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Corrosion in CO₂ capture unit using MEA-piperazine blends

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Abstract

This work investigated corrosion of carbon steel in the CO₂ capture unit using aqueous solutions of blended monoethanolamine (MEA) and piperazine (PZ). Results show the MEA/PZ solutions are more corrosive than the MEA solutions. Corrosion rate increases with PZ concentration, total amine concentration, CO₂ loading, solution temperature and heat stable salts. Formate is the most corrosive salt, followed by acetate, oxalate, and thiosulfate in the absence of oxygen (O₂), while acetate is the most corrosive salt followed by formate, oxalate, and thiosulfate in the presence of O₂. Sodium metavanadate (NaVO₃) and copper carbonate (CuCO₃) effectively suppress the corrosion rate to below 10 mpy

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Keywords: CO₂ corrosion; CO₂ capture; amine treating; piperazine; carbon steel; polarization

1. Introduction

Aqueous solutions of blended monoethanolamine (MEA) and piperazine (PZ) have demonstrated their promise as a cost-effective solvent for carbon dioxide (CO₂) capture from industrial flue gas streams due to their absorption performance and energy efficiency [1]. Although there are fundamental research data available on solvent stability, kinetics, solubility and mass-transfer of CO₂ into these blended solutions, no research has been done to investigate corrosiveness of these solutions. It was therefore our goal to further explore the promise of these blends in the aspect of corrosion, which is regarded as one of the most severe operational problems in the typical CO₂ capture plants using conventional solvents such as MEA. Emphasis of this work was placed on the determination of the level of corrosion rate and the understanding of corrosion behavior and mechanism under service conditions of this new blended MEA/PZ process. To achieve these objectives, electrochemical tests were carried out. All tested parameters and conditions are summarized in Table 1. All experiments were duplicated to ensure the reproducibility of the obtained data.

2. Experiments

Figure 1 illustrates the experimental setup for electrochemical corrosion tests. The corrosion cell was a one-litre standard three-electrode cell (model K47 from EG&G instruments corporation, Princeton Applied Research, NJ,

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USA) using a calomel reference electrode (SCE) (Hg/HgCl₂/ saturated KCl). Carbon steel 1018 working electrodes were cylindrical in shape with length, outside diameter, and hole diameter of 0.500 inch (1.270 cm), 0.375 inch (0.952 cm), and 0.210 inch (0.533 cm), respectively. They were prepared by wet grinding with 600 grit silicon carbide papers using deionized water in accordance with the ASTM standard G1-90 [2]. The potentiostat (model 273A EG& G Instruments Corporation, Princeton Applied Research, NJ, USA) provided an accuracy of $\pm 0.2\%$ of the potential and current readings. The data acquisition system, model 352 SoftCorr III (EG& G Instruments Corporation, Princeton Applied Research, NJ, USA), was used to control the potentiostat and also to record and analyze the produced corrosion data.

For each experiment, one litre of blended MEA/PZ solution with desired composition and CO₂ loading was prepared and transferred to a corrosion cell and a salt bridge. The corrosion cell was placed in a water bath to control the solution temperature at $80.0 \pm 0.1^\circ\text{C}$, connected to a condenser, and purged through a gas disperser with an appropriate mixture of N₂ and CO₂ to maintain a desired CO₂ loading of solution. After the cell reached the set environment, which took approximately 30 minutes, a prepared specimen was mounted to the holder. The corrosion cell was then connected to a potentiostat equipped with the data acquisition software. The polarization scan began when the potential of specimen reached equilibrium, or was constant with time. Three electrochemical techniques, Tafel plot, potentiodynamic polarization and cyclic polarization were used for corrosion measurements. Tafel plot involves polarizing a specimen in both anodic and cathodic directions in the potential range of ± 200 mV from equilibrium corrosion potential (E_{corr}) and generating an anodic/ cathodic polarization curve of the specimen. The obtained corrosion current density (i_{corr}), was used to calculate the corrosion rate of the specimen by using the following equation:

$$CR = \frac{(0.13 \times i_{\text{corr}} \times E.W.)}{A \times D} \quad (1)$$

where CR is corrosion rate in mils (thousandths of an inch) per year (mpy), i_{corr} is corrosion current density in $\mu\text{A}/\text{cm}^2$, $E.W.$ is equivalent weight of specimen, A is area of specimen in cm^2 , and D is density of the specimen in g/cm^3 . Before and after each experiment, samples of the solution were collected for solution analysis and both pH and conductivity of the solution were measured.

Table 1 Tested parameters and conditions for corrosion experiments

Parameter	Tested condition
Total amine concentration (kmol/m^3)	5.0, 6.2, 7.0, 8.7
CO ₂ loading of solution ($\text{mol CO}_2/\text{mol amine}$)	0.20, 0.40, 0.58, 0.63
Solution temperature ($^\circ\text{C}$)	40, 80
Partial pressure of O ₂ (kPa)	0.00, 5.07, 10.13
MEA/PZ Mixing ratio (mol : mol) @ Total amine concentration = $6.2 \text{ kmol}/\text{m}^3$	1:0, 1:1, 2:1, 4:1
Heat stable salt (1.00 wt%)	acetate, formate, oxalate, thiosulfate
Concentration of corrosion inhibitor (ppm):	
Sodium metavanadate (NaVO_3)	50, 100, 250
Copper carbonate (CuCO_3)	50, 100, 250

3. Results and discussion

3.1. Corrosion in uninhibited system

From Table 2, the blended MEA/PZ solution is more corrosive than the MEA solution when comparison is made at the identical total concentration of amine. This may be due to changes in reduction of oxidizing agent when PZ is present in the solution. Based on the principle of metal complexation, the iron dissolution occurs to produce Fe^{2+}

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