Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 19-20, 2022

Effect of Temperature and Acid Concentration on the Reductive Dissolution Kinetics of Magnetite Specimen in Oxalic Acid Solution

Hye Rim Kim [a*], Jae Kwan Park [a], Su In Lee [a], Jeongju Kim [b], Chorong Kim [b], Wonzin Oh [c*], Byung-Chul Lee [a*]
[a]*Department of Chemical Engineering, Hannam University, 1646 Yuseong-daero, Yuseong-gu, Daejeon 34054, Korea*
[b]*KHNP Central Research Institute, 1312-70 Yuseong-daero, Yuseong-gu, Daejeon 34101, Korea*
[c]*Research Institute of Advanced Energy Technology, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu 41566, Korea*
[*]*Corresponding author: wonzin@knu.ac.kr; bclee@hnu.kr*

1. Introduction

Chemical decontamination is a key technology to be able to remove more than 95% of the radionuclide inventory of the primary coolant system of NPP. Recently, extensive research on the current status and prospects for various decontamination technologies in NPPs has been conducted [1,2]. The removal of the radionuclides from the primary coolant system takes place with the dissolution of corrosion metal oxide layers deposited with the radionuclides. Chemical decontamination by the oxidative and reductive dissolutions of the metal oxides has so far been recognized as the most effective method [3-5]. The decontamination processes using oxalic acid have been most widely developed to reductively dissolve the magnetite oxide film [6,7].

The objective of this work is to investigate the effects of reaction temperature and acid concentration on the kinetics of reductive dissolution of magnetite. The dissolution experiments were conducted with a synthetic magnetite specimen in the form of a thin plate. The magnetite sample used is a specimen made by sintering magnetite powder at a high temperature. In addition, our experiments were also conducted at higher temperatures (120 °C).

2. Experimental Methods

The dimensions and surface image of the magnetite specimen, purchased from the Kojundo Chemical Laboratory Co., LTD (Saitama, Japan), are shown in Fig. 1. The magnetite specimen sample has a purity of 99.8%. Inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer model NexION 2000) was used to analyze the concentration of Fe^{2+} ions dissolved into the aqueous solution from the magnetite specimen during the reductive decontamination.

Fig. 1. Shape and dimensions of the magnetite specimen.

The leaching experiments were carried out in a stainless-steel cylinder-shaped reactor (500 mL internal volume) equipped with a thermostat to maintain constant temperature in the reacting mixture. Inside wall of the reactor, a thermocouple, an impeller and shaft, and a sampling line in the reactor are all Teflon-coated to prevent corrosion of materials by oxalic acid solution. In order to prevent the aqueous solution in the reactor from boiling or evaporating, the upper part of the reactor was connected to a nitrogen gas cylinder in which the pressure was kept constant at 1.5 bar.

The experimental procedure is as follows. First, the magnetite specimen is inserted into the reactor, and the prepared oxalic acid aqueous solution is introduced into the reactor. The reaction temperature is set by operating the band heater, and the dissolution reaction is conducted while stirring the reaction solution. During the dissolution reaction, samples were taken from the reaction solution at different time intervals, and diluted with DI water ten times to avoid any precipitation caused by changes in the temperature. Finally, the concentration of the dissolved Fe present in the sample solution was measured through the ICP-MS analysis.

3. Results and Discussion

3.1 Effect of Oxalic Acid Concentration

The oxalic acid concentration varied in the range of 10, 15, 20, 30, and 40 $mmol \cdot L^{-1}$, and the reaction temperature was kept constant at 94 °C. Noticeable differences in kinetics could be observed when using oxalic acid with concentrations of 10 to 40 $mmol \cdot L^{-1}$, as shown in Fig. 2. Increased oxalic acid concentration yielded increased dissolution of Fe from magnetite specimen. The dissolution reaction rates of Fe were calculated from the slops of the linear fits shown in Fig. 2, and the results are listed in Table I. The dissolution rate of Fe increased almost linearly, as the oxalic acid concentration increased.

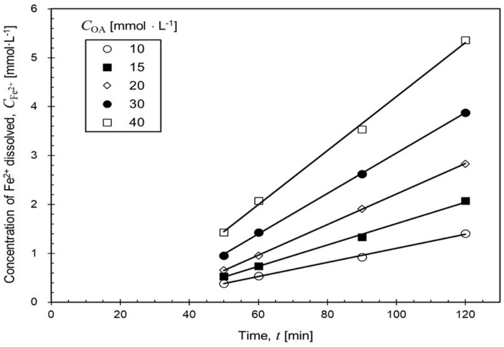

Fig. 2. The concentration of Fe^{2+} ion dissolved with respect to reaction time at different oxalic acid concentrations.

The data were fitted to a power equation. the dependence of the oxalic acid concentration of the dissolution reaction rate $[r(x)]$ of the magnetite specimen at 94 °C can be expressed by the following equation:

$$r(x)|_{T=94℃} = \left.\frac{dC_{Fe^{2+}}}{dt}\right|_{T=94℃} = 0.029x^{0.958}$$

Table I: Results for the linear fits of dissolution reaction rates of Fe at different oxalic acid concentration

C_{OA} [mmol·L^{-1}]	$x = \frac{C_{OA}}{C_{OA,R}}$ *	Dissolution reaction rate of Fe, $r(x)\left(=\frac{dC_{Fe^{2+}}}{dt}\right)$ [mmol·L^{-1}·min^{-1}]	R^2
10	0.50	0.014	0.998
15	0.75	0.022	0.997
20	1.00	0.031	0.999
30	1.50	0.041	0.999
40	2.00	0.055	0.998

* Reference oxalic acid concentration: $C_{OA,R} = 20$ mmol·L^{-1}

3.2 Effect of Reaction Temperature

Fig. 3 shows the experimental kinetic data for the reductive dissolution of the magnetite specimen at five different reaction temperatures. The concentration of oxalic acid in the aqueous solution was kept constant at 20 mmol·L^{-1}. The dissolution reaction rate of Fe^{2+} increased with the increase of the reaction temperature. That means that the dissolution of Fe^{2+} using oxalic acid could be thermally activated to improve its efficiency.

The dissolution reaction rate of Fe ($r(T)$) was obtained from the slope of the linear plot in Fig. 3, and the results are listed in Table II. The temperature dependency of the dissolution reaction rate, $r(T)$, can be expressed in a form of the so-called Arrhenius equation. Fig. 4 shows the result of the Arrhenius plot: $\ln r(T)$ vs. $1/T_{rxn}$. The activation energy (E_a) and rate constant (k_0) values were obtained from the slope and intercept of the straight line in Fig. 4, respectively, and are given in Table III. Consequently, the temperature dependence of the dissolution reaction rate of Fe at $x = 1$ (C_{OA} = 20 mmol·L^{-1}) is expressed as follows:

$$r(T)|_{x=1} = k_0 \exp\left(-\frac{E_a}{RT}\right) = 16.318 \exp\left(-\frac{19.726}{RT}\right)$$

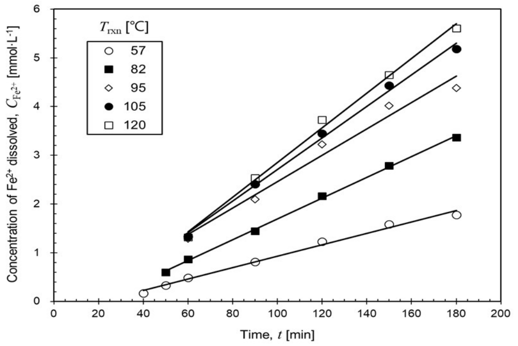

Fig. 3. The concentration of Fe^{2+} ion dissolved with respect to reaction time at different reaction temperatures.

Table II: Results for the linear plots of the dissolution reaction rates of Fe at different reaction temperatures

Reaction temperature, T_{rxn} [℃]	Dissolution reaction rate of Fe, $r(T)\left(=\frac{dC_{Fe^{2+}}}{dt}\right)$ [mmol·L^{-1}·min^{-1}]	R^2
57	0.012	0.991
82	0.021	0.999
95	0.027	0.975
105	0.032	0.996
120	0.036	0.996

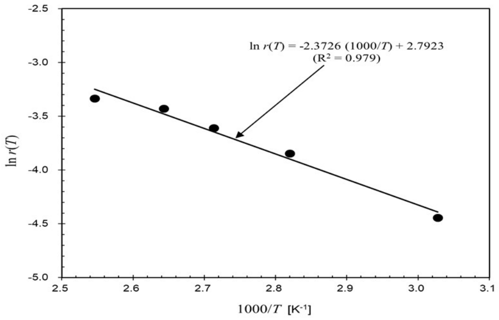

Fig. 4. Arrhenius plot of the dissolution reaction rate.

Table III: Data and results for the Arrhenius plot [$\ln r(T)$ vs. $1/T_{rxn}$] of the dissolution reaction rate of Fe with respect to the reaction temperature.

T_{rxn} [℃]	T_{rxn} [K]	$\frac{1000}{T_{rxn}}$ [K^{-1}]	$\ln r(T)$	E_a [kJ·mol^{-1}]	k_0 [mmol·L^{-1}·min^{-1}]	R^2
57	330.15	3.028	-4.443	19.726	16.318	0.979
82	355.15	2.820	-3.846			
95	368.15	2.713	-3.610			
105	378.15	2.643	-3.429			
120	393.15	2.546	-3.334			

3. Conclusions

The temperature and acid concentration were of importance for the determination of the dissolution reaction kinetics. The dissolution of Fe increased with acid concentration and temperature. According to the results for the acid concentration dependence of the dissolution reaction rate at a given temperature, the order of reaction was observed to be n = 0.958. The temperature dependence of the dissolution reaction rate of Fe from the magnetite specimen followed the Arrhenius formula well. The activation energy of the dissolution reaction was found to be 19.726 kJ·mol^{-1}.

REFERENCES

[1] C. Kim, H. Kim, Study on Chemical Decontamination Process Based on Permanganic Acid-Oxalic Acid to Remove Oxide Layer Deposited in Primary System of Nuclear Power Plant, J. Nucl. Fuel Cycle Waste Technol., Vol.17, p.15, 2019.

[2] J.K. Moon, S.B. Kim, W.K. Choi, B.S. Choi, D.Y. Chung, and B.K. Seo, The Status and Prospect of Decommissioning Technology Development at KAERI, J. Nucl. Fuel Cycle Waste Technol., Vol.17, p.139, 2019.

[3] B.-C. Lee, W. Oh, Temperature and Concentration Dependencies of Chemical Equilibrium for Reductive Dissolution of Magnetite Using Oxalic Acid, J. Nucl. Fuel Cycle Waste Technol., Vol.19, p.187, 2021.

[4] S.O. Lee, T. Tran, Y.Y. Park, S.J. Kim, and M.J. Kim, Study on the Kinetics of Iron Oxide Leaching by Oxalic Acid, Int. J. Miner. Process., Vol.80(2–4), p.144, 2006

[5] S.O. Lee, T. Tran, B.H. Jung, S.J. Kim, and M.J. Kim, Dissolution of Iron Oxide Using Oxalic Acid, Hydrometallurgy, Vol.87(3-4), p.91, 2007.

[6] R. Salmimies, M. Mannila, J. Kallas, and A. Hakkinen, Acidic Dissolution of Magnetite: Experimental Study on the Effects of Acid Concentration and Temperature, Clays Clay Miner., Vol.59, p.136, 2011.

[7] R. Salmimies, P. Vehmaanpera, A. Hakkinen, Acidic Dissolution of Magnetite in Mixtures of Oxalic Acid and Sulfuric Acid, Hydrometallurgy, Vol.163, p.91, 2016.

ACKNOWLEDGEMENT This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) (No. 20191510301310).