# Investigation of Carbon Steel Corrosion Behavior in Hydrazine-Based Reduction Metal Ion Decontamination

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## 1. Introduction

The corrosion of base metals plays a crucial role in determining the effectiveness of decontamination formulations. Carbon steel, a major structural material in nuclear power plant piping systems, is highly susceptible to corrosion during acidic decontamination processes [1]. As the advancement of hydrazine reduction decontamination process has been focused on enhancing dissolution of oxide layer during decontamination, this study aims to evaluate its impact on the corrosion of the base metal carbon steel SA106B.

## 2. Materials and Methods

Analytical grade reagents were utilized to prepare the hydrazine reductive solutions. The specific formulations of the hydrazine reduction solution employed is stipulated in Table 1, and the experimental setup is depicted in Figure 1.

Table 1: Composition of hydrazine reductive solutions employed.

| Sample | Hydrazine reductive solutions | pH |
|---|---|---|
| a | 29mM $H_2SO_4$ + 50 mM $N_2H_4$ | 2.14 |
| b | 29mM $H_2SO_4$ + 50 mM $N_2H_4$ + 0.5 mM Cu | 2.16 |

A setup comprising 250 mL glass reactor vessels, each containing 150 mL of the HyBRID solution, was assembled using stirred heating mantles. Each vessel was equipped with a thermostat and condensers connected to a water bath to establish and maintain a reaction temperature of 95°C (Fig.1). Unreactive magnetic bars were inserted into the glass vessels, and stirring was set to 500 rpm. Coupon SA106B samples were precision-cut to dimensions of 15 mm × 12 mm × 3 mm using a high-speed precision cutting machine (HPC-20, WOOSUNG E&I Co.) and subsequently washed ultrasonically with demineralized water for 10

minutes. The coupons were then suspended by stainless steel wire before being fully immersed in the solution for a 15-hour reaction period. Following the reaction, the coupons were removed, ultrasonically cleaned with demineralized water, and dried in a desiccator at 25°C. Subsequently, the coupons were weighed on an analytical balance before and after immersion, and the differences in weight were utilized to calculate the corrosion rate.

Characterization was carried out using EPMA (JXA-iHP200F Field Emission EPMA). Additionally, samples of the final reaction solution were collected, filtered using a 0.45 µm pore syringe, and the total iron content was analyzed using an Atomic Absorption Spectrophotometer (AAnalyst 400, PerkinElmer).
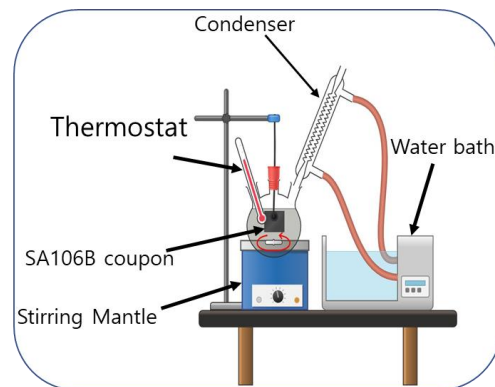


Fig. 1. Schematic diagram for the experimental setup

## 3. Result and Discussion

### 3.1 Corrosion rate of base metal SA106B in hydrazine reductive solutions

The weight loss measurements were used to calculate the corrosion rate [2]. The corrosion rate of the SA106B metal approximately ranged from 30 to 31.5 mm/year in hydrazine solutions, as demonstrated in Fig 2. These results indicate a significantly higher corrosion rate compared to the base metal coupons of Inconel l-600

and Stainless Steel 304SS, which exhibited corrosion rates of 0.1 and 0.02 mm/year [3] respectively under the same conditions (Fig. 3).
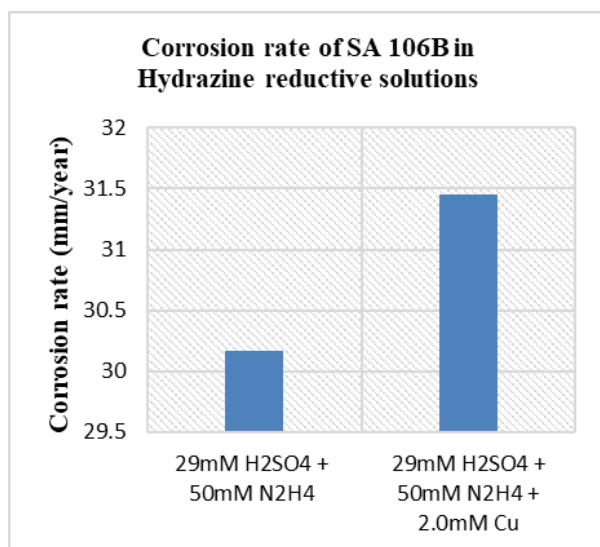


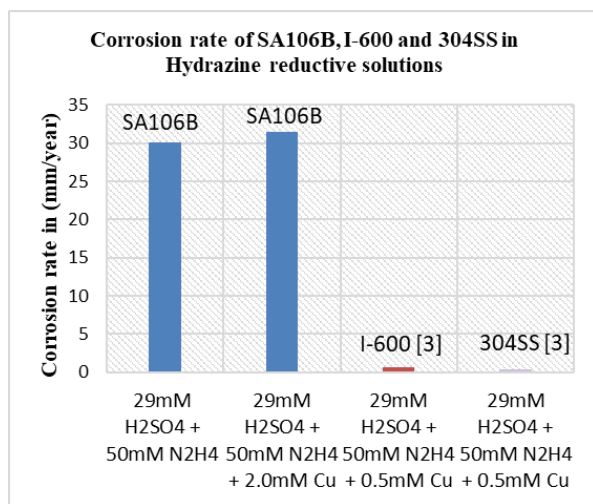Fig. 2. Corrosion rate of SA106B in hydrazine reductive solutions



Fig. 3. Comparison of corrosion rate of SA106B, I-600 [3], and 304SS [3] in hydrazine reductive solutions

### 3.2 Dissolution of Fe from base metal SA106B in hydrazine reductive solutions

In the hydrazine reduction system, Cu is proposed to be added in solution to enhance the further dissolution of the oxide layer (magnetite) up to 1250 ppm for PHWRs [1]. However, during this study, it was observed that the amount of Cu added, may also play a role in increasing the dissolution of Fe from the base metal SA106B, leading to more corrosion on the base metal. The amount of Fe dissolved increased from 19.7

ppm in Hydrazine solution without Cu to 194 ppm in hydrazine with 2.0 mM Cu, as shown in Fig. 4.



Fig. 4. Dissolution of Fe from base metal carbon steel SA106B in hydrazine reductive solutions

The dissolution of Fe from the base metal into the solution increases the unpredictable amount of metal ions in the final decontamination solution [4], leading to complications during waste disposal management.

### 3.3 Morphological characterization

Morphological characterization was conducted to assess the physical disruptions caused by corrosion on the surface of SA106B. As depicted in Fig. 5 below, an increase in corrosion debris on the metal surface provides evidence of increased corrosion with the addition of Cu in the hydrazine reductive solutions
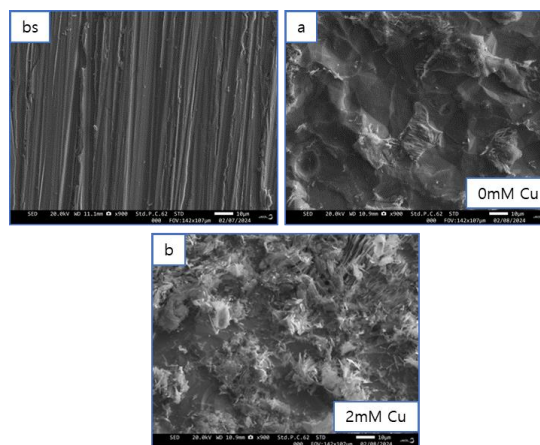


Fig. 5. SEM images for SA106B coupons in hydrazine reductive solutions with (a) 0mM Cu, (b) 2.0mM Cu. Here bs is means base metal

### 3.4 Surface elemental composition

Elemental compositional analysis of the surface was performed using EPMA. The results indicate a reduction in Fe content from 94% on the surface of base metal before immersion in hydrazine solutions to a range of 82.86% – 88.69% after immersion. Concurrently, O content increased from 0% to a range of 3.68% – 14.43%. These findings suggest the formation of a Fe oxide layer on the metal surface due to corrosion. Mn and Cr content were both below 1.0%, as illustrated in Table 2.
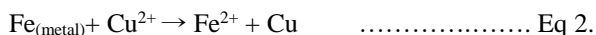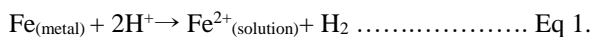
Table 2. Elemental composition (wt. %) on the surface of the SA106B before and after immersion in hydrazine

| Sample | Fe | O | C | Mn | Cr |
|---|---|---|---|---|---|
| Base (As received) | 94.12 | ND* | 4.77 | 0.64 | 0.09 |
| a | 82.86 | 14.43 | 1.84 | 0.77 | 0.1 |
| b | 88.69 | 3.98 | 6.39 | 0.71 | 0.23 |

*ND= Not Detected

### 3.5 Corrosion mechanism

The suggested corrosion mechanism in the hydrazine system on the base metal surface occurs through two pathways, as illustrated by Eq. (1) and (2) below. General corrosion is initiated by $H_2SO_4$ on the base metal, providing protons to the metal Fe (Eq. 1). In this scenario, $H_2SO_4$ serves as the primary corrosion agent when the base metal is immersed in hydrazine reductive solution without Cu. However, due to the variance in redox potential between Fe and $Cu^{2+}$, $Cu^{2+}$ directly oxidizes metal Fe to $Fe^{2+}$, leading to increased corrosion (Eq. 2) when Cu is added.

$$Fe_{(metal)} + 2H^+ \rightarrow Fe^{2+}_{(solution)} + H_2 \ldots\ldots\ldots\ldots\ldots Eq\ 1.$$

$$Fe_{(metal)} + Cu^{2+} \rightarrow Fe^{2+} + Cu \ldots\ldots\ldots\ldots\ldots Eq\ 2.$$

### 3.6 Comparison with other commercial system

The corrosion rate induced by hydrazine reductive solution on carbon steel SA106B (31mm/year) is notably higher than that induced by oxalic acid (0.792 mm/year) [5]. In the case of oxalic acid induced corrosion, the formation of a ferrous oxalate film serves to passivate the base metal, consequently reducing the corrosion rate.

### 4. Conclusion

In conclusion, this study investigated the corrosion behavior of the carbon steel base metal SA106B during hydrazine reductive decontamination process under simulated Nuclear power plants environments, yielding several significant findings as outlined below:

1. Corrosion rates derived from weight loss measurements exceeded those of I-600 and 304SS, indicating the susceptibility of carbon steel to corrosion in hydrazine reductive decontamination solutions;

2. Increasing Cu concentrations led to observed increased iron content in the hydrazine solution, directly confirming corrosion of the carbon steel SA106B base metal with rates reaching 31 mm/year;

3. EPMA images confirmed the General Corrosion effect on SA106B in hydrazine reductive solutions showing the formation of oxide layer on the surface of base metal;

4. Despite the corrosion observed, the corrosion rate in the hydrazine reductive decontamination solution was notably higher compared to the oxalic acid reductive system.

These findings highlight the necessity for further refinement of the hydrazine reductive decontamination system. Potential areas for enhancement include exploring the use of more dilute concentrations or incorporating corrosion inhibitors to mitigate carbon steel corrosion.

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