

A Comparative Study on the Dissolution of Magnetite

Hui-Jun Won*, Jung-Soon Park, Chong-Hun Jung, Wang -Kyu Choi and Jei-Kwon Moon,
Korea Atomic Energy Research Institute, 1045 Daedeokdaero, YuseongGu, Daejeon, 305-353, Korea

*Corresponding author: nhjwon@kaeri.re.kr

1. Introduction

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. 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 citric acid-hydrazine system, in nitric acid-hydrazine system and in dithionite-sodium citrate system were investigated. The objective of the study is to compare the dissolution performance of the 3 kinds of the candidate decontamination formulation.

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 maintained at 150 ± 2 °C(except $\text{Na}_2\text{S}_2\text{O}_4$ system). 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. The experimental apparatus is shown in Fig. 1.

2.2 Experimental condition

In all experiments, an amount of magnetite equivalent to 5.0×10^{-4} M (26.8 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). The crystal structure of the oxide before and after dissolution was determined by X-ray diffractometer (XRD).

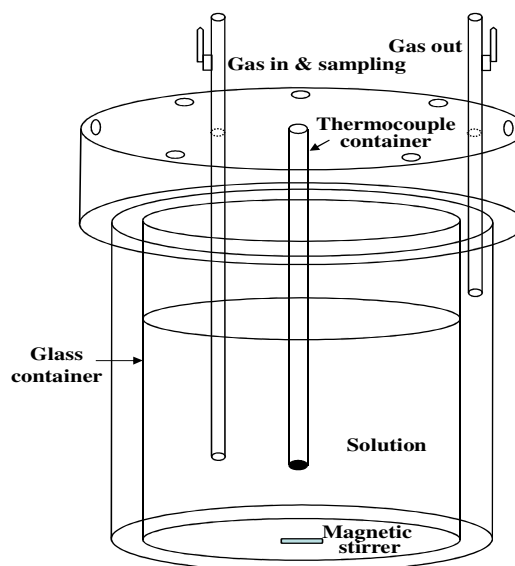


Fig. 1. Schematic diagram of the dissolution test equipment.

Table I: Experimental Condition

Reagents and Concentration	°C	pH
HNO_3 (pH control)	150	3.0
N_2H_4 0.007 M + HNO_3 (pH control)	150	3.0
C.A. 0.01 M + N_2H_4 0.007 M	150	3.5
Na_3CA 0.01 M + $\text{Na}_2\text{S}_2\text{O}_4$ 0.007 M	90	7.5

2.3 Test results

Fig. 2 shows the dissolved fraction of iron in magnetite in the presence of the various candidate decontamination solutions. Magnetite was hardly

dissolved only in a nitric acid solution at pH = 3. In the presence of reducing agents such as hydrazine or sodium dithionite, dissolution rate was greatly increased. 87 % of iron ion in magnetite was dissolved in two hours in nitric acid + hydrazine solution. 93 % of iron ion was dissolved in citric acid + hydrazine solution and 56 % of iron ion was dissolved in tri-sodium citrate + sodium di-thionite solution in two hours. Considering the fact that the reaction temperature was 90 °C, the dissolution performance of the tri-sodium citrate + sodium di-thionite solution was comparable with the citric acid + hydrazine solution and nitric acid + hydrazine solution.

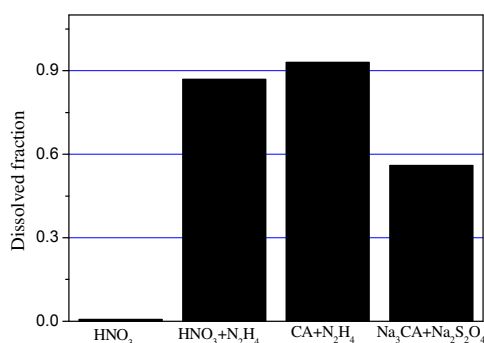
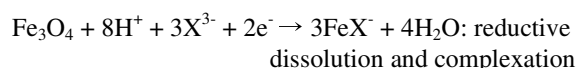
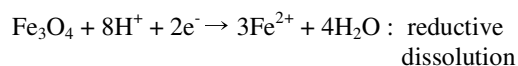
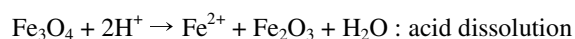


Fig. 2. Dissolved fraction of iron of magnetite in the presence of various candidate decontamination solutions.

The dissolution of magnetite can be occurred as followings:



Comparing the four kinds decontamination solution, we can assume that the reduction of lattice iron ion of magnetite affects the dissolution performance of magnetite.

3. Conclusion

The application of a decontamination solution to the primary coolant system before decommissioning is necessary to minimize the personnel dose rates. In foreign countries, system decontaminations were performed by applying the developed chemical decontamination process. 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, the dissolution of magnetite by the three kinds of decontamination solution was performed. All the test solutions showed good dissolution performance. The upgrading of the solution and the profound study on the dissolution kinetics are under consideration.

Acknowledgement

This work was carried out under the Nuclear R & D Program funded by the Ministry of Education, Science and Technology.

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).