CORROSION BY HEAT-STABLE SALTS IN AMINE-BASED CO_2 CAPTURE UNIT

Winyu Tanthapanichakoon and Amornvadee Veawab*

*Faculty of Engineering, University of Regina
Regina, Saskatchewan, Canada S4S 0A2
Tel: (306) 585-5665, Fax: (306) 585-4855
Email: veawab@uregina.ca

ABSTRACT

Amine treating units are currently being viewed as the immediate technology that can be used for CO_2 capture from flue gas streams emitted from coal-fired power plants, the major point source of greenhouse gases. Despite the fact that the amine treating units have been constantly rectified so as to improve their capture efficiency, they are encountering with many operational difficulties, including corrosion of process equipment and degradation of absorption solution. Recently, there has been a growing concern over the adverse impacts of heat stable amine salts on the corrosion of process equipment. No effective remedial method is presently applied to the amine treating units simply because the knowledge of the corrosion caused by heat stable amine salts is scarce and inconclusive. This contributes to an increased expenditure for unit operation and makes the amine treating units uneconomically viable. This work investigated the effect of fourteen heat stable amine salt compounds on the corrosion of process equipment made of both carbon steel and stainless steel in a 5 $kmol/m^3$ aqueous monoethanolamine (MEA)-CO_2 environment. The investigation was done by conducting a series of corrosion experiments at 80^oC under 0.2 mol/mol CO_2 loading using electrochemical techniques. The results show that most of the heat-stable salts tested were found to increase the system's corrosivity, while the others induced resistance to corrosion. The relationship between salt concentration and corrosivity was correlated.

INTRODUCTION

There is a great concern over corrosion caused by heat-stable salts in amine treating units. The heat-stable salts are essentially the reaction products of alkanolamines and the acids stronger than carbon dioxide (CO_2). These acids are usually introduced to the amine units with makeup water and feed gas streams or generated within the units by undergoing the chemical reactions with contaminants such as oxygen (O_2), carbon monoxide (CO), and sulfur dioxide (SO_2). For example, formate is generated by the reactions of amine and O_2, hydration and other reactions with CO as well as reactions with cyanides.

By nature, the heat-stable salts are non-regenerable under solvent regeneration condition. As such, they remain and accumulate in the absorbent throughout the plant. The accumulation of heat-stable salts not only causes a reduction in CO_2 absorption capacity, but also is claimed to cause a significant increase in the system corrosiveness [1-3]. The increased corrosion can lead to an increase in the amount of iron carbonate particles in the solution, thus causing other operational difficulties such as foaming, emulsions and fouling. This potentially undermines reliability of the amine units, particularly in terms of operation, throughput, treatment capacity, and productivity. At present, the knowledge of the influence of heat-stable salts on corrosion in this system is limited. This is basically an impediment to the development of cost-effective process. Therefore, this work was aimed at investigating the role of heat stable salt on corrosion so as to extend the knowledge in this area.

EXPERIMENTS

The corrosion experiments were carried out using an aqueous solution of 5.0±0.1 $kmol/m^3$ monoethanolamine (MEA) containing the CO_2 loading of 0.20±0.01 mol/mol at the temperature of 80.0±0.1^oC. MEA was chosen because it is the most extensively used and the most corrosive compared to other alkanolamines, thus representing a worst corrosion scenario under the test condition. In addition, the data obtained through laboratory experiments on corrosion caused by HSAS in the MEA system is currently not available.

The total of eleven HSAS anions commonly found in the amine treating unit was included in the investigation. They were acetate, chloride, formate, glycolate, malonate, oxalate, succinate, sulphate,

sulfite, thiocyanate, and thiosulfate. The first ten HSAS anions were made up by the dissolution of their acid forms (such as acetic acid, formic acid, glycolic acid and oxalic acid) in the aqueous solution of MEA as shown below:

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 + HA \leftrightarrow HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + A^- \qquad (1)$$

where $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$ = MEA
   HA = acid form of HSAS anion
   $OH\text{-}CH_2\text{-}CH_2\text{-}NH_3^+$ = protonated MEA
   A^- = HSAS anion.

The last two HSAS anions, thiosulfate and thiocyanate, were made up by another technique apart from the above because of the unavailability of their acid forms, while sodium chloride was also tested to investigate additional the corrosion effect of chloride in the presence of sodium. To facilitate the presence of HSAS anion, both sodium and ammonium forms of these anions, i.e. sodium chloride, sodium thiocyanate, ammonium thiocyanate, sodium thiosulfate and ammonium thiosulfate were used in solution preparation. The generic reactions are written below.

$$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 + AB + H_2O \leftrightarrow HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + A^- + B^+ + OH^- \qquad (2)$$
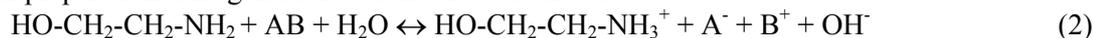
where   AB = sodium or ammonium form of chloride, thiocyanate and thiosulfate.
   B^+ = cation of sodium or ammonium

Thus, a total of 9 HSAS acids as well as 5 sodium/ammonium forms of HSAS anions were used in the investigation. Based on the typical concentrations of HSAS anion found in amine treating units, concentrations of the HSAS acids and sodium/ammonium forms of HSAS anions were prepared in ranges up to 50,000 ppm as summarized in Table 1.

Table 1: Chemicals and their concentrations used for solution preparation.

Type	Formula	Concentration (ppm)
Acetic acid	CH_3COOH	1000, 5000 and 10000
Ammonium thiocyanate	NH_4SCN	10000 and 50000
Ammonium thiosulfate	$(NH_4)_2S_2O_3$	10000
Formic acid	$HCOOH$	500, 1000, 5000, 10000 and 50000
Glycolic acid	$HOCH_2COOH$	1000, 5000 and 10000
Hydrochloric acid	HCl	1000, 5000 and 10000
Malonic acid	$(COOH)_2CH_2$	500, 1000, 5000 and 10000
Oxalic acid	$(COOH)_2.2H_2O$	500, 1000, 5000, 10000 and 50000
Sodium chloride	$NaCl$	10000
Sodium thiocyanate	$NaSCN$	10000 and 50000
Sodium thiosulfate	$Na_2S_2O_3$	10000
Succinic acid	$(COOH)_2(CH_2)_2$	1000, 5000 and 10000
Sulphuric acid	H_2SO_4	1000, 5000, 10000 and 50000
Sulphurous acid	H_2SO_3	1000, 5000 and 10000

RESULTS AND DISCUSSION

Carbon steel typically manifests active, passive, and transpassive behaviour depending upon the aggressiveness of the electrolyte solution or the potential of net oxidation/reduction reaction. These behaviors were obtained experimentally from Tafel and potentiodynamic polarization plots. Under the test condition, all carbon steels immersed in solutions with and without heat stable salt compounds

were clearly in an active state as shown in Figure 1. No passive film was developed to protect the metal surface, thus allowing a series of half-cell oxidation and reduction reactions to occur. This was evidenced by increases in anodic current density with potential. As the potential was raised beyond the primary passive potential (E_{pp}), film was passivated on the metal surface. As a result, the system corrosiveness reduced substantially, as indicated by decreases in current density. The passive film eventually broke down at transpassive potential (E_{trans}).

5 kmol/m³ MEA-0.2 CO_2 loading-10,000 ppm of various test heat stable salts, 80°C
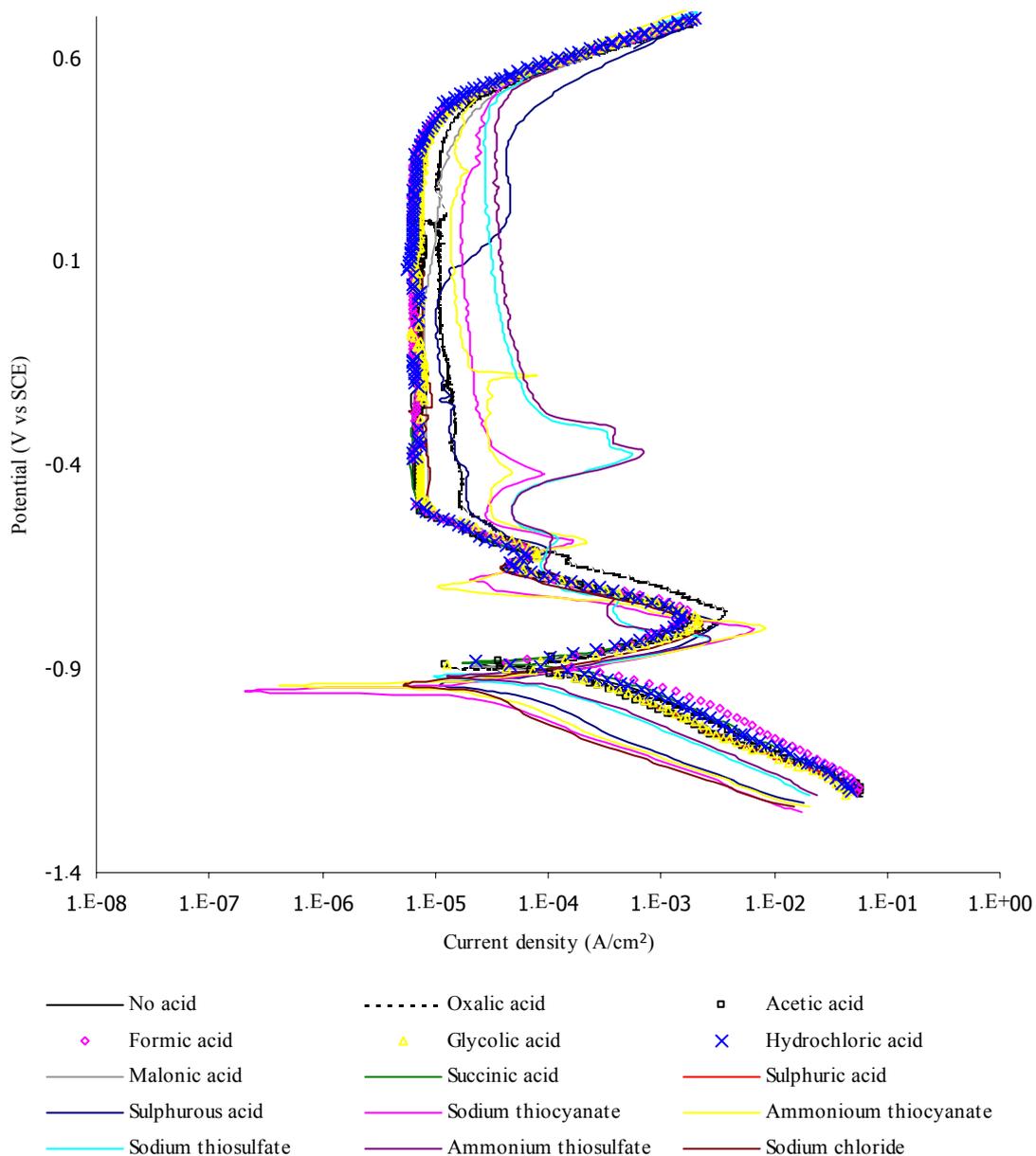
Figure 1: Comparison of potentiodynamic results at 1% of various compounds.

The actual corrosion degrees of the test systems were evaluated by analyzing the electrochemical data obtained from linear polarization resistance (LPR) plots. These plots gave values of corrosion resistance (R_p). A greater R_p reflects a lower corrosion rate and vice versa. Figure 2 shows the corrosive effects of heat stable salts presented in terms of corrosion rate. It was found that oxalate was the most corrosive salt among the test HSAS since it yielded the highest corrosivity, followed by malonate and formate, respectively. Glycolate, succinate, acetate, chloride (as HCl) and sulphate did not induce an increased corrosion rate. Chloride (as NaCl), sulfite, thiocyanate and thiosulfate inhibited corrosion to different degrees.
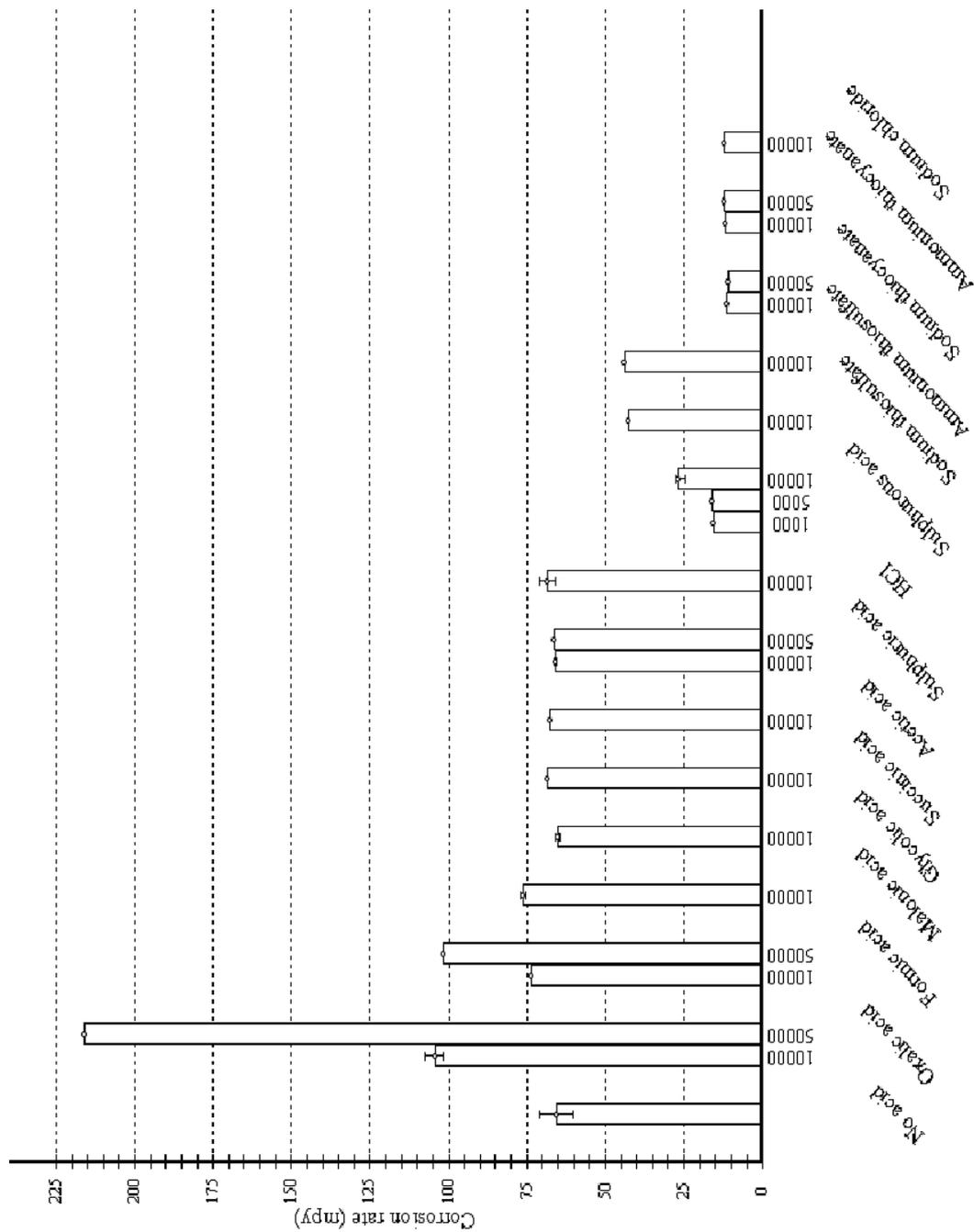
Figure 2: Corrosion rates at various concentrations of test compounds.

Remarks: 1000, 5000, 10000, 50000 in the Figure are the concentration in ppm of that chemical.

Since oxalic acid (oxalate) contributed to such a significant increase in corrosion rate compared to other acids, it was chosen as a representative of heat-stable salts in showing the effects of acid concentration on corrosion. From Figure 3, % increase in corrosion rate was plotted against the acid concentrations. Perspicuously, corrosion rate increased as the acid concentration rose. Neilson et al. [1] suggest that heat stable salts are corrosive because they lower the amine solution pH, increase solution conductivity and may also act as chelating agents, dissolving the protective film covering the base metal.
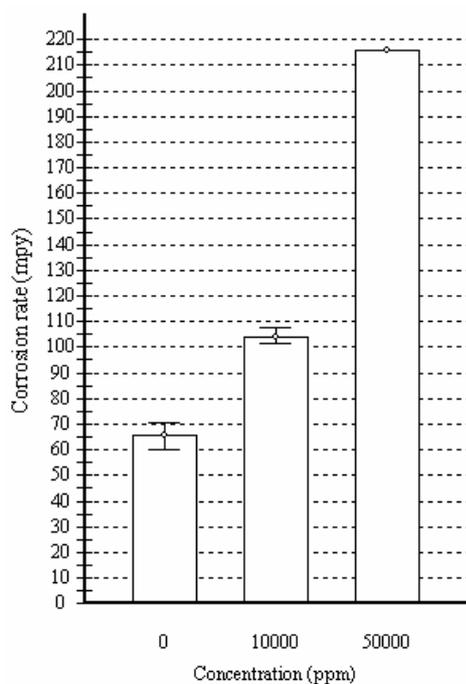
Figure 3: Effect of oxalic acid concentration on corrosion rate.

Cyclic polarization was also carried out to examine the pitting tendency. Since all acids behave similarly on carbon steel 1018 at the test conditions, oxalic acid was regarded as a good representative and presented here in the cyclic polarization curve. As seen in Figure 4A, the reverse scan was located on the left side of the anodic polarization curve. This indicated no localized pitting. As for stainless steel 316, oxalic and hydrochloric acids were suspicious of pitting tendency and therefore tested. The result also showed that none of them showed a pitting tendency under the test condition (Figure 4B).

CONCLUSIONS

The presence of heat stable salts did not alter the active state of the test metals, but it did have an apparent impact on corrosion in two manners. First, the heat stable salts, including oxalate, formate, malonate, glycolate, succinate, and acetate, sulphate and hydrogen chloride induced an increased uniform corrosion. Oxalate was the most corrosive salt, followed by formate and malonate. Higher salt concentration generally increased the rate of uniform corrosion. Second, the heat stable salts, including sulfite, sodium chloride, sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, and ammonium thiocyanate, retarded the rate of uniform corrosion or functioned as corrosion inhibitors. All test salts did not tend to induce pitting corrosion on both carbon steel and stainless steel.

ACKNOWLEDGEMENTS

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5N MEA + 1% Oxalic acid
80°C-0.2 CO_2 loading-CS 1018
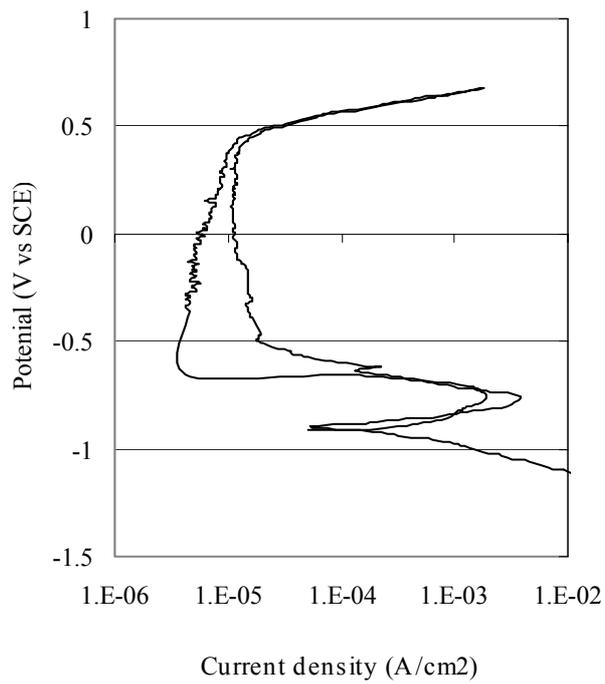
(a)

5N MEA + 1% Acid
80°C-0.2 CO_2 loading-SS 316

——— Oxalic acid - - -◇- - - Hydrochloric acid
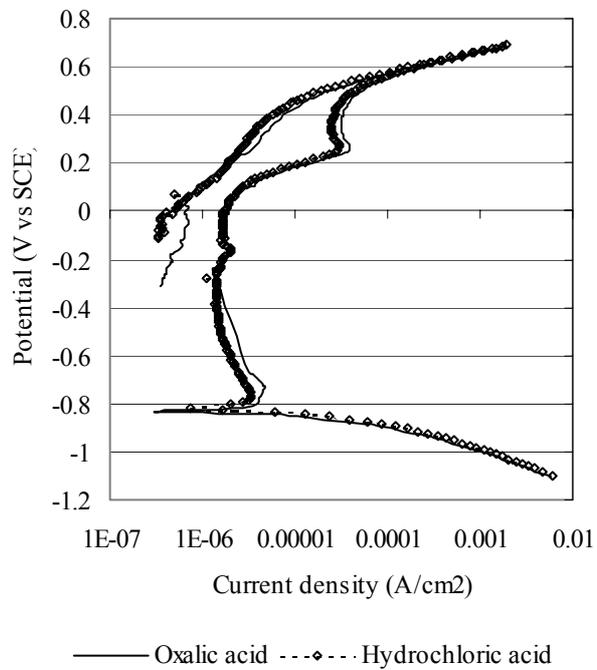
(b)

Figure 4: Cyclic polarization curve of (a) oxalic acid for CS 1018 and (b) oxalic acid and hydrochloric acid for SS 316.