

**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 is to evaluate the corrosion properties of carbon steel in MDEA / H₂O / CO₂ / O₂ / HSSs 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.% methyldiethanolamine (MDEA) solutions at 50°C under atmospheric pressure with different combinations of CO₂, O₂ and HSSs (bicine, formate, sulfate). Corrosion behavior of carbon steel was evaluated by using electrochemical methods (LPR, EIS and cyclic polarization), weight loss measurements, and surface analytical techniques (SEM and 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 active state. However, the corrosion rates of carbon steel did not change significantly with addition of O₂ and HSSs. 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/HSSs environments. The order of the corrosivity was MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂. The corrosion morphology of carbon steel in MDEA/CO₂ systems with O₂ and HSSs showed uniform attack with preferential dissolution of ferrite.

Key words: CO₂ capture, CO₂ corrosion, MDEA, O₂, heat stable salt, carbon steel

INTRODUCTION

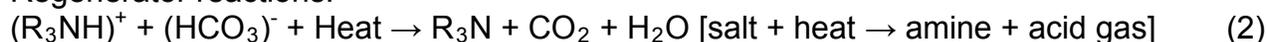
Emissions from fossil fuel-fired power plants represent a significant source of carbon dioxide emissions, a known greenhouse gas. To significantly reduce CO₂ emissions from power plants, CO₂ must be captured, compressed, and transported to a sequestration site. One of the most promising approaches for 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:



Regenerator reactions:



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 methyl-diethanolamine (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 with CO₂ while the tertiary amine, MDEA, does not.⁶ Carbamates have a great impact on the corrosivity of amine solutions.^{5,7} Thus, MDEA is the most forgiving amine from a corrosion standpoint.^{6,7} However, 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 amine type for the CO₂ capture process, the formation of heat stable salts (HSSs) in amine solutions has long been a problem. HSSs are formed in the presence of acids which are substantially stronger than CO₂. These acids can form directly from flue gas components such as SO₂ and 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:



Regenerator reactions:



The HSSs typically promote corrosion in the systems because they lower the pH and increase the conductivity of amine solutions. This can decrease the efficiency of CO₂ capture because of the irreversible reaction with the amine.

Many studies have been performed related to corrosion associated with removing acidic gases, usually hydrogen sulfide (H₂S) and carbon dioxide (CO₂), from natural and refinery gas streams. However, there are significant differences with exhaust gas applications, such as:⁸

- Near atmospheric operating pressure
- Oxygen-rich environment
- Contaminants from products of combustion (NO_x, SO_x, 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/HSSs mixtures related to the CO₂ capture process.

EXPERIMENTAL PROCEDURE

The specimens were made of carbon steel (ASTM⁽¹⁾ 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 as 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 paper, cleaned with isopropyl alcohol 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 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. In order to achieve equilibrium for the system, the solution was purged with gases for least 6 hours before the test. The heat stable salts (HSSs) 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 HSSs was fixed as 15,000 ppm (10,000 ppm bicine + 2818 ppm formic acid + 3002 ppm sulfuric acid).

Corrosion tests were carried out in a 2L glass cell at 50°C under atmospheric pressure. The setup consists of a: (1) three-electrode corrosion cell (CE: platinum wire, RE: Ag/AgCl electrode); (2) hot plate equipped with temperature controller; (3) gas (nitrogen, oxygen and carbon dioxide) supply set; (4) condenser; (5) potentiostat; and (6) pH meter. The schematic of experimental setup is shown in Figure 1.



FIGURE 1 – Experimental Setup for Corrosion Tests

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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 in order to investigate the effect of CO₂, O₂ and HSSs 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) measurements. 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. 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 potentiodynamically 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.

**TABLE 1
TEST CONDITIONS FOR SHORT-TERM CORROSION TESTS**

	Test condition
1	CS / 50 wt.% MDEA
2	CS / 50 wt.% MDEA / 6% O ₂
3	CS / 50 wt.% MDEA / 12% CO ₂
4	CS / 50 wt.% MDEA / 12% CO ₂ / 6% O ₂
5	CS / 50 wt.% MDEA / HSSs
6	CS / 50 wt.% MDEA / 6% O ₂ / HSSs
7	CS / 50 wt.% MDEA / 12% CO ₂ / HSSs
8	CS / 50 wt.% MDEA / 12% CO ₂ / 6% O ₂ / HSSs

* HSSs: 10,000 ppm Bicine + 2818 ppm Formic acid + 3002 ppm Sulfuric acid
CS: carbon steel, MDEA: Methyldiethanolamine

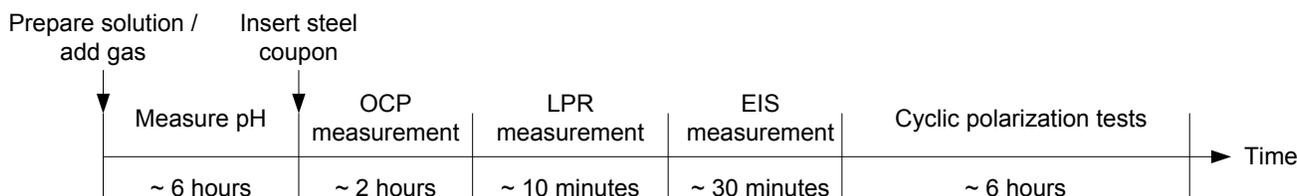


FIGURE 2 – Experimental Procedure for Short-Term Corrosion Tests

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 by electrochemical techniques (open-circuit potential (OCP), LPR, EIS measurements), weight loss measurements, and surface analytical techniques (SEM, EDS). 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.

**TABLE 2
TEST CONDITIONS FOR LONG-TERM CORROSION TESTS**

	Test condition
1	CS / 50 wt.% MDEA / 12% CO ₂
2	CS / 50 wt.% MDEA / 12% CO ₂ / 6% O ₂
3	CS / 50 wt.% MDEA / 12% CO ₂ / 6% O ₂ / HSSs

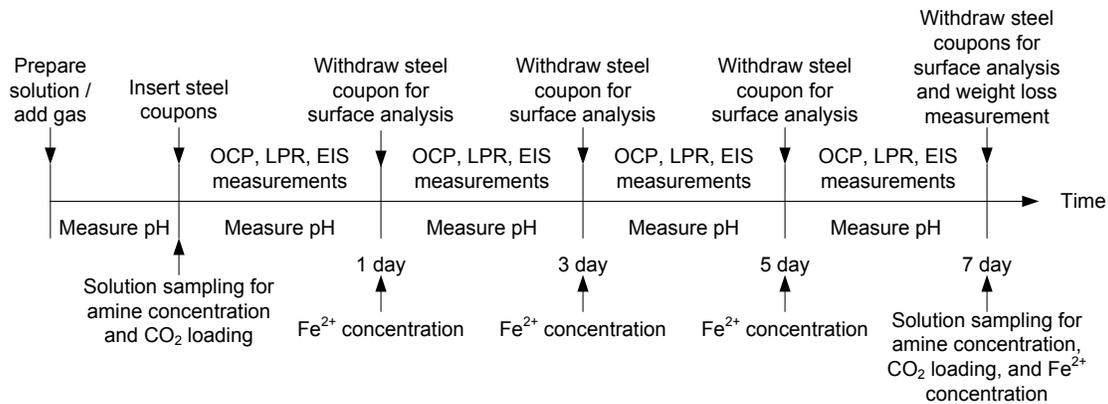


FIGURE 3 – Experimental Procedures for Long-Term Corrosion Tests

RESULTS

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 reciprocal polarization resistance ($1/R_p$) 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 with adding CO₂ into the system. These results indicate that CO₂ can obviously increase the system's corrosivity with the formation of H₂CO₃ or HCO₃⁻, which also led to decrease in pH. However, addition of O₂ did not change the corrosion pH 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 conditions which demonstrates no pitting tendency for carbon steel in MDEA systems with CO₂ and O₂.

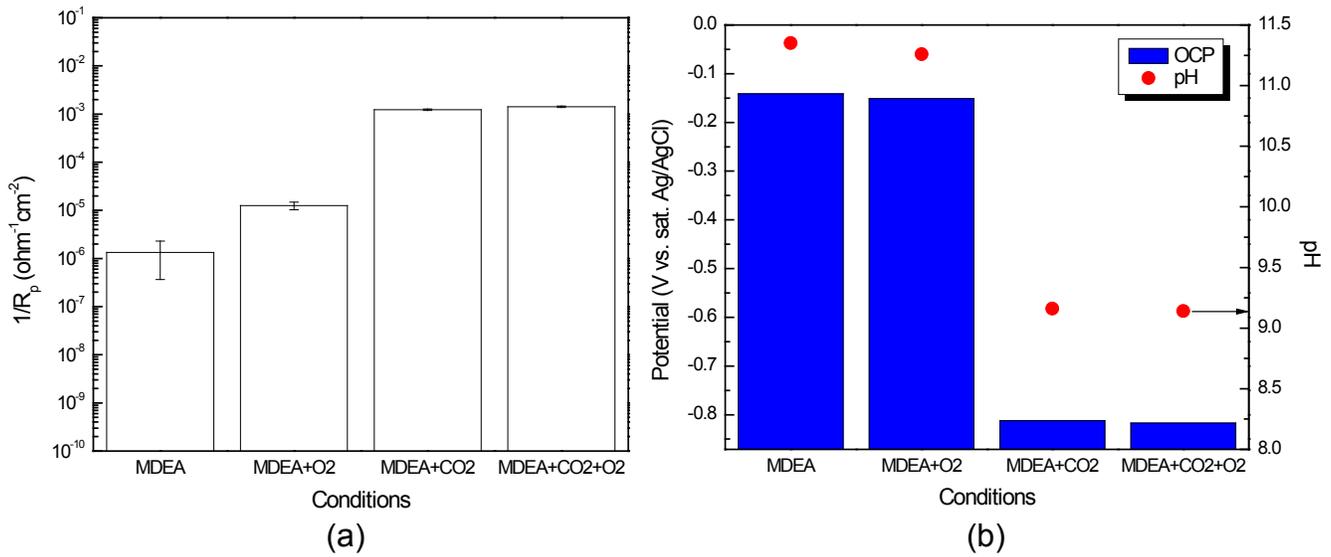


FIGURE 4 – Effect of CO₂ and O₂ on the Corrosion Properties of Carbon Steel in Aqueous MDEA Solutions: (a) Inverse of R_p, (b) OCP and pH

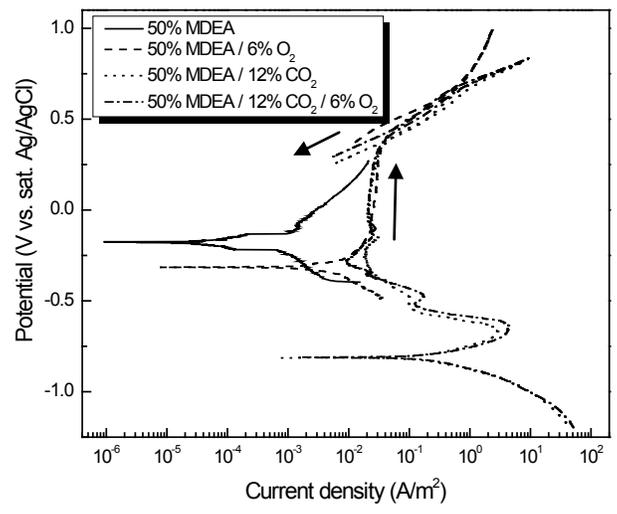


FIGURE 5 – Cyclic Polarization Curves of Carbon Steel in MDEA Systems with CO₂ and O₂

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

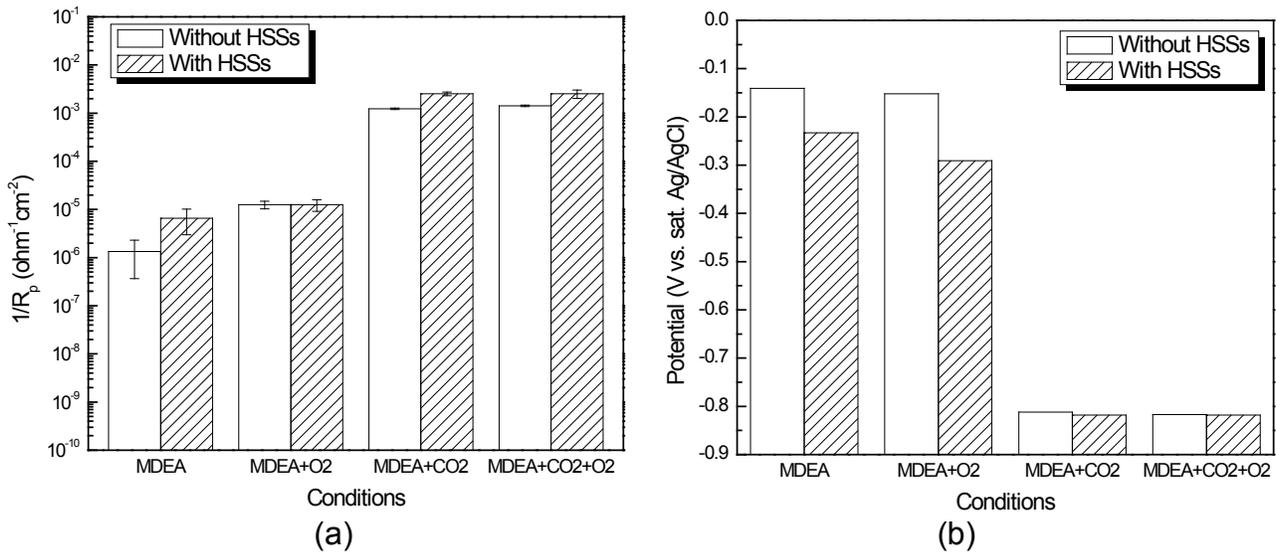


FIGURE 6 – Effect of HSSs on the Corrosion Properties of Carbon Steel in Aqueous MDEA Solutions: (a) Inverse of R_p , (b) OCP

Figure 7 illustrates the effect of HSSs on the polarization behavior of carbon steel in MDEA/CO₂ and MDEA/CO₂/O₂ conditions. In the active region, the cathodic current densities of the systems with HSSs were lower than those of the systems without HSSs with no obvious differences in anodic current densities. Such a difference in the cathodic behavior was probably due to changes in mechanism of reduction of corroding agents in the presence of HSSs. In the passive region, adding HSSs into the system increased the passive current density indicating the presence of HSSs 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.

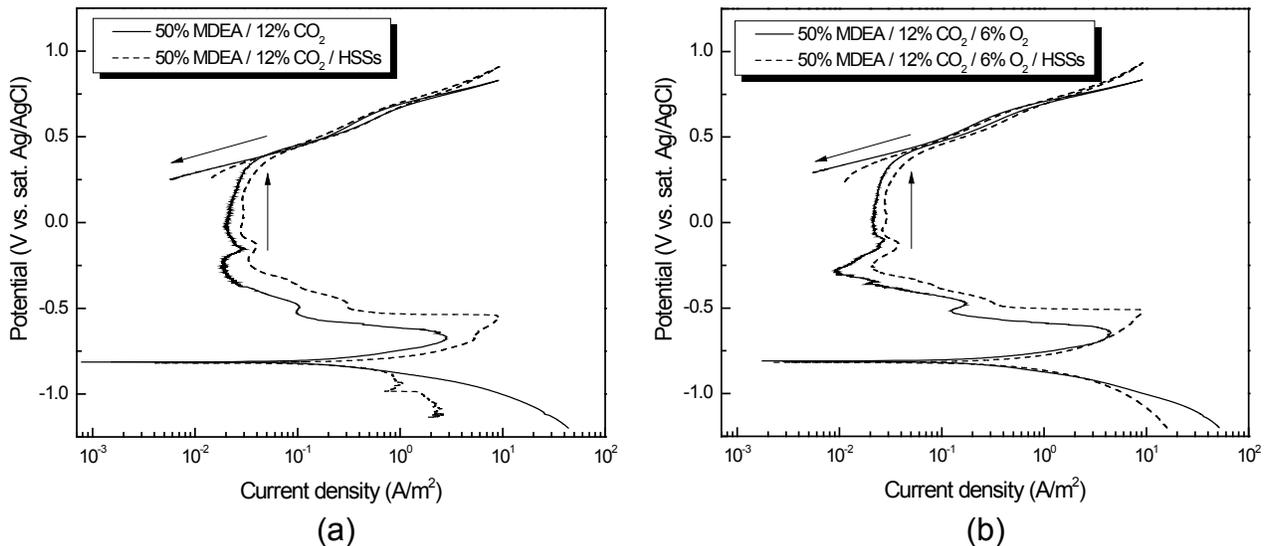


FIGURE 7 – Cyclic Polarization Curves of Carbon Steel in MDEA Systems with HSSs: (a) MDEA/CO₂, (b) MDEA/CO₂/O₂

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 / HSSs (MDEA/CO₂/O₂/HSSs). 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 MDEA/CO₂ condition whereas it maintained the initial values throughout the test periods in MDEA/CO₂/O₂ and MDEA/CO₂/O₂/HSSs conditions. The relative corrosivity of systems can be ranked as: MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂ with MDEA/CO₂ (least corrosive).

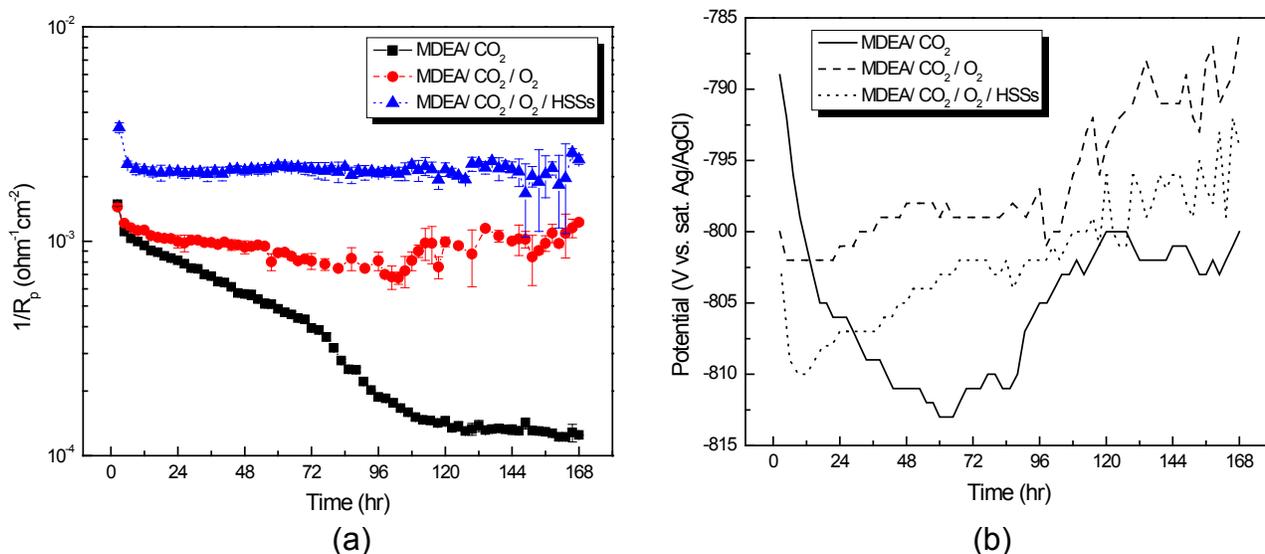


Figure 8: Variations of Polarization Resistance (a) and OCP (b) of Carbon Steel in MDEA Systems with Different Test Conditions

The results of pH and ferrous ion concentration measurements in MDEA systems are shown in Figure 9. The solution pHs decreased after 24 hours for all conditions and stabilized at 8.84 (MDEA/CO₂), 9.00 (MDEA/CO₂/O₂), and 8.91 (MDEA/CO₂/O₂/HSSs). However, as shown in Figure 8 (a) and Figure 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/HSSs systems due to 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 measured by weight loss have a similar trend with the results of electrochemical tests. Note that the corrosion rate obviously decreased from 0.21 to 0.08 mm/y in MDEA/CO₂, whereas it slightly changed from 0.25 to 0.20 mm/y in MDEA/CO₂/O₂ and from 0.43 to 0.41 in MDEA/CO₂/O₂/HSSs over 7 days.

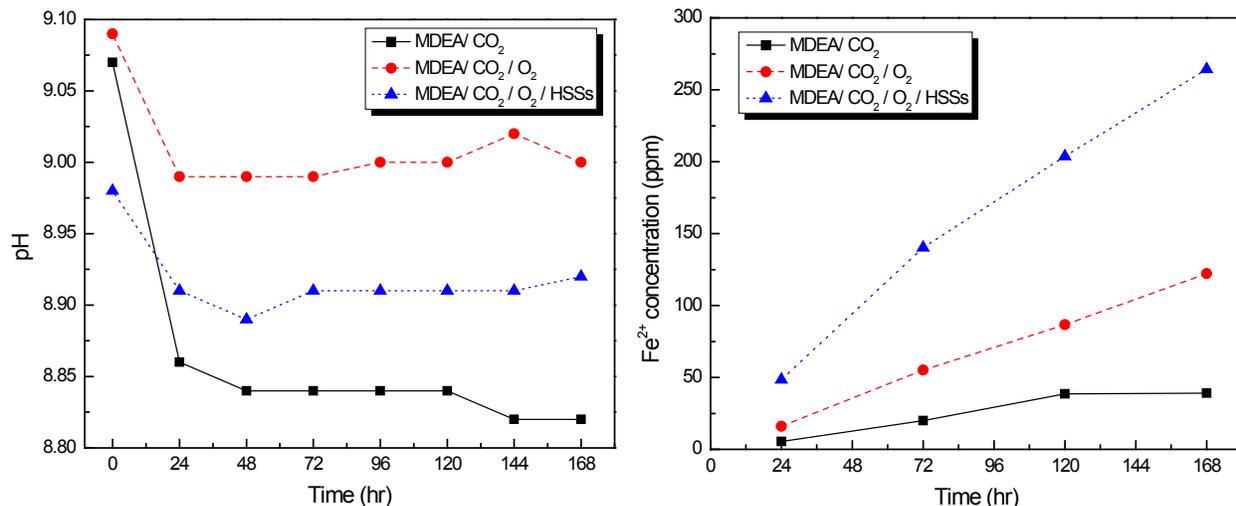


FIGURE 9 – Variations of MDEA Solution pH (a) and Ferrous Ion Concentrations (b) with Different Test Conditions

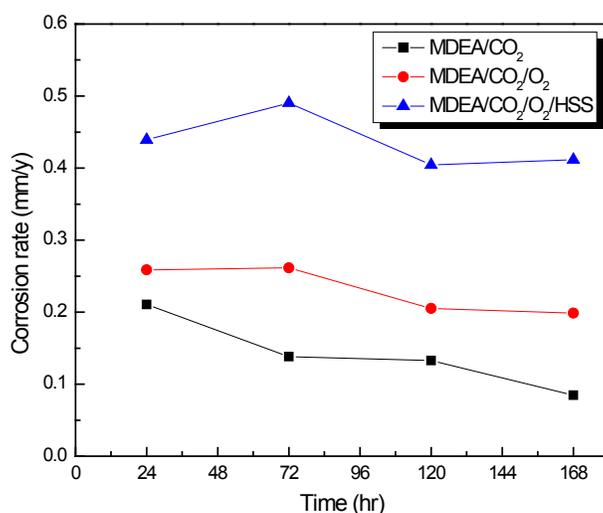
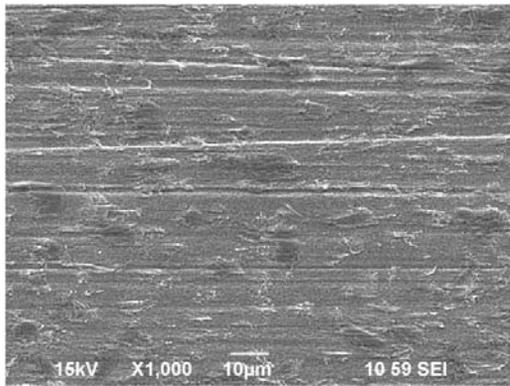
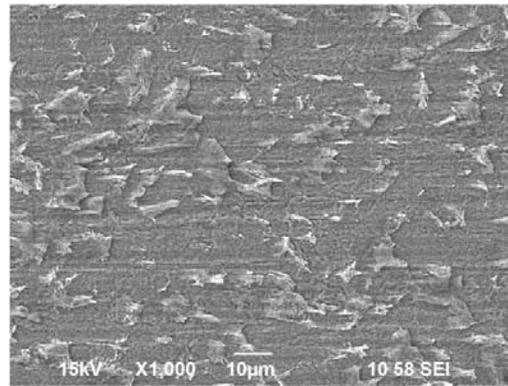


FIGURE 10 – Variation of Corrosion Rates of Carbon Steel with Time Measured from Weight Loss Measurements in MDEA Systems

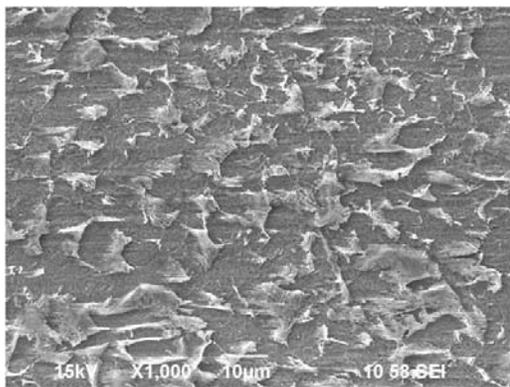
Figures 11 through 13 show the SEM images of the corroded surface of the samples after 1, 3, 5 and 7 days in MDEA systems with different test conditions. It can be seen that there are two distinct areas: one presenting dark color and other showing bright color which grows with time. Figure 14 shows a microstructure of A36 carbon steel which presented typical ferritic-pearlitic (F/P) microstructure. Based on the microstructure shown in Figure 14, it can be known that the dark and the bright regions in corroded surfaces represent ferrite phase and pearlite phases, respectively. Figure 15 shows EDS spectra of the selected parts of the sample after 7 days in MDEA/CO₂/O₂/HSSs system. More carbon content was detected in pearlite region than 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.⁹ In addition, more Fe₃C accumulated on the steel surface as increasing the corrosivity of the MDEA solutions.



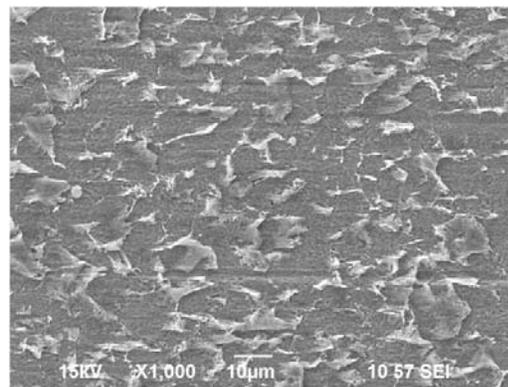
(a) Day 1



(b) Day 3

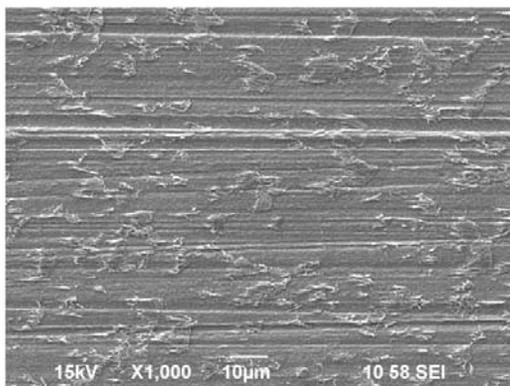


(c) Day 5

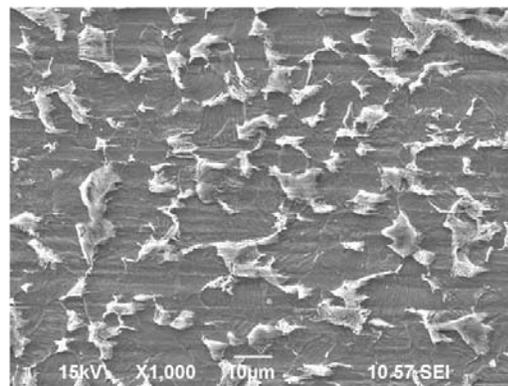


(d) Day 7

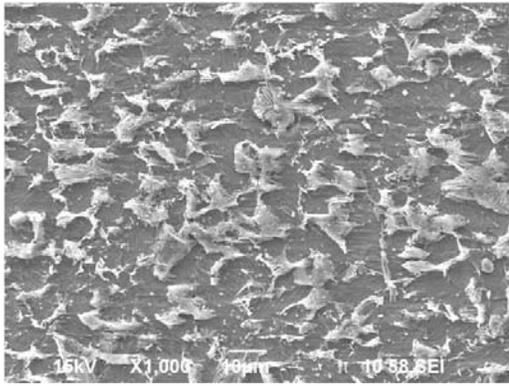
FIGURE 11 – SEM Surface Morphologies of Carbon Steel with Time in 50 wt.% MDEA / 12% CO₂ Condition



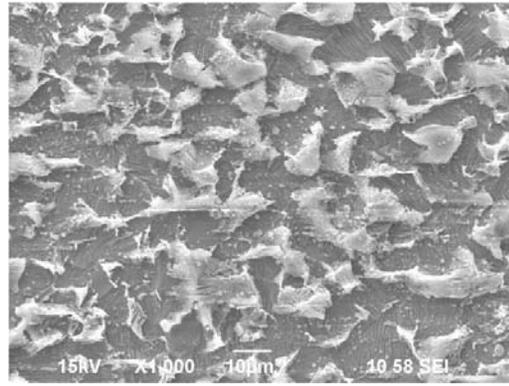
(a) Day 1



(b) Day 3

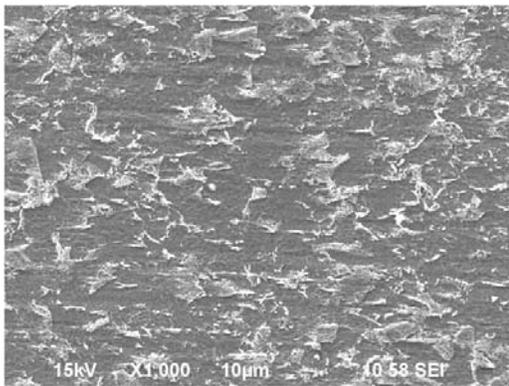


(c) Day 5

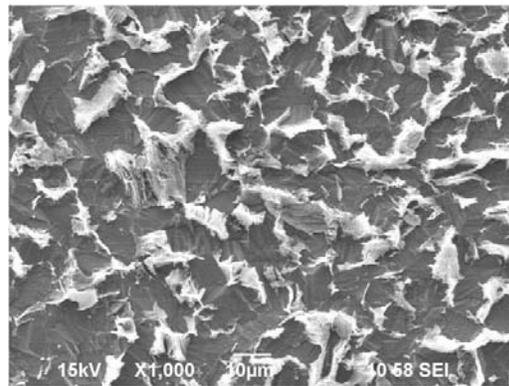


(d) Day 7

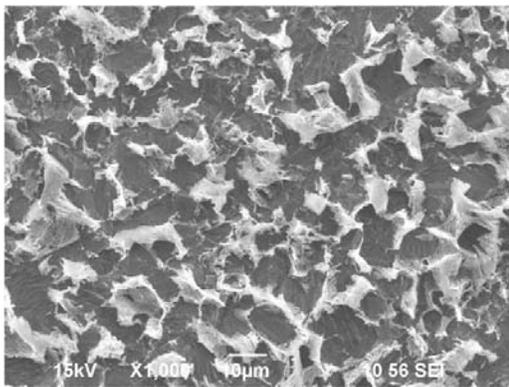
FIGURE 12 – SEM Surface Morphologies of Carbon Steel with Time in 50 wt.% MDEA / 12% CO₂ / 6% O₂ Condition



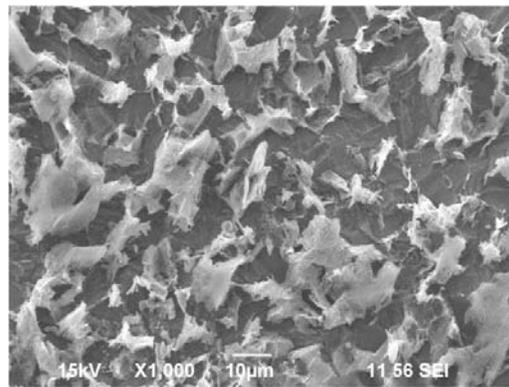
(a) Day 1



(b) Day 3



(c) Day 5



(d) Day 7

FIGURE 13 – SEM Surface Morphologies of Carbon Steel with Time in 50 wt.% MDEA / 12% CO₂ / 6% O₂ / HSSs Condition

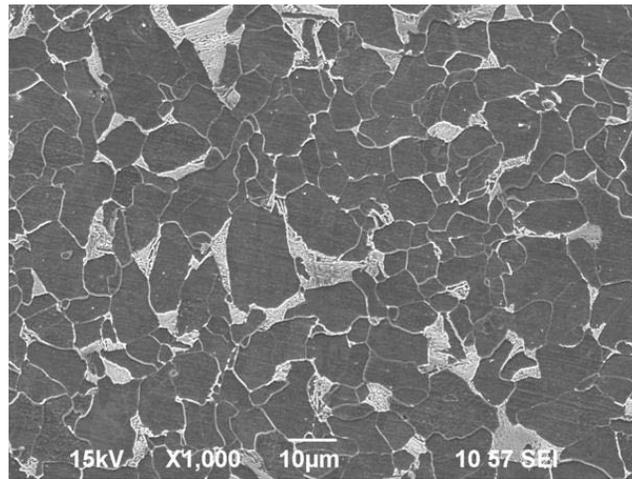


FIGURE 14 – Microstructure of A36 Carbon Steel

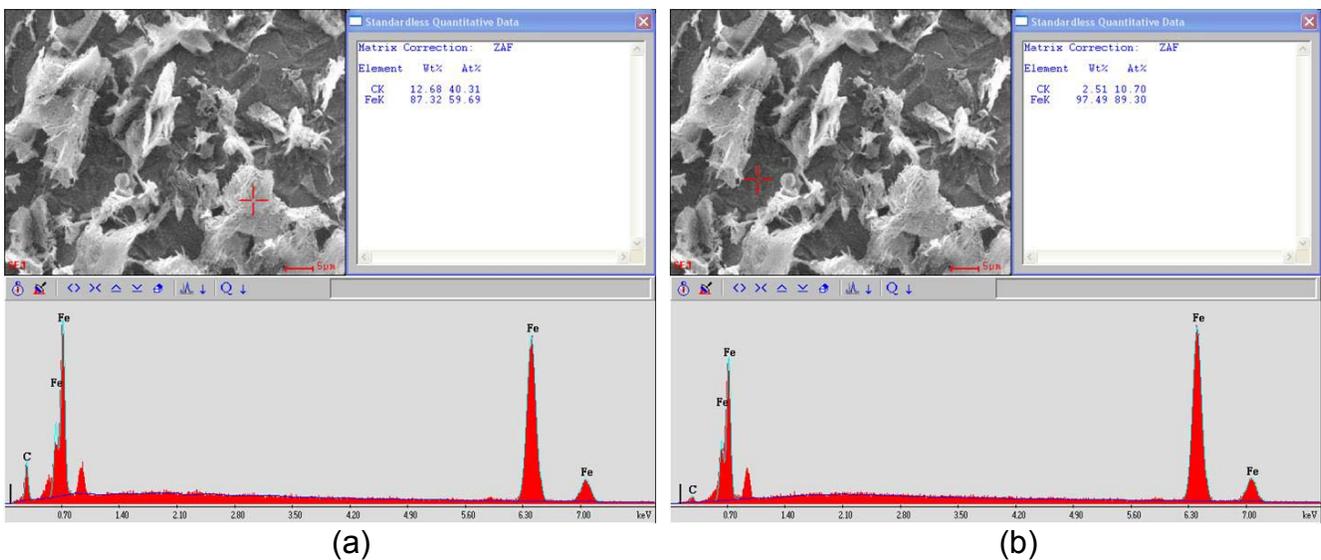
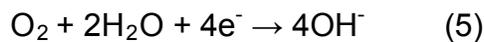


FIGURE 15 – Results of EDS Analyses for Corroded Sample after 7 Days in 50 wt.% MDEA / 12% CO₂ / 6% O₂ / HSSs: (a) Pearlite Region and (b) Ferrite Region

As shown in Figure 8 (a) and Figure 10, the corrosion rates of carbon steel in 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 FeCO₃ film may form on the surface and act as a diffusion barrier. However, when O₂ is dissolved into the MDEA solutions, another cathodic reaction became available to oxidize the iron according to the following reaction:



This additional reduction reaction resulted in a greater rate of iron dissolution and an acceleration of the corrosion process for MDEA/CO₂/O₂ systems.

When HSSs were added into MDEA/CO₂/O₂ systems, the corrosion rates evidently increased at the initial stage and changed slightly with time as shown in Figure 8 (a) and Figure 10. In the present study, formate, sulfate and bicine were chosen as HSSs and added in the MDEA systems. Formate and sulfate increase the corrosion rate of carbon steel by increasing the reduction rate of the oxidizing agent¹⁰, whereas bicine participates in the corrosion process as a chelator due to its high affinity toward iron.¹¹ Therefore, the addition of HSSs in the MDEA/CO₂/O₂ systems increased the corrosion rates of carbon steel by accelerating both the anodic and the cathodic reactions.

CONCLUSIONS

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

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