

Preferential Weld corrosion of carbon steel as Effect of Caustic in amine-CO₂ contained solutions

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Abstract

Technology to remove CO₂ gas from power plant emission are urgently required as wide impacts on environmental degradation. To date the primary compounds for CO₂ solvents are dominated by amines-based solvent such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). To improve adsorption system and prevent corrosion effect on metallic structure, Mitsubishi Heavy Industries (MHI) had developed solvent called KS-1. However, the use of KS-1 had caused several leakages on welding area in flue gas-CO₂ separation unit. It was reported that the failures occurred on different types of corrosion; carbonic acid and caustic corrosion. To investigate the corrosion rate on the weld area, it was conducted researches to determine the mechanism of the corrosion particularly on the roles of caustic and pH in relation with KS-1. In this research, the corrosion rate of carbon steel in KS-1 solvent solutions combined with saturated CO₂ gas and caustic solutions were studied. The experiments were carried out in static conditions and the linear polarization resistance (LPR) technique were used to measure the corrosion rate (as per ASTM G 5-94). It was found that the corrosion rate of base metal in the KS-1 mixed with caustic solutions did not show significant effects. At the base metal, the corrosion rate tends to be unvarying at adding caustic solution from 50 ppm to 500 ppm which was 0.05 mm/y. In contrast with on weld metal area, the corrosion rates were significantly high. The highest corrosion rate was at 500 ppm caustic solution which was 0.5 mm/y. The differences in microstructure and reaction activation of the samples may relate to the increase of corrosion process.

Keywords

CO₂ corrosion, Carbon steel, Amine solvent, Caustic solutions, Corrosion rate.

Introduction

At power plants, flue gas is often treated with a series of chemical processes and scrubbers to remove pollutants and reduce corrosive species. To treat the flue gas, the plant consists of three main equipment; namely; flue gas cooler, CO₂ absorber and CO₂ regenerator. To remove CO emission from the flue gas, they use amines in order to produce high purity CO. The flue typically consists of N₂ (67.79 vol%), O₂ (0.85 vol%), CO₂ (8.08 vol%), Ar (1.00 vol%), H₂O

(22.28 vol%), and impurities (NO_x, SO_x). Flue gas from the primary reformer is cooled in water-cooling tower. After cooled, CO₂ in the flue gas is absorbed by KS-1 solution in absorber (PFK, 2010).

Based on the process description, the piping from the CO₂ absorber to CO₂ regenerator contains KS-1 rich solution mixed with carbonic acid from the hydration of CO₂ gas with water (from water wash). In addition, the reclaiming process involving injection of caustic (Sodium Hydroxide) to reduce heat stable salts (HSS) which contribute to corrosion process. The use of amine-based solvent which are MEA, DEA, and MDEA are common in CO₂ capture plant. However, Both MEA and DEA form carbamate have a great impact on the corrosiveness of amine solutions. Corrosion process of carbon steel in amine solutions is suspected to the formation of heat stable salts (HSS) (Teeradet S., 2011). HSS are formed in the presence of acids which are substantially stronger than CO₂. These acids can form directly from flue gas components such as sulfur dioxide (SO₂) and sulfur trioxide (SO₃) or can be formed from amine degradation products. When formic acid is produced, it will react with MDEA to form a formate HSS. The HSS typically promote corrosion in the systems because they lower the pH and increase the conductivity of amine solutions. This can decrease the efficiency of CO₂ capture because of the irreversible reaction with the amine. Although there were extensive research on CO₂ corrosion (Asmara, 2012, 2015, 2018, 2019, Nesic, 2007, Nybork, 2006 Lee, 2004) have been conducted, measurement of corrosion rate related to real solutions are still limited.

This research aimed to test the effects of KS-1 on corrosion rate of carbon steel in CO₂ saturated gas combined with several concentration of caustic solution. In particular, corrosion rate on weld area.

Methodology

The experiments were performed both in stagnant (static test). The electrochemical technique measurements used linear polarization resistance (LPR). The procedure is similar to ASTM Experimental test G 5-94. The working electrodes were A-106 Gr B carbon steel. Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The experiments were repeated at least twice in order to ensure reasonable reproducibility.

Static Test

A typical experimental arrangement for the static test is illustrated in Figure below. The test assembly consists of one liter glass cell bubbled with CO₂. The required test temperature was set at the hot plate at 50°C. The electrochemical measurements were based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used was Ag/AgCl and the auxiliary electrode was a platinum electrode. Figure 1 shows the schematic illustration of static test. The Linear Polarization Resistance (LPR) technique was used to measure the corrosion rate. The procedure is similar to ASTM G 5-94.

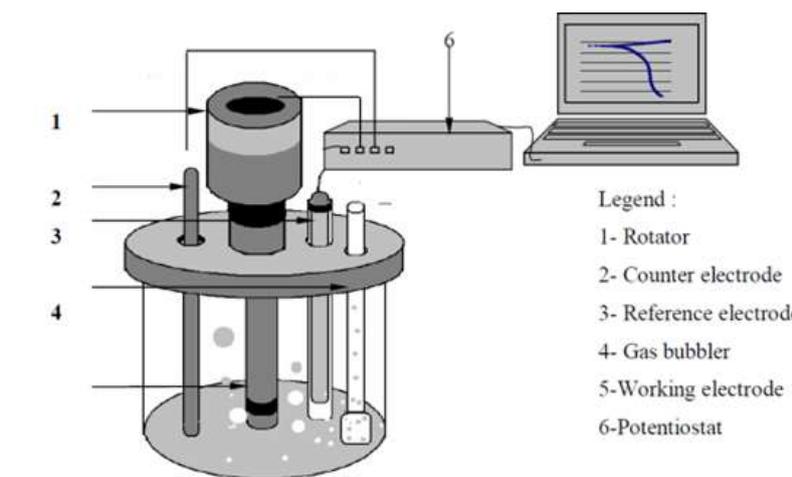


Figure 1. Experimental set-up for static test

Composition of Tested Solutions

Experiments were conducted in saturated CO₂ gas environment. In CO₂ gas system, the experiments used saturation condition of CO₂ gas where compositions and the pH solutions in the glass cell were described in Table 1.

Solution conditions	pH
KS-1+saturated CO ₂ + 50 ppm caustic	8.37
KS-1+saturated CO ₂ + 250 ppm caustic	8.3
Water/KS-1 (50:50) + CO ₂	7.9

KS-1 properties

Composition of the KS-1 as received from the plant was analysed with gas chromatography–mass spectrometry (GC-MS). The composition of the KS-1 is as shown in Figure 3 below which consist of active compound of methyl diethanolamine (MDEA) and piperazine.

Table 2. GCMS analytical result of KS-1 composition

Pk#	RT	Area%	Library/ID
1	1.727	4.90	C:\Database\NIST05a.L Ammonia Water
2	3.232	88.80	C:\Database\NIST05a.L Ethanol, 2-(ethylamino)- Ethanol, 2-(ethylamino)- N,N-Dimethyl-2-aminoethanol
3	3.822	6.30	C:\Database\NIST05a.L Piperazine Piperazine Piperazine

Results and Discussion

Corrosion rate of carbon steel in KS-1 solution

The corrosion behavior of A106Gr B with KS-1 at room temperature and 50°C was investigated and shown in Figure 1. It was recorded that corrosion rate of A106Gr B at room temperature and 50°C is negligible in the order of 0.0015 mm/yr and 0.018 mm/yr, respectively. Based on the results, it shows that KS-1 is not corrosive to carbon steel this is due to probably inhibitor properties (piperazine) of the solution.

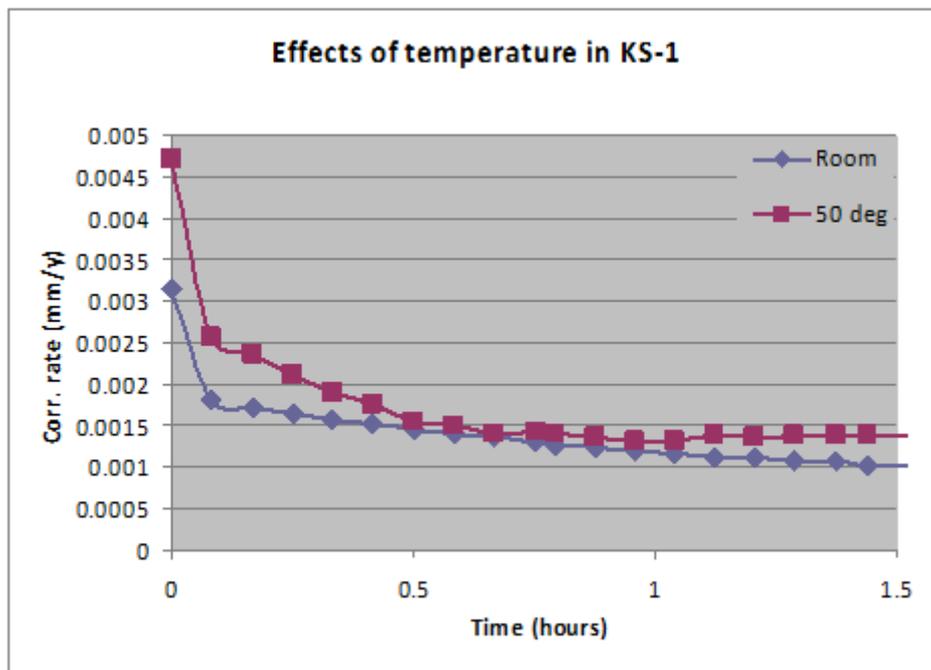


Figure 2. Corrosion rate of carbon steel in KS-1/water solution, 50°C and saturated CO₂ gas

Corrosion rate of welded carbon steel in KS-1 solution

The welded carbon steels were taken from single-vee welded joint of low carbon steel, ASTM 106 B pipeline. Based on the Figure 2 data, it shows that there are a significant differences of corrosion rate in weld and base metal region. The corrosion rate on weld metal can be double compared to base metal region in all conditions. Corrosion rate on base metal was recorded 0.05 mm/y and went to 0.11 mm/y on weld metal. The increase of corrosion rate as effects of weld were also happened on caustic mixed solutions. The more caustic concentration the more corrosion rate will occur. This higher corrosion rate of weld regions is due to microstructural heterogeneities caused by variation in heating and cooling process. The differences in microstructure can result in galvanic effect and initial stress of the samples. In addition to, the presence of corrosive species such as H₂S, CO₂ and organic acid in KS-1/water creates an aggressive environment which can cause severe preferential weld attack. (Asmara, 2015).

Effect of caustic on corrosion rate of welded carbon steel in KS-1 solution

The corrosion rate of welded carbon steel in KS-1 solution mixed with several concentration of caustic were studied under freely corroding potentials. The pH of the solutions were recorded and presented in Table 1. From the Figure 3 to Figure 5, it can be seen that effects of 50 ppm – 500 ppm have increased corrosion rate on weld metal from 0.15 mm/y to 0.3 mm/y. However, effect of 50 ppm – 500 ppm concentration caustic on base metal did not contribute in corrosion rate significantly. The highest increase of corrosion rate was recorded at 500 ppm caustic concentration where there was an increase of 9 times on weld metal. This was considered to be due to mixed rate control involving activation polarization and mass transport processes (Weisun, 2006). The corrosion mechanism will bring to corrosion cracking which was entirely consistent with metal dissolution at -0.76 VSHE and may involve hydrogen embrittlement and/or dissolution effects at E_{corr} (Anwar, 2009, Carter, 1977, Douglas, 1982).

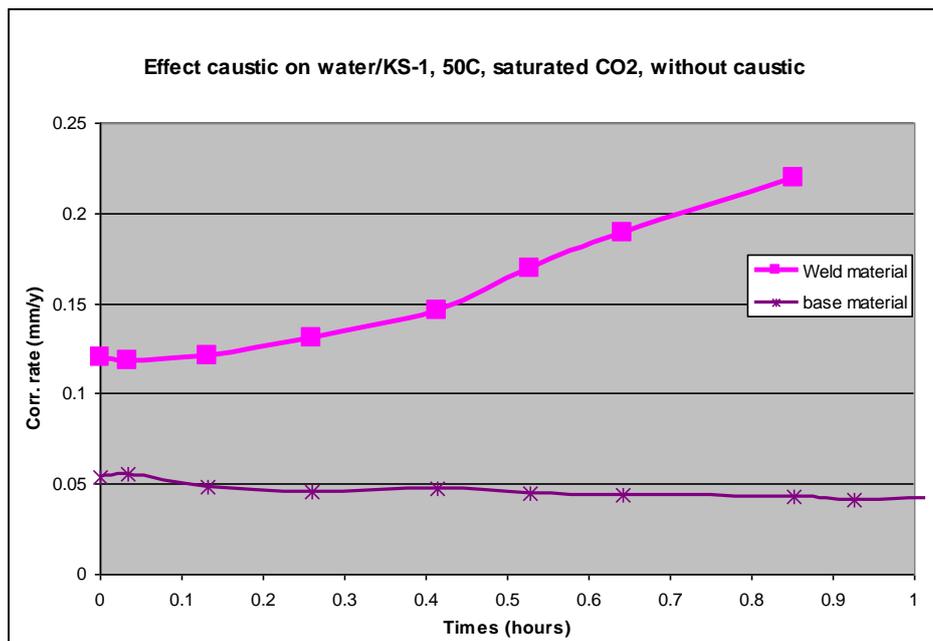


Figure 2. Effects of material welding on corrosion rate in KS-1/water solution, 50°C and saturated CO₂ gas

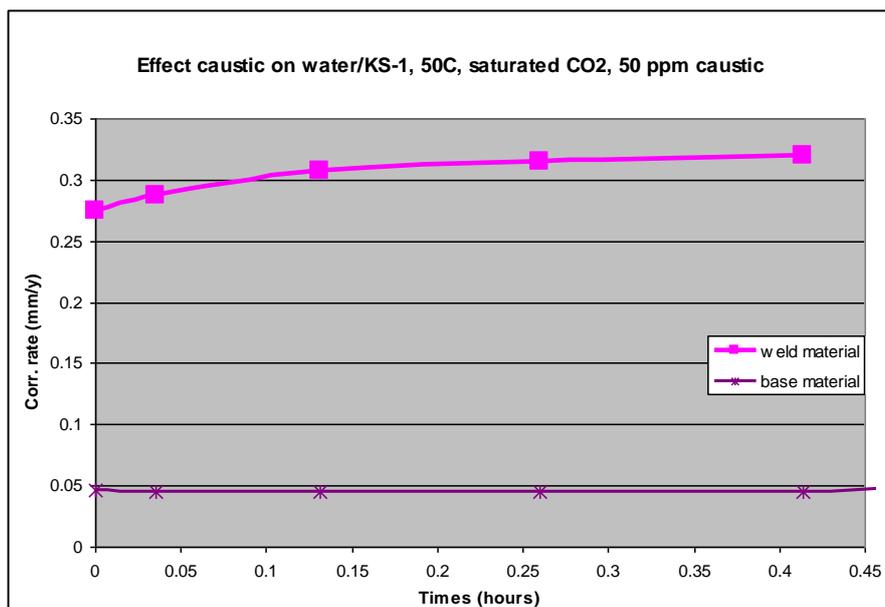


Figure 3. Effects of 50 ppm caustic on corrosion rate in material welding at conditions: KS-1/water solution, 50°C and saturated CO₂ gas

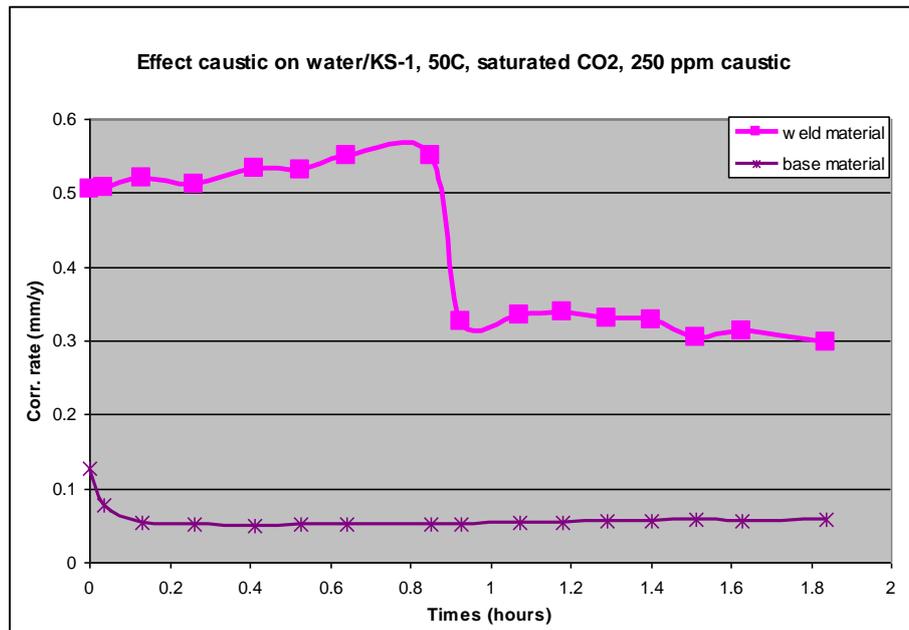


Figure 4. Effects of 250 ppm caustic on corrosion rate in material welding at conditions: KS-1/water solution, 50°C and saturated CO₂ gas

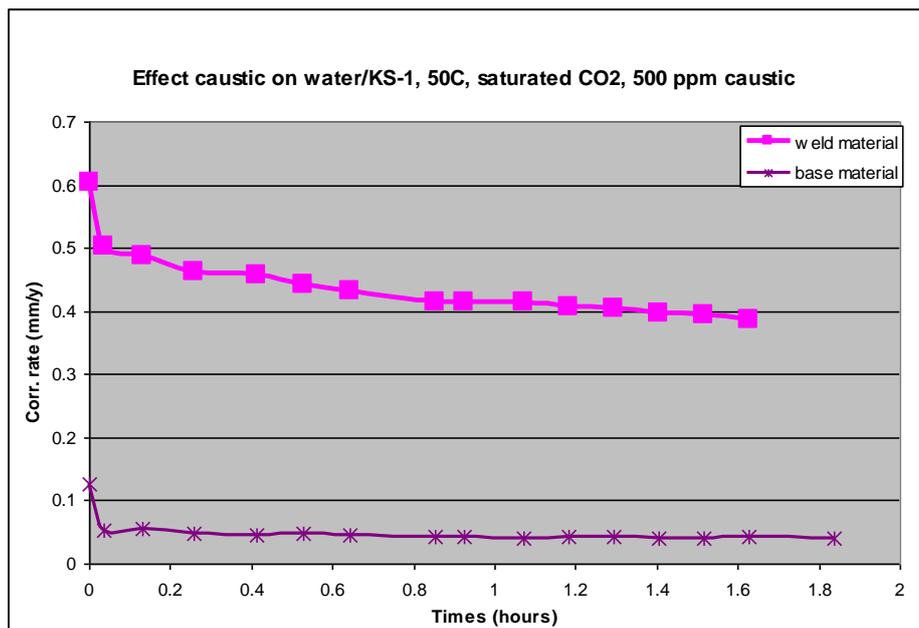


Figure 5. Effects of 500 ppm caustic on corrosion rate in material welding at conditions: KS-1/water solution, 50°C and saturated CO₂ gas

Conclusion

Corrosion rates were higher on weld area than base metal of carbon steel in solution consist of saturated CO₂ gas, caustic and KS-1 solvents. There were significant differences which can reach up to 5 times (500 ppm of caustic solution). Effect of caustic from 50 ppm to 500 ppm in KS-1 and CO₂ contained solutions on corrosion rate of base metal carbon steel were not

significant. The corrosion rate on base metal was 0.05 mm/y. On contrast on weld area, the corrosion rate increased remarkable from 0.11 mm/y (no caustic) to 0.5 mm/y (500 ppm of caustic concentration).

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