

Using sodium thiosulphate for carbon steel corrosion protection against monoethanolamine and 2-amino-2-methyl-1-propanol

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ABSTRACT

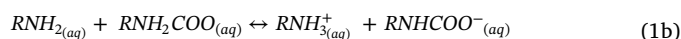
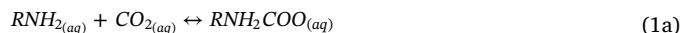
The corrosion performance of carbon steel (C1018) with inhibitor sodium thiosulphate (STS) has been compared to C1018 (without an inhibitor) and stainless steel (SS316 L) at 80 and 120 °C to determine the feasibility of use in a post-combustion CO₂ capture plant (PCCC). The corrosivity of variable ratio monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP) aqueous solvent blends were assessed after seven days using a gravimetric method for mass change, Fe ion solution concentration (ICP–OES), surface imaging (SEM) and analytical techniques (EDX and XRD). At low concentrations of MEA (25%), the use of the corrosion inhibitor is ineffective as it prevents the formation of protective films naturally developed by AMP. The performance of the inhibitor with MEA–AMP blends was noteworthy at higher MEA concentrations of 50 and 75%. In these cases, reduced corrosion rates were observed through gravimetric and ICP analyses. Imaging by SEM showed reduced surface corrosion and adsorption of STS-derived species. Since these higher MEA concentration solutions offer better CO₂ loadings, but still some exhibit corrosive effects when used alone on carbon steel, the use of STS can facilitate an economical usage of carbon steel for PCCC plants.

1. Introduction

Reduction in greenhouse gas emissions, specifically carbon dioxide (CO₂), is paramount in mitigating continued climate change. Since fossil fuel based power generation plants are one of the largest CO₂ emissions sources (Freund, 2003), development of technologies to reduce CO₂ concentrations from the flue gases emitted from these plants is essential. Due to its applications in natural gas sweetening, amine scrubbing is the most developed post-combustion CO₂ capture (PCCC) technology to date. Despite this experience, financial and technical limitations, including corrosion, still exist. Stainless steel is therefore the recommended material for PCCC pilot plants (Kittel and Gonzalez, 2014), but this is neither economically feasible nor a panacea due to localised corrosion concerns. Consequently, some recent studies have identified means of using carbon steel under specific process and solvent conditions (Campbell et al., 2016; Yu et al., 2016).

Importantly, amines are not inherently corrosive, only demonstrating this potential when exposed to CO₂ (DuPart et al., 1993). Since varied CO₂ uptake mechanisms exist for different amine classes, corrosive behaviour and the subsequent reaction between an Fe substrate and amines cannot be generalized. Both primary (1°) and secondary (2°) amines react with CO₂ to form carbamate ions (Eq. (1)) and increases solution pH through formation of a protonated amine (Belarbi et al.,

2016). One such 1° amine, monoethanolamine (MEA), has been historically used (30% by weight) due to its fast CO₂ uptake kinetics. However, it exhibits low loading capacity and undergoes thermal and oxidative degradation, all of which reduce its desirability as a solvent for the PCCC process. The corrosive behaviour of 1° amine solvents, on Fe substrates, is linked to the formation of carbamates by some studies (DuPart et al., 1993; Tomoe et al., 1996) which is favoured at reduced temperatures (Kittel and Gonzalez, 2014). This behaviour was observed in a previous study where 5 M MEA at 80 °C, proved to be more corrosive than 120 °C (Sadeek et al., 2018). By contrast to 1° amines, 3° amines react with CO₂ indirectly, requiring CO₂ hydrolysis (Eq. (2)).

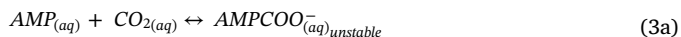


A subset of 1° amines are those which contain bulky side groups around the N atom, causing steric hindrance and are referred to as sterically-hindered (SH) amines. Such structures cause slow and unstable carbamate formation (Bougie and Iliuta, 2012; Dubois and Thomas, 2012; Mazari et al., 2014; Sartori and Savage, 1983; Zhao et al., 2011). The capture mechanism employed by SH amines, like 2-

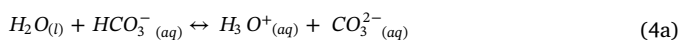
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amino-2-methyl-1-propanol (AMP), has been suggested to employ direct CO₂ capture, producing an unstable carbamate which is then hydrolysed to form bicarbonate (Sedransk Campbell et al., 2017) (Eq. (3)). The use of the SH amine AMP is popular due to its enhanced resistance to thermal (Hatchell, 2015) and oxidative (Wang and Jens, 2013) degradation.



The production of bicarbonate associated with SH amine CO₂ capture acts as a source of carbonate species (Eq. (4a)). These then react with Fe ions present from Fe substrate oxidation (Eq. (4b)) and results in Fe carbonate (FeCO₃, siderite) formation (Eq. (4c)). Siderite formation can be advantageous as it has been demonstrated to provide corrosion protection for the underlying metal substrate (Fe or a carbon steel with high Fe content) (Campbell et al., 2016; Farelas et al., 2013; Guo and Tomoe, 1999; Han et al., 2011; Tanupabrungsun et al., 2013; Yu et al., 2016).



In addition to the improved solvent performance demonstrated by AMP, relative to MEA, the reduced corrosion of Fe is highly beneficial. Two reports investigated the corrosion behaviour of 5 M AMP (and MEA) saturated with CO₂ at 80 and 120 °C using long term immersion testing and surface analytical techniques (SEM, EDX, XRD) (Campbell et al., 2016; Yu et al., 2016). In these tests, significant siderite layers formed on the surface with the concomitant corrosion reduction (as measured by Fe ion content in solution) relative to MEA. In agreement, using electrochemistry for 3 M AMP saturated with CO₂ at 80 °C (Veawab et al., 1999a), AMP was shown to be less corrosive than MEA. However, it has also been suggested to be more corrosive than MDEA, DEA and PZ (Gunasekaran et al., 2013). Some conflicting electrochemically determined corrosion rates have also shown that 3 M AMP at 80 °C has corrosion rates an order of magnitude lower than that of MEA for lean solutions (low CO₂-loading), but comparable to MEA under saturated CO₂ conditions (Veawab et al., 1999b).

Although the use of SH amines (e.g. AMP) has been suggested as an attractive solvent for amine scrubbing (Mandal et al., 2001), blending with 1° amines has proven advantageous (Xiao et al., 2000). The strategy of blending a 1° or 2° amine with a SH or 3° amine to improve solvent performance has been employed (Conway et al., 2015; Freeman et al., 2013; Kemper et al., 2011; Li et al., 2013; Mandal and Bandyopadhyay, 2006; Wang and Jens, 2013; Zhao et al., 2011). These mixtures take advantage of the fast reaction kinetics characteristic of 1° and 2° amines, and the high loading capacities and low regenerative requirements of SH and 3° amines. One such example which has shown promise are blends containing the SH amine AMP (Kemper et al., 2011; Mandal et al., 2001; Mandal and Bandyopadhyay, 2006; Xiao et al., 2000). In an investigation of the corrosive behaviour of 5 M amine blends containing MEA and AMP, Yu et al. (2016) observed: 1) reduced corrosion with decreased MEA concentration (demonstrated by decreased bulk Fe ions in solution) and 2) siderite crystal growth on coupons exposed to blends containing greater than 50% AMP. While promising, not all cases offer sufficient corrosion protection from siderite. As such, additional corrosion control methods may be required for some blend compositions.

In addition to blends, a complementary approach to facilitate the use of carbon steel in PCCC plants is inhibitor addition. Effective corrosion inhibitors for natural gas sweetening have been identified including arsenic, antimony and vanadium compounds, but these are being phased out due to environmental and health concerns (Kittel and

Gonzalez, 2014). Recent studies on low-toxic inhibitors have included copper carbonate (Soosaiprakasham and Veawab, 2009), 2-metapto-benzimidazole (Zheng et al., 2015) and sodium thiosulphate (STS) (Sadeek et al., 2018; Srinivasan et al., 2013). Long term testing and surface analyses were used to investigate the performance of STS in reducing corrosion rates in the presence of both 5 M MEA and MEA-MDEA blends at 120 and 80 °C. This inhibitor is inorganic and designed to impede corrosion by adsorption of the negative anion (S₂O₃²⁻ (TS)) (Roberge, 2012). Adsorption of TS was detected by EDX on coupons exposed to tested solvents with a high concentration of MEA. However, reaction of TS was observed and resulted in the formation of such species as Na₂CO₃, reducing the efficacy of the TS adsorption to the surface. Additionally, the promotion of metal-oxide products was also observed, though this proved to be less problematic than the formation of Na₂CO₃. However, in the 25% by weight MEA blended systems, the inhibitor presence altered the natural protective mechanism, siderite formation, characteristic of MDEA. That is, without the inhibitor, naturally growing siderite films offer good corrosion protection; by contrast, when the siderite was not formed in the presence of STS then corrosion was considerably worse (Sadeek et al., 2018).

The work reported herein assesses the performance of STS inhibited carbon steel, relative to both uninhibited carbon steel and stainless steel coupons, in MEA-AMP blended solutions at process conditions found in the high temperature units of PCCC plants. This industrially relevant study is essential to understanding the performance of 1) MEA-AMP blends relative to the MEA-MDEA blends and 5 M MEA, the current industry standard and 2) the performance of STS as an inhibitor with potentially usable blends under challenging PCCC process conditions. With a wider range of applications employing amines, particularly natural gas sweetening, the findings have even farther reaching implications.

2. Materials and method

2.1. Corrosion experiments

The chemicals monoethanolamine (MEA, Sigma ≥ 98%), 2-amino-2-methyl-1-propanol (AMP, Sigma ≥ 99%), sodium thiosulphate (STS, (Na₂S₂O₃), Sigma ≥ 99%) (Fig. 1) were used as received. Three 250 mL aqueous amine blends of solution composition 75, 50, 25 % by weight of MEA, and an MEA control were prepared each with a total amine content of 5 M (the balance being DI water). Two batches were prepared, where 0.625 g (2500 mg L⁻¹) of STS (inhibitor) was added to one batch. Round bottom double neck flasks (250 mL) with a reflux condenser (to minimise vapour loss) were used on Dry-syn blocks (with an aluminium heat transfer plate base) (Fig. 2). Purging with N₂ was conducted for two h (400 mL min⁻¹) at ambient temperature and pressure, thereby creating an O₂-free environment; the solution was subsequently loaded with CO₂ at 400 mL min⁻¹ for two h. After this period the CO₂ flow rate was reduced to 20 mL min⁻¹ and bubbled continuously for the duration of the experiment (i.e. maintaining a constant CO₂ loading). The addition of the inhibitor was by direct addition into the reaction vessel via single injection at the start of the experiment. The temperature was controlled at either 80 or 120 °C to mimic the conditions of a heat exchanger or stripper. All aqueous amine solutions saturated with CO₂ attained a pH of 7.81 ± 0.03.

Glass bead blast finished carbon (C1018) and stainless (SS316 L) steel coupons (Dimensions: 76.20 × 12.70 × 1.59 mm, Type C1018: Fe: 98.85%, C: 0.17%, Mn:0.80%, Cr: 0.04%, Al: 0.04%, ≤ 0.02%: P, S, Si, Cu, Ni, Sn, N, V, B, Ti, Co and Type SS316L: Fe: 67%, Cr:17%, Ni: 12%, Mn: ≤ 2%, Mo: 2.5%, Si: ≤ 0.75%, C ≤ 0.03%, P: ≤ 0.045%, S: ≤ 0.03%, N: ≤ 0.1%) (Alabama Specialty Products) were prepared by washing with DI water and acetone. The coupons were weighed and then suspended into the prepared aqueous amine solutions with a PTFE string through the top hole (radius of 6.35 mm) (Fig. 2).

Immersion of the coupons was for seven days (168 h), after which

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