

Effect of Dispersant on the Corrosion Behaviour of Carbon Steel and Magnetite in Simulated Secondary Water

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1. Introduction

Magnetite particles formed on the surface of secondary feed water pipe in pressurized water reactors (PWRs) are carried with the feed water flow to the secondary side of a steam generator (SG). They are deposited on heat transfer tubes and accumulated on the tube sheet and support plates in the secondary side of the SG. This phenomenon not only reduces heat transfer efficiency from the primary to the secondary side but also accelerates the corrosion degradation of SG tubes.

To mitigate these problems, a method using a polymeric dispersants for the removal of colloidal magnetite particles has recently been proposed [1,2]. Polyacrylic acid (PAA) has been considered as a potential dispersant to mitigate corrosion product accumulation in SGs of PWRs. If PAA is used as a polymeric dispersant to mitigate fouling phenomena in SGs, it is necessary to evaluate the effects of PAA on the corrosion behavior of carbon steel in secondary environments of PWRs. In this regard, there are some published papers, but the effect of PAA on the corrosion of carbon steel in simulated secondary water of PWRs are unclear [3-5]. Furthermore, the mechanism of interaction between PAA and carbon steel has not been elucidated.

Although magnetite is the root cause of SG fouling, it protects carbon steel piping from general corrosion and from flow-accelerated corrosion in secondary system environments. The surface of carbon steel is typically covered with magnetite under reducing operation conditions. The magnetite layer formed on the surface of carbon steel contains pores in nature, and the small area of carbon steel is exposed to the reducing secondary water due to the pores at the oxide/steel interface [6]. In addition, this layer are rapidly removed by flow accelerated corrosion in the turbulent flow region, and the exposed metal surface of carbon steel is electrically connected with the remaining magnetite layer. Consequently, a galvanic cell between carbon steel and magnetite can be formed, because magnetite shows almost metallic behavior with respect to electrical properties [7]. Recently, it has been reported that the galvanic coupling with magnetite accelerates the corrosion of secondary system materials, such as carbon steel [8], Alloy 600 [9], and Alloy 690 [10] in simulated secondary water of PWRs. Therefore, it is important to evaluate the effect of PAA on the corrosion behavior of magnetite as well as that of carbon steel.

In this work, the effect of PAA on the corrosion behavior of carbon steel and magnetite was investigated using electrochemical techniques under simulated wet layup conditions. The mechanism of interaction of PAA with carbon steel and magnetite is also discussed.

2. Experimental Procedures

2.1 Preparation of carbon steel and magnetite electrodes

Carbon steel specimens were machined from SA106Gr.B pipe material into a size of 10 mm × 5 mm × 1 mm. The specimens were ground using silicon carbide papers down to grit 1000, and then ultrasonically cleaned in acetone. After that, the specimen was spot-welded to a pure iron wire, which was then covered with a PTFE tube for electrical insulation. The area around the weld junction was coated with an epoxy resin to prevent crevice corrosion. This specimen was used as a carbon steel working electrode for electrochemical tests.

A magnetite working electrode was prepared by the electrodeposition of the magnetite layer on the whole surface of the carbon steel electrode stated above, as shown in Fig. 1. The electrodeposition solution consisted of 2 M NaOH, 0.1 M triethanolamine, and 0.043 M Fe₂(SO₄)₃. The electrodeposition process of magnetite was conducted at an applied potential of -1.05 V_{SCE} for 30 min at 80 °C in a three-electrode cell using a potentiostat. The detailed electrodeposition process of magnetite is given in previous studies [11,12].

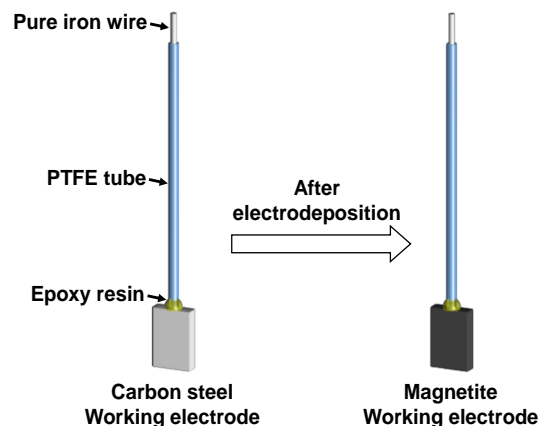


Fig. 1. Schematic for a magnetite working electrode prepared using the electrodeposition method.

2.2 Electrochemical corrosion test

The base test solution used in this work was deionized water with a pH of 9.5. To evaluate the effect of PAA, PAA with a molecular weight of 100,000 g/mol was added to the base solution. Regardless of PAA addition, the final pH of all test solutions at 25 °C was adjusted to 9.5 with ethanolamine, which is an organic chemical agent used to control the pH of secondary water in PWRs. All electrochemical corrosion tests were carried out under a deaerated condition at 25 °C. For a deaerated condition, the test solutions were continuously purged with high-purity nitrogen gas (99.999%) at a rate of 600 cm³/min during testing. This test environment was designed to simulate wet layup conditions in SGs.

Potentiodynamic polarization tests were performed using a potentiostat and a three-electrode cell. A saturated calomel electrode and platinum wire were used as a reference and counter electrode, respectively. After the open circuit potential (OCP) was stabilized, polarization scans for carbon steel and magnetite were started from 10 mV below the OCP to the anodic direction or from 10 mV above the OCP to the cathodic direction. The scan rate was 1 mV/s. Each anodic and cathodic polarization curve was finally combined in one graph.

3. Results and Discussion

Fig. 2 shows the polarization curves of carbon steel and magnetite in the test solution with and without 100 ppm PAA at 25 °C. The addition of 100 ppm PAA to the test solution shifted the corrosion potential (E_{corr}) of carbon steel from -0.769 V_{SCE} to -0.816 V_{SCE}. The overall polarization curves were also shifted in the direction of higher current density. The corrosion current density (i_{corr}) of carbon steel at the OCP increased from 1.4 $\mu\text{A}/\text{cm}^2$ to 4.1 $\mu\text{A}/\text{cm}^2$ with the addition of 100 ppm PAA. This result indicates that the addition of 100 ppm PAA increases the corrosion rate of carbon steel by approximately 2.9 times. The E_{corr} of magnetite was lowered from -0.424 V_{SCE} to -0.494 V_{SCE} with the addition of 100 ppm PAA to the test solution. However, the overall polarization curves were shifted in the direction of lower current density. The i_{corr} of magnetite at the OCP decreased slightly from 1.3 $\mu\text{A}/\text{cm}^2$ to 0.8 $\mu\text{A}/\text{cm}^2$ with the addition of 100 ppm PAA. This result indicates that the addition of 100 ppm PAA decreases the corrosion rate of magnetite by approximately 1.6 times.

To predict the galvanic corrosion behavior between carbon steel and magnetite using the mixed potential theory, the polarization curves of Fig. 2 were rearranged in Fig. 3. As shown in Fig. 3, the E_{corr} of carbon steel was lower than that of magnetite in the test solution both with and without PAA. This means that carbon steel behaves as an anode, if carbon steel and magnetite are

in electrical contact. The galvanic coupling with magnetite is expected to increase the i_{corr} of carbon steel from 1.4 $\mu\text{A}/\text{cm}^2$ to 8.3 $\mu\text{A}/\text{cm}^2$ in the test solution without PAA. In the 100 ppm PAA solution, the i_{corr} of carbon steel also increases slightly from 4.1 $\mu\text{A}/\text{cm}^2$ to 4.8 $\mu\text{A}/\text{cm}^2$ by the galvanic coupling with magnetite. From these results, it is expected that the presence of 100 ppm PAA will decrease the galvanic corrosion rate of carbon steel from 8.3 $\mu\text{A}/\text{cm}^2$ to 4.8 $\mu\text{A}/\text{cm}^2$.

Although the presence of PAA increases the corrosion rate of bare carbon steel, most of the carbon steel surface is covered with a magnetite layer under operating conditions. The electrochemical result shows that when carbon steel and magnetite are in electrical contact in equivalent area ratio, the corrosion rate of carbon steel increases. This type of galvanic corrosion occurs when the magnetite layer on carbon steel is partially removed. However, the extent of galvanic corrosion between carbon steel and magnetite is reduced in the presence of 100 ppm PAA. Therefore, it is expected that the use of PAA dispersant during wet layup will be beneficial in reducing magnetite deposits and will not cause corrosion-related problems.

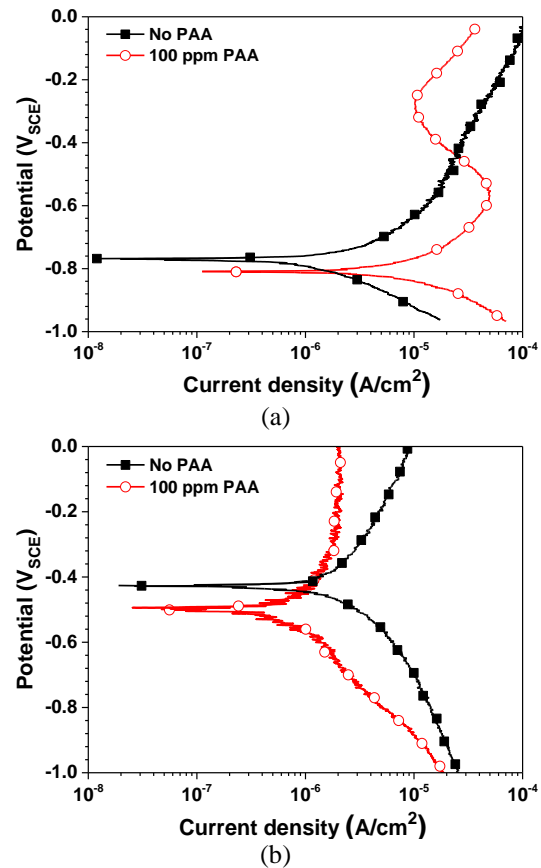


Fig. 2. Potentiodynamic polarization curves of (a) carbon steel and (b) magnetite in alkaline aqueous solutions of pH 9.5 with and without 100 ppm PAA at 25 °C.

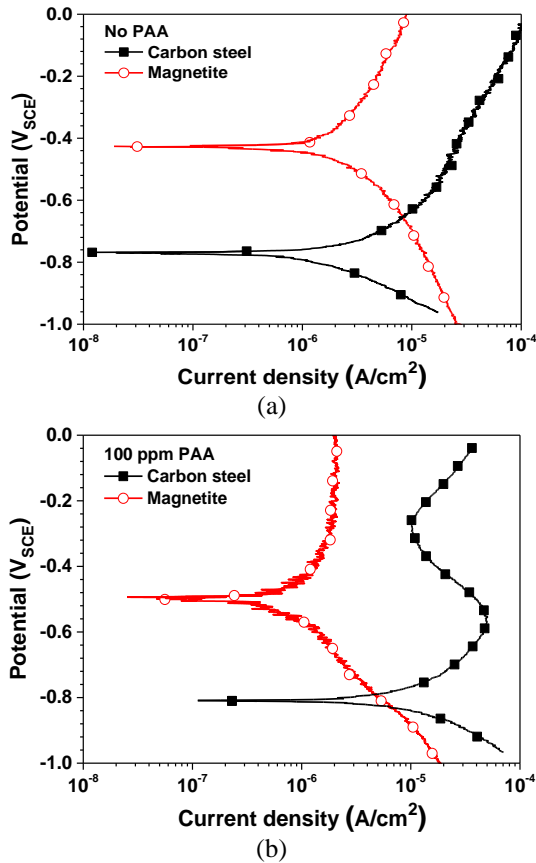


Fig. 3. Galvanic corrosion behavior between carbon steel and magnetite in alkaline aqueous solutions of pH 9.5 with and without 100 ppm PAA at 25 °C: (a) no PAA and (b) 100 ppm PAA.

4. Conclusions

- (1) The addition of 100 ppm PAA accelerated the corrosion rate of carbon steel. However, the addition of 100 ppm PAA slightly decreased the corrosion rate of magnetite.
- (2) The electrochemical behavior of carbon steel and magnetite showed that carbon steel acts as an anode of the galvanic couple with magnetite, regardless of the presence of PAA.
- (3) The galvanic coupling with magnetite increased the corrosion rate of carbon steel in the test solution both with and without PAA. In this couple, the extent of the galvanic corrosion of carbon steel was reduced by the addition of 100 ppm PAA.

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