



Technical Note

Electrochemical corrosion study on base metals used in nuclear power plants in the HyBRID process for chemical decontamination

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ABSTRACT

Base metal corrosion forms a significant issue during the chemical decontamination of the primary coolant loop in nuclear power plants as it is directly related to the economic and safety viability of decommissioning. In this technical note, potentiodynamic evaluations of several base metals (304 stainless steel, SA106 Grade B carbon steel, and alloy 600) were performed to determine their corrosion behavior during the hydrazine (N₂H₄)-based reductive ion decontamination (HyBRID) process. The results suggested that N₂H₄ protected the surface of the base metals in the HyBRID solution, which is primarily composed of H₂SO₄. The corrosion resistance of the carbon steel was further improved through the addition of CuSO₄ to the solution. The corrosion rate of carbon steel in the H₂SO₄-N₂H₄-CuSO₄ solution was lower than that exhibited in an oxalic acid solution, a commonly used reaction medium during commercial decontamination processes. These results indicate the superiority of the HyBRID process with respect to the base metal stability.

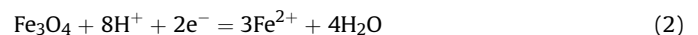
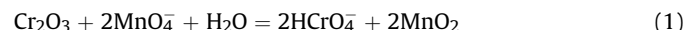
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1. Introduction

Chemical decontamination of the primary coolant loop systems in nuclear power plants (NPPs) is an important stage during decommissioning as highly radioactive nuclides (e.g., ⁶⁰Co) built up on the inner walls of the loop system during operation should be properly removed prior to disassembly of the core components [1–4]. Such radioactive nuclides are typically incorporated into the oxide layers that form on the inner surface of loop systems [1–4]. The oxide layers are primarily composed of Fe, Cr, or Ni oxides, which are the major components of base metals (e.g., stainless steel, carbon steel, and Ni alloy) within the primary loop [1–4]. It is hypothesized that removing the oxide layer from the loop system also removes the radioactive nuclides, thereby reducing the radioactivity of the system.

The oxide layers can be dissolved through a combination of several chemical pathways, depending on their chemical properties [1–4]. For instance, permanganate (MnO₄⁻) process that utilizes permanganates (e.g., KMnO₄ and HMnO₄) as oxidizing agents is a well-established method for the decomposition of Cr₂O₃ layers

(reaction 1). Fe-based spinel compounds, such as Fe₃O₄, NiFe₂O₄, and FeCr₂O₄, can be removed using reductive acid treatments (reaction 2). Such reactions could be repeated several times to ensure that decontamination had been performed to the required extent.



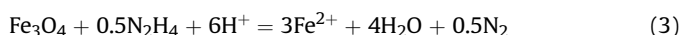
Conventional decontamination processes utilize organic acids as the reaction media, and additional organic complexes are introduced into the reaction media to inhibit metal ion precipitation [1–4]. However, the utilization of organic compounds may induce a safety issue as organic compounds are able to form mobile complexes [5,6]. If radioactive nuclides are present within these complexes, these can then be released into the environment upon underground disposal, where they will remain harmful for substantial periods of time [5,6].

Recently, the Korea Atomic Energy Research Institute suggested a hydrazine (N₂H₄)-based reductive ion decontamination (HyBRID) process for the chemical decontamination [6–8]. Organic acids and complexes are not introduced during the HyBRID process, and inorganic acids, such as H₂SO₄, are instead utilized as a base solution to minimize secondary waste generation. The net reaction of

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the oxide dissolution in the HyBRID process in the presence of N_2H_4 can be expressed as follows (reaction 3) [7].



Once the oxide layers have been removed via chemical decontamination, the fresh surface of the base metals is directly exposed to the decontamination solutions, which are typically acidic. Thus, it is critical to maintain the base metal's stability during the decontamination process from both an economic and safety perspective. Acidic dissolution of the base metals may increase the metal ion concentration within the decontamination solution, thereby increasing the volume of secondary waste generated during post-treatment of the waste solution, which, in turn, increases the cost of processing and disposal. In extreme circumstances, when a portion of the base metal is severely damaged, the decontamination solution, containing harmful radioactive nuclides, can leak out of the loop, resulting in a critical accident. Therefore, a comprehensive evaluation of the chemical stability of the base metals in acidic media should be conducted.

As the metal corrosion accompanies electron transfer, electrochemical techniques are widely used to study the corrosion behavior of metals. In this study, a potentiodynamic polarization test was performed to evaluate the corrosion stability of several base metals within the primary loop systems during the HyBRID process. Commonly utilized base metals in NPP loop systems, that is, 304 stainless steel (SS304), SA106 Grade B carbon steel (SA106B), and alloy 600 (A600), were selected as test candidates. To facilitate a performance comparison, an additional electrochemical investigation was performed within an organic oxalic acid (OA) solution, which is utilized as the base solution during conventional decontamination processes such as chemical oxidation reduction decontamination (CORD) [4]. The corrosion parameters such as corrosion current (I_{corr}) of the base metal candidates in the test solutions can be obtained through the polarization test. The I_{corr} value is strongly related to the corrosion rate and thus it was expected that the base metal stability can be evaluated by comparing the I_{corr} value of each candidate.

2. Material and methods

H_2SO_4 (Daejung Chemicals & Metals, 98%), $N_2H_4 \cdot H_2O$ (Junsei Chemical, 98%), and $CuSO_4 \cdot 5H_2O$ (Sigma Aldrich, 98%) were used to prepare the HyBRID test solution. 0.05 M H_2SO_4 (1 L) was prepared as a base solution, and $N_2H_4 \cdot H_2O$ (0.091 M) and $CuSO_4 \cdot 5H_2O$ (0.01–0.05 mM) were introduced in their required quantities for each electrochemical test. An additional electrochemical investigation was performed using a 2,000 ppm OA (Sigma-Aldrich, 98%) solution to determine a baseline performance.

A three-electrode test cell was fabricated to perform the electrochemical experiments. The surface of the circular (diameter = 16 mm, thickness = 2 mm) base metal specimens was ground using SiC polishing papers (up to 2000 grit size) to expose a fresh surface prior to assembly using an EG&G flat specimen holder kit (K0105), whose electrode opening area was 1.0 cm^2 , for their utilization as a working electrode. A platinum wire and saturated calomel electrode were used as the counter and reference electrodes, respectively. Potentiodynamic polarization measurements were obtained using a WonATech multichannel electrochemical workstation (ZIVE MP2) operated by corrosion analysis software (ZIVE Lab, SM6) at 23 ± 2 °C at a potential scan rate of 0.02 V s^{-1} . Typically the potential scan started at -0.1 to -0.3 V vs. open-circuit potential and ended at $+0.3$ to $+0.6$ V vs. open-circuit potential.

3. Results and discussion

Fig. 1 shows the potentiodynamic polarization curves obtained from the base metals using an H_2SO_4 solution, both with and without N_2H_4 . An analysis of the curves clearly demonstrates that the addition of N_2H_4 suppresses base metal corrosion. The I_{corr} and the corrosion potential (E_{corr}) were obtained through an extrapolation of the curves, and the results of which are listed in Table 1. The I_{corr} values, which correspond to the corrosion rates of SS304, SA106B, and A600, were reduced to 17.3%, 13.8%, and 26.0%, respectively, through the addition of N_2H_4 . N_2H_4 and its derivatives

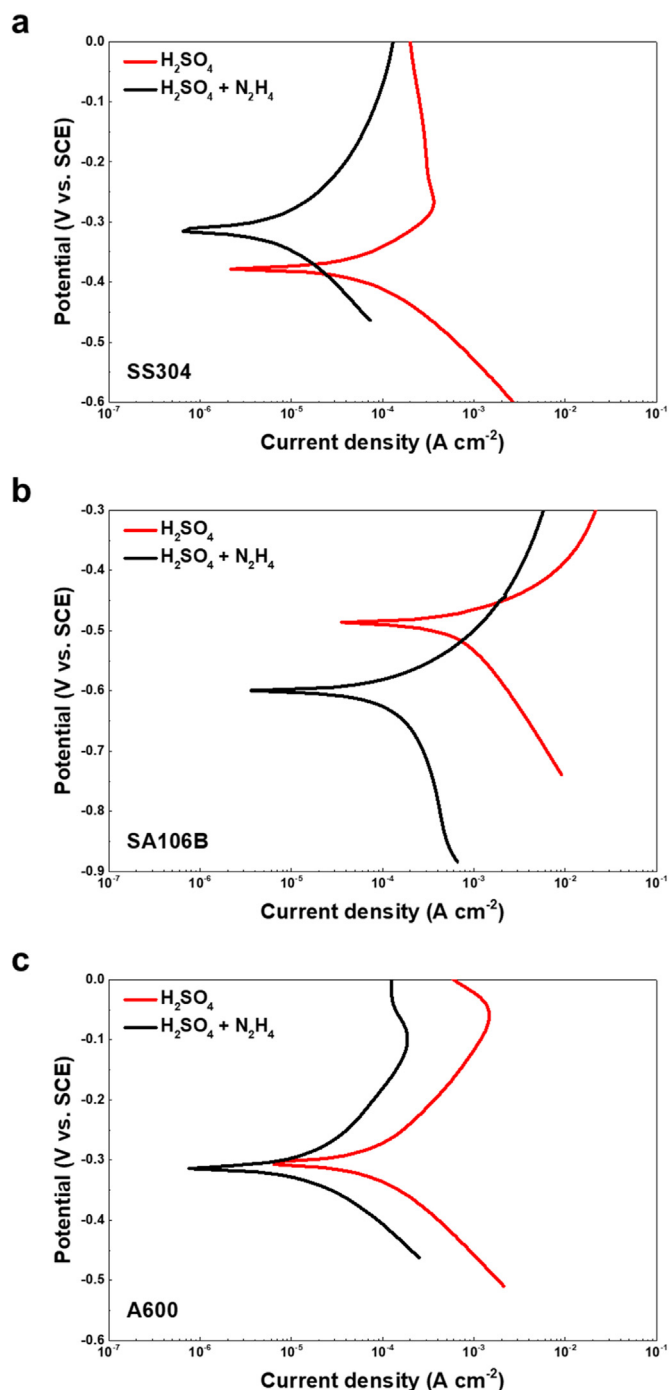


Fig. 1. Potentiodynamic polarization curves obtained from the base metals in the H_2SO_4 solution without and with N_2H_4 : (a) SS304, (b) SA106B, and (c) A600.

Table 1

I_{corr} and E_{corr} values of the base metals in the H_2SO_4 , $\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$, $\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4\text{-CuSO}_4$, and OA solutions ($\text{H}_2\text{SO}_4 = 0.05 \text{ M}$, $\text{N}_2\text{H}_4 = 0.091 \text{ M}$, $\text{CuSO}_4 = 0.05 \text{ M}$, OA = 2,000 ppm).

Material	Solution	I_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (V vs. SCE)
SS304	H_2SO_4	52.46	-0.377
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$	9.06	-0.316
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4\text{-CuSO}_4$	11.23	-0.396
	OA	10.70	-0.459
SA106	H_2SO_4	724.70	-0.488
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$	100.08	-0.598
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4\text{-CuSO}_4$	34.93	-0.542
	OA	137.08	-0.537
A600	H_2SO_4	77.87	-0.304
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$	20.21	-0.313
	$\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4\text{-CuSO}_4$	18.59	-0.344
	OA	35.20	-0.371

are well-established corrosion inhibitors [9–11]. Their ability to scavenge oxygen and bind metal surfaces via electron transfer imparts a protective coating on the metal surface that inhibits corrosion. For instance, it was reported that N_2H_4 provided complete inhibition of steel surface in various solutions [9]. Approximately 0.1, 0.3 and 0.05 M of N_2H_4 was required to protect the steel surface in chloride, sulphate, and sulphide media (0.01 M for each), respectively [9]. In addition, approximately 60% of inhibition efficiency was obtained in case of Pb corrosion by adding N_2H_4 (0.1 M) in acetic acid solution (0.1 M) and the inhibition efficiency was further improved when using the derivatives of N_2H_4 [10]. Consequently, the introduction of N_2H_4 to the H_2SO_4 solution during the HyBRID process provides two advantages, specifically enhanced oxide layer removal [6–8] and reduced base metal corrosion.

For the past decades, the CORD process has widely been used to decontaminate variety of NPP components fabricated using various metals, including stainless steel, carbon steel, and Ni alloy [4]. The corrosion behavior of the base metals in the OA solution, which is the organic base solution of the CORD process, was evaluated as shown in Fig. 2 for the comparison. The I_{corr} values of the base metals in the $\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$ solution were comparable to those obtained in the OA solution (Table 1). This suggests that the base metal corrosion induced during the HyBRID process would be in an adequate range, despite the fact that it utilizes strong inorganic acids (e.g., H_2SO_4) as the reaction medium as opposed to organic acids. As has previously been established, the use of inorganic compounds is advantageous with respect to long-term disposal [5,6].

Transition metal ions, such as Cu^{2+} , effectively promote the oxide dissolution reaction within the HyBRID solution [6,7]. With respect to reaction (3), it was found that the incorporation of Cu^{2+} induced an increase in the reaction rate as a result of the catalytic effect imparted by $\text{Cu}^+/\text{Cu}^{2+}$ redox cycling [6,7]. Cu^{2+} is reduced to Cu^+ through the N_2H_4 present in the solution (reaction 4). Cu^+ subsequently donates an electron to the Fe^{3+} present in the oxide layer (reaction 5), to make the solid-state oxide phase unstable. The overall dissolution reaction of Fe_3O_4 during the HyBRID process containing H_2SO_4 , N_2H_4 , and CuSO_4 is expressed in reaction 6 [7].

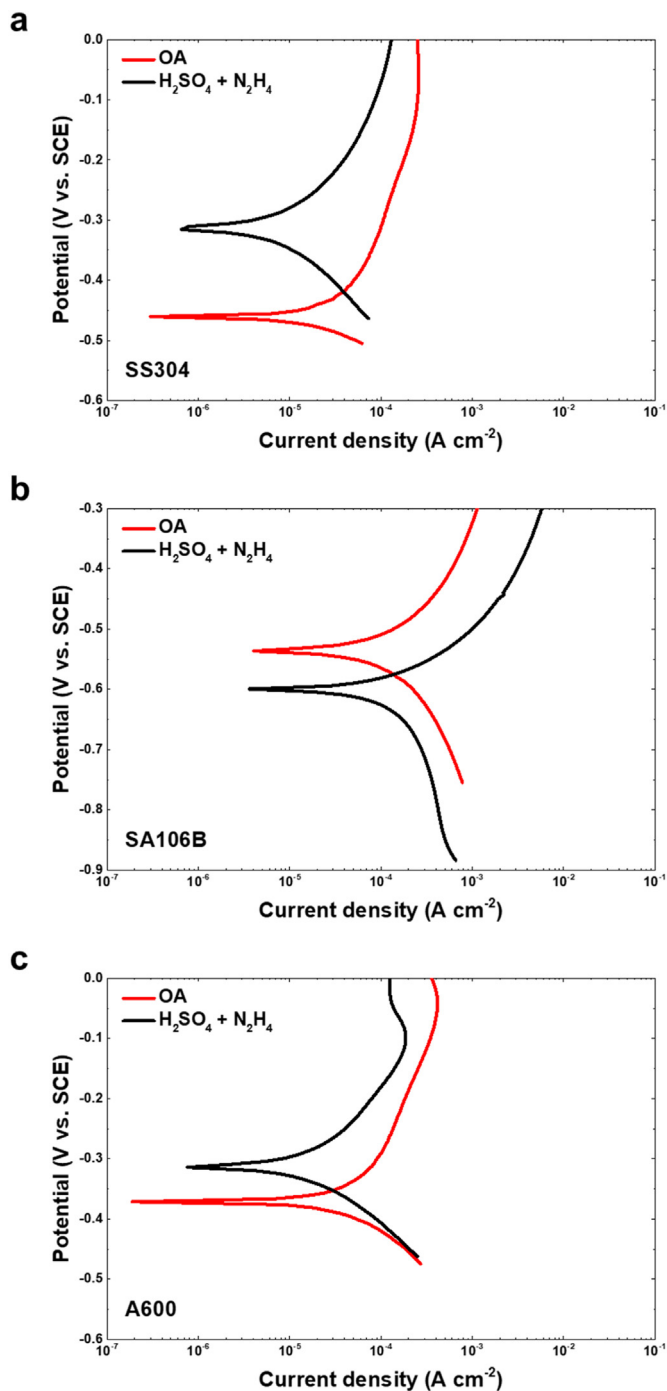
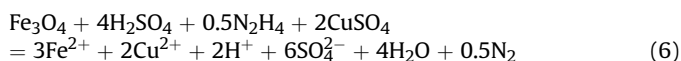
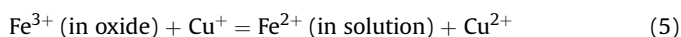
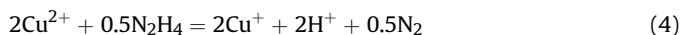


Fig. 2. Potentiodynamic polarization curves obtained from the base metals in the $\text{H}_2\text{SO}_4\text{-N}_2\text{H}_4$ and the OA solutions: (a) SS304, (b) SA106B, and (c) A600.

Cu^{2+} is able to act as a corrosion inhibitor in acidic solutions [12]. Furthermore, it has been reported that Cu^{2+} imparts a synergistic effect when combined with another inhibitor [12]. For instance, the inhibitory effect imparted by carboxymethyl chitosan (CMCT) on mild steel in an HCl solution was enhanced through the addition of CuSO_4 [12]. Cu^{2+} and CMCT form a complex compound to promote surface adsorption, resulting in an increased protection of the metal surface [12]. Owing to the existence of lone electron pairs, N_2H_4 can form several coordination complexes with metal ions [13]. During the HyBRID process, $\text{Cu-N}_2\text{H}_4$ complexes, such as $[\text{Cu}(\text{N}_2\text{H}_4)_2]^{2+}$ and $[\text{Cu}(\text{N}_2\text{H}_4)_2]^+$, can be present in the reaction

medium [7]. It is speculated that the formation of Cu-N₂H₄ complexes may effectively enhance the adsorption properties of N₂H₄ to increase the material's corrosion resistance.

The influence of the addition of CuSO₄ to the H₂SO₄-N₂H₄ solution on the overall corrosion behavior was evaluated, and the results are shown in Fig. 3 and Table 1. While there was no significant variation in the I_{corr} values of SS304 and A600, which already exhibit strong corrosion resistance, the corrosion rate of SA106B was significantly reduced through the addition of Cu²⁺. The I_{corr} value of SA106B in the HyBRID solution (H₂SO₄-N₂H₄-CuSO₄) was reduced to ~35% of the value obtained in the H₂SO₄-N₂H₄ solution. Furthermore, this value was only ~25% of that obtained in the OA solution, demonstrating the superior base metal stability imparted by the HyBRID process. There was no detectable CuSO₄ concentration dependency on the corrosion of SA106B, as shown in Fig. 3d, suggesting that a small volume of CuSO₄ is sufficient to induce a synergetic effect along with N₂H₄ to impart a protective coating at the surface of SA106B.

It was found that SA106B was most susceptible to corrosion during the HyBRID process, although its corrosion resistance was significantly improved through the introduction of N₂H₄ and CuSO₄. The I_{corr} value of SA106B was larger than those obtained from SS304 and A600 (~2–3 times greater) in the H₂SO₄-N₂H₄-CuSO₄ solution, as shown in Table 1. Carbon steels generally exhibit poor corrosion resistance in comparison to other alloys as no stable protective layer (e.g., Cr₂O₃ in stainless steels) is formed upon exposure to corrosive environments. Thus, it is thought that primary loop components fabricated using carbon steels may suffer from the corrosion within the HyBRID solution in comparison to other relatively stable components.

NPPs construction utilizes various structural materials as the material property demands required for each component vary

[14,15]. Stainless steel and Ni alloy constitute the major primary loop components in several varieties of NPPs [14]. Meanwhile, SA106B, a carbon steel, has been used in limited applications such as in the feeder pipes of Canadian deuterium uranium (CANDU) pressurized heavy water reactors [15]. The application of the HyBRID process in CANDU reactors requires a careful evaluation at this stage as the relatively rapid corrosion of the feeder pipes in comparison to other components (fabricated from metals exhibiting a high corrosion resistance) will result in several challenges upon chemical decontamination. Despite this, it is still significant that the degradation of SA106B was significantly reduced through the application of the HyBRID process as opposed to the conventional CORD process. However, further modification of the HyBRID solution to minimize the corrosion of SA106B is required. Optimizing the solution composition and/or introducing additional corrosion inhibitors forms a promising method for overcoming this issue.

4. Conclusions

In this study, electrochemical investigations of several base metals (i.e., SS304, SA106B, A600) used in NPPs were performed in a HyBRID solution to evaluate their corrosion behavior. Potentiodynamic studies revealed that the base metal corrosion was suppressed through the addition of N₂H₄ to the H₂SO₄ base solution. The degree of base metal corrosion induced in the H₂SO₄-N₂H₄ solution was comparable to that induced in the organic OA solution, which is the reaction medium used during the CORD process. This result suggests that the deterioration of the base metals during the HyBRID process is within an acceptable window. The corrosion resistance of SA106B (the material most susceptible to corrosion) could be further increased through the introduction of the CuSO₄

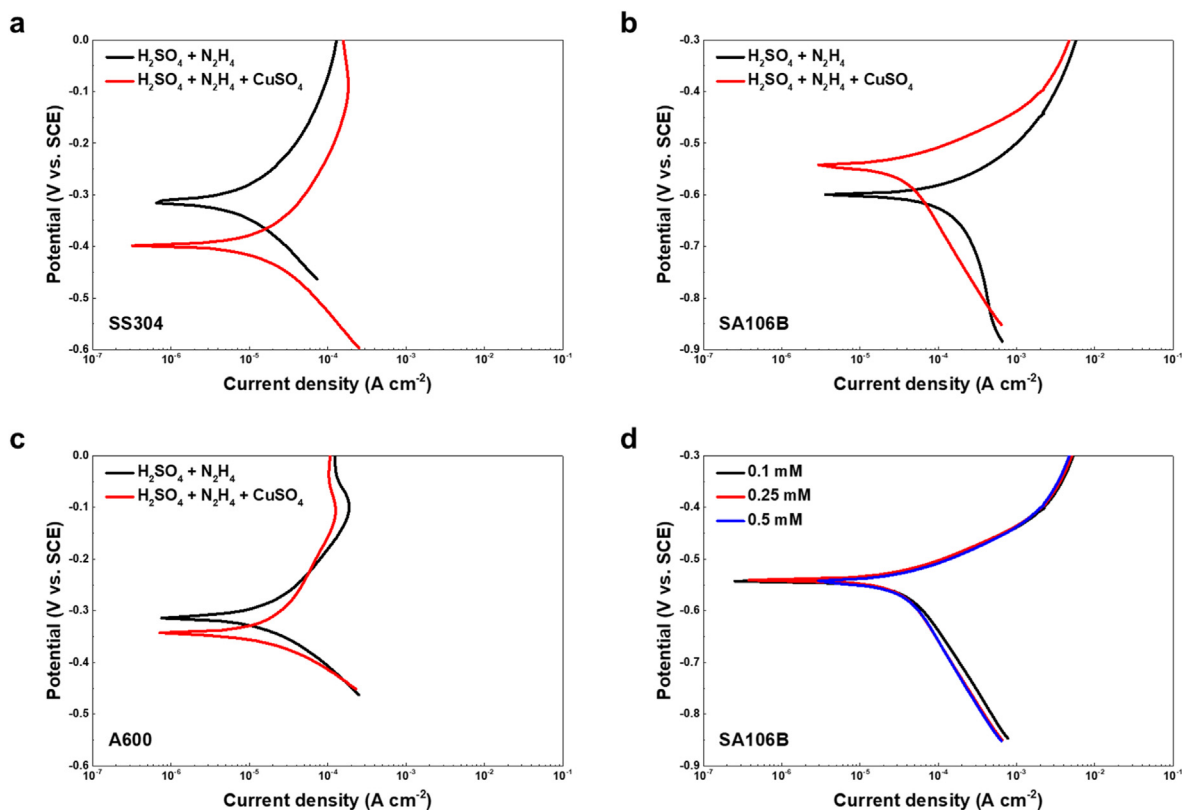


Fig. 3. Potentiodynamic polarization curves obtained from the base metals in the H₂SO₄-N₂H₄ without and with CuSO₄: (a) SS304, (b) SA106B, and (c) A600 at a fixed CuSO₄ concentration of 0.5 mM and (d) SA106B with various Cu concentrations.

additive, typically used during the HyBRID process to accelerate oxide layer removal. This result demonstrates the enhanced performance of the HyBRID process, inducing a reduced I_{corr} value ~24% lower than those obtained using the OA solution. Consequently, it was concluded that the addition of N_2H_4 and CuSO_4 to the HyBRID solution imparts a synergetic effect, not only with respect to the decomposition of the oxide layer (which contains the radioactive nuclides) but also for the corrosion protection of the exposed base metals during chemical decontamination.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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