

## Dissolution of Simulated Iron Oxide by HYBRID Solution

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### 1. Introduction

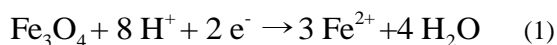
A new chemical decontamination agent applicable to the primary coolant system of a nuclear power plant is developed in KAERI. The decontamination agent is called HBRID (HYdrazine Base Reductive metal Ion for Decontamination). Hydrazine acts not only as a reducing agent of metal ion but also forms a coordination compound with metal ion. Furthermore, hydrazine is decomposed easily to nitrogen and water by hydrogen peroxide. The objective of the study is to evaluate the dissolution capability of  $\text{Cu}^+ \text{-N}_2\text{H}_4 \text{-HNO}_3$  system on magnetite particles and the oxide layer formed on Inconl-600.

### 2. Methods and Results

#### 2.1 Magnetite Dissolution

Magnetite particles (GR grade) were used as received. Before the test, they were characterized by XRD diffraction. Experiments were carried out in a magnetically stirred Erlenmeyer flask on the hot plate. For all experiments, an amount of magnetite equivalent to  $6.6 \times 10^{-4}$  M (35.5 ppm) of iron upon complete dissolution was employed. Hydrazine monohydrate was used as a main dissolution agent. 65 %  $\text{HNO}_3$  for pH control and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were used as received. The solution was de-aerated for 30 minutes by bubbling with high purity  $\text{N}_2$  gas.

Fig. 1 shows the plot of the dissolved fraction of magnetite vs. time under various  $[\text{N}_2\text{H}_4]$  at  $95^\circ\text{C}$ . The reproducibility in the dissolution data is within  $\pm 2.8\%$ . As shown in Fig. 1, dissolved fraction of magnetite increases with the increase of  $[\text{N}_2\text{H}_4]$  in an acid solution. It took 6 hours to dissolve the magnetite completely when  $[\text{N}_2\text{H}_4]$  is 0.07 M. This result is similar to that of the dissolution kinetic of magnetite in EDTA and NTA based dilute chemical formulation [1]. Keny et al. reported that it took longer than 5 hours to dissolve magnetite completely when the solution pH was 2.7-2.8 at  $80^\circ\text{C}$ . Baumgartner et al. [2] proposed that the reductive dissolution of magnetite can be expressed as written in Eq. (1).



Two possibilities may be considered in this system. 1) Hydrazine itself is a reducing agent that can be used to reduce the surface ferric ion of magnetite directly. 2)

Hydrazine can also behave as a reducing agent of  $\text{Cu}^{2+}$  ion, and then  $\text{Cu}^+$  ion reduces the surface ferric ion of magnetite.

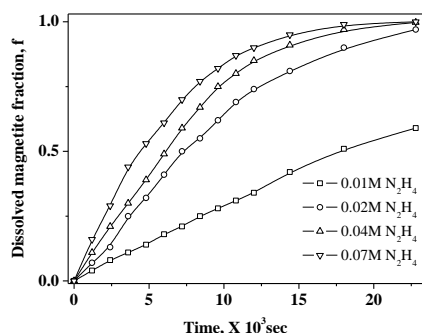


Fig. 1. Dissolved fraction of magnetite (f) as a function of time at different  $[\text{N}_2\text{H}_4]$ , pH=3, T=  $95^\circ\text{C}$  and  $[\text{Cu}^+] = 5 \times 10^{-4}$  M.

A shrinking core model of the form in Eq. (2) was found where f is the dissolved fraction of iron in magnetite at time t and k is the apparent rate constant.

$$1 - (1 - f)^{1/3} = kt \quad (2)$$

This law can be derived from the assumption that the dissolution rate is proportional to the instantaneous surface area and the approximation of uniform and spherical particles in heterogeneous reaction systems. A plot of  $1 - (1 - f)^{1/3}$  vs. time under various  $[\text{N}_2\text{H}_4]$  at  $95^\circ\text{C}$  is shown in Fig. 2. As shown in Fig. 2, deviation from linearity occurs during the reaction period except 0.01 M  $\text{N}_2\text{H}_4$  system. It was reported that the dissolution rate of magnetite increased with the initial  $[\text{Fe}^{2+}]$  in EDTA, ethylenediamine-disuccinic acid (EDDS) and  $\text{H}_2\text{SO}_4$  base solutions under the given condition [3, 4, 5]. From the interpretation of the results, Borghi et al. concluded that faster rate could be achieved at an  $[\text{EDTA}] : [\text{Fe}^{2+}]$  ratio significantly larger than 1 [3]. The deviation from the linearity can be explained by the increase of dissolution rate by  $\text{Fe}^{2+}$  ion generated from the dissolution of magnetite. The possibility of non-spherical magnetite particles cannot be excluded. Al-Mayouf et al. found that the dissolution rate of magnetite in EDDS solution decreased with time [4].

They suggested that the fall in dissolution rate was due to the decrease in the surface area of dissolving particles. Fig. 2 shows linear correlations during the whole reaction time. The linearity is based on surface chemical reaction control for the dissolution of magnetite by hydrazine base solution

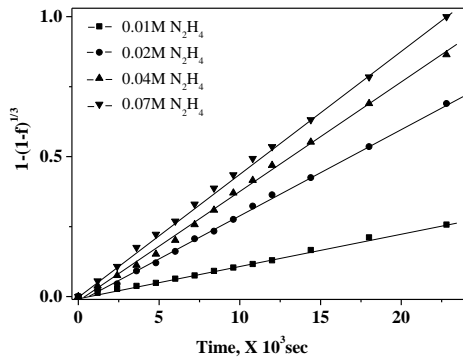


Fig. 2.  $1 - (1-f)^{1/3}$  as a function of time at different  $[N_2H_4]$ ,  $pH=3$ ,  $T=95\text{ }^\circ\text{C}$  and  $[Cu^+] = 5 \times 10^{-4}\text{ M}$ .

## 2.2 Dissolution of Oxide Layer on Inconel 600

Specimens ( $\sim 7.6\text{ cm}^2$ ) of Inconel-600 polished up to 600 grit/P1200 silicon carbide paper on the automatic grinder were used for the formation of oxide film. 4.5 L of semi-loop was filled with an aqueous solution containing LiOH (2.2 mg/L Li),  $H_3BO_3$  (650 mg/L B) and  $N_2H_4$  (90 mg/L). Specimens were located in a semi-loop and the solution circulated at  $350\text{ }^\circ\text{C}$  for 30 days. The pressure in a semi-loop was 2700 psi and dissolved oxygen concentration was maintained at 10 ppb. Specimens were treated with a solution containing  $HNO_3$  and  $KMnO_4$  at  $95\text{ }^\circ\text{C}$  for 12 hours before the reductive dissolution. The amount of the dissolved iron and nickel ions during the oxidation step was neglected.

Fig. 3 shows the amount of dissolved metal ions against time during the application of each step. When the oxidation pretreatment step was omitted, it had been observed earlier that the reductive dissolution reaction was extremely slow. The reductive dissolution step was performed under a given concentration ( $[N_2H_4] = 0.04\text{ M}$ ,  $[Cu^+] = 5 \times 10^{-4}\text{ M}$  and  $pH=3$ ) at  $95\text{ }^\circ\text{C}$ . As shown in Fig. 7, iron ions are continuously dissolved out from the oxide film in the first reductive dissolution step during 8 hours.  $30.53\text{ }\mu\text{g}/\text{cm}^2$  of iron ion was dissolved in the first reductive dissolution step and  $23.29\text{ }\mu\text{g}/\text{cm}^2$  of iron ion was dissolved in the second reductive dissolution step. It was reported that the difference in dissolution behavior between the magnetite powder and oxide film is attributed to the participation of the underlying base metal in the latter case that significantly promotes the kinetics of the dissolution [6]. As the increase of the iron ion concentration becomes saturated

after 8 hours, the effect of base metal dissolution on the dissolution rate of oxide film is negligible in  $N_2H_4-Cu^+-H^+$  system.

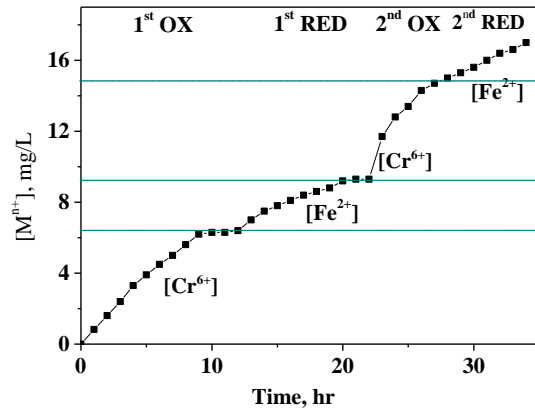


Fig. 3. Dissolved metal ion from Inconel-600 oxide layer against time.

## 3. Conclusions

$N_2H_4-Cu^+-H^+$  system efficiently dissolves the simulated oxide layer formed on Inconel 600 surface. From the results, we can infer that  $N_2H_4-Cu^+-H^+$  system does not cause any corrosion problem. The total concentration of the  $N_2H_4-Cu^+-H^+$  system used for the dissolution of simulated oxide layer is below 0.3 wt %.

It will be necessary to demonstrate the decontamination performance of  $N_2H_4-Cu^+-H^+$  system using Inconel 600 samples gathered from NPP.

## ACKNOWLEDGEMENTS

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