Modeling of Dissolution Rate of Magnetite in HyBRID Chemical Decontamination

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1. Introduction

The removal of radioactive isotopes from the primary coolant system takes place with the dissolution of corrosion metal oxide layers in which radioisotopes are deposited. Chemical decontamination by oxidative and reductive dissolution is considered to be the most effective method to date. Recently, KAERI has developed the HyBRID process without using any organic acids or organic chelating agents [1, 2]. The solution containing hydrazine, sulfuric acid and copper sulfate provided the acidic and reductive dissolution of transition metal ions from the corrosion oxides like magnetite. In this work we investigated the modeling of the kinetic data in the dissolution of metal oxides using the HyBRID method.

2. Modeling of Kinetic Data

The experimental data of reaction rate for dissolution of Fe ion from magnetite in HyBRID decontamination were analyzed by various kinds of kinetic models reported in literature for heterogeneous reactions such as the present work. Models are generally classified based on the graphical shape of their isothermal curves (dissolution vs time) or on their mechanistic assumptions [3]. Based on their shape, kinetic models can be grouped into acceleratory, deceleratory, linear, or sigmoidal models. Based on mechanistic assumptions, models are divided into nucleation, geometrical contraction, diffusion, or reaction-order. 12 different equations for dissolution are listed in Table 1 [3, 4].

The equations can be roughly divided into two categories: diffusion and reaction controlled [4]. For diffusion, the rate determining phenomenon is the transportation of reactants of reaction products to or from the reaction site. For chemical reaction, the rate determining step is, in turn, the actual chemical reaction taking place at the reaction site. In Table 1, x is the extent of reaction at time t, ranging from 0 to 1, k is the rate constant and a is a phase-specific constant. The x value is determined as the ratio of concentration of dissolved Fe ion to concentration of initially added Fe ion.

Table 1. Equations for modeling kinetics of dissolution

Eq. No.	Equation	Curve[1]	Physical Background	Remark
1	$x^2 = kt$	D	1D diffusion parabolic	
2	$(1-x)\ln(1-x) + x = kt$	D	2D diffusion for cylinder	
3	$[1-(1-x^{1/3})]^2 = kt$	D	3D diffusion for sphere	shrinking core model
4	$\left(1-\frac{2}{3}x\right)-(1-x)^{\frac{2}{3}} = kt$	D	3D diffusion for sphere	shrinking core model
5	$-\ln(1-x) = kt$	D	1st order random nucleation	1st order rate law
6	$[-\ln(1-x)]^{1/2} = kt$	V	random nucleation 2D	Avrami-Erofe'ev eq.
7	$[-\ln(1-x)]^{1/3} = kt$	V	random nucleation 3D	Avrami-Erofe'ev eq.
8	$\ln[-\ln(1-x)] = a\ln k + a\ln t$	V	modified 1st order random nucleation	Kabai eq.
9	$1-(1-x)^{1/2} = kt$	G	phase boundary control, shrinking disc	
10	$1-(1-x)^{1/3} = kt$	G	phase boundary control, contracting sphere	shrinking core model
11	$x^{1/3} = kt$	A	-	cubic root law
12	$\ln x = kt$	A	-	

[1]D = decelerator, V = variable, G = geometric, A = acceleratory

3. Results and Discussion

The kinetic data of dissolution of magnetite in HyBRID decontamination obtained from KAERI laboratory were correlated by all the model equations listed in Table 1. Fig. 1 shows the kinetic data of the dissolution of Ni and Fe ions from nickel ferrite ($NiFe_2O_4$) at five different hydrazine concentrations and at Cu ion concentration of 10-4 mol. The kinetic data of the dissolution of Fe ion from magnetite (Fe_3O_4) by the HyBRID solutions with various pH values are shown in Fig. 2.

The modeling results for the experimental data of Figs. 1 and 2 are given in Tables 2 and 3. When applying each model equation to each data set, the regression coefficient (R2) was calculated. The number of occurrences of the R2 value obtained by applying the model equation to each data is classified by the range of the R2 value. As shown in Table 2, the kinetic data of the dissolution of Ni and Fe ions from nickel ferrite measured at different N_2H_4 concentrations were quite well described (R2 > 0.90) by the 2D diffusion model (equation 2), the modified first-order Kabai equation (equation 8), and the shrinking core model (equation 10). Table 3 shows that the kinetic data of the Fe ion dissolution from magnetite were fitted the best by the modified first-order Kabai equation. The shrinking core model, the

Avrami-Erofe'ev equation, and the cubic-root law did not adequately describe the experimental data.

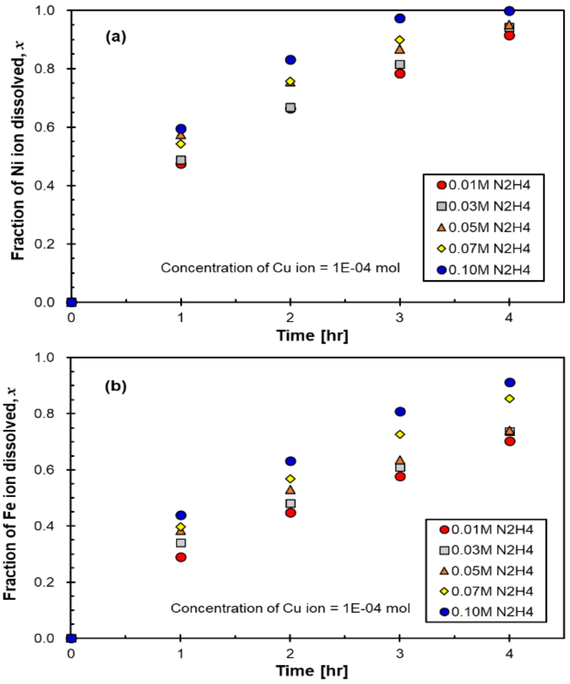

Fig. 1. Dissolution rate of Ni and Fe ions from nickel ferrite: (a) Ni ion; (b) Fe ion.

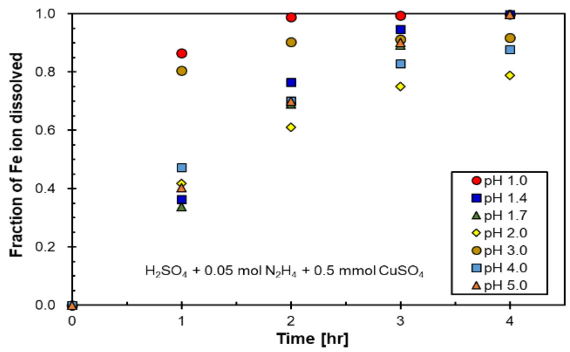

Fig. 2. Dissolution rate of Fe ion from magnetite at different pH values.

Table 2. Modeling results for the experimental kinetic data of Figure 1

Model equation	Number of data sets	Number of occurrences				
		R^2<0.80	0.80<R^2<=0.90	0.90<R^2<=0.95	0.95<R^2<=0.99	R^2>0.99
1	10	0	2	0	3	5
2	10	0	0	3	6	1
3	10	10	0	0	0	0
4	10	0	0	7	3	0
5	10	1	1	2	4	2
6	10	8	1	1	0	0
7	10	10	0	0	0	0
8	10	0	1	0	7	2
9	10	2	2	4	2	0
10	10	0	2	2	5	1
11	10	10	0	0	0	0
12	10	0	1	2	7	0

Table 3. Modeling results for the experimental kinetic data of Figure 2

Model equation	Number of data sets	Number of occurrences				
		R^2<0.80	0.80<R^2<=0.90	0.90<R^2<=0.95	0.95<R^2<=0.99	R^2>0.99
1	7	2	0	3	2	0
2	7	2	1	2	2	0
3	7	7	0	0	0	0
4	7	2	2	1	2	0
5	7	4	1	1	1	0
6	7	4	0	0	2	1
7	7	6	1	0	0	0
8	7	0	1	1	2	3
9	7	4	0	0	2	1
10	7	3	1	1	2	0
11	7	7	0	0	0	0
12	7	2	5	0	0	0

4. Conclusion

The kinetics of dissolution of magnetite and nickel ferrite by the HyBRID decontaminating agent was studied. The results showed that the concentration of hydrazine and copper sulfate and the pH of solution were of importance for the determination of the kinetics of dissolution reactions. The modeling results for the kinetic data showed that the dissolution rate data were correlated the best by the modified first-order random nucleation, represented by the Kabai equation.

ACKNOWLEDGEMENT

This work has been carried out under the Nuclear R&D Program (NRF-2018M2A8 A5024102) funded by Ministry of Science and ICT.

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