Using sodium thiosulphate for carbon steel corrosion protection against monoethanolamine and methyldiethanolamine

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ABSTRACT

Corrosion resistance against amine solvent monoethanolamine (MEA) and mixtures of MEA with methyldiethanolamine (MDEA) was studied. Stainless steel (SS316L) was tested as a baseline to compare with carbon steel (C1018) alone and with the inhibitor sodium thiosulphate (STS). Immersion testing used mass change, Fe ion concentration in solution (ICP–OES), surface imaging (SEM), and analytical techniques (EDX, XRD) to assess the corrosion. Generally, the use of STS improved C1018 resilience relative to C1018 alone, though SS316L was superior to both. Multiple inhibition mechanisms were observed, and are a function of temperature and solution composition. Whilst the surface adsorption mechanism was demonstrated in some cases, reactions between solution reactants and STS resulted in different outcomes.
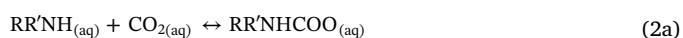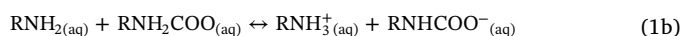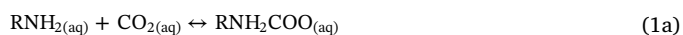
1. Introduction

Greenhouse gas emissions, specifically carbon dioxide (CO_2), are responsible for climate change. This has been observed not only through rising global temperatures, but also through increasing sea levels and escalating severe weather conditions. Fossil fuel based power generation plants are a major source of CO_2 emissions (Freund, 2003). Consequently, installation of abatement strategies, like post-combustion CO_2 capture (PCCC), are crucial. Post-combustion capture using amine scrubbing, is the most mature CO_2 capture technology. Remaining constraints still prevent PCCC deployment. One critical concern is the corrosive nature of aqueous amine solvents. To circumvent this, PCCC pilot (and natural gas sweetening) plants primarily use high grade stainless steel infrastructure materials (Li et al., 2017).

Studies comparing stainless and carbon steels show enhanced resilience against corrosion with stainless steel (Erfani et al., 2015; Rochelle et al., 2011; Sun et al., 2011). This benefit is presumed to be from the surface CrO layer providing corrosion protection. However, use of stainless steel is economically infeasible on a large scale for PCCC; as such, alternatives must be sought. Most reported studies on carbon steels demonstrate their vulnerability to corrosive attack (Gunasekaran et al., 2013; Sun et al., 2011; Veawab et al., 1999; Wattanaphan et al., 2013), rather than approaches to protect and utilise such materials. However, newer studies have taken a multifaceted approach to corrosion protection to facilitate the use of this more economical carbon steel material (Sedransk Campbell et al., 2016; Zheng et al., 2016a, 2014). Some have considered optimised solvents which can be not only more efficient but also less corrosive (Sedransk Campbell et al., 2016; Yu et al., 2016).

To address this possibility, it is critical to understand the behaviour of the specific solvent systems, as amine solvents do not all behave in the same way. The current baseline for solvent performance is against 30% by weight monoethanolamine (MEA), which has been used historically for its efficient reaction kinetics. Drawbacks include that MEA not only exhibits low CO_2 loading capacity but also undergoes thermal and oxidative degradation, reducing its long term efficacy. Primary (1°) amines, like MEA, and secondary (2°) amines, react with CO_2 to form carbamate ions (Eqs. (1) and (2)). Since these amines have at least one hydrogen atom bonded to the nitrogen atom, CO_2 uptake follows this kinetically fast pathway. However, two moles of amine are needed to absorb one mole of CO_2, giving inefficient loading capacities.
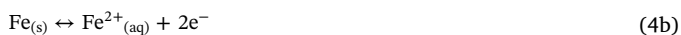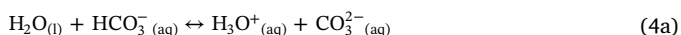
$$RNH_{2(aq)} + CO_{2(aq)} \leftrightarrow RNH_2COO_{(aq)} \tag{1a}$$

$$RNH_{2(aq)} + RNH_2COO_{(aq)} \leftrightarrow RNH_{3(aq)}^+ + RNHCOO^-_{(aq)} \tag{1b}$$

$$RR'NH_{(aq)} + CO_{2(aq)} \leftrightarrow RR'NHCOO_{(aq)} \tag{2a}$$

$$RR'NH_{(aq)} + RR'NHCOO_{(aq)} \leftrightarrow RR'NH_{2(aq)}^+ + RNHCOO^-_{(aq)} \tag{2b}$$

Unlike 1° and 2° amines, tertiary (3°) amines react indirectly with CO_2 via the hydrolysis of CO_2 (Eq. (3)). Importantly, only one mole of amine is needed to react with one mole of CO_2 thereby improving the loading efficiency.

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \tag{3a}$$

$$RR'R''N_{(aq)} + H_2CO_3 \leftrightarrow RR'NH^+HCO_{3\,(aq)}^- \tag{3b}$$
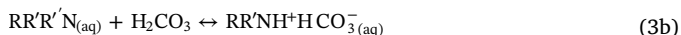
Amines are not intrinsically corrosive, but become corrosive when exposed to CO_2 (Kittel and Gonzalez, 2014). Consequently, the CO_2 uptake mechanisms are at the crux of the corrosive behaviour exhibited by different amine classes. The corrosivity of 1° amine solvents is thought to result indirectly from carbamate formation (DuPart et al., 1993a,b) and increases the likelihood of Fe hydroxide (Tomoe et al., 1996) and oxide (Yu et al., 2017; Zheng et al., 2016b) crystal growth. By contrast, Fe carbonate ($FeCO_3$, siderite) is one of the major corrosion products for 3° amines (Sedransk Campbell et al., 2016; Tomoe et al., 1996). This is due to formation of bicarbonate (HCO_3^-) ions through the indirect reaction with CO_2. Carbonate (CO_3^{2-}) ions can then be formed from the dissociation of HCO_3^- (Eq. (4)a), and subsequently react with available Fe ions (Eq. (4)b) to produce $FeCO_3$ (siderite) (Eq. (4)c).

$$H_2O_{(l)} + HCO_{3\,(aq)}^- \leftrightarrow H_3O^+_{(aq)} + CO_{3\,(aq)}^{2-} \tag{4a}$$

$$Fe_{(s)} \leftrightarrow Fe^{2+}_{(aq)} + 2e^- \tag{4b}$$

$$Fe^{2+}_{(aq)} + CO_{3\,(aq)}^{2-} \leftrightarrow FeCO_{3(s)} \tag{4c}$$

Methyldiethanolamine (MDEA), a 3° amine, is one of the most popular amines for natural gas sweetening (DuPart et al., 1993a,b). Studies have highlighted the distinct corrosion behaviour where decreased corrosion rates result from the formation of a protective, and sometimes passivating, siderite film

When used alone MDEA (or 3° amines more generally) is relatively inefficient, however blending a 1° (e.g. MEA) with a 3° amine (e.g. MDEA) increases efficiency. These mixtures take advantage of the fast reaction kinetics characteristic of the 1° amine, and the high loading capacities and low regenerative requirements of the 3° amine (Adeosun et al., 2013; Conway et al., 2015; Kemper et al., 2011; Li et al., 2013; Mandal and Bandyopadhyay, 2006; Roussanaly et al., 2013; Wang and Jens, 2014). Only limited research has been published on the corrosive behaviour of amine blends. Generally, the blend corrosivity decreases as the concentration of MEA decreases (Gunasekaran et al., 2013; Yu et al., 2017, 2016). Formation of a protective siderite film has also been observed for carbon steel coupons exposed to MEA-MDEA blends at, and greater than 75% by weight MDEA (25% by weight MEA), at 120 °C (total 5 M aqueous amine solution) (Yu et al., 2016). This study indicates that not all blend compositions may yield sufficient siderite protection (Yu et al., 2016). While this approach shows promise, a more comprehensive assessment of the formation of siderite as a protective mechanism, as both a function of temperature and blend composition, is required.

Traditionally, inhibitors have been used for protection against corrosion in natural gas sweetening; specifically compounds including arsenic, antimony and vanadium. Due to environmental and health concerns industrial use of these is unpopular (Kittel and Gonzalez, 2014). Consequently, identification of reduced toxicity inhibitors is essential, though there are very few studies in the literature. One study did establish the behaviour of copper carbonate in the presence of CO_2 loaded 5 M MEA at 80 °C (Soosaiprakasam and Veawab, 2009) where an inhibition efficiency of 80% was achieved, but O_2 was required to prevent pitting. In a second study using electrochemical experiments, sodium thiosulphate (STS) tested under the same conditions (Srinivasan et al., 2013) showed that this inhibitor was anodic in nature and provided superficial, intermittent protection.

The work reported herein assesses the performance of STS as an inhibitor for aqueous amine systems, considering both carbon and stainless steel. Aqueous amine solutions of 5 M MEA and MEA-MDEA blends are studied under process conditions normally found in the high temperature units of a PCCC plant.

2. Materials and method

2.1. Corrosion experiments

The chemicals monoethanolamine (MEA, Sigma ≥ 98%), methyldiethanolamine (MDEA, Sigma ≥ 99%), sodium thiosulphate (STS, ($Na_2S_2O_3$,) Sigma ≥ 99%) (Fig. 2) were used as received. Two batches of three 250 mL blends of each type (75%, 50% and 25% MEA), and a MEA control, were prepared by weight with a total amine content of 5 M (the balance was DI water). One batch also contained 0.625 g (2500 mg L^{-1}) of STS (inhibitor). The inhibitor was injected directly into the reaction vessel at the beginning of the immersion experiment. Solutions were transferred to 250 mL round bottom double necked flasks seated in Dry-syn blocks on an aluminium heat transfer plate (Fig. 3). Reflux condensers were used to prevent solution evaporation. Solutions were purged with N_2 for two hours at 400 mL min^{-1} at ambient temperature and pressure to remove any dissolved oxygen. Solutions were then loaded with CO_2 at 400 mL min^{-1} for two hours. The CO_2 flow rate was then decreased to 20 mL min^{-1} and left to continuously bubble for the duration of the experiment to maintain a constant CO_2 loading for the duration of the 7-day immersion. The temperature controller was set to 80 or 120 °C to mimic heat exchanger or stripper conditions respectively.

Steel coupons (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) (Fig. 1) with the dimensions 76.20 × 12.70 × 1.59 mm, two holes for attachment (radius of 6.35 mm), and a glass bead blast finish were washed with DI water and acetone, weighed and immersed in prepared amine solutions using PTFE string.

Coupons were corroded for seven days (168 h), removed from reaction vessels, weighed, washed and reweighed. The net mass change was computed by dividing the mass change of the coupon ($m_{initial}$-m_{final}) by the initial mass ($m_{initial}$), where a positive net mass change indicates net mass loss and negative change indicates net mass gain. The inhibition efficiency (IE) was then calculated by dividing the difference between the uninhibited and the inhibited mass change by the uninhibited mass change (Talati and Gandhi, 1983).

$$\text{Net Mass Change}(\%) = 100 \times \frac{m_{initial} - m_{final}}{m_{initial}} \tag{5}$$

$$IE(\%) = 100 \times \frac{(m_{initial} - m_{final})_{uninhibited} - (m_{initial} - m_{final})_{inhibited}}{(m_{initial} - m_{final})_{uninhibited}} \tag{6}$$

2.2. Analytical techniques

The solutions were retained and samples (triplicates) were prepared in HNO_3 matrix solution (7.433 M) and the Fe ion concentration was determined from ICP-OES (Perkin Elmer OES Optima 2000DV).

Coupons were then cut and mounted on SEM stubs, and then coated in 10 nm of Au. Surface imaging was done using SEM (Jeol JSM-6400). Surface chemical composition was determined using EDX detector calibrated with Co. Crystalline corrosion products were detected using XRD (PAnalytical X-Pert X-Ray Diffractometer). Scans were run between 2θ angles 10° and 100° at a step size of 0.0334 and 40 s scan time.

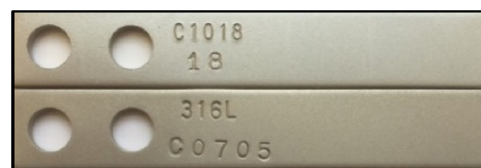**Fig. 1.** Uncorroded steel coupons (A) C1018 and (B) SS316L.