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## A Feasibility Study on the Decontamination of Type 304 Stainless Steel by $N_2H_4$ Base Solution†

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Dissolution tests of  $Fe_3O_4$  powders were performed in an acidic solution using a hydrazine base solution at a temperature range of 90–150 °C. The dissolved fraction of  $Fe_3O_4$  was calculated from the analysis of iron ion concentration in solution using an atomic absorption spectrometer. The dissolution rate of  $Fe_3O_4$  increased with  $[N_2H_4]$ , time and temperature. The addition of copper ions to the hydrazine base solution greatly increased the  $Fe_3O_4$  dissolution rate. This was explained by the complex formation between  $N_2H_4$  and Cu ions and the reducing power of the hydrazine-Cu complex to the ferric ions of  $Fe_3O_4$ . The solution was also applied to the decontamination of Type 304 stainless steel specimen which was radioactively contaminated with a spinel type oxide layer. The contact dose rate of the specimen was measured before and after application of the solution to evaluate the decontamination performance. The contact dose rate was greatly decreased by the repetitive application of nitric acid-permanganate and the hydrazine base solution.

**Keywords:** Dissolution,  $Fe_3O_4$ , Chelate free, Copper ion, Decontamination.

### INTRODUCTION

The commercial application of chemical decontamination technology has expanded significantly in recent years at nuclear power plants. From initial applications to components and small subsystems, to the current examination of full system decontamination, the entire technology has become sophisticated. Dilute chemical decontamination has been responsible for avoiding a substantial radiation exposure to personnel<sup>1</sup>.

The corrosion products in PWRs (Pressurized water reactor, nuclear power plant) operating under a normal reducing water chemistry condition consist of magnetite ( $Fe_3O_4$ ) and Ni, Cr substituted magnetite<sup>2,3</sup>. The best way to remove radionuclides such as Co-60 in the oxide layer is to dissolve the oxide without affecting the base metal. The dissolution of simple iron oxides is normally carried out using organic acid, a reducing agent and chelating agents. A chelating agent aids the dissolution process and increases the capacity of the solvent to hold the dissolved species in solution, while the reducing agent first initiates the dissolution by reducing the ferric ions in the oxide lattice. Commonly used chelating agents are EDTA, NTA and oxalic acid. It was recently reported that some of the chelating agent in a decontamination formulation affects the bad environmental effect during the disposal period of the radioactive waste.

The dissolution process of nickel ferrites in an acid solution proceeds similarly to that of magnetite, but its rate decreases markedly with an increasing nickel content. The decrease in the dissolution rates is due to the stabilization of oxide with increasing nickel content<sup>4</sup>. The dissolution of magnetite particles in solutions containing EDTA and Fe(II) was studied as a function of the total concentration of EDTA and Fe(II) and the influence of pH was also studied<sup>5</sup>. The results were interpreted in terms of a fast solution and surface complexation process followed by a slow heterogeneous electron transfer from adsorbed  $FeY^{2-}$  to surface  $>Fe(III)$  centers and the fast phase transfer of  $>Fe(II)$ . The dissolution rate increased with a decreasing pH of up to pH 3.1.

HANARO is a research reactor with a CNRF (cold neutron research facility) and FTL (fuel test loop) run in parallel. The FTL is a high-temperature (573K) and high-pressure (150 atm) facility. HANARO operates safely and effectively by improving its performance under advanced operation and maintenance technologies<sup>6</sup>. It has been 16 years since HANARO achieved its first criticality. The design review and suggestion of FTL for utilization are currently performed at KAERI. A chemical decontamination of the main internal loop of the FTL is also scheduled for this year.

In the present study, the dissolution characteristics of magnetite in the hydrazine base decontamination solution were

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investigated. In particular, the effect of copper ions on the dissolution of magnetite was emphasized. The objective of the study is to develop a new chemical decontamination agent safely applicable to the internal loop of FTL.

## EXPERIMENTAL

**Test equipment:** The dissolution experiments were performed in a magnetically stirred cylindrical glass vessel in a small autoclave provided with a thermostatic ceramic heater jacket. 200 mL of the dissolution mixture was de-aerated for 0.5 h by bubbling with high purity N<sub>2</sub> gas. Experiments were performed under an inert atmosphere by maintaining the inside of the autoclave with close packing throughout the duration of the dissolution.

**Condition:** 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. 65 % HNO<sub>3</sub> for pH control was used as received. The experimental conditions for magnetite dissolution are listed in Table-1. After the dissolution tests, the iron concentration in a solution was analyzed using an atomic absorption spectrometer (AA). The contact dose rate was measured from a  $\gamma$ -survey meter.

TABLE-1  
EXPERIMENTAL CONDITION  
FOR MAGNETITE DISSOLUTION

Reagents and concentration	Temp. (°C)	pH	Remark
HNO <sub>3</sub> , [N <sub>2</sub> H <sub>4</sub> ] 0.007M + HNO <sub>3</sub>	150	1-5	Fig. 1
[N <sub>2</sub> H <sub>4</sub> ] 0.007M + HNO <sub>3</sub>	70-150	3	Fig. 2,3
[N <sub>2</sub> H <sub>4</sub> ] $7 \times 10^{-6}$ M-0.14 M + HNO <sub>3</sub>	150	3	Fig. 4
[N <sub>2</sub> H <sub>4</sub> ] 0.07M + [M <sup>2+</sup> ] $5 \times 10^{-4}$ M+HNO <sub>3</sub>	95	3	Fig. 5

## RESULTS AND DISCUSSION

**N<sub>2</sub>H<sub>4</sub>-HNO<sub>3</sub> system:** Fig. 1 shows the plot of the dissolved fraction of iron in magnetite against the pH. The magnetite dissolution performance decreased with an increase in the solution pH. As shown in Fig. 1, the addition of a hydrazine in a nitric acid solution promotes the dissolution performance in a pH range of 1 to 3. However, the amount of dissolved magnetite looks almost the same when the solution pH exceeds 4.

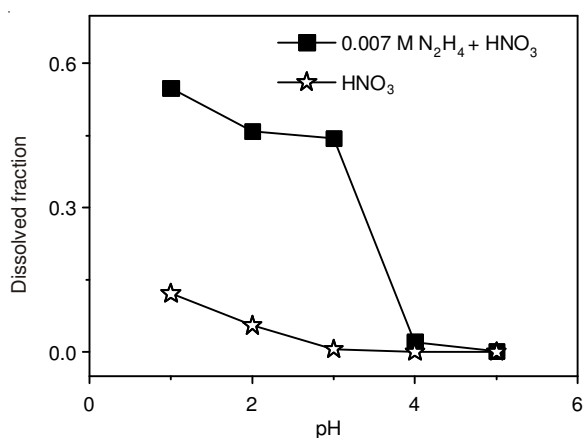


Fig. 1. Dissolved fraction of iron in magnetite against pH (2 h, 150 °C)

Fig. 2 shows a plot of the dissolved fraction of iron in magnetite against temperature. As shown in Fig. 2, a dissolution reaction occurs above 90 °C. The dissolution rate increases with an increase in the reaction temperature.

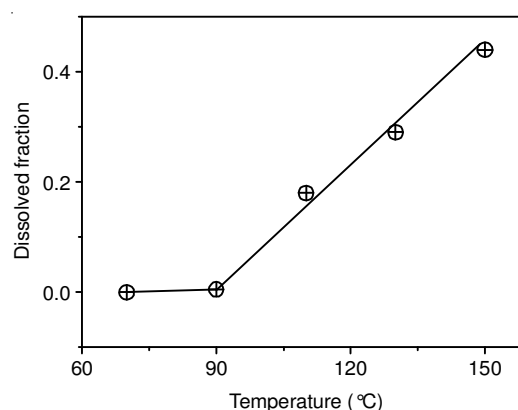


Fig. 2. Dissolved fraction of iron in magnetite against temperature ([N<sub>2</sub>H<sub>4</sub>] = 0.007 M, 2 h, pH = 3)

Fig. 3 shows a plot of the dissolved fraction of iron in magnetite over time. As shown in Fig. 3, the dissolution reaction in an early stage is fast. The reaction rate in the later stage is somewhat slow. The dissolution of magnetite, however, occurs continuously without any change in the reaction rate.

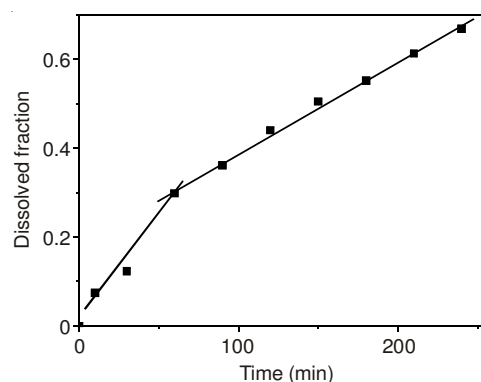


Fig. 3. Dissolved fraction of iron in magnetite over time ([N<sub>2</sub>H<sub>4</sub>] = 0.007 M, pH = 3, 150 °C)

Fig. 4 shows a plot of the dissolved fraction of iron in magnetite against the concentration of hydrazine. The dissolution rate slowly increases with an increase in the hydrazine concentration. As shown in Fig. 4, magnetite is fully dissolved when [N<sub>2</sub>H<sub>4</sub>] reaches 0.14 M.

**Effect of metal ion in N<sub>2</sub>H<sub>4</sub>-HNO<sub>3</sub> system:** The effect of metal ions on the dissolution of magnetite in a N<sub>2</sub>H<sub>4</sub>-HNO<sub>3</sub> system was investigated. The results are shown in Fig. 5. Most of the metal ions did not affect the dissolution of magnetite. In the case of Ni<sup>2+</sup> ions, the dissolution efficiency was decreased by the addition of metal ions. The magnetite dissolution efficiency of the N<sub>2</sub>H<sub>4</sub>-HNO<sub>3</sub> system was increased by the addition of copper ions.

Hydrazine and substituted hydrazine are potentially unidentate, bidentate, or bridging ligands. It was reported that transition metal ions form a complex with hydrazine in an aqueous solution or ethanolic solution<sup>7,8</sup>. From the visual

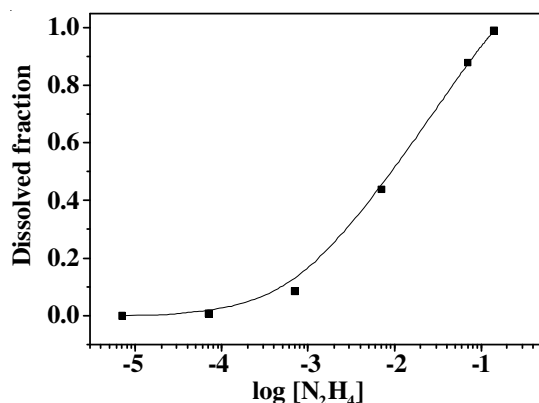


Fig. 4. Dissolved fraction of iron in  $Fe_3O_4$  against  $\log [N_2H_4]$ , (2 h, pH = 3, 150 °C)

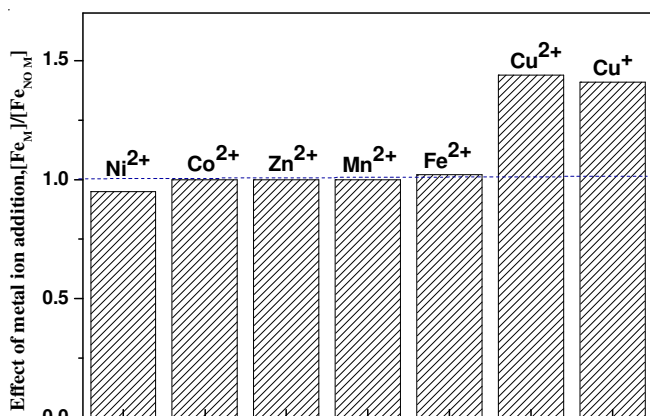


Fig. 5. Effect of metal ions on the dissolution of magnetite (2 h, pH = 3, 95 °C,  $[M^{n+}] = 0.0005$  M,  $[N_2H_4] = 0.07$  M)

inspection, the light blue colour of  $Cu(II)$  ion changed to colourless of  $Cu(I)$  ion at 95 °C. As shown in Fig. 6, there is a shift of N-H bend near  $1620\text{ cm}^{-1}$  by varying the anion species. This is explained by the fact that hydrazine and anion form a coordination compound with  $Cu(I)$  ion. The unpaired electrons of hydrazine and nitrate ion in a coordination compound can be attached to the ferric ion of magnetite. We, therefore, assume that the coordination compound of  $Cu(I)$  with hydrazine adhered to the ferric ion site of magnetite and the complex effectively reduced the ferric ions. Magnetite was quickly dissolved by reducing the ferric ions.

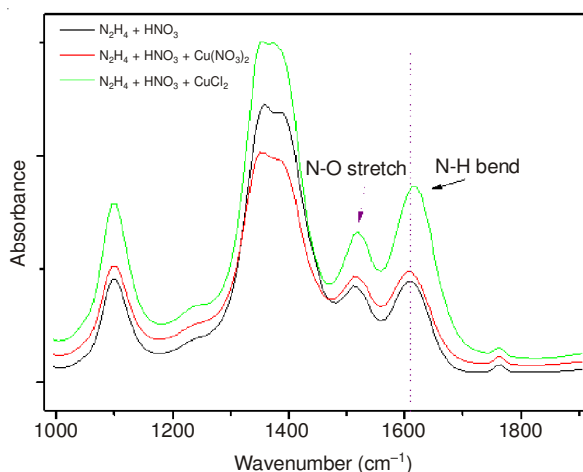


Fig. 6. FT-IR spectra of  $Cu-N_2H_4-NO_3(Cl^-)$  system

**Decontamination of Type 304 stainless steel:** The decontamination of a Type 304 stainless steel specimen was performed. The specimen was gathered from the primary loop of the FTL. The specimen was a tube type. The outer diameter was 5 cm and the height was 1.4 cm. Before decontamination, the contact dose rate of the specimen was 516 mSv/h.

Nitric acid + permanganate was used in the oxidation step.  $[KMnO_4]$  was 0.5 g/L and  $[HNO_3]$  was 0.315 g/L. In the reductive dissolution step, a hydrazine +  $Cu^{2+}$  ion +  $HNO_3$  (pH control) solution was used. Each oxidation step was performed at 93 °C for 10 h. Each reductive step was performed at 95 °C for 10 h.

Fig. 7 shows the change in contact dose rate after the application of each step. The contact dose rate decreased to 351 mSv/h after the first oxidation step. The contact dose rate decreased to 19.3 mSv/h after the first reductive dissolution step. Finally, the contact dose rate of the specimen decreased to 0.51 mSv/h after the second reductive dissolution step.

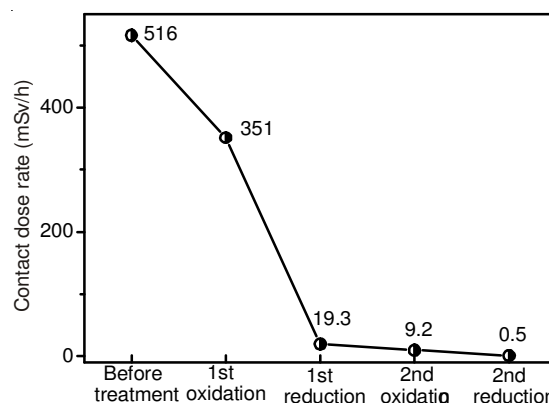


Fig. 7. Contact dose rate of FTL specimen against the application step

After the termination of the decontamination step, the specimen surface was investigated. No detrimental effect of the decontamination solution on the specimen was found.

## Conclusion

Magnetite is the main iron oxide formed on the surface of iron-based metals, especially when in contact with the coolant in nuclear power plants. Many solution formulations have been developed to decontaminate the internal loop of a nuclear power plant. The reductive decontamination agents commonly used, however, contain organic acid as a chelating agent. The possibility of not using organic acid was considered.

It was found that a chelate (organic acid) free reductive decontamination solution reasonably dissolves the magnetite powders. The magnetite dissolution rate was greatly increased by the addition of copper ions. The hydrazine base dilute reductive decontamination solution successfully decontaminated the radioactive Type 304 stainless steel.

If the main decontamination agent is decomposed into water and nitrogen, the generation of secondary waste is effectively reduced. The decomposition of hydrazine by the oxidizing agent, the radiation effect and material integrity of the candidate chemicals are being studied. The optimization of the decontamination process for the application of the hydrazine base decontamination solution to the FTL was also performed.

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