

Effect of Fluoride Ions on the Decontamination Performance of HyBRID

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1. Introduction

KAERI uses a dilute chemical decontamination agent called HyBRID(Hydrazine Base Reductive metal Ion Decontamination) which is applicable to the internal loop of a nuclear power plant. HyBRID dissolves the corrosion layer effectively without the much loss of base metal [1]. It, however, is known that small portion of the radioactivity is in the base metal [2]. To increase the decontamination performance, it is necessary to dissolve out the base metal during the decontamination.

The objective of the study is to investigate the change of decontamination performance when the fluoride ion is added to the decontamination solution. The effect of fluoride ion on the corrosion of Inconel 600 and stainless steel was also investigated.

2. Methods and Results

2.1 Experimental condition

80 % hydrazine monohydrate from Junsei Chemical Co., 99.99% of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ from Alfa Aseor and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from Showa were used as received, respectively. pH was adjusted by H_2SO_4 and HNO_3 . Tests were performed at pH = 3. The concentration of hydrazine was analyzed at 455 nm by the UV spectrophotometer from Hach Company (DR 5000). p-dimethylaminobenzaldehyde was used as an indicator. Iron ion concentration was analyzed by AAS from Perkin Elmer Co. (AAnalyst 400). Corrosion rate was measured by weight loss method.

2.2 Test results

Fig. 1 shows the plot of FT-IR spectrum of dissolved fraction of magnetite against time under various anions of copper ion. Irrespective of anions and acid, the tendency of magnetite dissolution is same. This means that anion does not affect the dissolution of magnetite.

Fig. 2 shows the FT-IR spectrum of a synthesized solid-state copper(I) hydrazine complex made from N_2H_4 - Cu(I)-HCl . N-H stretching frequencies were observed at 529, 1109, 1249, 1510, 1550 and 3200 cm^{-1} . N-H stretching frequency of NH_3^+ was also observed in the range of 2600–3300 cm^{-1} . The N-N stretching frequency observed at 960 cm^{-1} coincides with the N-N stretching frequency of hydrazinium ions (N_2H_5^+) observed in the

range of 958–965 cm^{-1} . In particular, Cu-N stretching frequency is also observed at 420 cm^{-1} [3].

From the investigation of FT-IR spectrum, it is anticipated that Cu and hydrazine form coordination compound in a HyBRID decontamination solution.

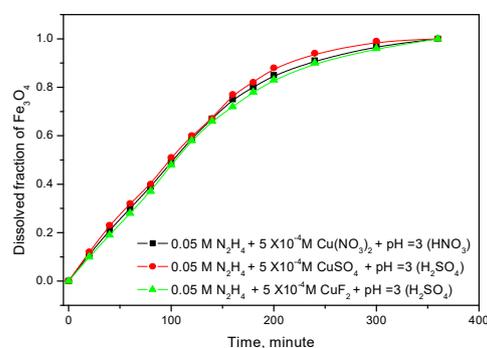


Fig. 1. Dissolution of Fe_3O_4 according to time under various anions and acids of HyBRID at 90°C.

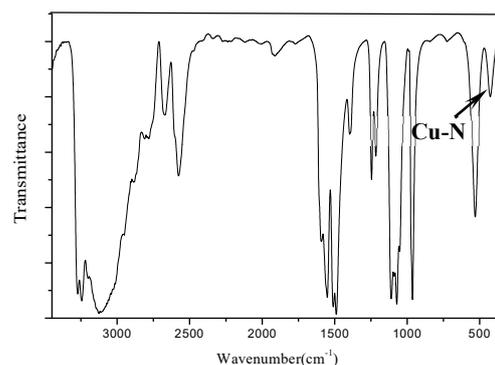


Fig. 2. FT-IR spectrum of synthesized N_2H_4 - Cu^+ - HNO_3 sample.

Fig. 3 shows a plot of charge vs. time under various incubation conditions. The charge values were obtained by integrating the electric current values measured via chronoamperometry. The charge of the 0.3 mM $\text{Cu}(\text{NO}_3)_2$ + 30 mM N_2H_4 and 0.3 mM $\text{Cu}(\text{NO}_3)_2$ + 30 mM NH_3BH_3

systems increased significantly after incubation. This means that $\text{Cu}^+ + \text{N}_2\text{H}_4$ system dissolves magnetite efficiently.

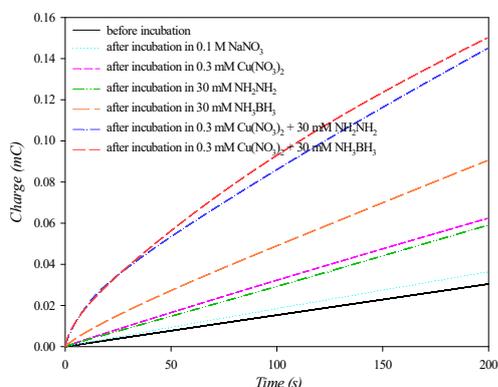


Fig. 3. Comparison of anodic charge of $\text{K}_4\text{Fe}(\text{CN})_6$ measured from chronoamperometry.

Fig. 4 shows a plot of corrosion depth vs. time under two anion conditions. Comparing stainless steel with Inconel 600, general corrosion rate of Inconel 600 is faster than that of stainless steel. For two anion conditions, general corrosion rate is faster when the fluoride ion is in HyBRID solution.

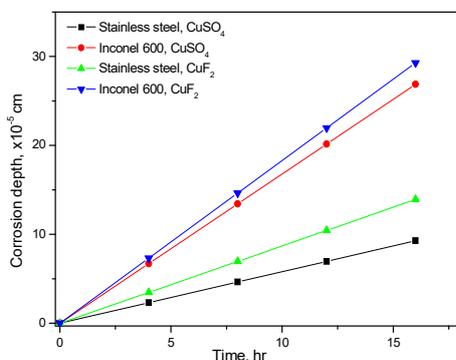


Fig. 4. Corrosion of Inconel 600 and stainless steel according to time.

Fig. 5 shows the potentiodynamic polarization curves of 316 SS in H_2SO_4 solutions with different content of F^- . At higher anodic potentials (higher than 800 mV vs. SCE), the rapid increase of current density with the applied potential can be identified. This is attributed to the transpassive behavior associated with the electro-oxidation of Cr(III) oxide present in the film to Cr(VI) rather than the

occurrence of stable pitting [4]. It can be found in the apparent polarization that F^- seems to mainly accelerate the anodic process at the potential ranging from the corrosion potential ($E_{\text{corr}} \sim -300$ mV vs. SCE) to ~ 0 mV [4].

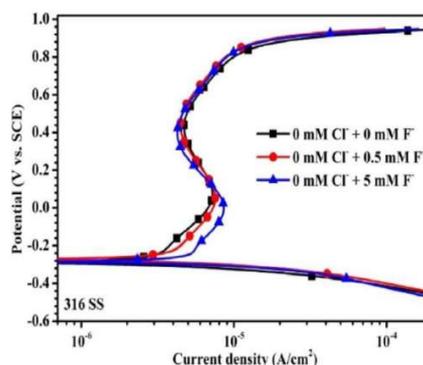


Fig. 5. Potentiodynamic polarization curves of stainless steel in H_2SO_4 solution [4].

3. Conclusion

Copper ions form coordination compounds with hydrazine. The compounds efficiently dissolved the magnetite powders irrespective of the change of anions in HyBRID solution. Because N_2H_4 reacts with hydrogen peroxide and easily decomposes into N_2 gas and H_2O , the generated volume of secondary waste can be significantly reduced by destroying the decontamination agent. F^- can accelerate the general corrosion of stainless steel and Inconel 600. The effect of F^- on the corrosion rate of stainless steel and Inconel 600 is attributed to the change of anodic polarization curves. In a previous study, we demonstrated the decontamination performance of the HyBRID solution. The application of F^- -HyBRID solution to the primary coolant system will increase the decontamination performance.

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