Corrosion mitigation via a pH stabilization method in monoethanolamine-based solutions for post-combustion CO₂ capture

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ABSTRACT

A pH stabilization method was investigated to mitigate corrosion in aqueous 5 M monoethanolamine for post-combustion CO₂ capture. The room temperature pH of a naturally aerated CO₂-loaded solution (i.e., 9.7) was adjusted with NaHCO₃ powders to 9.3 and 9.1, and its effect on corrosion of A106 carbon steel was studied. Lower pH initially accelerated corrosion but promoted protective FeCO₃ layer formation and subsequently A106 passivation (i.e., Fe₃O₄ formation). Dissolved oxygen also played a pivotal role by functioning as an additional oxidizer, retarding FeCO₃ formation via preferentially oxidizing Fe²⁺ to form rust, and promoting passivation of A106 under the FeCO₃ layer.

Keywords: A. carbon steel, B. polarization, B. ICP-OES, C. alkaline corrosion, C. rust, C. passivity

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1. Introduction

Post-combustion CO₂ capture, a method for the removal of CO₂ from flue gas streams derived from the combustion of fossil fuels such as coal, natural gas, or oil by application of aqueous alkanolamine solutions, is a commercially available technology to retrofit existing fossil fuel burning power plants to meet increasing regulations while meeting electricity demand [1-4]. Commonly used amine solutions, such as 5 M monoethanolamine (MEA), become very corrosive after capturing a certain amount of CO₂ under typical operating conditions [4-19]. The existence of 4-8% oxygen in flue gas exacerbates the situation by functioning as an additional oxidizer after dissolving in aqueous amine solutions during the capture process and by accelerating degradation of the amines to generate additional corrosive species [4-8, 19-24].

Corrosion can be inhibited if a protective layer of siderite (FeCO₃) and/or magnetite (Fe₃O₄) is formed on the surface of capture units which are made of carbon steels [6-9, 12-14, 24-26]. Formation of these protective layers depends on the operating conditions such as amine structure, temperature, dissolved O₂ concentration, and pH in the localized area near the carbon steel surface. A protective layer of FeCO₃ was formed in a naturally aerated CO₂-loaded secondary amine of piperazine solutions, which significantly decreased the corrosion of carbon steel under specific conditions [12-14]. Also, formation of a protective layer of FeCO₃ was reported in a CO₂-loaded tertiary amine of methyldiethanolamine (MDEA) solutions regardless of the presence of dissolved O₂ (i.e., with the O₂ partial pressure of 55 kPa) [24-26]. However, MEA, a primary amine, does not promote formation of this layer under similar naturally aerated conditions [7, 11-13, 26], which is due to its favorable carbamate formation and low equilibrium constant between carbamate and bicarbonate. This, overall, resulted in low concentrations of free Fe²⁺ and/or CO₃²⁻ to reach a minimum saturation degree (δ_{SD}) of FeCO₃ formation in the localized area near the carbon steel surface (reaction 1, and equations 2 and 3) [27-30]. That is, the δ_{SD} of FeCO₃, as shown in equation 3, must not be high enough to promote the precipitation and/or growth of FeCO₃ in MEA-based solutions.

$$K_{sp} = C_{\text{Fe}^{2+}} C_{\text{CO}_3^{2-}} \quad (2)$$

$$\delta_{SD} = \frac{C_{Fe^{2+}} C_{CO_3^{2-}}}{K_{sp}} \quad (3)$$

where K_{sp} is the solubility constant of $FeCO_3$, $C_{Fe^{2+}}$ and $C_{CO_3^{2-}}$ are the concentrations of free Fe^{2+} and CO_3^{2-} , respectively. Therefore, to promote $FeCO_3$ formation in MEA-based solutions, the concentrations of free Fe^{2+} and/or CO_3^{2-} in the localized area near the steel surface need to be increased.

Considering possible chemical reactions in MEA-based solutions, the concentration of CO_3^{2-} in [equation 3](#) can be adjusted based on its equilibrium with the concentration of HCO_3^- via reactions of [4-9](#) and their equilibrium constants ([equations 10-15](#)) [4, 31, 32]:

$$H_{CO_2} = \frac{P_{CO_2}}{C_{CO_2,aq}} \quad (10)$$

$$K_1 = \frac{C_{MEACOOH}}{C_{MEA} C_{CO_2,aq}} \quad (11)$$

$$K_2 = \frac{C_{MEACOOH}}{C_{MEACOO^-} C_{H^+}} \quad (12)$$

$$K_3 = \frac{C_{MEA} C_{H_2CO_3}}{C_{MEACOO^-} C_{H^+}} \quad (13)$$

$$K_4 = \frac{C_{H^+} C_{HCO_3^-}}{C_{H_2CO_3}} \quad (14)$$

$$K_5 = \frac{C_{H^+} C_{CO_3^{2-}}}{C_{HCO_3^-}} \quad (15)$$

where H_{CO_2} is the Henry's law constant for reaction 4, K_1 to K_5 are the reaction constants for reactions 5 to 9, respectively. P_{CO_2} is the partial pressure of CO_2 . $C_{\text{CO}_2,\text{aq}}$, C_{MEACOOH} , C_{MEA} , C_{MEACOO^-} , C_{H^+} , $C_{\text{H}_2\text{CO}_3}$, and $C_{\text{HCO}_3^-}$ are the concentrations of dissolved CO_2 , MEACOOH , MEA , MEACOO^- , H^+ , H_2CO_3 , and HCO_3^- , respectively. Combining equations from 10 to 15, equations 16-17 are obtained and gives a direct relationship between concentrations of CO_3^{2-} and HCO_3^- ,

$$C_{\text{CO}_3^{2-}} = K \frac{C_{\text{HCO}_3^-}^2}{P_{\text{CO}_2}} \quad (16)$$

$$K = \frac{K_2 K_5 H_{\text{CO}_2}}{K_1 K_3 K_4} \quad (17)$$

where K is the overall equilibrium constant for reactions 4 to 9. Substituting equation 16 into equation 3 gives equation 18,

$$\delta_{\text{SD}} = K \frac{C_{\text{Fe}^{2+}} C_{\text{HCO}_3^-}^2}{K_{\text{sp}} P_{\text{CO}_2}} \quad (18)$$

which shows the δ_{SD} is proportional to the Fe^{2+} concentration and the square of HCO_3^- concentration but inversely proportional to P_{CO_2} and the solubility constant in the system.

Therefore, in this work, sodium bicarbonate (NaHCO_3) was investigated as an environmentally benign additive to promote formation of a protective layer of FeCO_3 on a carbon steel surface in a corrosive solvent of CO_2 -loaded 5 M MEA solution. Before experimental study, a calculation of CO_2 :MEA: H_2O system using Aspen Plus[®] with the addition of various amounts of NaHCO_3 (from 0 to 2 M) was carried out to understand the effect of NaHCO_3 on the absorption efficiency of MEA. The simulation was carried out at a constant total CO_2 feed. To have net CO_2 absorption in 5 M MEA, i.e., mole absorbed CO_2 /mole amine, dissolved CO_2 from the contribution of NaHCO_3 in the solution was subtracted. The results, as presented in Figure S1, showed that no notable negative impact in CO_2 loading was observed at the absorber temperature of 40°C with addition of NaHCO_3 up to 1 M. However, the solution capacity decreases with increases in NaHCO_3 at a stripping temperature of 120°C. This indicates that the solution cyclic capacity, i.e., the difference in CO_2 loading between absorbing and stripping conditions, is increased. Considering this, the study was conducted with NaHCO_3 additions of no more than 1 M in this work. This method is known as pH stabilization and is

often used in gas-condensate pipelines to reduce corrosion by increasing the solution pH significantly to a level, normally around 7, to favor FeCO_3 formation [27, 33, 34]. However, pH stabilization, based on the authors' knowledge, is reported for the first time in amine solutions for post-combustion CO_2 capture in this work. The pH is shown to decrease for CO_2 -loaded 5 M MEA solutions with addition of NaHCO_3 (from 0.5 to 1 M), which is consistent with our previous observations that a lower pH is favorable for FeCO_3 formation in a MEA-based solution [9]. In addition, this work provides additional evidence to show how dissolved O_2 participates in the corrosion process in amine solutions for post-combustion CO_2 capture systems.

2. Experimental

2.1 Sample preparation

Considering the intrinsically corrosive characteristic of operated conditions in a real post-combustion CO_2 capture process, stainless steels are normally used for process units [19, 35]. However, the price for stainless steel is substantially higher than carbon steel (about 3-4 times). Therefore, to lower down the total capital cost for post-combustion CO_2 capture process, this work is seeking to develop protection technique for carbon steels which is likely to minimize the differences in corrosion as stainless steels. A106 grade B carbon steel, with chemical compositions (in weight percent) of 0.27 C, 0.26 Si, 0.86 Mn, 0.013 P, 0.022 S, 0.12 Cr, 0.04 Mo, 0.15 Ni, 0.21 Cu, 0.044 Al, and 0.001 V with the balance being Fe, was used for corrosion testing in this work. All of the tested samples, including cylinders with a diameter of 9.5 mm and a height of 13 mm and coupons with dimensions of 40 mm $\times$ 13 mm $\times$ 2 mm, were cut from A106 pipes. The cylinders were used for electrochemical testing, and the coupons were used for immersion corrosion testing in an autoclave type stainless steel corrosion cell. The samples were ground with SiC paper to a final 800 grit, and then ultrasonically cleaned with deionized water and acetone before corrosion testing.

2.2 Solution preparation and analysis

5 M MEA solution, with the balance being deionized water, was chosen and prepared for this study. The solution with a room temperature (RT, $22\pm 3^\circ\text{C}$) pH of 9.7 was obtained by introducing a mixture gas of 1.2 L/min CO_2 and 0.8 L/min N_2 into the previously prepared 5 M MEA solution for a set time, i.e., to obtain a dissolved CO_2 concentration of 0.43 mol CO_2 /mol amine (C/N). For MEA solutions, in which the dissolved CO_2 concentration is typically between 0.41 and 0.52 C/N at the bottom of an existing absorber column under the test conditions (around 50°C) with gaseous CO_2 concentration in the treating flue gas of 4-15 vol.%. While, after the stripping process (around 120°C), the typically achievable minimum dissolved CO_2 concentration in the solution is 0.2-0.3 C/N. Previously published work has shown that the most corrosive environment in the process is where the CO_2 loading is rich [6, 8, 12, 22], which is the reason for a selection of a rich solution with real measured 0.43 C/N in this work. Another reason for the selection of 0.43 C/N loaded solution is to show the negative effect of dissolved oxygen on the formation of protective layers when compared to previously published work in anoxic environments [9], i.e., protective layers are able to form in an anoxic solution but not in a naturally aerated solution with all the other conditions being constant. These reasons also led to our consideration towards developing a pH stabilization technique. To understand the effect of pH on the corrosion of carbon steel as well as formation of corrosion products on its surface, the pH was adjusted by addition of NaHCO_3 powders. Two additional solutions with RT pHs of 9.3 and 9.1 were obtained by addition of NaHCO_3 to reach initial concentrations of 0.5 M and 1.0 M, respectively, into the previously prepared pH 9.7 MEA solution. The actual concentration of NaHCO_3 will vary due to equilibrium between HCO_3^- and other species in the system. The solutions without addition of NaHCO_3 (with RT pH 9.7), and with addition of 0.5 M (with RT pH 9.3) and 1.0 M (with RT pH 9.1) NaHCO_3 are defined to be MEA-A, MEA-B, and MEA-C, respectively. To understand the effect of dissolved oxygen on the corrosion behavior of carbon steel in these solutions, no deaeration was used in this work, i.e., all the three solutions were naturally aerated.

The solutions were analyzed after all additives were fully dissolved. Solution alkalinity was determined by acid titration using a MetrohmTitrando 836. CO_2 content of the loaded solutions was analyzed by an acid-base method, as described in our previous work [9, 14]. Briefly, phosphoric acid liberates CO_2 from MEA solutions, which is transported by nitrogen gas to a CO_2 analyzer for quantitative determination. CO_2 loading values (mol CO_2 /mol amine, C/N)

reported herein are the CO₂ content from the CO₂ analyzer (mol CO₂/kg solution) divided by the total alkalinity obtained from the alkalinity measurement (mol amine/kg solution). The pH was measured at both RT and an operating temperature of 80°C using a temperature corrected probe and two point calibration. Calibration was conducted before the first measurement each day. Table 1 shows the prepared conditions of the three solutions for corrosion testing in this work. Lower pH was observed at higher temperature for each solution regardless of NaHCO₃ addition (Table 1), which can be explained as follows. Carbonic acid (H₂CO₃), bicarbonate ions (HCO₃⁻), and protonated amine are the main sources of protons in the CO₂ loaded aqueous alkanolamine solutions. Considering the endothermic nature of dissociation reactions of carbonic acid, bicarbonate ions, and protonated amines (i.e., all have $pK_a > 0$), a higher temperature will promote these dissociation reactions, and thus the production of protons, which, overall, shows a lower solution pH.

2.3 Electrochemical testing

A temperature of 80°C was selected in this work to mimic the operating temperature of the cross-over Lean/Rich solvent heat exchanger, which is around 80°C in a real CO₂ capture unit. This process stream would be both rich in dissolved CO₂ and at elevated temperature, i.e. under more corrosive conditions and protection is necessary [10-12, 22]. Moreover, dissolved CO₂ concentration can be maintained around 0.4 C/N for a longer time at 80°C but not at higher temperatures such as in the stripper (i.e., 120°C) without a pressurized system. A three-electrode setup was used for electrochemical corrosion testing with a saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode, as described elsewhere [11, 12, 14]. Briefly, a precathodization process was carried out at a potential of -1.2 V vs. SCE for 2 min to help remove air-formed oxides and to help initialize all corrosion samples to nearly equivalent starting conditions [36-38]. Since the potential used for this process is below the hydrogen equilibrium potential, reduced hydrogen was generated and would adsorb on the steel surface and evolve gas [39, 40]. After this process, visible bubbles were removed by slight vibration of working electrode by hand. Subsequently, linear polarization resistance (LPR) testing, with polarization from -10 mV to 10 mV vs. the corrosion potential (E_{corr}) and a scan rate of 0.166 mV/s, was carried out after E_{corr} was stable (approximately 15 min). LPR testing,

from which the polarization resistance (R_p) was calculated, was conducted for extended time periods to study corrosion over time. The LPR measurement was repeated for a total of three times at each time step, and data presented are an average of these three measurements. R_p values are normalized to the initial geometric surface area of the samples.

Electrochemical impedance spectroscopy (EIS) measurements, using an alternating potential signal at E_{corr} with a perturbation amplitude of 10 mV RMS (root mean square) and a frequency range from 100 kHz to 0.01 Hz, were performed. Similarly, the first EIS measurement was conducted approximately 15 min after reducing potentiostatically at -1.2 V vs. SCE for 2 min. All of the impedance plots shown in this paper have been normalized to the initial geometric surface area of the samples.

Also, E_{corr} was measured with changes in time to fully understand the effect of solution pH on the corrosion behavior of A106.

To verify reproduction of all the electrochemical results, all tests were repeated at least twice with reproducible results. Some of the repeated work is provided in the supplementary material ([Figure S3](#)). After corrosion testing, all samples were cleaned, dried, and stored in a vacuum desiccator to prevent further oxidation by air before surface characterization.

2.4 Characterization methods

To further understand the corrosion, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize samples before and after corrosion testing. A Hitachi S-4800 field emission SEM, with a voltage of 15 kV and a current of 20 μA , was used to characterize the surface of corroded A106 samples. XRD scans were carried out using a Rigaku Smartlab 1 kW powder system equipped with a Cu target. The operational tube voltage and current were 40 kV and 44 mA, respectively. Details of the operating procedure were described in our previous work [9]. A 2θ range from 10 to 90° was used with a scan rate of 0.5°/min. To make XRD patterns more reliable and comparable to each other, optical alignment was conducted every week, and sample alignment was conducted for each sample. Diffraction patterns were analyzed in the PDXL2 software with the database of ICDD PDF-2 release 2012.

In addition, *ex-situ* characterization of rust using SEM and XRD, which was formed during the corrosion tests in these naturally aerated CO₂-loaded 5 M MEA solutions regardless of pH (the red corrosion products shown in [Figure S2](#)), was conducted. The formed rust powders were collected with a 20 ml glass vial immediately after corrosion testing. Subsequently, the collected rust was cleaned with DI water with the help of a centrifuge, which was repeated more than three times. Further cleaning, similar to the previous step with DI water, was conducted with acetone. Finally, the cleaned rust was dried in an oven at 60°C for approximately 48 h. After drying, characterization was conducted by SEM and XRD.

2.5 Fe Concentration analysis

To understand the dissolved oxygen effect on the corrosion behavior of A106 carbon steel in a MEA-based solution, concentrations of total dissolved Fe from both anoxic and aerated solutions were analyzed intermittently on a Varian 720-ES spectrometer (inductively coupled plasma optical emission spectrometry, ICP-OES), of which the details were described in our previous work [9]. The experiments were repeated at least twice, and the average is reported.

2.6 Solution speciation

To better understand the corrosion behavior observed from the experiments, i.e., the solution pH effect, Aspen Plus[®] with the ENRTL-RK activity coefficient model was applied to investigate solution chemical behavior at a microscopic level in 5 M MEA solution at 80°C [9].

3. Results

Corrosion of A106 carbon steel in a naturally aerated CO₂-loaded 5 M MEA solution with an initial RT pH of 9.7 (MEA-A) at 80°C has been reported previously [11-13]. For the purpose of comparison as a baseline, some results, from previous work or parallel tests are presented and interpreted briefly in this work.

3.1 Electrochemical corrosion behavior

3.1.1 Polarization resistance

Figure 1 shows $\log(R_p)$ of A106 carbon steels obtained by LPR in naturally aerated CO₂-loaded 5 M MEA solutions with different pHs at 80°C and ambient pressure as a function of testing duration. For A106 in MEA-A (with an initial RT pH of 9.7), the $\log(R_p)$ was observed to decrease slightly from approximately 2.22 to 1.99 with increases in time to approximately 100 h, and subsequently stabilized up to a testing duration of approximately 185 h. Decreases in the $\log(R_p)$ before 100 h might be attributed to increases in galvanic corrosion, as evidenced by the Fe₃C residual phase as a result of preferential dissolution of the ferrite phase [11, 12, 20]. When the surface area of the Fe₃C residual maintains a balance between spallation and generation, galvanic corrosion is stabilized with dissolution of the ferrite phase.

For the case in MEA-B (with an initial RT pH of 9.3), the $\log(R_p)$ decreased slightly from approximately 2.01 to 1.87 with increases in time to approximately 100 h and stabilized thereafter, similar to that in MEA-A. The relative $\log(R_p)$ also decreased correspondingly with decreases in pH from 9.7 to 9.3.

The trend of corrosion behavior was similar with a further drop in an initial RT pH to 9.1 over the first 70 h (A106 in MEA-C), i.e., the $\log(R_p)$ decreased slightly from approximately 1.92 to 1.68. In addition, the relative $\log(R_p)$ was observed to decrease further with respect to that at higher pH. Interestingly, the $\log(R_p)$ subsequently increased to approximately 2.00 at 140 h and then a sharply increased to approximately 2.76. This might indicate that a protective layer of corrosion product was formed under the testing conditions. All the results showed good reproducibility, as shown in Figure S3.

3.1.2 EIS measurements

EIS measurements were conducted to further understand the effect of pH on the corrosion behavior of A106 carbon steel in the naturally aerated CO₂-loaded MEA solutions. Figure 2 shows Nyquist plots of A106 obtained after various exposure durations in the solutions with three different pHs. All of the solutions had high conductivity, meaning ohmic resistances were mostly insignificant, as can be seen from the almost zero intercepts on the real axis for high

frequencies. Moreover, most of the Nyquist plots depicted depressed semicircles characteristic of charge transfer resistance (R_{ct}). After 185 h, Warburg impedance was seen for A106 in MEA-C, indicating diffusion of species related to the corrosion process might be inhibited [16, 41-43]. This is consistent with the increase in R_p from the LPR data shown in Figure 1, and corroborates the hypothesis that a protective layer was formed.

Early in the experiment (i.e., approximately 0.25 h), the R_{ct} of A106 in the CO₂-loaded MEA solutions decreased with pH, as can be seen from the intercepts on the real axis for low frequencies (i.e., smaller diameter of the semicircles) in Figure 2, also in agreement with LPR results. Correspondingly, diffusion becomes more apparent with decreases in solution pH, as evidenced by the changes in the characteristic for low frequencies (Figure 2). With increases in time (to approximately 115 h and 185 h), the decreasing trend in R_{ct} was still observed with decreases in pH when comparing the cases of MEA-A to MEA-B. However, insignificant changes in R_{ct} were observed with further decreases in pH after 115 h (comparing A106 in MEA-B to MEA-C). When further increasing the duration to 185 h, the corrosion of A106 appears to have changed from a charge-transfer-dominated process in both MEA-A and MEA-B (i.e., depressed semicircle characteristics) to a diffusion-dominated process in MEA-C (i.e., Warburg characteristics) [16, 41-43].

Nyquist plots of A106 in these three solutions were re-plotted in Figure 3 to show the effect of testing duration on its corrosion behavior in each solution. For A106 in MEA-A and MEA-B, R_{ct} first decreases and subsequently stabilizes, consistent with the trend of R_p shown in Figure 1. However, for A106 in MEA-C, R_{ct} decreased and increased again from 70 h to 115 h, then became diffusion-dominated as indicated by Warburg characteristics beyond 115 h.

3.1.3 Corrosion potential measurements

To more fully understand pH effects as well as stability of the formed protective layer in naturally aerated CO₂-loaded MEA solutions, E_{corr} of A106 in solutions with different pHs was measured over time, as shown in Figure 4. Insignificant changes in E_{corr} were observed for A106 in MEA-A after approximately 600 h, i.e., E_{corr} stabilized around -0.84 V vs. SCE throughout the test.

E_{corr} for A106 in MEA-B was stable around -0.83 V vs. SCE for approximately 200 h, then gradually increased to approximately -0.78 V vs. SCE up to approximately 340 h. A sharp increase in the E_{corr} was observed thereafter and eventually reached -0.45 V vs. SCE after approximately 426 h and stabilized around that value up to the testing duration of approximately 500 h.

For A106 in MEA-C, increases in E_{corr} started earlier. E_{corr} was initially stable around -0.82 V vs. SCE for 100 h, then gradually increased to approximately -0.75 V vs. SCE at 185 h. Subsequently, a sharp increase in the E_{corr} occurred and reached an approximate value of -0.49 V vs. SCE after approximately 236 h and stabilized around that value up to the testing duration of approximately 340 h.

3.2 Surface characterization of as-corroded A106

Surface characterization of as-corroded A106 samples after 185 h at 80°C in CO₂-loaded 5 M MEA solutions was carried out by SEM (Figure 5 and Figure S4) and XRD (Figure 6). For A106 in MEA-A and MEA-B, no notable protective layer of corrosion products was observed but porous and discontinuous Fe₃C residual after preferential dissolution of the ferrite phase, as shown in Figure 5 (a) and (c), Figure S4 (a) and (b), and Figure 6 (a) and (b). The relative intensity of peaks for Fe₃C residual decreased with decreasing pH, which is contradictory to the decreased R_p and R_{ct} at the lower pH indicating a thicker Fe₃C residual layer. This may be explained by exfoliation of the fragile porous Fe₃C residual as it grew on the A106 surface under the severe corrosion conditions. Some spheroid-shaped precipitates were observed on the surface of A106 after corrosion in MEA-A (Figure 5 (b)), and a much higher density of these precipitates was observed in MEA-B (Figure 5 (d)). However, the amount of these precipitates was not large enough to be detected due to the resolution limit of the XRD (Figure 6 (a) and (b)). With further decreasing solution pH (A106 in MEA-C), a dense layer of FeCO₃ was formed (Figure 5 (e) and (f), and Figure 6 (c)), which might be responsible for the increase in R_p (Figure 1) as well as functioning as a diffusion barrier for the species involved in the corrosion process (Figure 2 and 3).

Based on the observation of precipitates in MEA-A and MEA-B, a dense layer of FeCO_3 might be formed if the set time for the corrosion process is long enough. Longer time periods were thus studied with all other conditions constant. Figure 7 shows the corresponding XRD patterns of the three long-term as-corroded A106 samples. As for the case in MEA-A, it still looks similar to the test after 185 h although a time period more than 3 times longer was used (600 h), i.e., the surface was still mainly covered by the Fe_3C residual and little/no layer such as FeCO_3 detected by XRD. This is consistent with the observation by SEM, i.e., a dense layer of FeCO_3 was formed only in some small areas but most of the surface area was still covered by the discontinuous Fe_3C residual (Figure S5). With decreased solution pH (A106 in MEA-B), the Fe_3C residual was nearly absent and a mixture layer of FeCO_3 and magnetite (Fe_3O_4) was observed after approximately 434 h, which is different from the test after 185 h where only Fe_3C residual was seen. This corroborated our initial speculation that a dense layer of FeCO_3 could be formed if longer time was given (Figures 7 and S5). Moreover, this mixed layer of FeCO_3 and Fe_3O_4 formed after a shorter duration of approximately 339 h if the solution pH was further decreased (A106 in MEA-C in Figures 7 and S6). The Fe_3O_4 corrosion product was only observed at time periods >185 h, and its formation, along with FeCO_3 , will be explained in the discussion section.

3.3 Rust formation

In addition to the formation of FeCO_3 and/or Fe_3O_4 , rust was observed during the corrosion tests in naturally aerated CO_2 -loaded 5 M MEA solutions regardless of pH, as can be seen in one example with red corrosion products in Figure S2. Normally, a visible rust layer, mainly on all the other solid surfaces away from A106 such as the inside wall of the electrochemical cell, was observed only after 48 h. To understand the corrosion mechanism including the formation of rust, characterization was conducted by SEM and XRD on the rust powders after the collecting, cleaning, and drying procedures as described in the experimental section. Figure 8 shows SEM surface morphologies of the rust. The rust is composed of spheroid clusters with an average size of approximately 300 nm. Combining the XRD result (Figure 9) with rust data from others [44-48], the rust was found to be mainly composed of hematite (Fe_2O_3). Although a small amount of other components of rust, e.g., goethite, lepidocrocite, and

magnetite is possible, these compounds could not be identified as clearly as hematite by this technique [44-48]. Interestingly, rust was not observed on the A106 surface after any of the tests in this work. The possible reasons for this phenomenon will be reviewed in the discussion section.

4. Discussion

4.1 pH effect on initial corrosion process

The initial corrosion of A106 carbon steel was observed to accelerate with decreases in solution pH, evidenced by decreased R_p and R_{ct} shown in [Figures 1 and 2](#). Normally, in an aerated MEA-CO₂-H₂O/A106 system, the corrosion process involves one oxidation reaction of iron ([reaction \(19\)](#)) and four possible reduction reactions ([reactions 20 to 23](#)) [6, 8, 10, 11, 14].

Among the available oxidizing agents, insignificant changes in the concentrations of H₂O and dissolved oxygen (measured to be approximately 0.4 ppm at 80°C) were expected to occur with changes in the solution pH. With decreases in solution pH, reduction [reaction \(21\)](#) would be promoted, however, H⁺ has been reported to play an insignificant role in the corrosion process as a result of its extremely low total concentration (approximately 10⁻⁸ M) [10]. Therefore, to better understand how solution pH affects the corrosion process, the pH-dependent speciation was estimated under the operating conditions (i.e., CO₂-loaded 5 M MEA solution) at 80°C by Aspen Plus[®]. [Figure 10](#) shows the log of mole fractions of ions of HCO₃⁻ and CO₃²⁻ versus solution pH. Monotonic increases in the concentrations of HCO₃⁻ and CO₃²⁻ were seen with decreasing solution pH from approximately 10.0 to 7.0. Experimentally ([Table 1](#)), solution pHs were 8.4, 8.2, and 8.0 at 80°C for MEA-A, MEA-B, and MEA-C, respectively. The pH of these solutions

at 80°C was in a range where significant increases in HCO_3^- concentration occur. HCO_3^- was identified to be one of the two primary oxidizing agents (HCO_3^- and H_2O) in the aqueous MEA- CO_2 - H_2O system by Veawab and Aroonwilas [10]. Therefore, the dramatic increase in HCO_3^- would contribute to higher exchange current densities (i_0) and reversible potentials for the corresponding reduction reactions, and eventually result in a faster dissolution of A106 (Figures 1-3) [10, 16, 32, 49].

Also, the increase in HCO_3^- with decreased solution pH should increase the solubility of Fe^{2+} via complexation of $\text{Fe}(\text{CO}_3)_2^{2-}$ from pathways shown in reactions 1 and 24 [36, 50],

which could also promote the initial corrosion of A106 in CO_2 -loaded MEA solutions with decreases in solution pH.

Therefore, we attribute the increase in initial corrosion of A106 to increased HCO_3^- concentration (i.e., decreased solution pH). The corrosion process was apparently dominated by charge transfer regardless of the solution pH at this stage (≤ 115 h), as seen from the depressed semicircles in the Nyquist plots shown in Figures 2 and 3.

4.2 Dissolved oxygen effect

Dissolved oxygen can significantly affect corrosion processes in our system. One of the possible effects of dissolved oxygen on the corrosion behavior of A106 carbon steel in CO_2 -loaded MEA solutions is that it takes part in the reduction process directly as shown in reaction 23. While this may not be the dominant reduction reaction in the system due to its low concentration [6, 10], it would still contribute to a higher i_0 and reversible potential and accelerate dissolution of A106.

A second effect of dissolved oxygen, considered in this work to be a main reason for the very high corrosion of A106 in CO_2 -loaded MEA solution over long time periods (Figure 1), was to retard formation of a protective corrosion layer such as FeCO_3 on the surface of A106. When dissolved oxygen is present in the corrosion system, Fe^{2+} becomes unstable and some of which

can further oxidize to Fe^{3+} (reaction 25). Subsequently, Fe^{3+} can form less soluble corrosion products such as $\text{Fe}(\text{OH})_3$ when compared to other possible precipitates such as FeCO_3 and $\text{Fe}(\text{OH})_2$. Thus, $\text{Fe}(\text{OH})_3$ are likely to precipitate giving rise to rust corrosion products possibly via reactions 26-28 [8, 44].

Competitive precipitation amongst FeCO_3 (reaction 1), $\text{Fe}(\text{OH})_3$ (reaction 26), and $\text{Fe}(\text{OH})_2$ (reaction 29) may occur in the system, depending on the concentrations of Fe^{2+} , Fe^{3+} , OH^- , and CO_3^{2-} . To better understand the competitive process, corresponding K_{sp} , and the concentrations of Fe^{2+} and Fe^{3+} in the bulk solution under the experimental conditions were calculated, as described in detail in the supplementary material [51-54]. Although the concentration of Fe^{2+} was calculated to be 4 orders of magnitude higher than that of Fe^{3+} in the bulk solution, for example, approximately 73 ppm Fe^{2+} and approximately 41 ppb Fe^{3+} after 220 h (Figure 11), $\text{Fe}(\text{OH})_3$ precipitation might be more preferable to reactions 1 and 29 as the result of an approximately 26 and 21 orders of magnitude lower in the solubility constant of $\text{Fe}(\text{OH})_3$ than that of FeCO_3 and $\text{Fe}(\text{OH})_2$ at 80°C, respectively. That is, the K_{sp} was calculated to be 5.78×10^{-37} for $\text{Fe}(\text{OH})_3$, 3.24×10^{-11} for FeCO_3 , and 1.85×10^{-16} for $\text{Fe}(\text{OH})_2$ if no ionic strength effect was considered. Thus, in aerated alkanolamine-based solutions, Fe^{2+} would likely be oxidized by dissolved O_2 in solution, with Fe_2O_3 as the major end product (other oxides and/or hydroxides being possible) [44], as shown in Figure 9 and Figure S2. This was a continuous process, and thus a significant Fe^{2+} concentration would be consumed despite the low instantaneous concentration of dissolved O_2 (i.e., approximately 0.4 ppm). Therefore, the presence of dissolved O_2 may not allow enough Fe^{2+} to accumulate to the point (minimum δ_{SD}) that a desirable protective layer of FeCO_3 would form.

To confirm this indirect effect of dissolved oxygen on the corrosion of A106 by retarding the formation of a protective layer such as FeCO_3 via consuming Fe^{2+} , total dissolved Fe concentration in the solution was analyzed by ICP after corrosion testing for different durations in MEA-A under naturally aerated and anoxic conditions. The anoxic condition was conducted in an autoclave type stainless steel corrosion cell by purging ultrahigh purity N_2 (99.999%) to remove residual air from the head space, and completely sealed thereafter, the details of which were described in our previous work [9]. Figure 11 shows the total Fe concentrations versus immersion duration of A106 in MEA-A under anoxic and aerated environments. The changes in total Fe concentration showed a similar trend for both tests in anoxic and naturally aerated environments. That is, the Fe concentration increased first, decreased subsequently after reaching a relative maximum value, and eventually reached a somewhat stable value. The increase in dissolved Fe concentration with time was the result of the continuous anodic dissolution of A106 at the beginning, which is consistent with the observations from other researchers [7]. At this stage, little to no precipitation occurred. After reaching supersaturation of some species such as Fe(OH)_3 and/or FeCO_3 , precipitation would occur and the dissolved Fe concentration would be consumed, i.e., the total Fe concentration decreased at this stage. The total dissolved Fe concentration stabilizes with steady-state between A106 dissolution and formation of corrosion products such as Fe(OH)_3 and/or FeCO_3 . Notably, the total Fe concentration was much higher at all times in the anoxic condition, especially for the maximum value which was more than 4 times higher than in the aerated condition. This further supports the hypothesis that dissolved O_2 accelerates the consumption of Fe^{2+} by further oxidation to Fe^{3+} to form rust and prevents the FeCO_3 layer formation.

Almost none of the rust was observed on the surface of A106 carbon steel but on all other solid surfaces in the test cell for all 185 h corrosion experiments (Figures 5-6) [11-13]. The reason for this phenomenon is that Fe^{3+} is known to be unstable at the metal surface under these corrosion potentials (e.g., around -0.8 V vs. SCE) [40, 44]. However, in these aerated solutions the Fe^{2+} ions can be oxidized in solution to Fe^{3+} by dissolved oxygen, and precipitation of Fe(OH)_3 can then occur [44]. Theoretically, the precipitation would mostly start and subsequently grow laterally on the surface of solids (such as the inner wall of the electrochemical cell) at nucleation points/defect where minimum concentrations of Fe^{3+} and/or OH^- were required.

A third positive effect of dissolved O_2 was to promote passivation of carbon steel underneath the protective layer of $FeCO_3$, i.e., the formation of a passive layer of Fe_3O_4 [6, 13, 17], as evidenced by results for A106 pre-coated with $FeCO_3$ before and after corrosion in both naturally aerated and anoxic MEA-A in [Figure 12](#) and [Figures S7-S9](#). This effect is consistent with observations from other researchers from potentiodynamic scans where passivation was promoted by dissolved O_2 [6, 17].

Another effect of dissolved O_2 , not a focus of this work, accelerates degradation of amines to generate heat stable salts (HSS) such as carboxylic acid, glycolic acid, and oxalate, which increase the conductivity of amine-based solutions and encourage corrosion of the process units [5, 20-23, 55]. As for the study system, dissolved oxygen has multiple reactions with MEA and iron [3, 44-48, 56, 57], and oxidation products from MEA can affect the iron oxidation process and the generated iron ions can accelerate MEA oxidation [20, 21, 24, 56]. Thus, it is impossible to single out an individual reaction in such a system with so many components. We can speculate on the overall effect of dissolved oxygen on Fe and MEA. Previous work on MEA oxidation in our group has shown that minimal MEA oxidation would take place at 80°C over the time duration of the studies carried out in this work, but a large amount of rust is found to readily form in the MEA solution ([Figure S2](#) in supplementary material). This might indicate that dissolved oxygen has a preferential effect on iron than that on MEA under the testing conditions. Further work with well-designed experiments and/or simulations is necessary to fully understand the dissolved O_2 effect on MEA degradation as well as iron oxidation in this system.

4.3 pH effect on protective layer formation

4.3.1 $FeCO_3$ formation

To build a protective layer of $FeCO_3$ on the surface of A106, high concentrations of Fe^{2+} and/or CO_3^{2-} in the localized area near its surface are necessary to reach a minimum δ_{SD} of $FeCO_3$ [27-30]. However, formation of rust was evidenced above to be more preferable to the formation of $FeCO_3$ due to the existence of dissolved O_2 in the solution. Therefore, based on the reasoning presented above, a pH stabilization method was carried out to promote the formation of $FeCO_3$. As shown in [Figure 10](#), a dramatic increase in the HCO_3^- concentration can be achieved by decreasing the solution pH. When the solution pH decreased to approximately 8.0 at

80°C, a dense and protective layer of FeCO_3 was formed after 185 h (A106 in MEA-C in [Figure 5 \(e\) and \(f\)](#), [Figure S4](#), and [Figure 6 \(c\)](#)). This phenomenon might be explained by the following reasons.

The localized concentration of Fe^{2+} would be increased by a decreasing solution pH ([Figures 1-3](#)). After the dissolution process, diffusion into the bulk solution relies on natural convection in this system and a concentration gradient, and thus the Fe^{2+} concentration would be higher in the localized area near the A106 surface than anywhere else away from this surface ([Figure S12](#)) [57].

Due to the occurrence of a reduction reaction with HCO_3^- ([reaction 20](#)), i.e., one of the primary reduction reactions during the corrosion process, the concentration of CO_3^{2-} increased near the A106 surface ([Figure S12](#)). In addition, slight increases in the CO_3^{2-} concentration in the bulk solution were estimated with decreases in solution pH, as can be seen from [Figure 10](#).

Therefore, according to [equation 3](#), the highest δ_{SD} of FeCO_3 , i.e., our experimental results (R_p and R_{ct} values) and calculations (HCO_3^- and/or CO_3^{2-} concentrations) indicate the highest possibility to form FeCO_3 , would be near the A106 surface in the solution with the lowest pH (i.e., in MEA-C). Precipitation rates for alternative CO_2 -saturated solutions have been reported previously, demonstrating the dependence of precipitation on K_{sp} and δ_{SD} [28-30]. This is consistent with the observation from SEM micrographs that an increased density of FeCO_3 precipitates was observed with decreases in solution pH ([Figure 5 \(b\), \(d\), and \(f\)](#)). Precipitation of FeCO_3 would most likely start on the A106 surface at defect sites where the minimum concentrations of Fe^{2+} and/or CO_3^{2-} were required. Subsequently, more precipitates and lateral growth of FeCO_3 occurred and eventually a complete protective layer formed on the A106 surface.

4.3.2 *Passive layer formation*

For A106 in MEA-B and MEA-C, substantial increases in the E_{corr} occurred, and eventually the values stabilized around -0.45 V vs. SCE (after 426 h) and -0.49 V vs. SCE (after 236 h), respectively ([Figure 4](#)). These values indicated that spontaneous passivation of A106

beneath the formed FeCO_3 layer occurred [13, 27, 58, 59]. The ultimately resulting spontaneous passivation potential slightly decreased at a lower pH value, which is consistent with the results obtained by Han et al. in a CO_2 -loaded NaCl solution [59]. With a further increase in pH (i.e., A106 in MEA-A), insignificant changes in E_{corr} or no noticeable passivation occurred for nearly 600 h. These results exhibit that the time to reach spontaneous passivation was shorter at a lower pH, which suggests that the lower pH not only promoted FeCO_3 formation as mentioned but also the spontaneous passivation behavior of carbon steel in the aerated CO_2 -loaded MEA solution afterwards. This is consistent with previous observations by others that FeCO_3 could facilitate passivation of carbon steel [13, 58, 59]. This passivation behavior further inhibited corrosion of the underlying carbon steel as indicated by the apparent change to a diffusion-limited process corrosion behavior shown in [Figures 2 and 3](#).

Based on the characterization results shown in [Figures 7 and 12](#), a FeCO_3 layer might be gradually transformed into a passive layer of Fe_3O_4 via a further oxidation process shown in [reaction 30](#) [13, 27, 40].

Therefore, initial corrosion of A106 carbon steel in naturally aerated CO_2 -loaded 5 M MEA solution was accelerated by decreasing the solution pH. However, formation of a protective layer of FeCO_3 and subsequently a passive layer of Fe_3O_4 , which resulted in a dramatic decrease in the corrosion of A106, were promoted. This indicated that corrosion mitigation of process units made of carbon steel for post-combustion CO_2 capture may be achieved by a pH stabilization method. Also, to promote formation of a protective layer on the surface of carbon steel, methods which could retard rust formation could be pursued. From a corrosion point of view, [equation 18](#) should be considered in solvent design to enhance a protective FeCO_3 layer formation.

5. Conclusions

Corrosion of A106 carbon steel in naturally aerated CO_2 -loaded 5 M MEA solutions with addition of NaHCO_3 to adjust solution pH was evaluated at 80°C by electrochemical corrosion testing methods such as linear polarization resistance (LPR) testing, electrochemical impedance

spectroscopy (EIS), corrosion potential measurements, immersion corrosion in an autoclave type stainless steel cell, scanning electron microscopy (SEM), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectrometry (ICP-OES). The results showed that:

1. Initial corrosion, i.e., before formation of a complete protective layer of corrosion products such as FeCO_3 and Fe_3O_4 on the A106 surface, was accelerated in solution with lower pH.
2. Formation of a dense layer of FeCO_3 on the A106 surface, which provided diffusion resistance for oxidizing agents from solution to and the generated Fe^{2+} from the A106 surface, was promoted by decreasing the solution pH.
3. Spontaneous passivation of A106, which, together with the previously formed FeCO_3 layer, resulted in a dramatic decrease in corrosion and a change in the corrosion process from an apparent charge-transfer-limited process to a diffusion-limited process, was also promoted by decreasing the solution pH.
4. Dissolved oxygen was observed to play an important role in the overall corrosion process by (i) participating in the reduction process, (ii) retarding formation of a protective layer of FeCO_3 on the A106 surface via further oxidizing Fe^{2+} to form rust away from A106 surface, and (iii) promoting passivation of A106 underneath the FeCO_3 layer. Effect (ii) was expected to be a dominant effect with dissolved oxygen substantially changing the corrosion behavior of carbon steel in a post-combustion CO_2 capture system.
5. A pH stabilization method, obtained by adding a pH stabilizer such as NaHCO_3 , was shown to be an effective way to mitigate corrosion in MEA-based solutions. This method could be extended to other corrosive solvents for post-combustion CO_2 capture.

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Figure 1. Log of polarization resistance (R_p , $\Omega \text{ cm}^2$) as a function of time for A106 in naturally aerated CO_2 -loaded 5 M MEA solutions at 80°C to show the effect of pH.

Figure 2. Nyquist plots for A106 in naturally aerated CO_2 -loaded 5 M MEA solutions at 80°C after different time durations. The plot for A106 in MEA-A after 185 h is from our previous work [11].

Figure 3. Nyquist plots for A106 in naturally aerated CO_2 -loaded 5 M MEA solutions at 80°C after different time durations. The plot for A106 in MEA-A after 185 h is from our previous work [11].

Figure 4. Corrosion potential as a function of time for A106 in naturally aerated CO₂-loaded 5 M MEA solutions at 80°C. The curve for A106 in MEA-A is from our previous work [13].

Figure 5. SEM surface morphologies of A106 after approximately 185 h at 80°C in naturally aerated MEA-A ((a) and (b)), MEA-B ((c) and (d)), and MEA-C ((e) and (f)).

Figure 6. XRD patterns (obtained with 2Theta/Omega scan) for A106 after approximately 185 h at 80°C in naturally aerated (a) MEA-A, (b) MEA-B, and (c) MEA-C.

Figure 7. XRD patterns (obtained with 2Theta/Omega scan) for A106 in naturally aerated (a) MEA-A, (b) MEA-B, and (c) MEA-C after approximately 601 h, 434 h, and 339 h at 80°C, respectively.

Figure 8. SEM micrographs of rust powders collected from the solution from the electrochemical corrosion cell as shown in Figure S1.

Figure 9. XRD patterns (obtained with 2Theta/Omega scan) of rust from electrochemical corrosion cell shown in Figure S1. Peak positions for standard of hematite (Fe_2O_3 , PDF card No.: 00-001-1053) are also provided at the bottom of the figure.

Figure 10. Estimated speciation of HCO_3^- and CO_3^{2-} , i.e., log of mole fractions, versus solution pH of CO_2 -loaded 5 M MEA-based solutions at 80°C . The presented mole fraction is a function of all species in solution, including all molecular (e.g., H_2O and MEA) and ionic species.

Figure 11. Fe concentration vs. immersion duration of A106 in both anoxic and naturally aerated MEA-A at 80°C.

Figure 12. XRD patterns (obtained by grazing incidence X-ray diffraction with the incidence angle of 1°) of (a) as-fabricated FeCO_3 -precoated A106 from 0.43 C/N CO_2 -loaded 4 M piperazine solution at 80°C for 48 h. (b) and (c) are (a) after 1769 h in anoxic and 1152 h in naturally aerated MEA-A at 80°C , respectively.

Table 1 Solution conditions of aerated 0.43 C/N CO₂-loaded 5 M MEA with addition of different amounts of NaHCO₃

Solutions	NaHCO ₃ concentration (M)	Alkalinity at RT (mol amine/kg solution)	CO ₂ at RT (mol CO ₂ /kg solution)	CO ₂ loading at RT (C/N)	pH at RT	pH at 80°C
MEA-A	0	4.48	1.94	0.43	9.7	8.4
MEA-B	0.5	4.86	2.27	0.47	9.3	8.2
MEA-C	1.0	5.12	2.50	0.49	9.1	8.0