Effect of Oxygen and Heat Stable Salts on the Corrosion of Carbon Steel in MDEA-Based CO₂ Capture Process

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ABSTRACT

The objective of the present study was to evaluate the corrosion properties of carbon steel in MDEA/H₂O/CO₂/O₂/HSS (methyldiethanolamine/water/carbon dioxide/oxygen/heat stable salts) mixtures related to the CO₂ capture process in fossil fuel-fired power plants. Short-term and long-term corrosion tests were performed in 50 wt% MDEA solutions at 50°C under atmospheric pressure with different combinations of CO₂, O₂, and HSS (bicine [C₆H₁₃NO₄], formate [HCOO⁻], sulfate [SO₄²⁻]). Corrosion behavior of carbon steel was evaluated using electrochemical methods (linear polarization resistance [LPR], electrochemical impedance spectroscopy [EIS], and cyclic polarization), weight-loss measurements, and surface analytical techniques (scanning electron microscopy [SEM] and energy-dispersive spectroscopy [EDS]). The results of short-term corrosion tests indicated that the addition of CO₂ in the MDEA systems significantly increased the corrosion rate and changed the corrosion behavior from a passive to an active state. However, the corrosion rates of carbon steel did not change significantly with the addition of O₂ and HSS. The corrosion rates of carbon steel decreased with time under MDEA/CO₂ systems, whereas it maintained the initial values throughout the tests in MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSS environments. The order of the corrosiveness was MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂. The corrosion morphology of carbon steel in MDEA/CO₂ systems with O₂ and HSS showed uniform attack with preferential dissolution of ferrite.

KEY WORDS: carbon dioxide capture, carbon dioxide corrosion, carbon steel, heat stable salt, methyldiethanolamine, oxygen

INTRODUCTION

Emissions from fossil fuel-fired power plants represent a significant source of carbon dioxide (CO₂) emissions, a known greenhouse gas. To reduce significantly CO₂ emissions from power plants, CO₂ must be captured, compressed, and transported to a sequestration site. One of the most promising approaches for capturing CO₂ from a conventional coal-fired boiler is the use of an aqueous amine (alkanolamine)-based solution to absorb CO₂ from the flue gas stream. In amine-based CO₂ capture processes, the amine system is designed to form soluble salts from the reaction of amine with acid gas (CO₂) in the absorber and to reverse the process in the regenerator, releasing the acid gas to the regenerator overhead:¹ ²

Absorber reactions:

\[ R₃N + CO₂ + H₂O \rightarrow [R₃NH]⁺ + [HCOO⁻]⁻ \]  \hspace{1cm} (1)  
\[ \text{[amine + acid → salt]} \]

Regenerator reactions:

\[ [R₃NH]⁻ + [HCOO⁻]⁻ + \text{heat} \rightarrow R₃N + CO₂ + H₂O \]  \hspace{1cm} (2)  
\[ \text{[salt + heat → amine + acid gas]} \]
Removing CO₂ with alkanolamine-based exhaust gas conditioning solvents poses its own problems—notably, corrosion.³ On the basis of plant experiences, corrosion seems to take place in several plant locations including the bottom portion of the absorber, the rich-lean heat exchanger, the regenerator, and the reboiler. Both uniform and localized corrosion such as pitting, galvanic, erosion, stress cracking, and intergranular corrosion have been detected.⁴,⁵ Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are commonly used for CO₂ capture processes. The use of primary amines such as MEA leads to a more corrosive environment than secondary (DEA) and tertiary (MDEA) amines because it is a stronger Lewis base than DEA and MDEA, which is the weakest. Both MEA and DEA form carbamate (R₂NCOO⁻) with CO₂ while the tertiary amine, MDEA, does not.⁶ Carbamates have a great impact on the corrosiveness of amine solutions.⁵,⁷ Thus, MDEA is the most forgiving amine from a corrosion standpoint.⁶,⁸ Although there are extensive research data available on corrosion and corrosion inhibition in MEA systems,⁹,¹² minimal information has been reported in the literature concerning the electrochemical behavior and corrosion mechanisms of carbon steel in CO₂-loaded MDEA solutions.

Regardless of the amine type for the CO₂ capture process, the formation of heat stable salts (HSS) in amine solutions has been a problem for a long time. HSS are formed in the presence of acids, which are substantially stronger than CO₂. These acids can form directly from flue gas components such as sulfur dioxide (SO₂) and sulfur trioxide (SO₃) or can be formed from amine degradation products. For example, if formic acid is produced, it will react with MDEA to form a formate HSS:²

Absorber reaction:

\[ \text{R}_n \text{N} + \text{H}_2\text{O} \rightarrow [\text{R}_n \text{NH}]^+ + [\text{O}_2\text{CH}]^- \]  

[amine plus acid → salt]  

(3)

Regenerator reactions:

\[ [\text{R}_n \text{NH}]^+ + [\text{O}_2\text{CH}]^- + \text{heat} \rightarrow \text{no change} \]  

(4)

The HSS typically promote corrosion in the systems because they lower the pH and increase the conductivity of amine solutions.¹³ This can decrease the efficiency of CO₂ capture because of the irreversible reaction with the amine.¹⁴ Numerous studies have been performed that are related to corrosion associated with removing acidic gases, usually hydrogen sulfide (H₂S) and CO₂, from natural and refinery gas streams. However, there are significant differences with exhaust gas applications, such as:¹⁵

—near atmospheric operating pressure
—oxygen-rich environment
—contaminants from products of combustion (NOₓ, SOₓ, particulates, etc.)

These particular conditions involving flue gas can introduce more complicated corrosion problems in alkanolamine systems. However, there is little information about corrosion issues in exhaust gas applications. In this work, tests were designed to simulate corrosion environments in the absorber. Short-term tests were focused on the evaluation of the corrosion behavior of carbon steel under operating conditions in the absorber and identifying the effect of all possible components present in the system. Long-term tests were used to evaluate the corrosion behavior with time and the corrosion mechanism of carbon steel in MDEA/CO₂/O₂/HSS mixtures related to the CO₂ capture process.

**EXPERIMENTAL PROCEDURES**

The specimens were made of carbon steel (A36) with a chemical composition of 0.23% C, 0.79% Mn, 0.02% P, 0.03% S, 0.29% Cu, 0.20% Si, and balance Fe. Carbon steel was chosen because it is generally used in the absorber, lean amine cooler tubes, reflux drum, and regenerator shell. The specimens were ground with 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol (C₃H₈O) in an ultrasonic bath, and dried.

An aqueous solution of MDEA with a concentration of 50% by weight was prepared from a 99% MDEA reagent and deionized (DI) water. The test solution was purged with 12% CO₂ (0.12 bar: CO₂ loading = 0.13 mol CO₂/mol amine) and/or 6% O₂ (0.06 bar) depending on the test conditions. To achieve equilibrium for the system, the solution was purged with gases for at least 6 h before the test. The heat stable salts (HSS) were prepared as a mixture of bicine anion, formate, and sulfate, which were made up by the dissolution of their acid forms in an aqueous MDEA solution. The total concentration of HSS was fixed as 15,000 ppm (10,000 ppm bicine [C₆H₁₃NO₄] + 2,818 ppm formic acid [HCOOH] + 3,002 ppm sulfuric acid [H₂SO₄]).

Corrosion tests were carried out in a 2-L glass cell at 50°C under atmospheric pressure. The setup consists of a three-electrode corrosion cell (CE: platinum wire, RE: silver/silver chloride [Ag/AgCl] electrode), a hot plate equipped with a temperature controller, gas (nitrogen, oxygen, and CO₂) supply set, condenser, potentiostat, and a pH meter. The schematic of the experimental setup is shown in Figure 1.

**Short-Term Corrosion Experiments**

Table 1 and Figure 2 demonstrate the test conditions and procedures for the short-term corrosion test. The test conditions were set to investigate the
The effect of CO₂, O₂, and HSS on the corrosion of carbon steel in an aqueous MDEA solution. The corrosion rate was measured using linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). LPR measurements were performed within ±10 mV with respect to the corrosion potential with a scan rate of 0.166 mV/s. EIS measurements were conducted in the frequency range between 10 kHz and 10 mHz. A sinusoidal voltage of ±10 mV was supplied at the corrosion potential. The cyclic potentiodynamic polarization tests were carried out after conducting LPR and EIS measurements. The specimen was scanned potentiodymanically at a rate of 0.166 mV/s to a potential corresponding to a current density of 10 A/m². At this point, the scan direction was reversed. The downscan was continued until the initial corrosion potential.

**Long-Term Corrosion Experiments**

This part of the study is focused on the evaluation of the corrosion behavior of carbon steel with time in an aqueous MDEA solution. The testing conditions shown in Table 2 were selected from the results of the short-term corrosion study. The corrosion properties of carbon steel were evaluated using electrochemical techniques (open-circuit potential [OCP], LPR, and EIS measurements), weight-loss measurements, and surface analytical techniques (scanning electron microscopy [SEM] and energy-dispersive spectroscopy [EDS]). The corrosion rates were determined from the weight-loss method at the end of a 7-day exposure. Specimens were removed and cleaned for 5 min in the Clarke solution (20 g antimony tri-oxide [Sb₂O₃] + 50 g stannous chloride [SnCl₂] and hydrochloric acid [HCl] to make 1,000 mL). The specimens then were rinsed in distilled water, dried, and weighed to 0.1 mg. The corrosion rate can be calculated using the following equation:

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

In addition, ferrous ion concentrations and solution pH were measured to monitor the water chemistry with time. Figure 3 shows experimental procedures for the long-term corrosion tests.

**RESULTS AND DISCUSSION**

**Short-Term Corrosion Experiments**

**Effect of CO₂ and O₂** — The results of LPR, EIS, OCP, and pH measurements for 50 wt% MDEA (MDEA), 50 wt% MDEA/6% O₂ (MDEA/O₂), 50 wt% MDEA/12% CO₂ (MDEA/CO₂), and 50 wt% MDEA/12% CO₂/6% O₂ (MDEA/CO₂/O₂) are described in Figure 4. The polarization resistance values obtained from LPR and EIS were averaged for each condition and represented in reciprocal form. The polarization resistance reciprocal (1/R_p) for MDEA and MDEA/O₂ conditions showed very low values with noble OCP values, indicating spontaneous passivation of carbon steel. However, the 1/R_p had a significant increase.

![Figure 2. Experimental procedure for short-term corrosion tests.](image-url)
with adding CO₂ into the system. These results indicate that CO₂ obviously can increase the system’s corrosiveness with the formation of carbonic acid (H₂CO₃) or HCO₃⁻, which also led to a decrease in pH. However, addition of O₂ did not change the corrosion rate and OCP in MDEA/CO₂ systems.

Figure 5 illustrates the cyclic polarization curves for carbon steel in different test conditions. Carbon steel showed spontaneous passivation without CO₂, whereas it presented typical active-passive corrosion behavior with CO₂ in MDEA systems. There are no significant shifts of the polarization curves of carbon steel in MDEA/CO₂ systems with and without O₂; this indicates O₂ has little influence on the corrosion behavior of carbon steel in the short-term corrosion tests. In addition, as shown in Figure 5, the reverse polarization curve is on the left of the forward curve for all of the conditions, which demonstrates no pitting tendency for carbon steel in MDEA systems with CO₂ and O₂.

**Effect of Heat Stable Salts** — Figure 6 shows the comparison of the polarization resistance and OCP with/without heat stable salts (HSS) in MDEA systems. The addition of HSS slightly increased the corrosion rates of carbon steel in MDEA systems, but it did not change the corrosion behavior of carbon steel. This indicates that among CO₂, O₂, and HSS, CO₂ is a primary factor for the corrosion of carbon steel in MDEA systems because it changes the corrosion behavior from a passive to an active state.

![Experimental procedure for long-term corrosion tests.](image)

**TABLE 2**

<table>
<thead>
<tr>
<th>Test Condition</th>
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<tr>
<td>1 CS/50 wt% MDEA/12% CO₂</td>
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<tr>
<td>2 CS/50 wt% MDEA/12% CO₂/6% O₂</td>
</tr>
<tr>
<td>3 CS/50 wt% MDEA/12% CO₂/6% O₂/HSS</td>
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**Figure 3.** Experimental procedure for long-term corrosion tests.

**Figure 4.** Effect of CO₂ and O₂ on the corrosion properties of carbon steel in aqueous MDEA solutions: (a) inverse of R_p and (b) OCP and pH.
MDEA/CO2/O2 conditions. In the active region, the cathodic current densities of the systems with HSS were lower than those of the systems without HSS, with no obvious differences in anodic current densities. Such a difference in the cathodic behavior was probably a result of changes in the mechanism of the reduction of corroding agents in the presence of HSS. In the passive region, adding HSS into the system increased the passive current density, indicating that the presence of HSS reduced the protection ability of the passive film covering the metal surface. However, the polarization behavior in the transpassive region was almost identical with no pitting tendency.

**Long-Term Corrosion Experiments**

Figure 8 shows the variations of polarization resistance and OCP with time for 50 wt% MDEA/12% CO2 (MDEA/CO2), 50 wt% MDEA/12% CO2/6% O2 (MDEA/CO2/O2), and 50 wt% MDEA/12% CO2/6% O2/HSS (MDEA/CO2/HSS).
For all three conditions, the OCP changed within an active potential region during 7 days, and there is little difference in each condition. However, as shown in Figure 8(a), the corrosion rate decreased with time in the MDEA/CO₂ condition, whereas it maintained the initial values throughout the test periods in MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSS conditions. The relative corrosiveness of systems can be ranked as: MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂, with MDEA/CO₂ being least corrosive.

The results of pH and ferrous ion concentration measurements in MDEA systems are shown in Figure 9. The solution pHs decreased after 24 h for all conditions and stabilized at 8.84 (MDEA/CO₂), 9.00 (MDEA/CO₂/O₂), and 8.91 (MDEA/CO₂/O₂/HSS). However, as shown in Figures 8(a) and 9(a), there is no relationship between the corrosion rate and the solution pH for all conditions. The ferrous ion concentrations increased with time for MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSS systems as a result of the continuous anodic dissolution of carbon steel with time. For the MDEA/CO₂ system, ferrous ion concentrations increased slowly up to 5 days and it remained constant for up to 7 days.

Figure 10 shows the variation of the corrosion rates with time obtained from weight-loss measurements for MDEA/CO₂, MDEA/CO₂/O₂, and MDEA/CO₂/O₂/HSS conditions. The corrosion rates mea-
Corrosion rates measured by weight loss have a similar trend with the results of electrochemical testing. Note that the corrosion rate obviously decreased from 0.21 mm/y to 0.08 mm/y in MDEA/CO₂, whereas it slightly changed from 0.25 mm/y to 0.20 mm/y in MDEA/CO₂/O₂ and from 0.43 mm/y to 0.41 mm/y in MDEA/CO₂/O₂/HSS over 7 days.

Figures 11 through 13 show the SEM images of the corroded surface of the samples after 1, 3, 5, and 7 days in MDEA systems with different test conditions. It can be seen that there are two distinct areas: one presenting a dark color and the other showing a bright color that grows with time. Figure 14 shows a microstructure of A36 carbon steel that presented a typical ferritic-pearlitic (F/P) microstructure. Based on the microstructure shown in Figure 14, it can be shown that the dark and bright regions in the corroded surfaces represent ferrite phase and pearlite phase, respectively. Figure 15 shows EDS spectra of
the selected parts of the sample after 7 days in a MDEA/CO₂/O₂/HSS system. More carbon content was detected in the pearlite region than the ferrite region. This indicates that a preferential dissolution of ferrite into Fe²⁺ took place and that only iron carbide (Fe₃C) from the pearlite was left on the steel surface. In addition, more Fe₃C accumulated on the steel surface as corrosiveness increased in the MDEA solutions.

As shown in Figures 8(a) and 10, the corrosion rates of carbon steel in the MDEA/CO₂ system decreased with time. However, SEM and EDS analyses of the samples showed no indication of the formation of a protective scale on the sample surface. Instead, less preferential dissolution of ferrite and accumulation of carbides on the corroded surfaces after 7 days, compared with MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSS systems, were observed. This can introduce a hypothesis that a very thin iron carbonate (FeCO₃) film may form on the surface and act as a diffusion barrier, even though the solubility of FeCO₃ in the alkanolamine is much higher than that in water. This suggests that carbon steel is acceptable when used for the absorber condition with CO₂.

Nevertheless, when O₂ is dissolved into the MDEA solutions, another cathodic reaction became available to oxidize the iron according to the following reaction:

\[
O₂ + 2H₂O + 4e^- \rightarrow 4OH^- \quad (6)
\]

This additional reduction reaction resulted in a greater rate of iron dissolution and an acceleration of the corrosion process for MDEA/CO₂/O₂ systems. According to laboratory tests and field data, in addition to the direct role of O₂ on corrosion, O₂ in the feed gas has been linked to the degradation of MDEA and the formation of bicine.

When HSS were added into MDEA/CO₂/O₂ systems, the corrosion rates evidently increased at the
FIGURE 13. SEM surface morphologies of carbon steel with time in 50 wt% MDEA/12% CO₂/6% O₂/HSS condition: (a) Day 1, (b) Day 3, (c) Day 5, and (d) Day 7.

CONCLUSIONS

- The addition of CO₂ in the MDEA systems significantly increased the corrosion rates and changed the corrosion behavior from a passive to an active state.
- However, the corrosion rates of carbon steel did not change significantly upon addition of O₂ and HSS in the short-term corrosion tests.
- No pitting trend was observed from cyclic polarization curves in MDEA systems with CO₂, O₂, and HSS.
- The corrosion rates of carbon steel decreased with time in the MDEA/CO₂ condition, whereas it maintained the initial values throughout the test periods in MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSS conditions.
- The relative corrosiveness of systems was ranked as follows: MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂.
- The presence of O₂ in the MDEA/CO₂ systems accelerated the corrosion process with the addition of the O₂ reduction reaction, whereas HSS increased both anodic and cathodic reactions for the corrosion of carbon steel.
- Corrosion morphologies of carbon steel in MDEA/CO₂ systems with O₂ and HSS showed uniform attack with preferential dissolution of ferrite.

initial stage and changed slightly with time, as shown in Figures 8(a) and 10. In the present study, formate, sulfate, and bicine were chosen as HSS and added in the MDEA systems. According to the literature, formate and sulfate increase the corrosion rate of carbon steel by increasing the reduction rate of the oxidizing agent, whereas bicine participates in the corrosion process as a chelator because of its high affinity toward iron. Therefore, the addition of HSS in the MDEA/CO₂/O₂ systems increased the corrosion rates of carbon steel by accelerating both the anodic and cathodic reactions. However, the detailed mechanism for the individual effect of HSS is not understood, and further investigations are needed.
REFERENCES