

Analysis of magnetite-coated Carbon Steel by hydrazine based chemical decontamination reagent

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***Keywords:** Chemical Decontamination, Hydrazine, Magnetite-coated Carbon Steel, Corrosion, Magnetite dissolution.

1. Introduction

Contamination of nuclear power plant cooling circuits, particularly with radionuclides like ⁶⁰Co, poses significant challenges. Within pressurized heavy water reactors (PHWR), carbon steel (CS) is utilized as the main alloy in the cooling circuit. Distinct from alloys like SUS 304 due to its chromium-deficient composition¹, resulting in a notably thicker oxide layer, almost 75 μm². CS oxide layer is formed by Wüstite (FeO), magnetite, and a thin layer of Hematite³⁻⁴, extending from the base metal outward. Due to the presence of precipitated radionuclides in it, dissolution of the thick contaminated oxide layer becomes essential. The decontamination factor (DF) calculated by pre- and post-dissolution activity measurements, indicated a direct relationship between DF and dissolution rate. Thus, a study on an effective dissolution procedure is vital. This study, however, seeks to elucidate the impact of the hydrazine-based solution, developed by the Korea Atomic Energy Research Institute (KAERI) for NPPs, on CS Magnetite-Coated coupon due to there is no well-known and industrial procedure for decontamination of PHWR system thus, hydrazine-based procedure is adjusted for this purpose⁵⁻⁷. Notably, the primary concern lies in base metal corrosion, particularly concerning less resistant CS, which can entail substantial additional expenses. This article investigates the dissolution efficiency of Magnetite and the corrosion effects to assess the merits and drawbacks of the hydrazine-based process.

2. Methods and Results

In order to have an obvious result and a similar situation of the decontamination process in a Nuclear Power Plant's (NPP) Primary Cooling Circuit (PCC), Magnetite-coated coupons were cut into two parts to simulate thinner magnetite-coated parts in PCC, such as bends due to the Flow Accelerated Corrosion (FAC), where hydrazine-based solution would face to base metal faster than the other parts. In this case, magnetite causes more corrosion due to the galvanic effect of magnetite^{8,9}. The reaction conditions of immersing cut

Table 1: Reaction conditions used for dissolution in this study

| # | Solution | Temp. | Time |
|---|---|-------|------|
| 1 | 29mM H ₂ SO ₄ + 50mM N ₂ H ₄ | 95 °C | 18 h |
| 2 | 29mM H ₂ SO ₄ + 50mM N ₂ H ₄ + 0.5mM Cu | 95 °C | 18 h |
| 3 | 29mM H ₂ SO ₄ + 50mM N ₂ H ₄ + 2mM Cu | 95 °C | 18 h |

Table 2: Corrosion results from solution #1-3 for 18h

| # | Δ V (mm ³) | Δ W (g) | pH _i | pH _f | mg.cm ⁻² .h ⁻¹ |
|---|------------------------|----------|-----------------|-----------------|--------------------------------------|
| 1 | -44.36 | -0.2397 | 2.15 | 6.55 | 2.6040 |
| 2 | -27.53 | -0.2590 | 2.14 | 5.40 | 2.8070 |
| 3 | -25.76 | - 0.2752 | 2.14 | 5.50 | 2.9858 |

coupon in the hydrazine-base solutions with and without CuSO₄ and sulfuric acid are presented in Table 1. Various analytical techniques including weighing, measuring the dimensions, Atomic Absorption Spectroscopy (AAS), Energy Dispersive X-ray(EDX), and Scanning Electron Microscopy (SEM) were employed to analyze dissolution and corrosion phenomena and to compare the surface of coupons

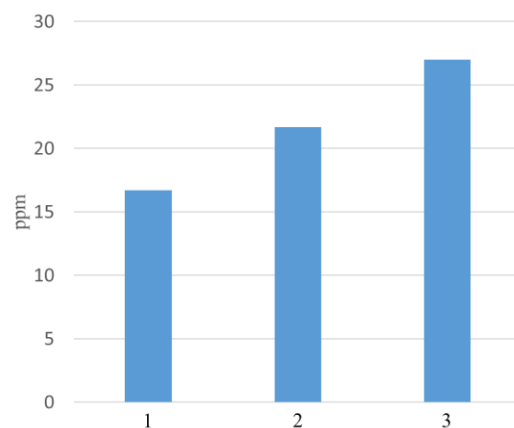


Figure 1: Fe ions concentration after dissolution test

before and after 18h immersing in hydrazine-based solution with and without CuSO_4 . Corrosion data of coupons, pH, and weight loss in solutions 1-3 are reported in Table 2. Figure 1 exhibits the AAS data of the dissolution test which is supported by the corrosion rate by Weight change based on surface area by time. Also, the corrosion differences are obvious in SEM and SEM-EDX images before and after immersing in solutions 1 to 3 which are presented in Figure 2 and Figure 3. The observed increase in corrosion rates upon the introduction of Cu^{2+} ions into the solution is notable and indicative of their influence on the corrosion process. This phenomenon finds explanation through the standard electrode potentials of Cu^{2+} and Cu^+ , which show a higher thermodynamic propensity to react with the base metal (Fe) compared to H^+ . Consequently, the presence of Cu^{2+} ions facilitates accelerated corrosion reactions with the base metal, contributing to the observed rise in corrosion rates. Furthermore, Eh-pH simulation with HSC program do not show the possibility of generating Cu^+ at any pH and potential and higher tendency to convert to the metallic copper which goes out form the solution due to its stability. Existence of Cu in EDX spectrum of 2A in Figure 4 support that Cu ion in solution react on the surface and increases the corrosion rate not reacting with Hydrazine and being as a part of the $\text{Cu}^{2+} \leftrightarrow \text{Cu}^+$ cycle.

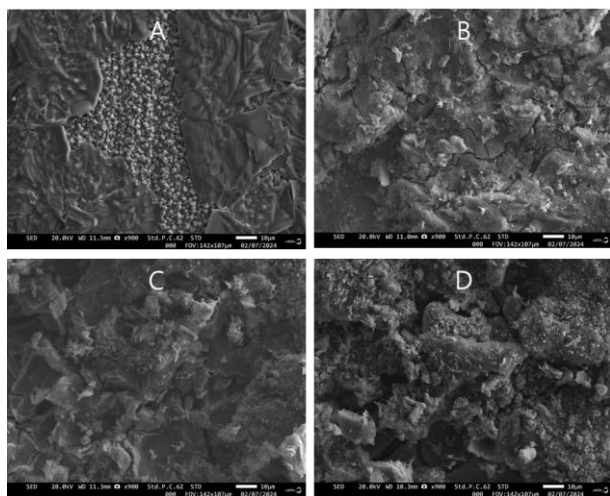


Figure 2: SEM images of Magnetite-coated coupon before (A) and after dissolution in solution 1-3 (B-D)

Various analytical techniques including weighing, measuring the dimensions, atomic absorption spectroscopy (AAS), Energy Dispersive X-ray (EDX), electron probe microanalysis (EPMA), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) were employed to analyze dissolution and corrosion phenomena and to compare the surface of coupons before and after 18h immersing in hydrazine-based solution with and without CuSO_4 . Corrosion data of coupons, AAS data, and SEM images in solutions 1-3

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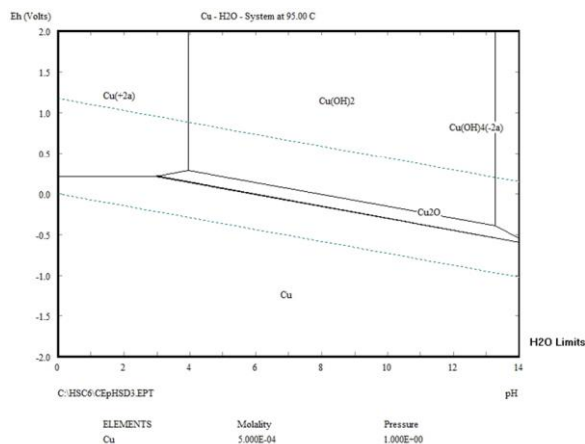


Figure 3 Pourbaix diagram of 0.5 mM Cu

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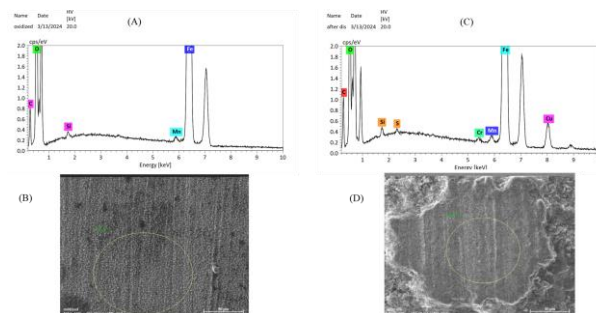


Figure 4 SEM-EDX of Magnetite-coated coupon before (A,B) and after dissolution in solution 2 (C,D)

3. Conclusions

In conclusion, the investigation into the dissolution efficiency of magnetite and the corrosion effects resulting from the hydrazine-based solution's application has provided valuable insights into potential decontamination procedures for pressurized heavy water reactors (PHWRs). The study highlights the importance of addressing base metal corrosion concerns, particularly in less resistant CS components, which

could incur significant additional expenses in maintenance and operation. Through various analytical techniques, including AAS, EDX, and SEM, the impact of the hydrazine-based solution on CS Magnetite-coated coupons was thoroughly examined. The results indicate a notable increase in corrosion rates attributed to the presence of Cu^{2+} ions in the solution, elucidating their role in accelerating corrosion reactions with the base metal (Fe). This understanding underscores the necessity for further research to optimize decontamination procedures and develop effective corrosion mitigation strategies tailored to the unique challenges posed by PHWR cooling circuits-based carbon steel materials. Additionally, the study underscores the importance of considering dissolution efficiency alongside corrosion effects in evaluating the overall efficacy and feasibility of chemical decontamination processes for nuclear power plant systems.

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