

Dissolution of Magnetite by the Hydrazine Base Solution

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1. Introduction

During the operation of nuclear power plants, build-up of radiation field in reactor coolant system happens. Magnetite is the main iron oxide formed on the surface of iron-based metals especially in contact with coolant in nuclear power plants. It reduces the efficiency of water lines in water-cooled nuclear reactors. Many solution formulations have been developed to dissolve or to decontaminate metal surfaces from the oxide layers formed on the surface [1, 2, 3]. The presence of Cr in the structural materials such as stainless steel could result in the formulation of Cr-substituted iron oxides, as Fe^{3+} (0.067 nm) and Cr^{3+} (0.064 nm) have similar ionic radii. The formation of solid solution between Cr_2O_3 with hematite and magnetite is reported [4]. The best method of removing the radioactive nuclides such as Co-60, impregnated / embedded in these oxides, is to dissolve the oxide deposit without affecting the base metal. Dissolution of simple iron oxides is normally carried out using organic (inorganic) acid, reducing agent and chelating agent. The commonly used chelating agent is EDTA, NTA and oxalic acid. Recently, it was reported that the chelating agent in a decontamination formulation affects the bad environmental effect during the disposal period of the radioactive waste. In the present study, the dissolution characteristics of magnetite in the hydrazine base system were investigated. The objective of the study is to prepare the decontamination agent applicable to the contaminated facility in KAERI.

2. Methods and Results

2.1 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 dissolution mixture was de-aerated for 30 minutes by bubbling with high purity N_2 gas. Experiments were performed under an inert atmosphere by keeping an inside of the autoclave with the close packing throughout the duration of dissolution.

2.2 Experimental condition

In all experiments, an amount of magnetite equivalent to 6.6×10^{-4} M (35.5 ppm) of iron on complete dissolution was employed. The concentration of decontamination solution is listed in Table 1. After dissolution tests, the iron concentration in a solution was analyzed by atomic absorption spectrometer (AA).

Table 1: Experimental Condition

Reagents and Concentration	$^{\circ}\text{C}$	pH
HNO_3 , N_2H_4 0.007 M + HNO_3 (pH)	150	1 - 5
N_2H_4 0.007 M + HNO_3 (pH)	70-150	3.0

2.3 Test results

Fig. 1 shows the plot of the dissolved fraction of iron in magnetite against pH. Magnetite dissolution performance is decreased with the increase of the solution pH. As shown in Fig. 1, the addition of hydrazine in nitric acid solution promotes the dissolution performance in the pH range from 1 to 3. However, the dissolution of magnetite is almost same when the solution pH exceeds 4.

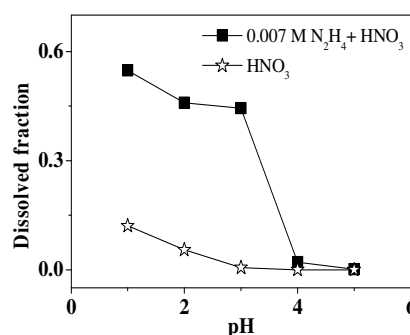


Fig. 1. Dissolved fraction of iron in magnetite against pH (2hrs, 150°C).

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

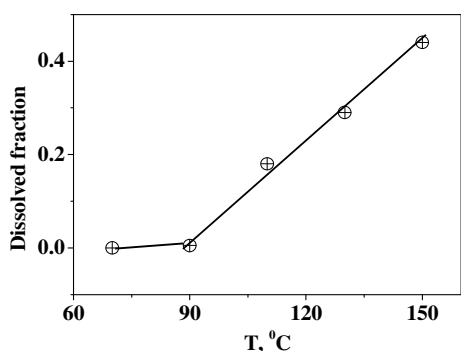


Fig. 2. Dissolved fraction of iron in magnetite against the temperature (2hrs, pH=3 [N₂H₄]=0.007M).

Fig. 3 shows the plot of the dissolved fraction of iron in magnetite against time. 30 % of the magnetite was dissolved in one hour after the initiation of reaction. The reaction rate is fast in an early stage of reaction. Then, the reaction becomes to decrease. However, magnetite is dissolved constantly without the change of reaction rate in the experimental range.

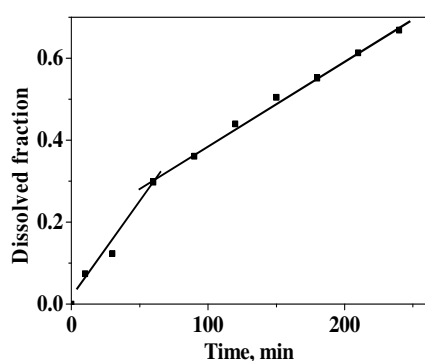


Fig. 3. Dissolved fraction of iron of magnetite against time (pH=3, [N₂H₄]=0.007M, 150 °C).

3. Conclusion

Good radiation field reduction can be achieved by carrying out full primary coolant system chemical decontamination in PWRs. To prepare against the decommissioning of the nuclear power plant, it is necessary to develop the unique domestic chemical decontamination process. As a candidate chemical decontamination solution, hydrazine base decontamination solution was chosen and the dissolution of magnetite by the solution was performed. By the addition of hydrazine to the acid solution, dissolved fraction of magnetite was greatly increased. Magnetite becomes to dissolve when the solution temperature

was above 90 °C. Magnetite dissolution rate was almost same and the reaction proceeds persistently even after 4 hours of reaction at 150 °C. However, the reaction was very slow under 100 °C. The effort to lower the reaction temperature is necessary.

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REFERENCES

- [1] E. B. Borghi, A. E. Regazzoni, A. J. G. Maroto, and M. A. Blesa, Reductive Dissolution of Magnetite by Solutions Containing EDTA and Fe(II), *Journal of Colloid and Interface Sciences*, Vol. 130, p. 299, 1999.
- [2] J. Manjanna, G. Venhateswaran, B. S. Sherigara, and P. V. Nayak, Dissolution Studies of Chromium Substituted Iron Oxides in Reductive-Complexing Agent Mixtures, *Hydrometallurgy*, Vol. 60, p. 155, 2001.
- [3] A. M. al-Mayouf, Dissolution of magnetite coupled Galvanically with Iron in Environmentally Friendly Chelant Solutions, *Corrosion Sciences*, Vol. 48, P. 898, 2006.
- [4] S. Music, M. Lenglet, S. Popovic, B. Hannoyer, I. Czakonagy, J. Ristic, D. Balzer, F. Gashi, Formation and Characterization of the Solid Solutions (Cr_xFe_{1-x})₂O₃, 0 ≤ x ≤ 1, *Journal of Material Science*, Vol. 31, p. 4067 (1996).