Effect of altered Antifreeze to Component Materials Cooling Water System for an Emergency Diesel Generator

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1. Introduction

A nuclear power plant had reached the end of its design life and is now permanently shut down and is being dismantled. However, the spent fuel pool is not dismantled and is still functioning to store the spent fuel. Spent fuel is in a state in which the fuel has not been physically completely consumed, but rather the toxic substances from the reaction have accumulated and the nuclear fission reaction can no longer continue. Therefore, spent fuel in the storage tank continuously releases residual heat and radioactive materials due to nuclear fission. And then cooling and purification are important for safe storage of spent fuel. The cooling and purification system is operatiing for this purpose. And the plant also maintains an emergency diesel generator (EDG) to prepare for unexpected power outages. In addition, EDG is subject to periodic testing in accordance with the technical specification. But the EDG was shutdown by an automatic high-high temperature stop signal in the cooling water during the periodic testing. It was assumed that one of the causes of shutdown was that the altered antifreeze did not effectively prevent material corrosion. As part of the root cause analysis, this study evaluated the impact of the altered inhibitor on the components of the cooling system.

2. Methods and Results

Electrochemical experiments (Poteniodynamic Polarization) and immersion tests were used to evaluate the effectiveness. The experimental temperature was 70°C, which is the average temperature of the cooling water when the emergency diesel generator is operating. The specimens used in the experiment were manufactured from SA106 Gr.B (carbon steel), a cooling system piping material, and Cu (copper), a heat exchanger material. The surfaces of the manufactured specimens were polished to 1㎛ using a diamond suspension solution to minimize evaluation errors. After polishing, the specimens were sonicated in acetone to remove any residual surface impurities. The test solutions used were inhibited ethylene glycol (EG) and ethylene glycol containing additives (EGA).

Initially, in the electrochemical experiment, 100% ethylene glycol concentration was used, but data measurement was impossible (overload state) due to low conductivity, so the ethylene glycol concentration was diluted to 30% and the experiment was conducted again. The potential applied to calculate the current density is from -0.5 V to +1.5 V compared to OCP (Open Circuit Potential), and the data sweep rate was 1 mV/s. The current density was calculated from the measured polariaztion curve using the Tafel extrapolation method. And the corrosion rate was calculated using equation 1.

$$CR(\text{Corrosion Rate}) = 3272 \cdot i_{corr} \cdot EW/\rho \quad \text{Equation 1}$$

where, i_{corr} is corrosion current density (A/cm^2)
EW is equivalent weight (g/equivalent)
ρ is density of each material (g/cm^3). The density of carbon steel used 7.85 g/cm^3, and copper used 8.94 g/cm^3.

The immersion time was 1,000 hours. The corrosion rate was calculated using the weight loss of the specimens after the immersion test. After the experiment, the specimens were analyzed using SEM (Scanning Electron Microscope) and XRD (X-ray Diffraction) to evaluate the surface integrity and oxide properties.

2.1 Results of Potentiodynamic Curve

Figure 1 shows the polarization curves measured for each solution and specimen. Table I shows the corrosion rates calculated using the measured current densities. In both materials, the current density and corrosion rate were lower in the EGA solution than in the EG solution.

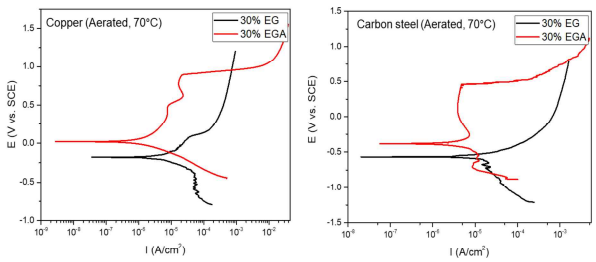


Fig. 1. Polarization curves for copper (left) and carbon steel (right) and in EG and EGA solutions, respectively.

Table I: Calculated corrosion rate using measured current density

Material	Antifreeze	I_{con}(A/cm^2)	E_{con}(V)	CR(mm/yr)
Copper	EG	7.79E-06	-0.178	0.09034

SA106 Gr.B	EGA	1.67E-06	0.021	0.01937
	EG	1.33E-05	-0.567	0.15522
	EGA	2.76E-06	-0.388	0.03221

From a material perspective, copper was calculated to have a lower corrosion rate than carbon steel. Compared to the corrosion allowance presented in the EPRI guidelines, both materials were evaluated as within the margin (>0.08~0.14 mm/yr) in the EG solution, and both materials were evaluated as good (<0.08 mm/yr) in the EGA solution[1].

2.2 Results of Corrosion Rate after the Immersion Test

Figure 2 shows the results of weight measurements ovet time for carbon steel and copper materials in the EG and EGA solutions. Regardless of the solution, carbon steel and copper materials initially showed a tendency for increased corrosion, but after 24 hours of immersion, the corrosion rate decreased sharply. This trend was more evident in the EGA solution. The reason for this tendency is that corrosion occurs rapidly in the beginning, and as corrosion products accumulate on the specimen surface which plays a role in inhibiting corrosion[2]. In the EG soultion, the corrosion rate of copper decreased with immersion time, but was remained higher than that of carbon steel.

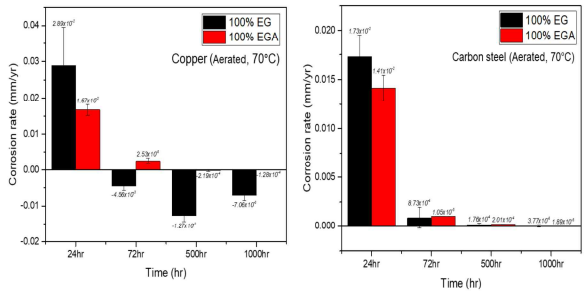
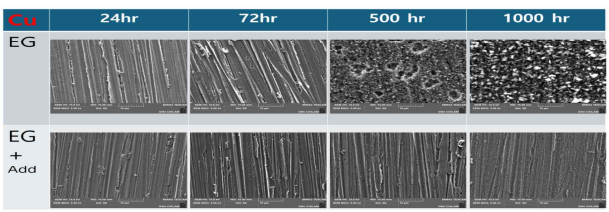


Fig. 2. Corrosion rate trends according to immersion time by material and solution

2.3 Results of Surface Analysis

Figure 3 shows the surface condition of each material after the immersion test. In the EG solution, copper showed traces of pitting after 74 hours, and particulate oxides were distributed on the surface after 1,000 hours. However, in the EGA solution, no traces of pitting or oxides were observed on the surface regardless of the immersion time. For carbon steel, no traces of formula or corrosion oxide formation were observed, regardless of the solution.



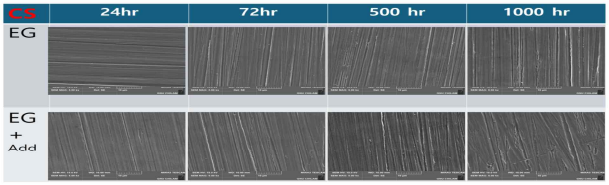
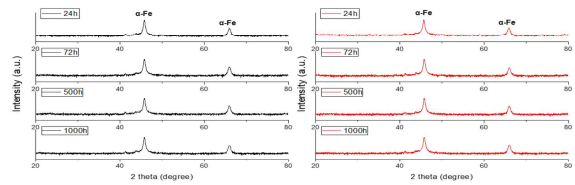
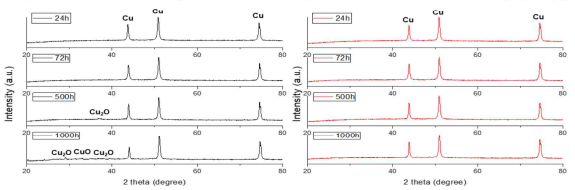


Fig. 3. Surface analysis results using a SEM. Copper (top) vs Carbon steel (bottom)

Figure 4 shows the results of the analysis of the crystal state of the oxide formed on the surface of the specimens. The crystal state of the oxide formed on the surface of carbon steel was goethite(α-FeOOH) regardless of the solution, and the formed oxides remained stable without growing or changing overtime. However, the crystal state of the copper oxide produced differed depending on the solution. In the EGA solution, there was no trace of oxide on the surface of copper. But in the EG solution, Cu_2O was formed after 72 hours. Finally, it can be seen that crystalline oxides such as Cu_2O and CuO are ultimately formed.



(a) Carobon steel[EG solution (left), EGA solution (right)]



(b) Copper[EG solution (left), EGA solution (right)]

Fig. 4. Surface crystal state analysis results using XRD

3. Conclusions

To analyze the cause of corrosion of the components of cooling system for an emerency disel generator. It was assumed that one of the causes of corrosion was due to a change in the antifreeze. For evaluation, electrochemical experiments and immersion test were conducted. The evaluation results showed that overall, the corrosion rates of copper and carbon steel in the EG solution were high. In particular, corrosion of copper was increased as the immersion time increased. In Contrast, copper and carbon steel corrosion was nearly absent in the EGA solution. This is likely due to the presence of trace amounts of chemicals among the additives in the EGA that act as corrosion inhibitors

REFERENCES

[1] Closed Cooling Water Chemistry Guideline: Revision 2. EPRI, Palo Alto, CA: 2013. 3002000590.
[2] Denny A. Jones, Principles and Prevention of Corrosion, Second Edition, p.8, 1996.