CO₂ loading-dependent corrosion of carbon steel and formation of corrosion products in anoxic 30 wt.% monoethanolamine-based solutions

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Abstract

Corrosion of A106 carbon steel in anoxic 30 wt.% monoethanolamine-based solutions (one example of a corrosive solvent for post-combustion CO₂ capture) with CO₂ loadings ranging from 0.24 to 0.53 mol CO₂/mol amine is investigated. Results show that the corrosion and formation of a protective layer of corrosion products on the A106 surface are strongly CO₂ loading-dependent. That is, initial corrosion is accelerated with increased CO₂ loading. However, the formation of chukanovite and subsequently siderite, which dramatically inhibits the corrosion, was promoted with increasing CO₂ loading. Chukanovite is a metastable intermediate corrosion product which transforms into siderite. Possible mechanisms are discussed.

Keywords: A. carbon steel, B. weight loss, B. XRD, B. SEM, B. ICP-OES, C. alkaline corrosion

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1. Introduction

With an increasing understanding of global warming, the Intergovernmental Panel on Climate Change (IPCC) reported that scientists were more than 95% certain that global warming is exacerbated by increasing concentrations of greenhouse gases (mostly CO₂) produced by anthropogenic activities [1]. Fossil fuel burning sources such as power plants have produced about three-quarters of the total increase in CO₂ over the past 20 years [2]. One of the most promising technologies to mitigate these emissions from large-scale fossil fuel burning power plants is a post-combustion CO₂ capture process with application of aqueous alkanolamine solutions [3, 4]. Generally, the capture of CO₂ from flue gas involves two processes, scrubbing and stripping, with working temperatures in the range of 40-50°C and 110-120°C, respectively [3-6]. However, a major issue for this technique is that most amine solutions become highly corrosive after capturing a certain amount of CO₂ at these temperatures [4-11]. The case is made worse by the coexistence of 4-8% of oxygen and traces of SO₂ in flue gas after the desulfurization pretreatment process, some of which dissolves in the amine solution during the capture process. Subsequently, these additional oxidizing agents can take part in electrochemical reactions directly and/or cause the formation of heat stable salts (HSS) such as carboxylic acid, glycolic acid, and oxalate, which increases the conductivity of the amine-based solution and encourages corrosion of the process units [3, 8, 9, 11, 12].

A significant decrease in corrosion was observed with the formation of a dense layer of corrosion products on the surface of carbon steel such as siderite (FeCO₃), maghemite (γ-Fe₂O₃), magnetite (Fe₃O₄), goethite (FeOOH), or a combination of them, and their formation is dependent on factors such as CO₂ loading, O₂ and SO₂ concentration, amine-structure, and temperature [5, 6, 10, 11, 13, 14]. For example, a thick, dense, and protective layer of FeCO₃ was formed quickly (less than 15 h) in a CO₂-loaded piperazine-based solution, a heterocyclic secondary amine [5, 14]. However, no notable layer was observed under similar conditions with a primary amine solution, monoethanolamine (MEA), after 200 h [5, 7]. Also, O₂ and HSS were reported to retard the formation of a protective layer of FeCO₃ in a MEA-based solution [13].

Thus, for the purpose of better protecting process units such as the absorber and stripper columns from corrosion, a comprehensive understanding of the effect of these factors such as CO₂ loading, O₂, and other trace impurities of SO₂, SO₃, and NO_x on corrosion as well as formation of

corrosion products is required. Extensive research data are available in the open literature about the effect of these factors on the corrosion mechanism of carbon steel in CO₂-loaded amine-based solutions normally under short-term electrochemical measurements at temperatures no higher than 80°C and atmospheric pressure or long-term pilot scale CO₂ capture conditions [5-14]. However, long-term evaluation of a single or combination of factors on the corrosion behavior as well as the formation of corrosion products in a unit that can simulate conditions such as temperature, pressure, and solution flow more relevant to utility CO₂ capture systems, which will provide a more comprehensive understanding on corrosion and protection in a post-combustion CO₂ capture process, is still lacking.

In this work, the effect of CO₂ loading on the corrosion of carbon steel as well as the formation of corrosion products was studied over extended time periods in an anoxic closed system with the application of an autoclave-type corrosion cell in 30 wt.% MEA-based solutions. These conditions were chosen to avoid corrosion products resulting from O₂ in an effort to investigate protective carbonate-based corrosion products. The 30 wt.% MEA-based solutions were chosen for this study due to its corrosivity [5-13], and also because it is one of the most recognized benchmark industrial solvents due to its cost-effectiveness, high capacity for CO₂, fast reaction kinetics, and high removal efficiency [3]. The solvent temperatures of 80°C and 120°C were selected to simulate the cross-over heat exchanger operating condition (between the stripper and absorber) as well as the stripping condition. Under certain circumstances, chukanovite (Fe₂(OH)₂CO₃) was observed to be formed and likely to transform into FeCO₃. Furthermore, the formed corrosion layer was protective. To this end, if no significant increase in the total capital cost for CO₂ capture is required, a pretreatment process to remove oxygen (that retards the formation of a protective layer of FeCO₃ [13]) from the flue gas is recommended in this paper. To our knowledge, this is the first time Fe₂(OH)₂CO₃ formation has been observed in an amine-based solution for post-combustion CO₂ capture. This work contributes to a better understanding of corrosion, in-situ corrosion protection, and ultimately process cost reduction in an amine-based post-combustion CO₂ capture system. In this study, the corrosion rates were measured by a mass loss method. Surface characterization, solution analysis, and simulation of solution speciation were conducted to understand the corrosion as well as the formation of Fe₂(OH)₂CO₃ and FeCO₃.

2. Experimental

2.1 Sample preparation

A106 grade B carbon steel, usually designed to be used as seamless pipe at high temperature and pressure, was used for corrosion testing in this work. The nominal chemical compositions (in weight percent) of A106 are 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. Previous characterization results showed that A106 is composed of two different phases, ferrite and pearlite [5, 7]. Overall, it is composed of two phases of ferrite and a lamellar structured Fe_3C . All of the tested coupons with dimensions of 40 mm $\times$ 13 mm $\times$ 2 mm were cut from A106 pipes. The samples were ground with SiC paper to a final 800 grit, and then ultrasonically cleaned with deionized water and acetone.

2.2 Immersion corrosion testing

After measurements of the dimensions and weight, coupons were hung onto non-conductive racks and separated by PTFE spacers with a length of 10 mm. The racks with coupons were put into a stainless steel autoclave-type corrosion cell and fully submerged into prepared volumes of solution (approximately 4 L) according to ASTM G4-95 [15]. Figure 1 shows a schematic of the corrosion cell, the details of which were described in our previous work [7, 14]. Briefly, the solution was circulated by a pump between a heat exchanger cell and the reactor where the coupons were placed. To minimize the effect of O_2 on the corrosion for this study, the system was purged with high purity N_2 or CO_2 with a flow rate of 4 L/min for 1 h to remove residual air in the head zone of the pressure vessel before every run. Corrosion experiments were conducted in 30 wt.% MEA-based solutions (with the balance being deionized water) with different CO_2 loadings and temperatures.

A set of samples (three coupons) was removed at set intervals to study the impact of time on corrosion. After being removed, the coupons were cleaned. To prevent destruction of the corrosion product from the sample surface by force, the samples were submerged carefully in DI water and acetone sequentially, and then placed in individually labeled plastic sealed sample bags after being slowly dried by compressed air. To prevent further oxidation, the corroded samples were stored in a vacuum desiccator until further analysis was conducted. Two of the three corroded coupons were used to calculate the average corrosion rates after each run from various CO_2 -loaded

MEA-based solutions by the mass loss method described elsewhere [7, 14]. The third corroded coupon was used for surface and cross-section characterization.

2.3 Characterization methods

To understand the corrosion mechanisms for A106 in CO₂-loaded MEA-based solutions under different durations, the collected coupons were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

A Hitachi S-4800 field emission SEM was used to characterize surface morphologies of the corroded samples. Also, select samples were sealed using a non-destructive resin and subsequently ground and polished for cross-sectional characterization. A voltage of 15 kV and a current of 20 μ A were used for SEM characterizations.

All 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. A parallel beam X-ray source was selected by using a cross beam optics (CBO) selection slit. The soller-slit 5.0° was used as an incident parallel slit. The size of the beam-defining collimating slit was 10 mm $\times$ 10 mm. To reduce the background from peak to background ratio (P/B ratio), a diffracted beam monochromator (DBM), which was made of graphite, was used to eliminate the white X-rays, fluorescent X-rays, and K β from the diffraction beam. Also, a receiving optical device of PSA 0.114° was used. The penetration of X-rays can be varied by different scan modes, which provide information on corrosion products formed under different stages. Thus, with all the aforementioned optical components as well as conditions being the same, both the scan modes of $2\theta/\Omega$ by which an offset can be put in for Ω to avoid the effect of roughness of samples and grazing incidence X-ray diffraction (GIXRD) with an incidence angle (Ω) of 1° by which a thin layer of corrosion products from the outside surface could be identified were applied. With this incidence angle, the penetration depth for the grazing incidence diffraction was calculated to be less than 1 μ m for a FeCO₃ matrix [16]. For the $2\theta/\Omega$ scan, Ω also changes in a way that is linked to 2θ . The 2θ ranges from 10 to 90° with a scan rate of 0.5°/min for both scan modes. To make XRD patterns reliable and comparable to each other, optical alignment was conducted every week, and sample alignment was conducted for each sample.

All the diffraction patterns were analyzed in the PDXL2 software with the database of ICDD PDF-2 release 2012. Quantitative analysis for phases of the formed corrosion products was carried out for most of the samples by determining the relative intensity ratio (RIR) from the corresponding diffracted patterns.

The effect of air exposure on the surface of the as-corroded samples from drying, sample transfer, and XRD analysis was observed to be beyond the resolution for these applied characterization methods. No measurable oxidation effect from these processes on the presented results was expected in this work.

2.4 Liquid analysis

Solution alkalinity, CO₂ loading, and pH were analyzed at room temperature before and after each run. The alkalinity of the solution, i.e., the ability of a solution to accept a proton (or neutralize an acid) which in our system is nearly directly the total amine content in the solution (mol amine/kg solution), was determined by acid titration using a MetrohmTitrand 836. The CO₂ content of the loaded solutions (mol CO₂/kg solution) was analyzed by an acid-base method. In this method, phosphoric acid liberates CO₂ from MEA solutions which is transported by nitrogen gas to a CO₂ analyzer for quantitative determination. CO₂ loading values reported herein are the CO₂ content from the CO₂ analyzer divided by the total alkalinity obtained from the alkalinity measurement (mol CO₂/mol amine, C/N). The pH was measured at ambient temperature using a temperature corrected probe and two point calibration. Calibration was conducted every time before the first measurement in a day.

2.5 Fe concentration analysis

The concentration of dissolved Fe in MEA-based solutions after certain durations (normally after each run) was analyzed on a Varian 720-ES spectrometer (inductively coupled plasma optical emission spectrometry, ICP-OES), where the solution sample was nebulized and subsequently the aerosol was carried by an argon gas stream into an argon plasma. Before measurement, the instrument was calibrated using certified reference materials (CRMs) for iron which are manufactured by VHG. The radio frequency (RF) signal generator power is 1300 W. The rates for sample intake, plasma flow, and auxiliary gas are 1 mL/min, 15 L/min, and 1.5 L/min, respectively. Each sample solution, with a weight of 2.5-5.0 g, was digested using a combination

of nitric acid (50 vol.%) and hydrochloric acid (50 vol.%) for analysis. The experiments were repeated at least two times and the average is reported in this work. Because the experiments were designed and conducted under anoxic conditions (dissolved oxygen was measured to be <0.4 ppm at 80°C), Fe^{3+} concentration was expected to be insignificant in the solution compared to Fe^{2+} after corrosion. Thus, Fe concentration obtained by ICP analysis was assumed to be mainly of Fe^{2+} unless difference mentioned.

2.6 Solution speciation

To better understand the corrosion behavior observed from the experiments, Aspen Plus® with the ENRTL-RK activity coefficient model was applied to investigate solution chemical behavior at a microscopic level for given operating conditions such as CO_2 loading, temperature, and pressure as for the experiments. Since the total iron ion concentration obtained from ICP analysis was very small (e.g. <300 ppm) when compared to the major species in solution, it was expected that the dissolution of iron into the solutions would make no noticeable quantitative effect on the solution speciation as well as on the solution ionic strength (Figure S1 in supplementary material). Therefore, little to no change of the solution speciation (i.e., the major species) in the bulk solution was expected with changes in immersion duration.

3. Results

The 30 wt.% MEA-based solutions with CO_2 loadings of 0.24 C/N and 0.43 C/N were prepared by sparging a mixture gas of 1.2 L/min CO_2 and 0.8 L/min N_2 at room temperature. Solutions with desired CO_2 loadings were put into the corrosion cell and subsequently high purity N_2 was used as a purging gas to remove residual air in the head zone. Solutions with a CO_2 loading of 0.53 C/N were obtained first by pouring a previously prepared 0.43 C/N CO_2 -loaded solution into the corrosion cell followed by purging with high purity CO_2 to remove residual air in the head zone. Dissolved O_2 can have a strong effect on these corrosion systems, as noted in Figures S8-S14 and was therefore purged from the system to better investigate the effect of CO_2 loadings. All the operational conditions are listed in Table 1. The details of each operation process were described in the experimental section.

3.1 CO_2 effect

Figure 2 shows corrosion rates of A106 carbon steels in 30 wt.% MEA-based solutions with different CO₂ loadings at 80 and 120°C. The initial corrosion rate (after 147 h) was $5.9 \pm 0.1 \text{ g m}^{-2} \text{ d}^{-1}$ in the solution with low CO₂ loading of 0.24 C/N at 80°C. Corrosion data were not collected at earlier time periods due to the low overall corrosion rate for the 0.24 C/N system. Insignificant changes in the corrosion rate were observed with increases in immersion duration to 384 h. With increased CO₂ loadings, however, initial corrosion rates were significantly higher, $76.7 \pm 1.8 \text{ g m}^{-2} \text{ d}^{-1}$ (after 50 h) and $97.5 \pm 2.3 \text{ g m}^{-2} \text{ d}^{-1}$ (after 50 h) for 0.43 C/N and 0.53 C/N, respectively, at 80°C. This is consistent with results reported by others previously and might be due to an increased cathodic reaction rate by increasing CO₂ loading [5, 9, 11]. For corrosion in solution with a CO₂ loading of 0.43 C/N, insignificant changes in the corrosion rate were observed from 50 h to 125 h, but a sharp decrease in corrosion rate occurred thereafter (up to 383 h). The corrosion rate was $39.9 \pm 0.2 \text{ g m}^{-2} \text{ d}^{-1}$ and approximately half its initial rate ($76.7 \pm 1.8 \text{ g m}^{-2} \text{ d}^{-1}$). However, for the case with a CO₂ loading of 0.53 C/N, a monotonic decrease in corrosion rate with time was observed, and the corrosion rate after 383 h ($31.6 \pm 0.5 \text{ g m}^{-2} \text{ d}^{-1}$) was one third of its initial rate ($97.5 \pm 2.3 \text{ g m}^{-2} \text{ d}^{-1}$). Interestingly, the corrosion rate after 383 h was slightly lower in the solution with a CO₂ loading of 0.53 C/N than that with a CO₂ loading of 0.43 C/N. This might be due to formation of a denser layer of corrosion products such as FeCO₃ in the case with a higher CO₂ loading of 0.53 C/N [5, 14].

To further understand the effects of CO₂ loading on corrosion, surface characterization by SEM as well as XRD was carried out on the corroded samples. Figure 3 shows SEM surface morphologies of corroded A106 in 0.24 C/N CO₂-loaded 30 wt.% MEA-based solutions at 80°C after different immersion durations. Combined with their corresponding XRD patterns (Figures S2 and S3 in supplementary material), no notable protective layer such as FeCO₃ was observed in addition to the customary Fe₃C residual. This might be the reason for its insignificant changes in the corrosion rate with changes in immersion duration up to 384 h (Figure 2) although the surface coverage by the porous Fe₃C residual increased (Figure 3).

Similarly, no layer of FeCO₃ and/or Fe₂(OH)₂CO₃ was formed before 125 h in the case with a CO₂ loading of 0.43 C/N, but the porous and lamellar-structured Fe₃C remained ((a) and (b) in Figures 4 and 5), and this might be the reason that little change in corrosion rate was observed during this period (Figure 2). However, with further increases in immersion duration to 383 h,

$\text{Fe}_2(\text{OH})_2\text{CO}_3$ with a blade-shape morphology develops in addition to Fe_3C residual, as can be seen from Figures 4 (c) and (d) and XRD in Figure 5 (c). The morphology of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ formed in our system is similar to that reported by others in CO_2 -loaded brine and contaminated groundwater treatment systems [17-19]. Also, the disappearance and/or weakening of iron peaks located at approximately 45° , 65° , and 82° indicated that the mixture layer, mostly $\text{Fe}_2(\text{OH})_2\text{CO}_3$ (Table S1 in supplementary material), was thick enough that X-rays could not penetrate it to reach the A106 carbon steel substrate. This result is consistent with a thickness of approximately 60 μm from its corresponding cross-sectional morphology as given in Figure S4 in the supplementary material. Formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ led to a decrease in corrosion rate by blocking the A106 surface from corrosive species.

With increases in CO_2 loading to 0.53 C/N, similar to 0.43 C/N, only Fe_3C residual was seen after 50 h ((a) in Figures 6 and 7). However, a mixture layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ (blade-shaped as labeled in Figure 6 (c)) and FeCO_3 (spheroid-shaped as arrowed in Figure 6 (c)) was formed after 125 h and remained with increasing duration up to 383 h (Figure 6 (b)-(e), and Figure 7 (b) and (c)). This resulted in a sharp decrease in the corrosion rate as shown in Figure 2. In addition, from their corresponding RIR calculations, the content of FeCO_3 in the top layer that was able to be penetrated by X-rays increased from approximately 40% to approximately 60% with increases in duration from 125 h to 383 h (Table S1 in supplementary material). Combining all of these results from the anoxic sealed corrosion cell, it shows that the corrosion of carbon steel in MEA-based solutions as well as the formation of corrosion products of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and/or FeCO_3 on its surface were strongly dependent on the CO_2 loading. The change in CO_2 loading could affect kinetics of cathodic reactions by changing concentrations of HCO_3^- and H^+ (pH) and also hasten the formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and/or FeCO_3 and subsequently reduce the corrosion rate.

3.2 Temperature effect

Formation of a protective layer of FeCO_3 was expected to be favored under higher temperature due to its decreased solubility limit [20]. Therefore, in addition to simulating the cross-over heat exchanger operating condition, i.e., approximately 80°C , corrosion experiments were conducted at 120°C to simulate the conditions at the top of the stripper in the capture process with a CO_2 loading of 0.53 C/N. For the case at 120°C , the corrosion rate decreased sharply from $33.0 \pm 0.3 \text{ g m}^{-2} \text{ d}^{-1}$ to $12.9 \pm 0.5 \text{ g m}^{-2} \text{ d}^{-1}$ with increasing duration from 150 h to 368 h, and then

gradually decreased to $7.9 \pm 0.2 \text{ g m}^{-2} \text{ d}^{-1}$ up to a duration of 595 h. This is comparable to the corrosion rate in the solution with a much lower CO_2 loading of 0.24 C/N and a lower temperature of 80°C ($8.0 \pm 0.6 \text{ g m}^{-2} \text{ d}^{-1}$ after 384 h), as shown in Figure 2. Notably, when compared to the corrosion at 80°C with a same CO_2 loading of 0.53 C/N, the corrosion rate was approximately 4 times lower at 120°C with similar immersion durations (Figure 2). This might be due to favorable kinetics resulting in the formation of a denser layer with more spheroid-shaped FeCO_3 on the A106 surface at 120°C than that at 80°C (Figures 6 and 8 and Table S1 in supplementary material).

A number of nodules with an approximate size of $5 \mu\text{m}$ as well as blade-shaped clusters were observed on top of the surface (Figure 8 (a)). Higher magnification showed that the nodules had a spheroid morphology which was similar to most of the corrosion products formed on the surface (Figure 8 (b)). Combined with the corresponding XRD patterns in Figure 9 (a) and previous results at 80°C , the spheroid-shaped product was mainly composed of FeCO_3 and the blade-shaped product was mainly $\text{Fe}_2(\text{OH})_2\text{CO}_3$, as indicated in Figure 8 (a)-(c). Notably, with increases in immersion duration, the blade-shaped $\text{Fe}_2(\text{OH})_2\text{CO}_3$ disappeared gradually on the surface (Figure 8 (d) and (e)). This is consistent with the XRD patterns shown in Figure 9 where the peaks for $\text{Fe}_2(\text{OH})_2\text{CO}_3$ around 12° and 14° disappear gradually and suggest that the formed $\text{Fe}_2(\text{OH})_2\text{CO}_3$ was metastable and transformed into a more stable phase of FeCO_3 with increases in immersion duration [17, 18, 21, 22]. FeCO_3 nodules were still seen on the surface after 595 h as shown by arrows in Figure 8 (d). Moreover, the lower magnification surface view after corrosion (Figure 8 (a) and (d)) showed a similar microstructure morphology to A106 carbon steel after etching in nital solution [5, 7], which indicates the preferential dissolution of the ferrite phase occurs during the corrosion process. This is consistent with the curved interface between A106 carbon steel and the formed layer showing that the corrosion was non-uniform (see cross-section in Figure 8 (f)). However, the curved interface would increase contact area to the A106 substrate, which might be able to increase adhesion of the formed corrosion layer to A106 and subsequently increase resistance to erosion from spray as well as movement of solution in a CO_2 capture system. In addition, the corresponding cross-sectional morphology showed that the formed mixture layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and FeCO_3 (mostly FeCO_3) was dense, which would function as a physical barrier for transport of corrosive species and corrosion products such as dissolved iron ions to and from the surface of the A106, where both anodic and cathodic reactions occur. Eventually, this dense

layer resulted in a low corrosion rate of A106 at 120°C, comparable to the case with a much lower CO₂ loading of 0.24 C/N at 80°C (Figure 2).

To obtain an enhanced diffraction from the very outside thin layer of the corroded surface as well as to more fully understand the formation of Fe₂(OH)₂CO₃ and FeCO₃ during different stages, diffraction patterns for the samples after corrosion in 0.53 C/N loaded 30 wt.% MEA-based solutions at 120°C were obtained by GIXRD in addition to the 2 θ / Ω scans, as shown in Figure 10. When compared to the XRD patterns obtained by 2 θ / Ω scans (Figure 9), the peaks for A106 carbon steel around 45°, 65°, and 82° as well as the peaks for Fe₂(OH)₂CO₃ around 24°, 34°, 35°, 49°, and 58° were nearly absent. Although the peaks for Fe₂(OH)₂CO₃ around 12° and 14° remained, a significant decrease in the relative intensities was seen. From the corresponding RIR calculations (as given in Table S1 in supplementary material), the FeCO₃ content in the very outside thin layer of <1 μ m (calculated from the XRD patterns by the GIXRD scan) was approximately 95 %, which was higher than that of approximately 85% in a relatively thicker layer from the outside surface (calculated from the XRD patterns by the 2 θ / Ω scan). This indicated that the very outside thin layer was mainly composed of FeCO₃.

4. Discussion

4.1 CO₂ loading effect on initial corrosion

The initial corrosion rate, prior to formation of a notable layer of corrosion product (Fe₂(OH)₂CO₃ and/or FeCO₃) on the surface of A106 carbon steel, was observed to increase from 5.9±0.1 g m⁻² d⁻¹ (after 147 h) to 76.7±1.8 g m⁻² d⁻¹ (after 50 h) and to 97.5±2.3 g m⁻² d⁻¹ (after 50 h) with increases in CO₂ loading from 0.24 C/N to 0.43 C/N and to 0.53 C/N, respectively (Figure 2). Normally, in an aqueous amine-CO₂ system, the corrosion process involves one oxidation reaction of iron (reaction (1)) and three reduction reactions (from reaction 2 to 4), i.e, reduction of bicarbonate ions (HCO₃⁻), reduction of protons (H⁺), and reduction of water (H₂O) [7, 9, 14].

Dissolution of iron:

Reduction of corrosive species:

Among the three oxidizing agents, insignificant changes in the concentration of H_2O was expected to occur with changes in CO_2 loading. However, dramatic changes in the speciation of H^+ and HCO_3^- are known to depend on CO_2 loading. Although H^+ was reported to play an insignificant role in the total reduction reaction as a result of its extremely low total concentration, HCO_3^- was identified to be one of the two primary oxidizing agents (HCO_3^- and H_2O) in the aqueous amine- CO_2 system by Veawab and Aroonwilas from their simulation results [9]. Therefore, to better understand how CO_2 loading affects the total reduction reactions and subsequently the corrosion of A106, the solution speciation was estimated under operating conditions at different CO_2 loadings at 80°C . Figure 11 shows the mole fractions of ions of HCO_3^- and CO_3^{2-} as well as pH obtained from the calculation. Significant increases in the concentration of HCO_3^- (in mole fraction) from 5.6×10^{-4} to 5.4×10^{-3} and to 8.6×10^{-3} were seen with increasing CO_2 loading from 0.24 C/N to 0.43 C/N and to 0.53 C/N, respectively. Correspondingly, the pH at 80°C decreased from 8.36 to 7.04 and to 6.85. These increasing amounts of HCO_3^- and H^+ would contribute to higher exchange current densities (i_0) and reversible potentials for the corresponding reduction reactions, and eventually result in a higher corrosion rate of A106 [9]. This phenomenon was also observed in other aqueous amine systems such as 30 wt.% piperazine solutions [5].

In addition, the increasing amount of HCO_3^- was reported to increase the solubility of Fe^{2+} by forming a stable complex of $\text{Fe}(\text{CO}_3)_2^{2-}$ from pathways shown in reactions (5) and (6) [23, 24],

Formation of $\text{Fe}(\text{CO}_3)_2^{2-}$ complex $\therefore$

which is consistent with the initial observation of higher dissolved Fe concentration with higher CO_2 loading, as shown in Figure 12. This might be one of the reasons contributing to the higher initial corrosion rate with increases in CO_2 loading.

4.2 Formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$

A significant decrease in corrosion rate was observed when a layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and/or FeCO_3 was formed on the surface of A106 (Figure 2). Nearly no precipitates of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and/or FeCO_3 on the surface of A106 were observed after corrosion in the solution with low CO_2 loading of 0.24 C/N up to the testing duration of 384 h at 80°C (Figure 3 (b)). However, with increases in CO_2 loading to 0.43 C/N, a layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ (mixed with some Fe_3C residual) was formed after a similar testing duration of 383 h (Figure 4 (c) and (d), and Figure 5). Moreover, with further increases in CO_2 loading to 0.53 C/N, a mixture layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and FeCO_3 (mixed with some Fe_3C residual) formed earlier after only 125 h (Figure 6 (b) and (c), and Figure 7).

The formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$, the first time it has been observed in a CO_2 -loaded amine-based solution, was previously found on carbon steel surfaces in anoxic corrosion environments such as clay media [17, 19, 21, 22]. This is consistent with the operating conditions in this work where residual air was removed in the head zone by purging with N_2 or CO_2 . $\text{Fe}_2(\text{OH})_2\text{CO}_3$ was reported to be formed via the reactions shown in (7) and (8) [17-19, 21-24].

Formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$:

The precipitation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ in the aqueous amine solution required minimum concentrations of Fe^{2+} and CO_3^{2-} to reach the solubility constant (K_{sp}) of $\text{Fe}_2(\text{OH})_2\text{CO}_3$. The faster dissolution of Fe (i.e. higher corrosion rate) at the very beginning would generate more Fe^{2+} in solutions with higher CO_2 loadings (Figure 12). This is especially the case in localized areas near the A106 surface. The speciation of CO_3^{2-} was shown to increase slightly from 1.2×10^{-2} mol/L to 3.3×10^{-2} mol/L and to 3.7×10^{-2} mol/L with increases in CO_2 loading from 0.24 C/N to 0.43 C/N and to 0.53 C/N. In addition, reaction (9), obtained by combining reactions (7) and (8), shows that the formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ is dependent on the localized pH near the steel surface. Although the localized pH was unavailable, the bulk pH decreases from 8.36 to 7.04 and to 6.85 at 80°C with increases in CO_2 loading from 0.24 C/N to 0.43 C/N and to 0.53 C/N.

Dissolution of $\text{Fe}_2(\text{OH})_2\text{CO}_3$:

There is a lack of thermodynamic data and K_{sp} for $\text{Fe}_2(\text{OH})_2\text{CO}_3$ at 80°C in the open literature, but, according to Refait's group [25, 26], the formation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ is strongly dependent on the relative concentrations of Fe^{2+} , OH^- , and CO_3^{2-} in the system. That is, a unique layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ was able to be formed if the ratio of Fe^{2+} concentration to OH^- concentration ($[\text{Fe}^{2+}]/[\text{OH}^-]$) is greater than 1 and at the same time the ratio of CO_3^{2-} concentration ($[\text{CO}_3^{2-}]$) to $[\text{OH}^-]$ is greater than 0.5. In the solutions with CO_2 loadings of 0.24 C/N, 0.43 C/N, and 0.53 C/N at 80°C, the analyzed maximum $[\text{Fe}^{2+}]$ were approximately 1.6×10^{-4} mol/L, 5×10^{-4} mol/L, and 5×10^{-4} mol/L (calculated from Figure 12); the $[\text{OH}^-]$ were 2.9×10^{-4} mol/L, 2.7×10^{-5} mol/L, and 1.7×10^{-5} mol/L (simulated by Aspen Plus®); and the $[\text{CO}_3^{2-}]$ were 1.2×10^{-2} mol/L, 3.3×10^{-2} mol/L, and 3.7×10^{-2} mol/L (simulated by Aspen Plus®), respectively. Therefore, for the cases with CO_2 loadings of 0.24 C/N, 0.43 C/N, and 0.53 C/N, $[\text{Fe}^{2+}]/[\text{OH}^-]$ are approximately 0.6, 19, and 29, and $[\text{CO}_3^{2-}]/[\text{OH}^-]$ are approximately 41, 1222, and 2176, respectively. These concentrations are consistent with the observations that $\text{Fe}_2(\text{OH})_2\text{CO}_3$ was formed in solutions with CO_2 loadings of 0.43 C/N as well as 0.53 C/N.

4.3 Formation of FeCO_3

In addition to $\text{Fe}_2(\text{OH})_2\text{CO}_3$, FeCO_3 was observed to be formed on the A106 surface only after 125 h in the solution with a CO_2 loading of 0.53 C/N and a temperature of 80°C, as can be seen from Figures 6 and 7. One possible pathway for the formation of FeCO_3 is by its precipitation directly in the solutions as shown in reaction (5). This requires that the area near the A106 surface reaches the solubility limit of FeCO_3 or to reach a minimum saturation degree (i.e. supersaturation) in this aqueous amine system [20, 27]. Assuming the solubility constant (K_{sp}) of FeCO_3 in the CO_2 -amine- H_2O system is similar to that in a CO_2 -NaCl- H_2O system, the K_{sp} for FeCO_3 was calculated with CO_2 loadings of 0.24 C/N, 0.43 C/N, and 0.53 C/N at 80°C according to the equation reported by Sun et al. [20]. The reaction quotient of reaction (5) (Q), obtained by multiplying concentrations of Fe^{2+} and CO_3^{2-} as given in equation (11), is introduced here to show changes in concentration with changes in experimental conditions. In the special case that the system reaches equilibrium, Q is constant and equal to K_{sp} for FeCO_3 .

$$Q = [\text{Fe}^{2+}][\text{CO}_3^{2-}] \quad (11)$$

Because corrosion was conducted in an anoxic environment, the Fe concentration obtained from ICP analysis was assumed to be only from Fe^{2+} in the solution which was free and available for the precipitation of FeCO_3 . To demonstrate the possibility for precipitation of FeCO_3 in solutions with different CO_2 loadings at 80°C , the maximum Q values are calculated and listed in Table 2. The results showed that all the Q values were more than 3 orders of magnitude larger than K_{sp} indicating the system was at supersaturation, and FeCO_3 would precipitate at all tested conditions [20, 27]. Precipitation rates for alternative CO_2 -saturated solutions have been reported previously, demonstrating the dependence of precipitation on K_{sp} and saturation degree (Q/K_{sp}) [28-30]. Furthermore, the Q values or the ratios of Q to K_{sp} are very close to each other for the cases with CO_2 loadings of 0.43 C/N and 0.53 C/N at 80°C , which indicates that the formation behavior of FeCO_3 should be similar. However, no notable FeCO_3 was formed on the A106 surface in the solutions with CO_2 loadings of 0.24 C/N as well as 0.43 C/N up to a duration of 383 h as it did in the solution with a CO_2 loading of 0.53 C/N after only 125 h (Figures 3-7 and Figures S2-S3 in supplementary material). This indicates that FeCO_3 observed in the solution with a CO_2 loading of 0.53 C/N might not be formed via direct precipitation from solution. The assumptions made for the calculation, such as the iron concentration obtained by ICP analysis was Fe^{2+} and free for FeCO_3 formation, may explain the discrepancy between the calculation and the experimental results. For example, Fe^{2+} might be stabilized in complexes such as $\text{Fe}(\text{CO}_3)_2^{2-}$ and might not be available for FeCO_3 formation.

The other possible pathway for formation of FeCO_3 might be from the transformation of the formed $\text{Fe}_2(\text{OH})_2\text{CO}_3$ as shown in reaction (12),

Transformation from $\text{Fe}_2(\text{OH})_2\text{CO}_3$ into FeCO_3 :

which was associated with a decrease in pH [18, 19, 21, 25, 31]. Electrochemical reactions were shown earlier to retard after formation of a layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ in the cases with CO_2 loadings of 0.43 C/N and 0.53 C/N (Figure 2), which would lower the localized pH as well as the difference between localized pH and bulk pH, relatively. Although the localized pH was unavailable since it is inherently difficult to measure, the speciation simulation results in Figure 11 show the bulk pH decreases with increases in CO_2 loading. This indicates that the localized pH is slightly lower in the case with a CO_2 loading of 0.53 C/N than that with a lower CO_2 loading of 0.43 C/N [18, 32].

The localized pH may be low enough to trigger transformation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ to FeCO_3 (reaction (12)) for the case of a CO_2 loading of 0.53 C/N but not low enough for cases with CO_2 loadings less than 0.53 C/N, at least for a testing duration of 383 h at 80°C.

The transformation from $\text{Fe}_2(\text{OH})_2\text{CO}_3$ into FeCO_3 was observed for corrosion testing in a solution with a CO_2 loading of 0.53 C/N at a higher temperature of 120°C (Figures 8-10). Blade-shaped $\text{Fe}_2(\text{OH})_2\text{CO}_3$ was seen on the A106 surface after 150 h (Figure 8 (a) and (c)) but disappeared gradually with increases in duration to 595 h (Figure 8 (d) and (e)), Figures 9 and 10). Meanwhile, FeCO_3 nodules were formed (Figure 8 (a), (b), and (d)). The formation of FeCO_3 nodules was most likely the result of a transformation of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ clusters (at terminal surface points) into FeCO_3 . Also, a higher content of FeCO_3 in the very outside thin layer ($<1\text{ }\mu\text{m}$) than that in a relatively thicker layer from the outside surface was observed (Table S1 in supplementary material). This helps to confirm the hypothesis that $\text{Fe}_2(\text{OH})_2\text{CO}_3$ formed as a metastable intermediate in the pathway to protective FeCO_3 formation. In addition, the content of FeCO_3 increased in the mixture layer with increases in temperature from 80°C to 120°C (Table S1 in supplementary material), which might be the result of a slightly decreased pH at higher temperature (from 6.85 at 80°C to 6.60 at 120°C) that favored the transformation from $\text{Fe}_2(\text{OH})_2\text{CO}_3$ into FeCO_3 .

The formation of a mixture layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and FeCO_3 in 30 wt.% MEA-based solutions is in contrast to that in 30 wt.% piperazine-based solutions, where a unique, dense layer of FeCO_3 forms under similar conditions [5, 14]. This might be due to a slightly lower pH, a slightly higher initial corrosion rate, and/or higher concentrations of HCO_3^- and CO_3^{2-} in piperazine-based solutions compared to MEA-based solutions. These results indicate that the formation of a protective layer of FeCO_3 was favored by a lower pH in a CO_2 -loaded aqueous amine system. A pH stabilization method was reported to be able to push formation of a dense layer of FeCO_3 in sour environments by the addition of alkaline chemicals such as NaOH to increase the system pH [27, 33]. However, in a post-combustion CO_2 capture system using corrosive amine solvents (alkaline aqueous solutions), a protective layer of FeCO_3 might be achieved in the system without affecting its capture efficiency by a similar pH stabilization method by the addition of chemicals to decrease the system pH to a certain range near the A106 carbon steel surface.

In addition, dissolved oxygen was observed to retard formation of the FeCO_3 layer by promoting formation of other corrosion products which are less/not protective [5, 7, 13], as shown in one example in the supplementary material (Figures S8-S14). This will result in more severe corrosion in a post-combustion CO_2 capture system due to the coexistence of 4-8% of O_2 in the flue gas. From a corrosion point of view, without significantly increasing the total capital cost for post-combustion CO_2 capture process, a pretreatment process to remove oxygen in the flue gas might be better for protecting the process units by allowing initial formation of the protective FeCO_3 layer. Long-term studies on oxygen effects are necessary.

5. Summary

Corrosion of A106 carbon steel in anoxic 30 wt.% monoethanolamine-based solutions (one example of a corrosive solvent for post-combustion CO_2 capture) with a range of CO_2 loadings from 0.24 C/N (mol CO_2 /mol amine) to 0.53 C/N at temperatures of 80°C and 120°C has been investigated by the mass loss method, scanning electron microscopy, X-ray diffraction with scan modes of $2\theta/\Omega$ and GIXRD, inductively coupled plasma optical emission spectrometry, and solution speciation simulations. The results showed that the corrosion as well as formation of a protective layer of corrosion products such as chukanovite ($\text{Fe}_2(\text{OH})_2\text{CO}_3$) and siderite (FeCO_3) on the A106 surface were strongly CO_2 loading-, temperature-, and O_2 -dependent. Major findings include:

1. Initial corrosion, before formation of a notable layer of corrosion products such as $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and FeCO_3 , was accelerated from approximately $6 \text{ g m}^{-2} \text{ d}^{-1}$ (after 147 h) to approximately $77 \text{ g m}^{-2} \text{ d}^{-1}$ (after 50 h) and to approximately $98 \text{ g m}^{-2} \text{ d}^{-1}$ (after 50 h) with increases in CO_2 loading from 0.24 C/N to 0.43 C/N and to 0.53 C/N at 80°C , respectively.
2. The formation of a layer of corrosion products of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and FeCO_3 , which could dramatically decrease the corrosion, were promoted with increasing CO_2 loadings as a result of faster generation of Fe^{2+} during initial corrosion as well as slightly increased CO_3^{2-} speciation and decreased pH.
3. The formed layer of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ and/or FeCO_3 on the surface of A106 from solutions with high CO_2 loadings (such as 0.53 C/N) and/or temperatures (such as 120°C) was protective, which could eventually result in a comparable low corrosion rate to that without this layer from

solutions with a much lower CO₂ loading (such as 0.24 C/N) and/or a lower temperature (such as 80°C).

4. Fe₂(OH)₂CO₃ was formed prior to FeCO₃ as a result of its more favorable localized conditions such as pH. However, Fe₂(OH)₂CO₃ was unstable, and eventually transformed into a more stable product of FeCO₃ protecting the underlying steel from further corrosion.

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Figure captions

Figure 1. Schematic for immersion corrosion testing in a stainless steel autoclave-type corrosion cell.

Figure 2. Corrosion rates of A106 carbon steel in 30 wt.% MEA-based solutions at different CO₂ loading (mol CO₂/mol amine, C/N) and temperature.

Figure 3. SEM surface morphologies of A106 in 0.24 C/N loaded 30 wt.% MEA-based solutions at 80°C after immersion durations of (a) 147 h and (b) 384 h.

Figure 4. SEM surface morphologies of A106 in 0.43 C/N loaded 30 wt.% MEA-based solutions at 80°C after (a) 50 h, (b) 125 h, (c) and (d) 383 h to show the formation of Fe₂(OH)₂CO₃.

Figure 5. XRD patterns (obtained by 2 θ / Ω scan) of A106 in 0.43 C/N loaded 30 wt.% MEA-based solutions at 80°C after (a) 50 h, (b) 125 h, and (c) 383 h to show the formation of Fe₂(OH)₂CO₃. Peak positions as well as PDF card No. for standards of Fe, Fe₃C, and Fe₂(OH)₂CO₃ are also provided at the bottom of the figure.

Figure 6. SEM surface morphologies of A106 in 0.53 C/N loaded 30 wt.% MEA-based solutions at 80°C after (a) 50 h, (b) and (c) 125 h, (d) and (e) 383 h to show the formation of Fe₂(OH)₂CO₃ and FeCO₃.

Figure 7. XRD patterns (obtained by 2 θ / Ω scan) of A106 in 0.53 C/N loaded 30 wt.% MEA-based solutions at 80°C after (a) 50 h, (b) 125 h, and (c) 383 h to show the formation of FeCO₃ and Fe₂(OH)₂CO₃. Peak positions as well as PDF card No. for standards of Fe, Fe₃C, Fe₂(OH)₂CO₃, and FeCO₃ are also provided at the bottom of the figure.

Figure 8. SEM surface morphologies of A106 in 0.53 C/N loaded 30 wt.% MEA-based solutions at 120°C after 150 h ((a), (b), and (c)) and 595 h ((d) and (e)) to show the formation of FeCO₃, Fe₂(OH)₂CO₃, and nodules. (f) shows an example of the corresponding cross-sectional morphology to (d).

Figure 9. XRD patterns (obtained by 2 θ / Ω scan) of A106 in 0.53 C/N loaded 30 wt.% MEA-based solutions at 120°C after (a) 150 h, (b) 368 h, (c) 535 h, and (d) 595 h to show the formation of

FeCO_3 and $\text{Fe}_2(\text{OH})_2\text{CO}_3$. Peak positions as well as PDF card No. for standards of Fe, Fe_3C , $\text{Fe}_2(\text{OH})_2\text{CO}_3$, and FeCO_3 are also provided at the bottom of the figure.

Figure 10. XRD patterns (obtained by GIXRD) of A106 in 0.53 C/N loaded 30 wt.% MEA-based solutions at 120°C after (a) 150 h, (b) 368 h, (c) 535 h, and (d) 595 h to show the formation of FeCO_3 and $\text{Fe}_2(\text{OH})_2\text{CO}_3$. Peak positions as well as PDF card No. for standards of Fe, Fe_3C , $\text{Fe}_2(\text{OH})_2\text{CO}_3$, and FeCO_3 are also provided at the bottom of the figure.

Figure 11. Simulated speciation of HCO_3^- (red dash curve) and CO_3^{2-} (blue dash-dot curve) and bulk pH (black solid curve) vs. carbon loading in 30 wt.% MEA-based solutions at 80°C.

Figure 12. Fe concentrations vs. immersion durations of A106 carbon steel in MEA-based solutions under different conditions.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Tables

Table 1. Experimental conditions for immersion corrosion testing in various CO₂-loaded 30 wt.% MEA with the balance being deionized water

Test	1	2	3	4
Alkalinity (mol/kg)	4.73	4.50	4.33	4.33
CO ₂ loading (C/N)	0.24	0.43	0.53	0.53
Room temperature pH	10.37	9.56	9.01	9.01
Operated temperature (°C)	80	80	80	120
Total pressure (Pa)	1.7×10 ⁵	2.3×10 ⁵	4.0×10 ⁵	9.1×10 ⁵

Table 2. Calculated ionic strength, solubility constant (K_{sp}) of FeCO₃, and maximum solubility ($Q^{\max}$) of FeCO₃ with the simulated speciation and Fe concentration from ICP analysis in the 30 wt.% MEA-based solutions at 80°C

CO ₂ loading (C/N)	Ionic strength (mol/L)	K_{sp} (mol ² /L ²)	$Q^{\max}$ (mol ² /L ²)	$Q^{\max}/K_{sp}$
0.24	1.78	6.8×10 ⁻¹⁰	1.9×10 ⁻⁶	2.8×10 ³
0.43	3.06	1.1×10 ⁻⁹	1.6×10 ⁻⁴	1.5×10 ⁵
0.53	3.42	1.1×10 ⁻⁹	1.7×10 ⁻⁴	1.5×10 ⁵