

A Review of Magnetite-Accelerated Corrosion of Secondary Side Materials in PWRs

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1. Introduction

The main feedwater system of the secondary side in pressurized water reactors (PWRs) is operated under reducing water chemistry conditions at a room-temperature pH (pH_{RT}) of 9.5–9.8 in order to suppress corrosion of piping and steam generator materials [1]. The main feedwater piping, predominantly composed of carbon steel, is subject to flow-accelerated corrosion under high-velocity flow conditions, whereby the magnetite layer formed on the pipe surface dissolves and can subsequently be transported into the steam generator. The resulting dissolved iron species and magnetite particles deposit onto the surfaces of the steam generator tubes and their supporting structures.

Notably, deposits formed on the tube surfaces exhibit a highly porous structure containing numerous pores, generated by the nucleation and departure of steam bubbles during the boiling process [2]. These pores can serve as sites for the accumulation of impurity species, or as so-called hideout sites, thereby creating localized water chemistry environments that promote material corrosion. Furthermore, because magnetite have a lower thermal conductivity than the underlying tube material, their presence can elevate the outer surface temperature of the tubes, potentially further accelerating corrosion.

Another important consideration is that magnetite exhibits relatively high electrical conductivity, with a room-temperature conductivity of approximately $2.5 \times 10^4 \text{ S/m}$ [3]. This indicates that magnetite can provide an electrically conductive path for galvanic coupling with metallic materials. Therefore, when magnetite deposits are present on a metallic surface, the magnetite and the underlying metal may form a galvanic couple, potentially altering the electrochemical corrosion behavior of the substrate. The present study aims to review the effects of such galvanic couples on the corrosion behavior of carbon steel and steam generator tube materials.

2. Preparation of Magnetite Specimens

A compact and rigid magnetite working electrode is needed to evaluate the electrochemical corrosion behavior of magnetite itself. In this study, various types of these magnetite-deposited specimens were prepared by the electrodeposition of the magnetite layer on a material matrix. The electrodeposition solutions

consisted of 2 M sodium hydroxide, 0.1 M triethanolamine, and 0.043 M ferric sulfate hydrate. The magnetite layer was electrodeposited in the solution at an applied potential of $-1.05 \text{ V}_{\text{SCE}}$ at 80°C . The detailed electrodeposition process of magnetite is given elsewhere [4,5].

3. General Corrosion

Fig. 1 shows the potentiodynamic polarization curves of carbon steel SA106 Gr.B and magnetite in a solution with a pH_{RT} of 9.5 at 60°C [6]. The corrosion potential (E_{corr}) of magnetite was approximately 380 mV more positive than that of carbon steel. Therefore, when electrically connected, carbon steel acts as the anode of the galvanic couple. The corrosion rate can be calculated from the corrosion current density at each E_{corr} using the Tafel extrapolation method. The galvanic corrosion rate can also be estimated using the mixed potential theory. As expected, the corrosion current density increased by a factor of 3.6 (from 3.42 to $12.42 \mu\text{A}/\text{cm}^2$) upon galvanic coupling.

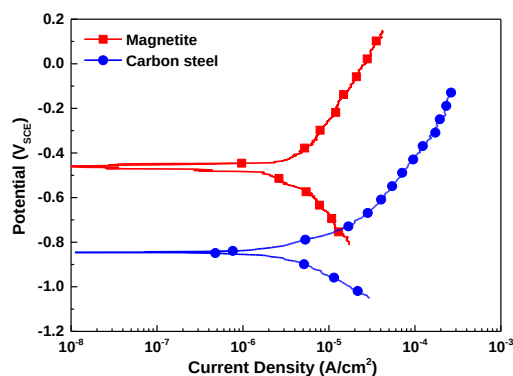


Fig. 1. Potentiodynamic polarization curves of SA106 Gr.B and magnetite in a solution with a pH_{RT} of 9.5 at 60°C .

As shown in Fig. 2, the E_{corr} of magnetite was also more positive than that of Alloy 690 in a solution with a pH_{RT} of 9.5 at 60°C [7]. As a result, the corrosion rate of Alloy 690 increased by a factor of approximately 2.6 when Alloy 690 and magnetite were galvanically coupled at an equal area ratio. Alloy 600 also showed similar electrochemical behavior in the same test solution [8].

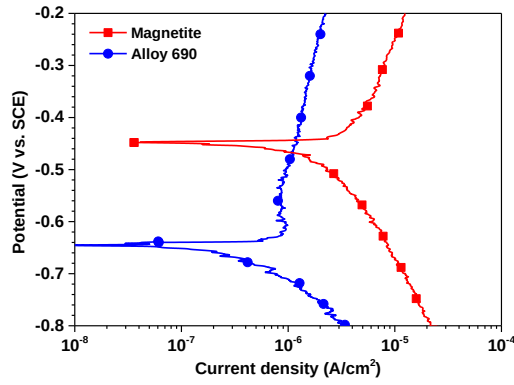


Fig. 2. Potentiodynamic polarization curves of Alloy 690 and magnetite in a solution with a pH_{RT} of 9.5 at 60 °C.

4. Flow-Accelerated Corrosion

The polarization curves of magnetite and SA 106 Gr. B were obtained under both stagnant and flowing conditions in a solution with a pH_{RT} of 9.5 at 60 °C. As shown in Fig. 3 [9], the E_{corr} of carbon steel was always lower than that of magnetite. This means that carbon steel and magnetite will act as an anode and cathode, respectively, when these two materials are electrically connected. Under flowing conditions, the E_{corr} values of both carbon steel and magnetite shifted in the positive direction compared with those under stagnant conditions. The corrosion current densities of carbon steel and magnetite also increased. This is because the mass transfer rate is increased by the presence of a fluid flow.

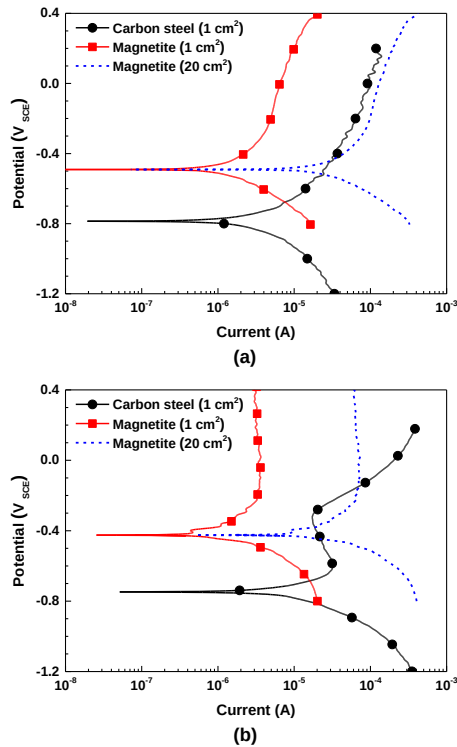


Fig. 3. Potentiodynamic polarization curves of SA106 Gr.B and magnetite under both stagnant and flowing conditions in a solution with a pH_{RT} of 9.5 at 60 °C.

To evaluate quantitatively the effects of a fluid flow, the galvanic coupling with magnetite and the area ratio (AR) of magnetite to carbon steel on the corrosion rate of carbon steel, corrosion parameters were estimated from the polarization curves. The changes in the corrosion current density of carbon steel caused by the three factors mentioned above were summarized in Fig. 4. The corrosion current density of carbon steel is expected to increase by a factor of approximately 5 due to fluid flow. The corrosion current density increases by a factor of approximately 11 when both fluid flow and galvanic coupling with magnetite (AR=1) are considered. Furthermore, the corrosion acceleration caused by these two factors becomes more pronounced, increasing to approximately 16 times as the AR increases from 1 to 20. Consequently, the corrosion rate of carbon steel can be drastically accelerated in a region where these three factors are combined.

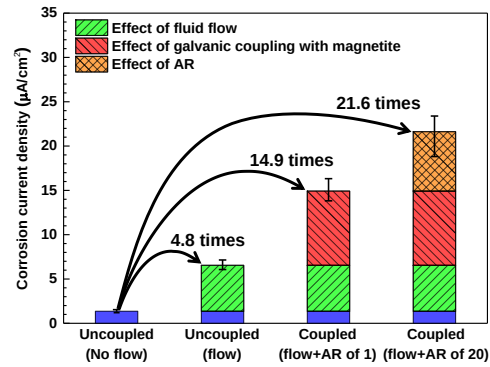


Fig. 4. The change in the corrosion current density of carbon steel caused by effects of a fluid flow, the galvanic coupling to magnetite and the AR in the test solutions at 60 °C.

5. Stress Corrosion Cracking (SCC)

To evaluate the effects of magnetite on the SCC behavior of Alloy 600, a magnetite layer was electrodeposited over the entire surface of U-bend specimens except for a region approximately 0.8–1 mm wide at the apex. Fig. 5 shows typical stress corrosion cracks in Alloy 600 U-bend specimens uncoupled and coupled with magnetite after 1000 h of testing in a solution containing 100 ppm PbO at 315 °C. The coupled specimens exhibited much deeper cracks than the uncoupled specimens.

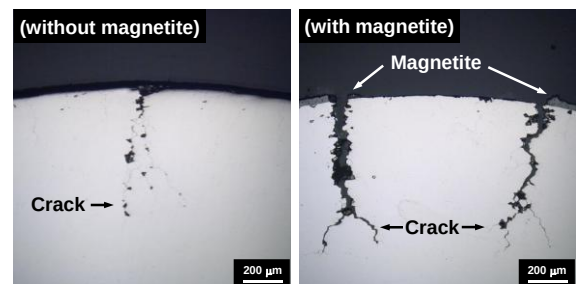


Fig. 5. Stress corrosion cracks of Alloy 600 without magnetite and coupled with magnetite in a solution containing 100 ppm PbO at 315 °C after 1000 h.

Fig. 6 shows the cross-sectional images of the U-bend specimens exposed to 10 wt.% NaOH solution for 300 h [11]. No stress corrosion cracks were generated in any of the magnetite-free specimens. However, stress corrosion cracks with depths of 150–280 μm were observed in all magnetite-deposited specimens. Furthermore, the deepest crack was always observed near the junction between the exposed Alloy 600 surface and magnetite layer, not the apex with the greatest stress in the U-bend specimen. These results indicate that magnetite coupled to Alloy 600 induces the rapid SCC of Alloy 600.

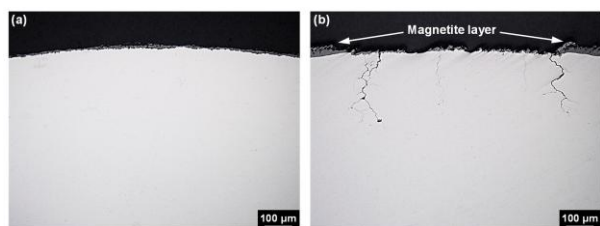


Fig. 6. Stress corrosion cracks of Alloy 600 without magnetite and coupled with magnetite in 10 % NaOH solution at 315 °C: (a) magnetite-free U-bend specimen and (b) magnetite-deposited U-bend specimen.

6. Conclusions

Magnetite exhibited a more positive corrosion potential than carbon steel and Ni-based alloys in simulated PWR secondary water. As a result, magnetite coupled to the materials significantly accelerates the general corrosion, flow accelerated corrosion, and stress corrosion cracking of the materials in various aqueous environments. Actual corrosion phenomena occur under conditions where the surfaces of the materials are covered with porous magnetite deposits. Therefore, the magnetite-accelerated corrosion effects should be considered in evaluating the corrosion behaviors of the secondary side materials in PWRs.

Acknowledgements

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