for evaluation under high-pressure CO\(_2\) environments with and without H\(_2\)S based on the results of preliminary tests.\(^{(2)}\) In this instance, “imidazoline” is shorthand for tall oil fatty acid (TOFA) imidazoline-type inhibitor. The formulation of the corrosion inhibitor packages is shown in Table 2.\(^{(3)}\)

The experimental procedure is outlined in Figure 2. Initially, 1 wt% of NaCl solution was placed in an autoclave and the electrolyte purged with a high flow rate of CO\(_2\) for 1 h to 3 h in order to remove dissolved O\(_2\). 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, additional purging with CO\(_2\) or a mixture of CO\(_2\)/10% H\(_2\)S was performed for 1 h to 2 h to ensure the removal of O\(_2\) and the saturation of CO\(_2\) or CO\(_2\)/H\(_2\)S, and then the working H\(_2\)S partial pressure was achieved by pressurizing with the mixture of CO\(_2\)/10% H\(_2\)S for the CO\(_2\)/H\(_2\)S conditions. High-pressure CO\(_2\) was then injected with a booster pump.

![FIGURE 1. Schematic of autoclave system equipped for electrochemical measurements.](image)

### Table 1. Chemical Compositions of Materials Used in the Present Study (wt%, balance Fe)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>0.065</td>
<td>0.05</td>
<td>1.54</td>
<td>0.013</td>
<td>0.001</td>
<td>0.25</td>
<td>0.04</td>
<td>0.04</td>
<td>0.007</td>
<td>0.041</td>
</tr>
<tr>
<td>1Cr</td>
<td>0.3</td>
<td>0.85</td>
<td>0.91</td>
<td>0.015</td>
<td>0.008</td>
<td>0.29</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3Cr</td>
<td>0.08</td>
<td>3.43</td>
<td>0.54</td>
<td>0.006</td>
<td>0.003</td>
<td>0.30</td>
<td>0.16</td>
<td>0.06</td>
<td>0.32</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 2. Chemical Composition of the Corrosion Inhibitor Packages

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>Active ingredient</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI1</td>
<td>Inhibitor blend</td>
<td>tail oil fatty acid/diethylenetriamine (TOFA/DETA) imidazoline + Sodium thiosulfate</td>
<td>10% CH(_3)COOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13% C(_4)H(_9)OCH(_2)CH(_2)OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20% TOFA/DETA imidazoline</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.28% Na(_2)S(_2)O(_3)5H(_2)O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Balance water</td>
</tr>
<tr>
<td>CI2</td>
<td>Generic inhibitor</td>
<td>tail oil fatty acid/diethylenetriamine (TOFA/DETA) imidazoline</td>
<td>10% CH(_3)COOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13% C(_4)H(_9)OCH(_2)CH(_2)OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24% TOFA/DETA imidazoline</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Balance water</td>
</tr>
</tbody>
</table>

\(^{(1)}\) 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.
In order to ensure that no oxygen contamination occurred during the test, indirect evidences were checked at the end of each test:

- No change of color for the solution was observed. If the system was contaminated with oxygen, the solution color should change to orange due to the formation of iron oxide.
- Elemental sulfur could form when the system has both H₂S and O₂. In the present tests, elemental sulfur was not observed in the autoclave.
- Iron oxide was not detected in the corrosion product.

During the experiment, corrosion rates and corrosion potentials were monitored with linear polarization resistance (LPR) measurement made at regular time intervals using the range of ±5 mV with respect to the open circuit potential, and a scan rate of 0.125 mV/s. The polarization resistance (R_p) obtained from LPR measurement was used to calculate the corrosion current density (i_corr) by using Equation (1):

$$i_{\text{corr}} = \frac{B}{R_p} = \frac{\beta_a \times \beta_c}{2.3 \times R_p \times (\beta_a + \beta_c)}$$  \hspace{1cm} (1)

where $\beta_a$ is the anodic Tafel constant and $\beta_c$ is the cathodic Tafel constant. In the present study, empirical B value of 23 mV for the CO₂-H₂S corrosion was used for all conditions.\(^{39}\) Then, the $i_{\text{corr}}$ was converted into corrosion rate using Equation (2):

$$\text{Corrosion rate}(\text{mm/year}) = \frac{0.00327 \times i_{\text{corr}}(\mu\text{A/cm}^2) \times \text{EW}}{\text{density}(\text{g/cm}^3)}$$  \hspace{1cm} (2)

where EW is the equivalent weight in grams and 0.00327 is a constant factor used for dimension and time conversion.

During the experiment, the solution pH was measured periodically by using commercial high-pressure glass pH electrodes.

**Table 3. Test Conditions for Corrosion Testing**

<table>
<thead>
<tr>
<th>Condition</th>
<th>CO₂ Pressure (MPa)</th>
<th>H₂S (ppm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</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>CO₂/H₂S</td>
<td>8</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>200</td>
<td>80</td>
</tr>
</tbody>
</table>

**FIGURE 2.** Experimental procedures for evaluating the corrosion behavior of materials in high-pressure CO₂ environments with H₂S.

**FIGURE 3.** Corrosion rate and corrosion potential of CS in CO₂ saturated 1 wt% NaCl solution at 12 MPa CO₂ and 80°C.
FIGURE 4. pH measurement data during corrosion experiment of CS in CO2 saturated 1 wt% NaCl solution at 12 MPa and 80°C.

FIGURE 5. SEM and EDS cross-sectional analysis of CS in CO2 saturated 1 wt% NaCl solution at 12 MPa and 80°C.

FIGURE 6. LPR data of CS, 1Cr, and 3Cr steels in CO2 saturated 1 wt% NaCl solution at 120 bar and 80°C: (a) corrosion rate and (b) corrosion potential.
The electrodes and Ag/AgCl reference electrode. The electrodes were calibrated prior to each test by the procedure supplied by the manufacturer.\textsuperscript{40}

After each test, the specimens were removed from the autoclave, rinsed with DI water and isopropyl alcohol, dried with N\textsubscript{2} and stored in a desiccator cabinet in an inert atmosphere until surface analyses could be conducted. The surface morphology and compositions of corrosion products were analyzed with scanning electron microscopy (SEM), energy

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Element & CS (at\%) & 1Cr (at\%) & 3Cr (at\%) \\
\hline
C & 31 & 42 & 66  \\
O & 35 & 28 & 17  \\
Cr & 0 & 1.3 & 17  \\
Fe & 25 & 29 & 2  \\
\hline
\end{tabular}
\caption{EDS Surface Analysis of CS, 1Cr, and 3Cr steels after Corrosion Experiment in CO\textsubscript{2} Saturated 1 wt\% NaCl Solution at 12 MPa and 80°C.}
\end{table}

\textbf{FIGURE 7.} SEM surface and cross-section analysis of CS, 1Cr, and 3Cr steels after corrosion experiment at 12 MPa and 80°C in CO\textsubscript{2} saturated 1 wt\% NaCl solution.

\textbf{FIGURE 8.} Result of XRD analysis for CS, 1Cr, and 3Cr steels exposed to 12 MPa CO\textsubscript{2} and 80°C.
dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and Raman spectroscopy. In addition, the cross-sectional SEM and EDS analysis were performed by using the samples cold-mounted in the epoxy. For testing with inhibitors, the procedure was the same as shown in Figure 2, except the inhibitor was added to the solution before inserting the specimens.

Table 3 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. For CO2 environments, the corrosion behavior and inhibition strategy were evaluated at the inlet condition, whereas it was investigated at both inlet and outlet conditions for the CO2/H2S environments.

RESULTS AND DISCUSSION

3.1 | Corrosion Inhibition Strategies Under High-Pressure CO2 Environments

Figure 3 shows the variations of corrosion rate and corrosion potential for CS with time under 12 MPa CO2 and 80°C. The corrosion rate of CS is about 90 mm/y at the beginning of the experiment and then sharply decreases after 20 h. In addition, the corrosion potential increased when the corrosion rate started to decrease. This indicates that protective iron carbonate (FeCO3) layers formed on the steel surface. pH values were also monitored during the experiment, as shown in Figure 4. pH data represent the bulk pH of the solution, which suggests a considerable change in bulk water chemistry because of initial high corrosion rate and the small volume of solution in the autoclave. This considerable change in water chemistry is
responsible for the drop in corrosion rate after 20 h of experimentation. Cross-sectional analysis using SEM and EDS (Figure 5) shows the formation of FeCO$_3$ layer on the steel surface, which caused the drop in corrosion rate. However, in actual field conditions, this considerable change in water chemistry would not be happening because at any given location in the line the water is being continuously replenished. Therefore, it must be stated that in this case, the decrease in corrosion rate because of changes in water chemistry and formation of FeCO$_3$ is an artifact of experimental design.\textsuperscript{22,41-42} Therefore, the initial measured corrosion rate of 90 mm/y is the best representative of the corrosion rate of CS at 12 MPa and 80°C expected in the field conditions.

Figure 6 shows the corrosion behavior of different materials (CS, 1Cr, and 3Cr) at 12 MPa and 80°C. 3Cr steel shows a lower corrosion rate compared with CS and 1Cr steel at the
end of the experiment. This layer is Cr-rich, based on the EDS analysis shown in Table 4 but XRD only shows a weak peak of Fe. Therefore, this layer is amorphous as well as being chromium-rich. Raman spectroscopy analysis (Figure 9) detected a strong peak at around 1,000 cm⁻¹ originates from the O-H deformation and, thus, can be used as a fingerprint for identifying corrosion products of 3Cr steel as chromium hydroxide, Cr(OH)₃. Formation of Cr(OH)₃ is very fast and can reduce the corrosion rate, but is insufficiently protective to reduce the corrosion rate significantly under this condition.

Corrosion rates and corrosion potentials of CS at 12 MPa and 80°C in CO₂ saturated 1 wt% NaCl solution with the presence of 0 ppm, 200 ppm, and 400 ppm of Cl₁ are shown in Figure 10. With the presence of 200 ppm of Cl₁, the initial corrosion rate was much lower than the uninhibited condition, however, the corrosion rate increased with time, indicating insufficient inhibition for the Cl₁ concentration of 200 ppm. With 400 ppm of Cl₁, the corrosion rate decreased with time to below 0.1 mm/y with more noble corrosion potential, which is the targeted inhibited corrosion rate.

The results of the surface analysis for samples after corrosion experiments with different concentrations of Cl₁ are shown in Figure 11. On the sample surfaces with 200 ppm and 400 ppm of Cl₁ there was a very thin layer of corrosion products containing sulfur, possibly FeS formed indirectly via disproportionation of the thiosulfate component in the inhibitor. There is a stronger peak of S with 400 ppm of Cl₁ because of the doubled thiosulfate concentration for the 400 ppm experiment compared to that conducted for 200 ppm of Cl₁.

Based on the current understanding and the experimental results above, we propose an inhibition mechanism for high-CO₂ aqueous environment, having two main steps:

- Step 1 (Figure 12[a]): As CO₂ saturated aqueous solution is acidic, thiosulfate (one of the main component of inhibitor) disproportionates to form sulfide which rapidly reacts with Fe to form FeS on the steel surface, as summarized by the following reaction:⁴³
  \[
  \text{Fe} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{FeS} + \text{SO}_4^{2-} + \text{H}_2 \quad (3)
  \]
It is assumed that this process is very fast based on the kinetics of the FeS formation reaction (order of seconds and minutes).

- Step 2 (Figure 12[b]): Following the formation of a thin layer of FeS on the steel surface, adsorption of the imidazoline (the main component of the inhibitor) would happen. The adsorption kinetics is much slower (order of hours). Moreover, the adsorption of the organic inhibitors on the steel surface covered by a thin FeS layer has been hypothesized to be stronger than on the bare steel surface.
80°C with different H2S concentrations. In the presence of 100 ppm 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 the addition of a small amount of H2S reduced the corrosion rate almost 10 times under high-pressure CO2 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 decreases to a low value, in the range of 1 mm/y to 2 mm/y. Figure 14 shows the change of pH during the experiments in the presence of H2S. Unlike the pure CO2 condition (Figure 4), the solution pH was constant for the condition with 200 ppm H2S indicating that bulk water chemistry has not appreciably changed. Therefore, the corrosion rate decrease, in this case, is not an artifact of the experimentation and the same result would have obtained in a field condition.

Figure 15 shows the surface and cross-section SEM images of the corroded samples after 2 d 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 16 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.

Although the addition of H2S provided a certain degree of protection to CS in the high-pressure CO2 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 17 shows LPR corrosion data of CS, 1Cr, and 3Cr steels in the CO2/H2S 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 CO2/H2S 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 CO2 and 80°C) with 200 ppm H2S, contrary to the case of the pure CO2 system. SEM and EDS surface analysis of specimens after corrosion experiments was conducted and the results are shown in Figure 18 and Table 5. CS formed a compact corrosion product layer, which is a combination of FeS and FeCO3 and reduces the corrosion rate. However, 1Cr and 3Cr steels formed a Cr-rich layer on the surface (Table 5), which could be identified as Cr(OH)3.44 It can be hypothesized that this layer reduces the adherence of the FeS layer to the metal surface, and, consequently compromises the corrosion resistance.45 Adherence of corrosion product layer to the metal surface is a key element in corrosion protectiveness of corrosion product layers. Furthermore, the severe localized attack was observed on the surface of 1Cr steel.

CIs were added to reduce the corrosion rate of CS in high-pressure CO2 with H2S. Corrosion behavior of CS with different CIs in the CO2/H2S environment (12 MPa, 80°C, 200 ppm H2S) is shown in Figure 19. The concentration of the CIs was fixed at 400 ppm based on the above result in the pure CO2 environments. Although both CIs showed similar inhibition performance at the beginning of the test, only CI2 (“imidazoline” generic) reduced the corrosion rate to lower than 0.1 mm/y at the end of the test.

According to the surface analysis, Figure 20, 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 6). This can be postulated to be due to the formation of elemental S resulting from the reaction between thiosulfate and H2S, as described by Siu and Jia:46

\[ S_2O_3^{2-} + 2H_2S + 2H^+ \rightarrow 4S + 3H_2O \]  

(4)

This formation of elemental S could be a reason for insufficient inhibition with CI1. Furthermore, localized corrosion with a maximum depth of around 150 μm was observed after removing corrosion product using Clarke’s solution (20 g antimonyp oxide, 50 g stannous chloride, and hydrochloric acid to make 1,000 mL) on the sample with CI1 (Figure 21).
FIGURE 18. SEM surface analysis of different materials after corrosion experiments in NaCl electrolyte at 12 MPa CO₂ and 80°C with 200 ppm H₂S.

Table 5. EDS Surface Analysis of Materials After Corrosion Experiment in CO₂ Saturated 1 wt% NaCl Solution at 12 MPa CO₂ Containing 200 ppm H₂S 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>Cr</td>
<td>0</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>Fe</td>
<td>22</td>
<td>53</td>
<td>7</td>
</tr>
</tbody>
</table>
FIGURE 19. LPR data of CS in CO₂ saturated brine with and without Cls at 12 MPa CO₂ and 80°C (200 ppm H₂S): (a) corrosion rate and (b) corrosion potential.

FIGURE 20. SEM images of the sample surface in CO₂ saturated 1 wt% NaCl solution with the presence of 400 ppm of inhibitors at 12 MPa and 80°C (200 ppm H₂S): (a) Cl1 and (b) Cl2.

| Table 6. EDS Surface Analysis of the Sample After Corrosion Experiments with Cl1 and Cl2 at 12 MPa CO₂ and 80°C (200 ppm H₂S) |
|-----------------|-----------------|-----------------|
| Element        | Cl1 (at%)       | Cl2 (at%)       |
| C              | 52              | 18              |
| O              | 11              | 2               |
| S              | 11              | 1               |
| Fe             | 20              | 79              |
FIGURE 21. SEM and optical profilometry analysis of the CS sample surface in CO₂ saturated 1 wt% NaCl solution with the presence of 400 ppm of Cl⁻ at 12 MPa and 80°C (200 ppm H₂S).

FIGURE 22. LPR data of CS in CO₂ saturated brine containing 0 ppm, 100 ppm, and 200 ppm H₂S at 8 MPa CO₂ and 25°C: (a) corrosion rate and (b) corrosion potential.
FIGURE 23. SEM and EDS surface analysis of CS after corrosion experiment at 8 MPa CO₂ and 25°C with different H₂S concentrations.

FIGURE 24. LPR data of different materials in CO₂ saturated brine containing 200 ppm H₂S at 8 MPa CO₂ and 25°C: (a) corrosion rate and (b) corrosion potential.
3.3 | Corrosion Inhibition Strategies Under High-Pressure CO2 Environments with H2S: 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 ppm, 100 ppm, and 200 ppm of H2S are shown in Figure 22. Without H2S, the corrosion rate is constant at 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.

SEM surface and cross-section analysis for the effect of H2S at 8 MPa and 25°C is shown in Figure 23. 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 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 (Fe2C) 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.

Figure 24 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 25 shows the SEM surface analysis of CS and 3Cr steel after removing corrosion product using Clarke's solution. In the case of CS, SEM surface analysis shows uniform corrosion attack on the surface. However, it shows that localized corrosion occurs for 3Cr steel. High-resolution optical profilometry was used to study the depth of the surface features associated with the observed localized corrosion attack. Figure 26 shows the results of high-resolution optical profilometry analysis of several pits observed on the cleaned 3Cr steel exposed to 8 MPa 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/yr, which is 26 times higher than the general corrosion rate.

The corrosion rate and corrosion potential of CS as a function of time with and without H2S and CI2 in the outlet condition are shown in Figure 27. The addition of 200 ppm of H2S decreased corrosion rate significantly from about 10 mm/yr to about 0.3 mm/yr, and the addition of CI2 in the CO2/H2S environment decreased the corrosion rate to much lower values (less than 0.1 mm/yr).

SEM surface analysis of the sample surface before and after removing corrosion products once again confirms the superior inhibition performance of CI2 in the outlet condition (Figure 28).
CONCLUSIONS

The corrosion mechanisms and corrosion protection of CS in a high-pressure 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:

➣ At least 400 ppm of corrosion inhibitor was needed in order to control the aqueous corrosion rate below 0.1 mm/y at 12 MPa CO\textsubscript{2} and 80°C condition.

➣ Insufficient protection was achieved from low-Cr alloy steels at 12 MPa CO\textsubscript{2} and 80°C condition.

➣ 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 low-pressure 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


FIGURE 27. LPR data of CS in CO\textsubscript{2} saturated brine with and without H\textsubscript{2}S and CI\textsubscript{2} at 8 MPa CO\textsubscript{2} and 25°C: (a) corrosion rate and (b) corrosion potential.

FIGURE 28. SEM images of the sample surface in CO\textsubscript{2} saturated 1 wt% NaCl solution with the presence of 400 ppm of CI\textsubscript{2} at 8 MPa CO\textsubscript{2} and 25°C with 200 ppm H\textsubscript{2}S.