Investigation of the cathodic mechanism for 316L stainless steel corrosion in a mixed SO\textsubscript{2}/CO\textsubscript{2} aqueous environment

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Abstract

Carbon capture and storage is regarded as one of the most promising ways to address the global climate change problems. Sulfur dioxide (SO\textsubscript{2}) is one of the main impurities in the captured carbon dioxide (CO\textsubscript{2}) from the coal-fired power plants. Although SO\textsubscript{2} corrosion has been extensively investigated in atmospheric environment, its electrochemical mechanism still needs to be figured out, especially when it is coexisting with CO\textsubscript{2} in the carbon capture and storage system. In this work, experiments were conducted by adding a certain amount of sulfurous acid to the CO\textsubscript{2}-saturated solution at 25 °C under different pH value conditions. The effect of sulfurous acid on the cathodic reactions of 316L stainless steel in CO\textsubscript{2}-saturated solution was investigated by electrochemical method. It was found that there was a significant difference in the cathodic polarization curves between the case with 100 ppmw sulfurous acid in CO\textsubscript{2}-saturated solution at pH 3.0 and the corresponding case without sulfurous acid. The charge-transfer current of the cases containing 100 ppmw sulfurous acid was higher than these without sulfurous acid at the same pH, and the cathodic limiting currents increased. It was found that a second "wave" appeared before the cathodic limiting current. This new "wave" was most likely caused by the direct reduction of sulfurous acid or bisulfite on the steel surface. Under the pH 2.0 condition, the hydrogen ion concentration was high, and the direct reduction of hydrogen ions was the dominate cathodic reaction, thus there was no significant change in cathodic polarization curve between the cases with and without 100 ppmw sulfurous acid.

Keywords: CCS CO\textsubscript{2}; Sulfurous acid; Cathodic mechanisms; 316L stainless steel

Introduction

The greenhouse effect has been paid more and more attentions due to the increase of carbon dioxide (CO\textsubscript{2}) emission [1]. Carbon dioxide capture and storage (CCS) is regarded as an effective way to reduce CO\textsubscript{2} content in the atmosphere. Coal-fired power plant is one of the main sources of CO\textsubscript{2} emissions. When CO\textsubscript{2} is collected from the flue gas from coal-fired power plants, kinds of impurities (such as NO\textsubscript{x}, SO\textsubscript{2}, H\textsubscript{2}S and O\textsubscript{2}) are inevitably contained in the CO\textsubscript{2} stream [2]. The presence of gas impurities causes great harm to the integrity of the pipeline during the transportation of supercritical or liquid CO\textsubscript{2}.

SO\textsubscript{2} is one of the main products of coal and oil combustion, so it is also one of the main impurity gases in the CO\textsubscript{2} stream captured from the coal-fired power plants. At the same time, SO\textsubscript{2} is also the main air pollutant, which is the main cause of acid rain [3]. Therefore, SO\textsubscript{2} is harmful to the environment. Dry SO\textsubscript{2} has no obvious corrosion effect to the metal, and the corrosion rate of steel is less than 0.1 mil/y [4]. When SO\textsubscript{2} is dissolved in water to produce

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sulfurous acid, it has a significant effect on the metal integrity. Sulfurous acid is a medium strong acid, which is stronger than H₂S, carbonic acid and acetic acid. At the same pH, the corrosion rate of steel in weak acid is higher than that in HCl acid [5]. Vernon [6] found that sulfurous acid can further increase the corrosion rate of steel in atmospheric environment.

It is crucial to study the mechanism of SO₂ corrosion because it is important for establishing the corrosion prediction model in order to better predict and prevent SO₂ corrosion. Although steel corrosion in atmospheric environment with SO₂ and the synergistic corrosion effect of SO₂ and CO₂ in CCS system have been widely studied [7-17], the study on the electrochemical mechanism of steel in SO₂-containing environment is rare. In particular, the role of SO₂ on the corrosion of steel when CO₂ is present need to be further investigated. At present, there are many reports on the electrochemical mechanism of metals in H₂S, carbonic acid or acetic acid solutions [18-23]. Many explanations have been put forward about how the weak acids accelerate the corrosion rate of metals [22, 23]. There are two mechanisms existing for the weak acid corrosion: the "buffering effect" and "direct reduction". The "buffering effect" mechanism means when hydrogen ions are consumed in the solution, the undissolved weak acid molecules provide hydrogen ions by ionization to supplement the consumption of hydrogen ions in the solution, creating a buffering effect to accelerate corrosion of the steel; the "direct reduction" mechanism means the buffering effect mechanism still exists, and at the same time, the undissolved weak acid molecules are directly adsorbed on the steel surface and reduce directly to accelerate the steel corrosion.

In this paper, the mechanism of cathodic reaction of 316L austenitic stainless steel in CO₂/sulfurous acid solution under ambient pressure was studied. Electrochemical method was applied to investigate whether undissolved sulfurous acid molecules are directly reduced in the cathodic reaction or only provided hydrogen ions as the buffering acid.

Materials and Methods

Materials and pretreatment

The working electrodes were machined from the 316L austenitic stainless steel. The chemical composition of the 316L austenitic stainless steel was as follows (by wt.%): C, 0.013; Si, 0.07; Mn, 0.06; P, 0.023; Mo, 2.30; Cr, 17.14; Ni, 12.65; S, 0.075; Fe in balance. In the experiment, the work electrode (WE) was machined from the parent steel material and mounted in epoxy resin, with a working surface area of 0.78 cm². The working surface was polished with a series of silicon carbide papers progressively reaching 600 grit, washed with acetone and then dehydrated by ethanol. All work electrodes were dried in a vacuum oven for 24 h.

Experimental setup and Methods

The experimental setup is illustrated in Figure 1. The experiment was carried out under atmospheric pressure at 25 °C using a 3 L glass cell. The test solution was a 1 wt.% sodium sulfate (Na₂SO₄) deionized solution. The electrochemical experiment used a standard three-electrode setup. Saturated calomel (Hg/Hg₂Cl₂) reference electrode (RE) was used which was connected by a Luggin capillary. A platinum plate was employed as the counter electrode (CE). The pH was measured by using a pH meter (METTLER TOLEDO, FE20). A potentiostat (Gamry, Reference 3000) was used for electrochemical testing. Before the experiment, high-purity (99.999 vol.%) N₂ was purged into the solution for at least 2 h to deoxygenate. High-purity CO₂ (99.999 vol.%) was purged into the solution for at least 1 h to reach saturation conditions, and then 100 ppmw sulfurous acid was added to the solution on the basis of the test conditions. CO₂ was continuously purged into the glass cell with a relatively low flow rate during the test. The initial pH of the solution was adjusted by sulfuric acid (H₂SO₄) or sodium hydroxide (NaOH). Potentiodynamic scanning was carried out to
study the mechanism of the cathodic reaction with a scanning rate of 0.2 mV/s. An exhaust gas treatment tower was used for SO₂ exhaust gas treatment. The tests were carried out under static conditions. The experimental conditions are given in Table 1.

![Schematic diagram of the setup for electrochemical measurements.](image)

Table 1. Test conditions

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>CO₂ (bar)</th>
<th>Sulfurous acid (ppmw)</th>
<th>NaHSO₃ (ppmw)</th>
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<td>2</td>
<td>0.97</td>
<td>0</td>
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<tr>
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<tr>
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<td>4</td>
<td>4</td>
<td>0.97</td>
<td>100</td>
<td>26,000</td>
</tr>
</tbody>
</table>

Results and discussion

The cathodic polarization curves of 316L austenitic stainless steel in a CO₂-saturated solution with and without sulfurous acid at pH 4.0 were shown Figure 2. When 100 ppmw sulfurous acid appeared in CO₂-saturated solution, the cathodic polarization curve shifted to the right, indicating that the addition of sulfurous acid promoted the cathodic reaction. The addition of sulfurous acid increased the charge transfer current, and a new "wave" appeared before the limiting current. The charge transfer current increased and the new "wave" may be related to the direct reduction of sulfurous acid or bisulfite ions in the cathodic reaction. The possible reactions are:

\[
2\text{SO}_2 \cdot \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{HSO}_3^- \quad (1)
\]

\[
2\text{HSO}_3^- + 2e^- \rightarrow \text{H}_2 + 2\text{SO}_4^{2-} \quad (2)
\]
When sulfurous acid was added to the CO₂-saturated solution, the limiting current increased and the corresponding potential range also increased. The change of the limiting current may be affected by the diffusion of sulfurous acid or bisulfite ions to the metal surface. The final stage of the cathodic polarization curve was mainly controlled by the reduction of water. When sulfurous acid was added into the CO₂-saturated solution, the cathodic reaction includes: reduction of hydrogen ions (H⁺), direct reduction of sulfurous acid or bisulfite ions and reduction of H₂O. When only 100 ppmw sulfurous acid was added to the solution, The cathodic polarization curve with only 100 ppmw sulfurous acid was significantly different from the polarization curve of the CO₂-saturated solution. It can be concluded that the cathodic reaction mechanism of 316L in CO₂-saturated solutions is different from that with only sulfurous acid.

A new case, NaHSO₃ was used to adjust the solution to pH 4.0 rather than NaOH after adding sulfurous acid to the CO₂-saturated solution, and the amount of NaHSO₃ was 26,000 ppmw. The comparison of results between this new case and the case that used NaOH to adjust the CO₂-saturated solution with 100 ppmw sulfurous acid indicates that when a large amount of NaHSO₃ was present, the charge transfer current was further increased and no limiting current was observed in the test potential range. The cathodic polarization curve was mainly controlled by activation process, further proving that a new cathodic reaction occurs. The formation of sulfurous acid was promoted simultaneously in solution owing to the addition of large amount of NaHSO₃:

$$\text{HSO}_3^- + \text{H}^+ \Leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O} \quad (3)$$

Whether the direct reduction of sulfurous acid, bisulfite ions, or both of them existing in cathodic reaction needs further verification.

The cathodic polarization curves of 316L austenitic stainless steel in a CO₂-saturated solution with and without 100 ppmw sulfurous acid at pH 3.0 are illustrated in Figure 3. The cathodic polarization curve of CO₂-saturated solution with sulfurous acid at pH 3.0 is similar to the cathodic polarization curve of steel in CO₂-saturated solution with sulfurous acid at pH 4.0.
condition, presenting as shifting of cathodic polarization curve to the right and the increase of the charge transfer current, compared to the case without sulfurous acid under the same pH value condition. Under the pH 3.0 conditions, the cathodic polarization curves of CO$_2$-saturated solution with sulfurous acid can better distinguish between the direct reduction of sulfurous acid or bisulfite ions and reduction of hydrogen ions. There are two stages of limiting current and a new "wave" in the CO$_2$-saturated solution with sulfurous acid under the pH 3.0 conditions. The first limiting current of CO$_2$-saturated solution with sulfurous acid is close to the limiting current of CO$_2$-saturated solution, and it can be deduced that this diffusion current mainly reflects the diffusion of H$^+$. The new wave reflects the direct reduction of sulfurous acid or bisulfite ions, which is similar with the results by Zheng et al. [18], who investigated the H$_2$S corrosion mechanism. The second stage of the limiting current is dominated by the diffusion of sulfurous acid or bisulfite ions, and the final stage of the cathodic reaction is the reduction of H$_2$O.

\[ E'(V) \text{ vs. saturated Hg/Hg}_2\text{Cl}_2 \]

\[ i(A/m^2) \]

**Figure 3.** Comparison of potentiodynamic curves with and without 100 ppmw sulfurous acid at 25 °C, pH 3.0, aqueous solution saturated with CO$_2$, 1 wt% Na$_2$SO$_4$.

Figure 4 shows the cathodic polarization curve of 316L austenitic stainless steel in a CO$_2$-saturated solution with and without sulfurous acid at pH 2.0. Under the condition of pH 2.0, the cathodic polarization curve had no obvious change when sulfurous acid appeared. For the pH 4.0 conditions, the H$^+$ content is limited in the solution, and H$^+$ is mainly supplied by H$_2$CO$_3$ and sulfurous acid. Therefore, the direct reduction of sulfurous acid or bisulfite ions directly affects both the charge transfer current and the limiting current. At pH 3.0, the content of hydrogen ion in the solution was increased and additional H$_2$SO$_4$ was required to adjust the pH to the desired value. The diffusion of H$^+$ was reflected in the first stage of the limiting current platform. In the pH 2.0 conditions, the H$^+$ concentration in the solution was high, 100 ppmw sulfurous acid played a negligible role in the cathodic process, and H$^+$ reduction dominated during the whole cathodic process. The limiting current of sulfurous acid or bisulfite ions is obscured by the limiting current of hydrogen ions, which can also be similarly explained by the illustration of Kahyarian et al. [23]. This phenomenon is also similar to the results by Morris et al. [24]. They found that a limit current gradually disappeared with the addition of H$_2$S.
Figure 4. Comparison of potentiodynamic curves with and without 100 ppmw sulfurous acid at 25 °C, pH 2.0, aqueous solution saturated with CO₂, 1 wt% Na₂SO₄.

Figure 5 shows the cathodic polarization curves of 316L austenitic stainless steel in CO₂-saturated solution without sulfurous acid under the different pH conditions. The cathodic polarization curve of Figure 5 is the same as that in Tran et al.'s work [25]. With the decrease of pH, both the charge transfer current and limiting current increased.

Figure 5. Comparison of potentiodynamic curves for different pH at 25 °C, aqueous solution saturated with CO₂, 1 wt% Na₂SO₄.
The cathodic polarization curves of 316L austenitic stainless steel in CO₂-saturated solution containing sulfurous acid under the different pH conditions are depicted in Figure 6. The second stage of the limiting current at pH 3.0 is substantially the same as the limiting current at pH 4.0. It is further proved that sulfurous acid or bisulfite ions are directly involved in the cathodic reaction, and the limiting current platform is mainly affected by the diffusion of sulfurous acid or bisulfite ions.

![Graph showing cathodic polarization curves](image)

*Figure 6. Comparison of potentiodynamic curves with 100 ppmw sulfurous acid for different pH at 25 °C, aqueous solution saturated with CO₂, 1 wt% Na₂SO₄.*

**Conclusions**

In this paper, the cathodic corrosion mechanism of 316L austenitic stainless steel in CO₂/sulfurous environment was studied, and the following conclusions are obtained:

1. When sulfurous acid appeared in CO₂-saturated solution, the cathodic reaction was promoted. A large amount of NaHSO₃ can further promote the cathodic process.
2. When sulfurous acid presented, a new cathodic reaction was present, presenting as a second wave on the cathodic polarization curve. Further verification is required to determine which is the new cathodic reaction, the direct reduction of sulfurous acid or bisulfite ions.

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