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Using pre-treated carbon steel for post-combustion carbon capture infrastructure

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Abstract

The reduction of capital cost in building post-combustion CO_2 capture is necessary to realize its widespread use. Cheaper steels, *e.g.* carbon steel, are attractive but lack the necessary corrosion resistance. To protect from corrosion, one approach is to implement a protective coating on the surface. Particularly, a coating like siderite ($FeCO_3$) is appealing because it can be formed by amines and therefore could be regenerated. This study investigates the formation, over seven days at 40 and 80 °C, of such siderite layers formed in methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and a K_2CO_3 solution. When tested against 2.5 M monoethanolamine for 28 days, the coatings formed at 80 °C in MDEA and AMP appear the most resilient. There is a substantial siderite crystal layer remaining on the surface and only minimal weight loss.

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Keywords: post-combustion capture, corrosion, carbon steel, siderite, monoethanolamine, methyldiethanolamine, 2-amino-2-methyl-1-propanol

1. Introduction

Reduction of the capital costs associated with the construction of post-combustion CO_2 capture (PCCC) infrastructure is essential to the future large-scale worldwide deployment of this technology. In demonstration facilities, stainless steels remain the construction material of choice due to their robustness against corrosion from CO_2-loaded aqueous amine solvents. However, the high cost of this material and the popularity of amine solvents

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are incompatible. As such, the use of less expensive steels which resist corrosion is essential and is the long-term goal of this work. The approach presented herein uses the pre-treatment of carbon steel with siderite ($FeCO_3$), which can be formed in some aqueous amine solution environments. The crystalline siderite layer offers protection to the surface of the metal. In this study, the siderite-producing amine solution is replaced with an alternative amine solution which shows corrosive behaviors.

Amines are not inherently corrosive, but rather some show corrosive behaviours in the presence of CO_2 [1,2]. Previous research has demonstrated that tertiary (3°) (*e.g.* methyldiethanolamine, MDEA) and sterically-hindered (SH) (*e.g.* 2-amino-2-methyl-1-propanol, AMP) CO_2-loaded amines form siderite crystals on the surface of carbon steel at 80 °C [3-6]. This results from the indirect (*via* hydrolysis) reaction of the amine with CO_2 which causes the formation of bicarbonate ions (Equation 1). The conversion of bicarbonates to carbonates occurs readily (Equation 2). In the presence of Fe oxidized at the surface of the metal (Equation 3), the carbonate or bicarbonate reacts to form siderite (Equation 4).

$$RR'R''N + H_2CO_3 \rightarrow RR'R''NH^+ + HCO_3^- \quad (1)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad (2)$$

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \quad (3)$$

$$2Fe_{(aq)}^{2+} + 2HCO_{3(aq)}^{2-} \rightarrow 2FeCO_{3(s)} + H_{2(aq)} \quad (4)$$

Ionic solutions, such as K_2CO_3, are also viable to create an excess of bicarbonate into solution. Such solutions can even serve as an alternative to amines, particularly given their resistance to degradation [7]. By contrast, primary (1°) (e.g. monoethanolamine, MEA) (Equations 5 and 6) and secondary (2°) amines (Equations 7 and 8) do not have the same propensity to produce bicarbonate ions when reacted with CO_2.

$$RNH_2 + CO_2 \rightarrow RNH_2COO \quad (5)$$

$$RNH_2 + RNH_2COO \rightarrow RNH_3^+ + RNHCOO^- \quad (6)$$

$$RR'NH + CO_2 \rightarrow RR'NHCOO \quad (7)$$

$$RR'NH + RR'NHCOO \rightarrow RR'NH_2^+ + RR'NCOO^- \quad (8)$$

While more corrosive, these amines demonstrate significantly more rapid CO_2 capture kinetics. As such, their use is often preferred but could be cycled with another amine in the hopes of regularly regenerating the protective siderite layer and while still maintaining some CO_2 capture.

Nomenclature

1°	primary amine
2°	secondary amine
3°	tertiary amine
SH	sterically-hindered amine
MEA	monoethanolamine
MDEA	methyldiethanolamine
AMP	2-amino-2-methyl-1-propanol
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
XRD	X-ray Diffraction
MSCR	mass size change rate (mm y^{-1})
m	mass
ρ	density
A	exposed surface area

t	time of exposure

2. Methods

Solutions were made from: 2-amino-2-methyl-1-propanol (AMP, ≥90% Sigma), methyldiethanolamine (MDEA, ≥99% Sigma), potassium carbonate (K_2CO_3, ≥99% Sigma), and monoethanolamine (MEA, ≥99% Sigma) with deionized water. All solvents were used as received. Corrosion coupons of carbon steel C1018 (76.25×12.62×1.63 mm, 98.83-99.13% Fe, 0.18% C, 0.6-0.9% Mn, ≤0.04 P and ≤0.05 S, Alabama Specialty Metals) were first washed with acetone and air dried then weighed. Five coupons were mounted on a custom made PTFE coupon mount (Imperial College Department of Chemical Engineering Workshop).

Three 2L pre-treatment solutions of 5 M AMP, 5 M MDEA and 1 M K_2CO_3 (lower concentration due to solution saturation limits) were prepared in custom glass reactors (Cambridge Glass). Solutions were purged of oxygen by continuously bubbling nitrogen gas (N_2) at 50 mL min-1 for four hours at room temperature. The solutions were subsequently loaded by bubbling CO_2 at 100 mL min-1 for two hours at either 40 or 80 °C, as dictated by the experiment, at atmospheric pressure. The temperature was maintained using a hot plate (IKA) with individual water baths, of a height equal to the reaction vessels, and a temperature probe inside the reaction solution. Upon completion of loading, the coupon mount was submerged into the pre-treatment solution (Figure 1). Throughout the experiment, CO_2 was continuously bubbled into the solution at a rate of 50 mL min-1 to maintain CO_2 saturation.

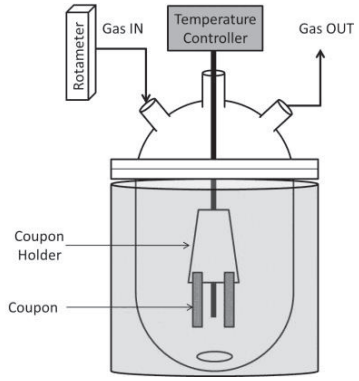


Figure 1: Corrosion vessel

After the seven days allocated for pre-treatment one coupon was removed, the solution was then sampled and changed to 2.5 M MEA. Each subsequent week, one coupon was withdrawn for four weeks. After removal, the coupons were first weighed, then washed with deionized water and acetone, then reweighed. Given the experiment

produced and destroyed product layers, net coupon weight change served as a simple means to gauge coupon mass change (mm y^{-1}). The mass size change rate (MSCR) is calculated from the difference between coupon initial mass (m_{INITIAL}) and final mass (m_{FINAL}), divided by coupon initial surface area (A), density (ρ) and the time spent in solution (t) (Equation 9).

$$Mass\ Size\ Change\ Rate\ (mm\ y^{-1}) = \frac{m_{FINAL} - m_{INITIAL}}{\rho A t} \tag{9}$$

The coupons were cut to separate a 5×5 mm square, which was then coated in 10 nm thick gold and mounted on aluminum stubs for imaging using scanning electron microscopy (SEM) (JEOL 6400). The surface composition was also measured using Energy Dispersive X-ray (EDX) against a cobalt standard.

3. Results and Discussion

The impact of pre-treatment on carbon steel coupons is demonstrable. At 40 °C very little siderite is observed using SEM for either 5 M MDEA or AMP (Figure 2a,c). However, siderite formation is observed for 1 M K_2CO_3 (Figure 2e). In contrast, at 80 °C the formation of siderite is significant with complete surface coverage and minimal defects for all three pre-treatment solutions (Figure 2b,d,f). However, the quality of the crystals is variable, with those formed in K_2CO_3 considerably inferior.

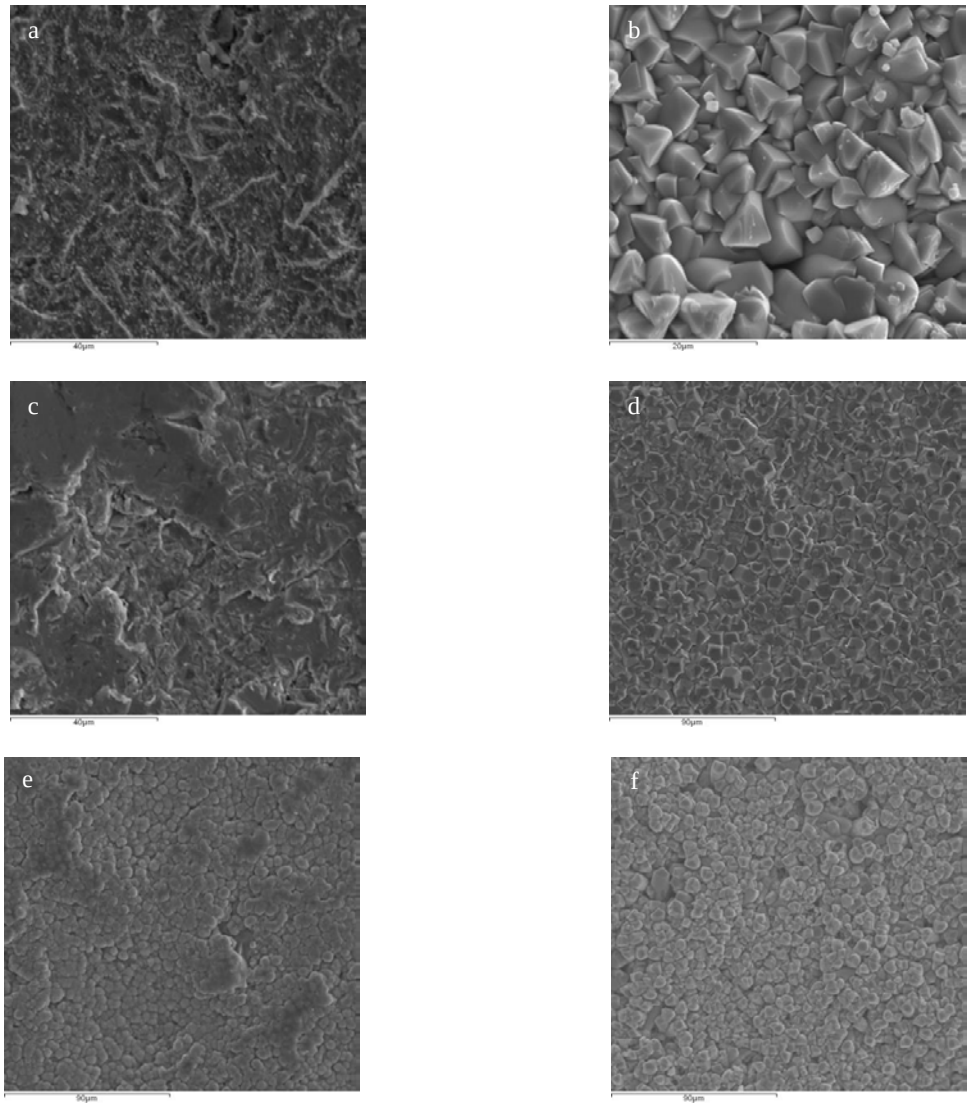


Figure 2: Carbon steel surface after pre-treatment. 5M MDEA at (a) 40 °C at 1000x and (b) 80 °C at 2000x; 5 M AMP at (c) 40 °C at 1000x, and (d) 80 °C at 500x; 1 M K_2CO_3 at (e) 40 °C at 500x and (f) 80 °C at 500x.

The weight change of the individual coupons at both 40 and 80 °C was recorded (Figure 3). While siderite formation was not notable at 40 °C, a reduced corrosion rate in the case of pre-treatment is evident. All three pre-treatment approaches appear to have a similar impact. Most importantly, there remains apparent continued protection from corrosion for the four weeks tested. This could indicate the presence of a protective iron oxide layer. At 80 °C, the significant improvement resulting from pre-treatment is most evident early on. The use of 5 M AMP and MDEA appear better than K_2CO_3. However, the nominal increase over the course of the four weeks is apparent and, critically, may point to some loss in efficacy of the protective layer.

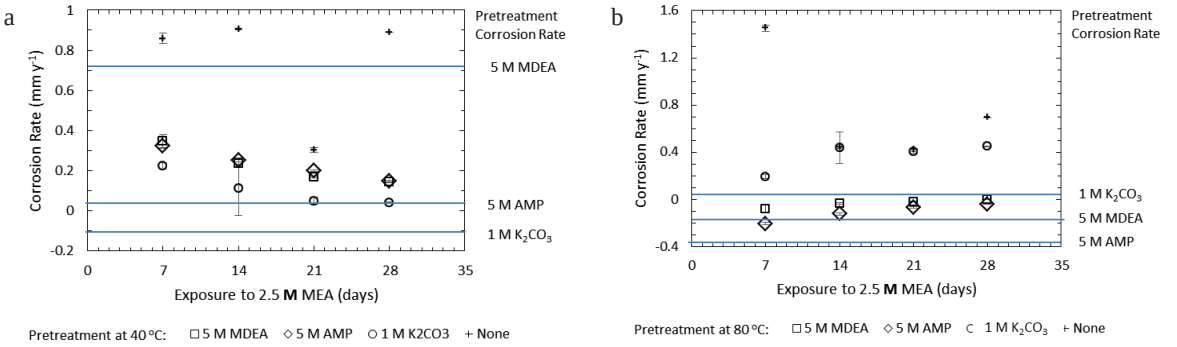
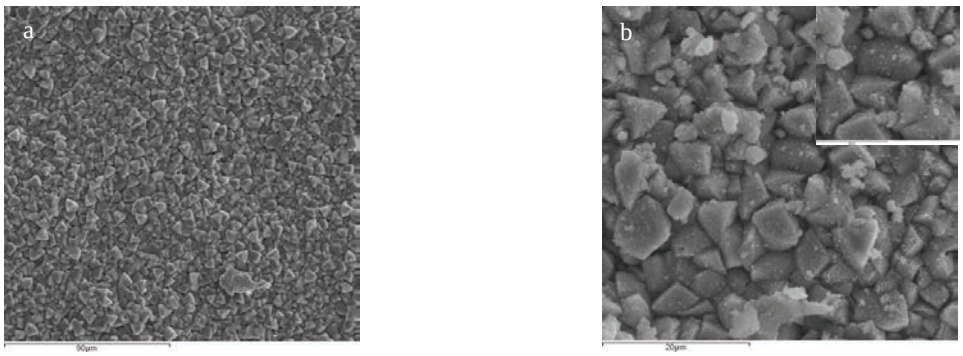


Figure 3: Weight change of carbon steel coupons due to 2.5 M MEA after a one week pre-treatment at (a) 40 and (b) 80 °C, where horizontal lines indicate corrosion rate for relative pre-treatments (as listed on the right of each graph).

The apparent beneficial reduction of corrosion at 80 °C is clearly due to a substantial crystalline siderite layer (Figure 4a,c,e). The possible loss in efficacy demonstrated by the weight change can be observed using SEM imaging. Most noticeable is the significant destruction of the siderite layer formed in 1 M K_2CO_3, even after one week of exposure (Figure 4e). At longer exposure to 2.5 M MEA there is some damage to the crystalline structure formed in 5 M MDEA and AMP (Figure 4b,d); however, the integrity of the layer, in both cases, remains intact.



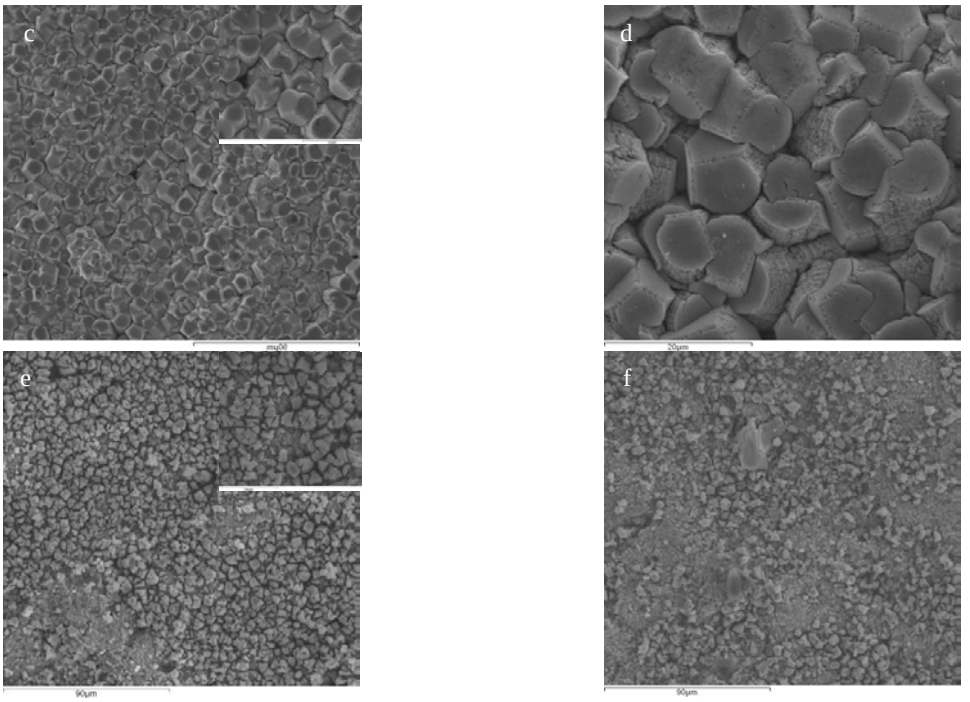


Figure 4: Carbon steel surface after pre-treatment when exposed to 2.5 M MEA. 5 M MDEA pretreatment at 80 °C: (a) one (500x) and (b) three weeks (2000x, 4000x); 5 M AMP pretreatment at 80 °C: (c) one (500x, 4000x) and (d) three weeks (2000x); 1 M K_2CO_3 pretreatment at 80 °C: (e) one (500x, 2000x) and (f) three weeks (500x)

4. Conclusions

The efficacy of pre-treatment, using 5 M MDEA or AMP, shows great promise towards protecting carbon steel from corrosion when 2.5 M MEA is used for PCCC processes. The interesting protective behaviors observed at absorber temperatures, particularly the mechanism, should be considered for future investigation. However, the complexities of flue gas impurities further complicate this case. Most promising is the formation of strong siderite layers on the carbon steel at temperatures relevant to the heat exchanger and cool sections of the stripper. These results establish a justification to further pursue innovative approaches using amine-generated siderite layers as a protective mechanism for carbon steel.

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