Leaching kinetics of neodymium in sulfuric acid from E-scrap of NdFeB permanent magnet

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Abstract−The leaching kinetics of neodymium in NdFeB permanent magnet powder was analyzed for the purpose of recovery of neodymium in sulfuric acid (H_2SO_4) from E-scrap (electric scrap) of NdFeB permanent magnet powder treated by oxidation roasting to form a reactant. The reaction was conducted with H_2SO_4 concentrations ranging from 2.5 to 3.5 M, a pulp density of 110.8 g/L, an agitation speed of 750 rpm, and a temperature range of 30 to 70 °C. After 4 h of leaching, the neodymium content in the E-scrap powders was completely converted into a neodymium sulfate ($Nd_2(SO_4)_3$) solution phase in H_2SO_4 in the condition of 70 °C and 3.0 M H_2SO_4. Based on a shrinking core model with sphere shape, the leaching mechanism of neodymium was determined by the rate-determining step of the ash layer diffusion. Generally, the solubility of pure rare earth elements in H_2SO_4 is decreased with an increase in leaching temperatures. However, the leaching rate of the neodymium in E-scrap powders increased with the leaching temperatures in this study because the ash layer included in the E-scrap powder provided resistance against the leaching. Using the Arrhenius expression, the apparent activation energy values were determined to be 2.26 kJmol^{-1} in 2.5 M H_2SO_4 and 2.77 kJmol^{-1} in 3.0 M H_2SO_4.

Keywords: NdFeB Permanent Magnet, Leaching, E-scrap, Neodymium Sulfate, Ash Layer Diffusion

INTRODUCTION

NdFeB permanent magnets have been broadly used in various fields requiring magnets with high magnetism, such as cranking motor of automobiles, computers, audio-visual components, magnetic separators, and military and aerospace systems. The average annual growth in the magnet market has increased to 70% due to the increase in world demand over the last decade. About 30 wt% of the NdFeB magnetic used is generated as scraps during the magnet preparation processes, and the amount of end-of-life scrap has also increased [1-7].

Therefore, it has been important to develop the separation and recycling technology for the recovery of neodymium from E-scrap, and the use of recycled neodymium could affects the supply and demand of raw neodymium materials [8].

This study was conducted in an effort to recover high value-added neodymium from the E-scrap of NdFeB permanent magnets. The leaching of E-scrap powders was hypothesized by a shrinking core model with a constant size and ash layer diffusion, because the NdFeB permanent magnetic scrap powder was oxidized by roasting in an electric muffle furnace. For the leaching mechanism, it was assumed that the H_2SO_4 solution diffuses into the inner ash layers until only the ash layers remain after the completion of neodymium leaching, as shown in the leaching behavior diagram of Fig. 1.
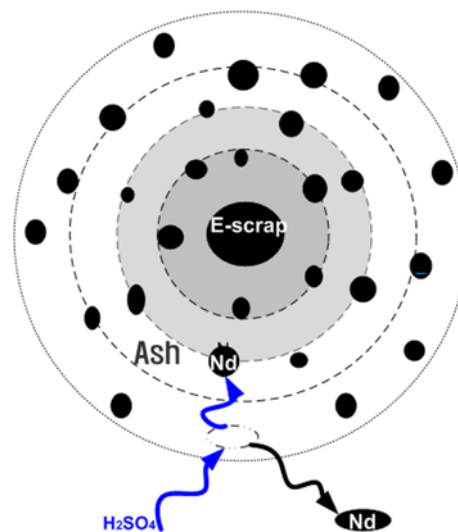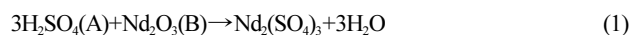

Fig. 1. Schematic diagram for the leaching behavior of E-scrap powder.

The Nd_2O_3 existing in the E-scrap powders of oxidized NdFeB permanent magnets is converted into a $Nd_2(SO_4)_3$ phase in H_2SO_4 solution, as described in Eq. (1). The reaction has a stoichiometric ratio of 3 mol H_2SO_4 per 1 mol Nd_2O_3.

$$3H_2SO_4(A) + Nd_2O_3(B) \rightarrow Nd_2(SO_4)_3 + 3H_2O \qquad (1)$$

The neodymium component existing on the surface of E-scrap

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powders was leached out, but the effect of chemical reaction did not appear, because the neodymium amount revealed on the surface was negligible. Then, the ash layer provided a resistance for the H_2SO_4 solution to penetrate toward the core of the ash layer. Therefore, the ash layer diffusion could be considered as a rate-determining step. In the ash layer diffusion model, there are many kinetic equations [9,10], but in this study the reaction rate was applied as Eq. (2) in terms of the diffusion rate of H_2SO_4 through the ash layer by shrinking core model with a constant sized spherical particle, as shown in the leaching behavior of Fig. 1.

$$1-3(1-X_B)^{2/3}+2(1-X_B)=k_{ash}t \tag{2}$$

X_B is fractional conversion of neodymium in E-scrap and k_{ash} is the apparent rate constant for ash layer diffusion and inverse of the time required for complete conversion of a particle, $r_c=0$.

$$k_{ash}=\frac{2D_eC_{Ao}}{\rho_BR^2} \tag{3}$$

D_e is the effective diffusion coefficient of H_2SO_4 in the ash layer, R is the radius of initial E-scrap particle. C_{Ao} is initial concentration of H_2SO_4. X_B is the fractional conversion of neodymium in E-scrap and ρ_B is the molar density of neodymium in E-scrap.

EXPERIMENT

The E-scrap powders and sulfuric acid solution could react explosively during leaching process due to exothermic reaction. Accordingly, it is difficult to control reaction temperature. Therefore, the E-scrap powder was roasted into a metal oxide under the atmosphere condition for 5 h at 600 °C. For the effective leaching of neodymium, and then the powder was ground with a shatter box fusing a tungsten carbide grinding barrel. As a raw material, the 50% mean diameter of powder was 9.4 μm before the leaching, and Table 1 shows the composition of the metals in E-scrap powder.

A double-jacketed Pyrex glass reactor with three baffles and condenser was used for sulfuric acid leaching, and the reaction temperature was constantly controlled by supplying water from water bath to the double jacked reactor. The leaching tests were performed under the following conditions: 110.8 g/L pulp density; 750 rpm agitation speed; 2.5 M to 3.5 M sulfuric acid concentration.

Sulfuric acid concentrations were adjusted to 2.5 M to 3.5 M. The stoichiometric concentration was calculated to be 2.4 M to dissolve all the metal components from E-scrap powder.

The metal composition of the E-scrap powders of NdFeB permanent magnets was analyzed after digesting the scraps with sulfuric acid with inductively coupled plasma-mass spectrometer (ICP-MS, X-series (X5), Thermo Elemental, UK). Sampled neodymium solution was filtrated by a syringe filter with 0.2 μm pores, and then the leached solution was analyzed by ICP-AES.

The crystal structure of the E-scrap powder was analyzed by X-ray diffraction spectroscopy (D8 ADVANCE, BRUKER AXS). The concentration of neodymium ion was analyzed by inductively
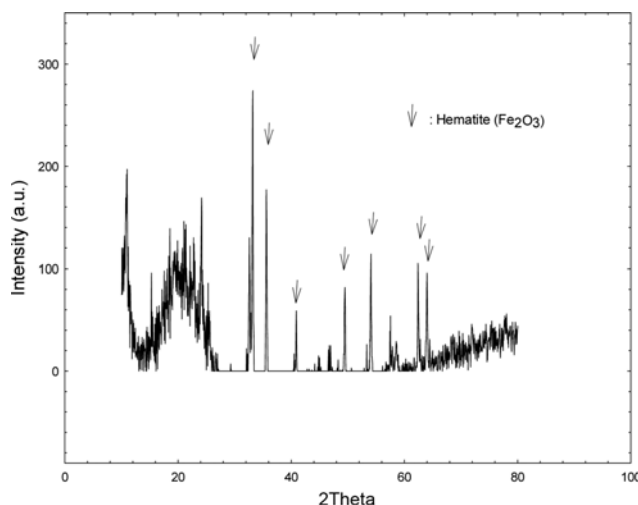

Fig. 2. XRD patterns of E-scrap powders of NdFeB permanent magnet.

coupled plasma-atomic emission spectrometry during the leaching (ICP-AES, iCAP6000, Thermo Fisher, UK).

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the E-scrap powder roasted from NdFeB permanent magnets. The main peak has a hematite crystalline structure, as confirmed by JCPDS reference card (33-0664). Table 1 shows the elemental compositions of E-scrap powder analyzed by ICP-MS. As shown in Table 1, the content of neodymium is 19.10% in E-scrap powder. Since neodymium is a main component among REEs (rare earth elements) in E-scrap powder, neodymium was selected in the experiment as a leaching objective.

The leaching experiment was carried out under the condition of 110.8 g E-scrap powder per L of H_2SO_4, with agitation at a temperature of 30 °C to 70 °C. If metal components exist as simple metal oxide, the stoichiometric ratio of H_2SO_4 required to be converted into sulfate forms is about 2.4 M. Although there was no change in size of the E-scrap powder of NdFeB permanent magnets before and after the leaching, the neodymium component in the E-scrap powder was completely leached out in the solution after the leaching.

Fig. 3 shows the leaching results as a function of sulfuric acid concentration from 2.5 to 3.5 M. The neodymium in E-scrap powder was completely leached out after the leaching of 4 h at the condition of the sulfuric acid concentration of 3.0 M, pulp density of 110.8 g/L, and leaching temperature of 70 °C. With increasing H_2SO_4 concentration from 3.0 M to 3.5 M, the leaching yield decreased, because the solubility of $Nd_2(SO_4)_3$ was decreased by means of the common ion effect of SO_4^{2-} in the solution. In the case of 3.5 M sulfuric acid, the increase of SO_4^{2-} concentration in the solution exceeded the concentration of neodymium. Therefore, it seems that the formation of $Nd_2(SO_4)_3$ crystal decreases the leaching yield of

Table 1. Elemental compositions of NdFeB permanent magnetic scraps analyzed by ICP-MS

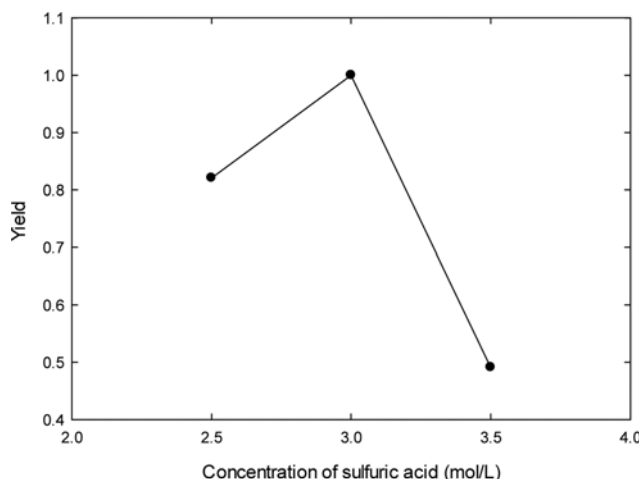| Element	Nd (%)	Dy (%)	Fe (%)	Ni (%)	Co (%)	Al (%)
E-scrap powder	19.10	4.17	55.90	<0.008	1.11	0.50

Fig. 3. Leaching yield of neodymium according to concentrations of sulfuric acid (leaching temp., 70 °C; leaching time, 4 h; pulp density, 110.8 g/L; agitation speed, 750 rpm).
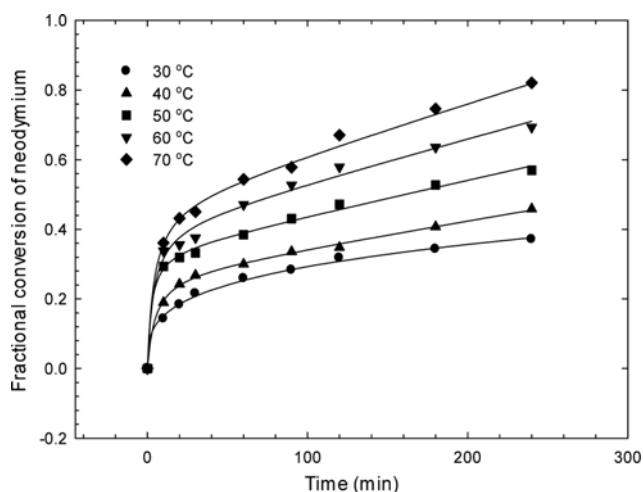

Fig. 5. Evolution of fractional conversion of leached neodymium in 3.0 M H$_2$SO$_4$.

Fig. 4. Evolution of fractional conversion of leached neodymium in 2.5 M H$_2$SO$_4$.

Fig. 6. Particle size distribution before and after leaching.

neodymium in the case of 3.5 M sulfuric acid. Accordingly, the optimum concentration of sulfuric acid for the most effective leaching was found to be 3.0 M.

Figs. 4 and 5 show the fractional conversion of neodymium with the concentration of H$_2$SO$_4$ during the leaching period. The leaching yield of neodymium increased with the reaction temperature. As shown in Fig. 5, the Nd$_2$O$_3$ in the NdFeB permanent magnetic scrap was completely leached out into the Nd$_2$(SO$_4$)$_3$ solution after the reaction for 4 h under the condition of 70 °C and 3.0 M H$_2$SO$_4$.

As mentioned, the leaching reaction was determined by ash layer diffusion. The mean diameter of NdFeB permanent magnets was about 9.4 μm before the leaching, and there was no change in the size after the leaching reaction, as shown in particle size analysis of Fig. 6 and SEM image of Fig. 7. The results show that the NdFeB permanent magnetic scrap remains only in the ash layer after the leaching, and the layer provides resistance against the penetration of sulfuric acid into the core of E-scrap.

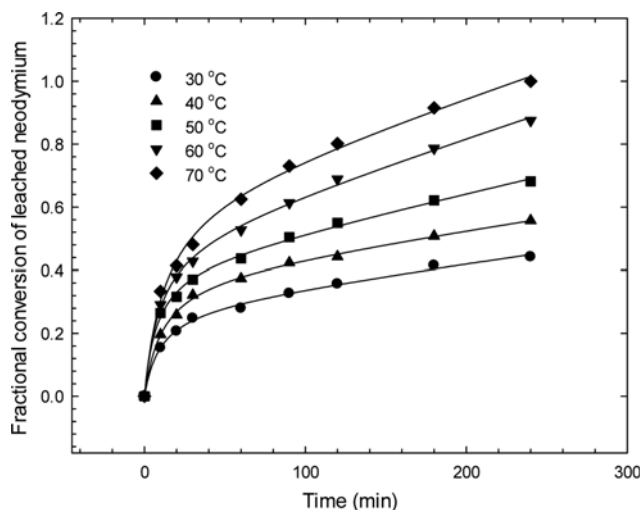In the experiment, it was assumed that there was no change of

concentration during the leaching reaction, because excessive H$_2$SO$_4$ was added with concentrations of 2.5 M to 3.5 M, which is higher than the stoichiometric ratio of 2.4 M necessary for the complete leaching of all the metals according to ICP-MS. The real conversion of the Fe component was shown to have a leaching efficiency of 20% in the experiment. Accordingly, the acid concentration is excessive in the leaching solution, and the solutions indicated a pH range less than 1.0 after the leaching. Therefore, it could be assumed that the concentration of H$_2$SO$_4$ is constant during the leaching reaction.

The rate equation can be summarized as in Eq. (2) using the shrinking core model with same size before and after the leaching, which considers a spherical particle [11,12]. The neodymium component on the surface of the E-scrap reacts with H$_2$SO$_4$, and is rapidly leached out during the first step of the leaching. The surface of the E-scrap becomes rough, and the thickness of the ash layer gradually increases according to the progress of leaching. The ash layer provides resistance against H$_2$SO$_4$ penetrating into the core of the E-scrap.

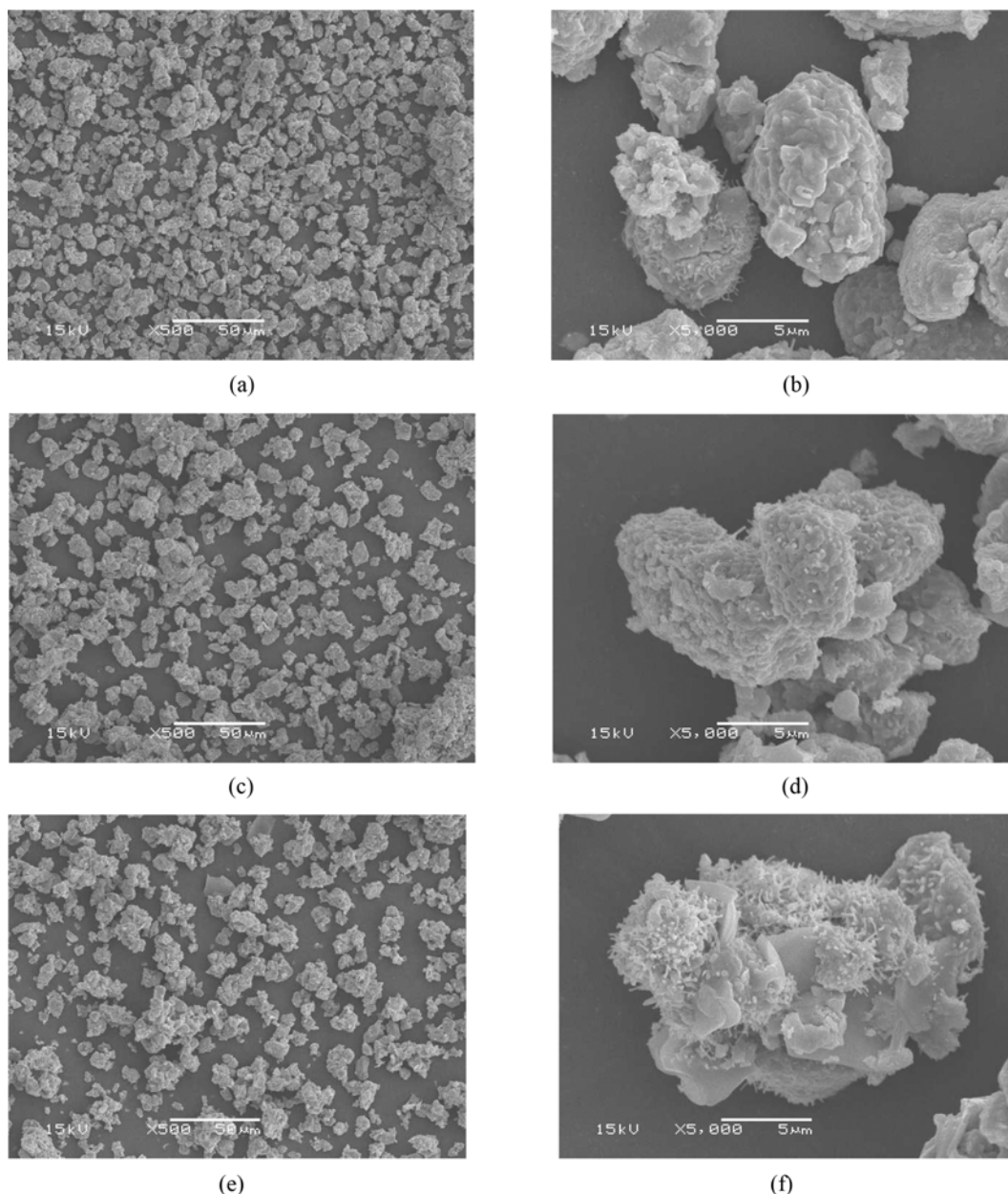The rate equation can be summarized as in Eq. (2) for the ash

Fig. 7. SEM photographs of E-scrap powders according to leaching times: (a), (b) 0 min (c), (d) 60 min (e), (f) 240 min.

layer diffusion rate-determining step using the shrinking core model that considers a spherical particle. Based on Eq. (2), the apparent rate constant can be calculated by the least square method at various reaction temperatures, as shown in Fig. 8. Table 2 is the result of the apparent rate constant (k_{ash}) obtained from the slope of each graph of Fig. 8 in 2.5 M sulfuric acid. To investigate the effect of leaching temperatures, the apparent activation energy was calculated from the rate constants shown in Table 2. In the ash layer diffusion stage, the slope was -2.717×10^2, as shown in Fig. 9. Finally, the apparent activation energy appeared as a value of 2.26 kJmol^{-1} in the range of 30 to 70 °C. The small activation energy value shows that this leaching reaction is insensitive to temperature change for the leaching of neodymium.

Fig. 10 presents a graph obtained from the relationship of $1-3(1-X_B)^{2/3}+2(1-X_B)$ according to the leaching times based on ash layer diffusion in 3.0 M H$_2$SO$_4$. The rate equation is summarized as in Eq. (2) for the ash layer diffusion rate-determining step using the shrinking core model, which has the shape of a spherical particle. Based on Eq. (2), the apparent rate constants were calculated by the least square method from the graph, as shown in Fig. 10. Table 3 is the result of apparent rate constant (k_{ash}) obtained from the slope of each graph of Fig. 10 in 3.0 M sulfuric acid. The apparent activation energy was calculated from rate constants shown in Table 3. In the ash layer diffusion stage, the slope was -3.332×10^2 as shown in Fig. 11. Finally, the apparent activation energy was calculated as 2.77 kJmol^{-1} in the range of 30 to 70 °C.

Table 4 is the summary of leaching kinetics of neodymium from E-scrap powders of NdFeB permanent magnet. These results show that the leaching yield and apparent reaction rate constant, k_{ash} for 3.0 M are higher than values of 2.5 M, because it was assumed that
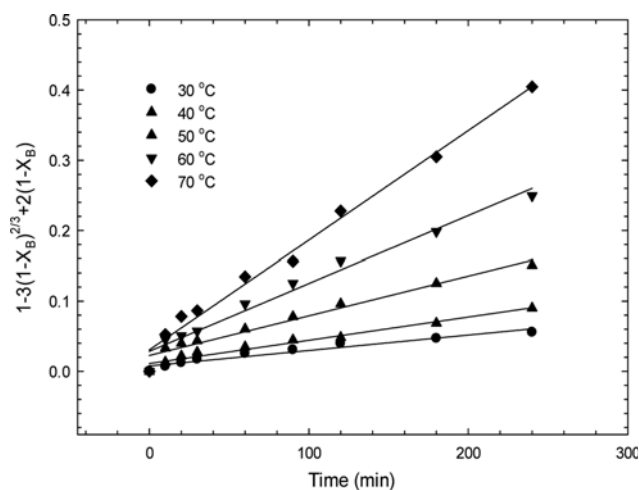
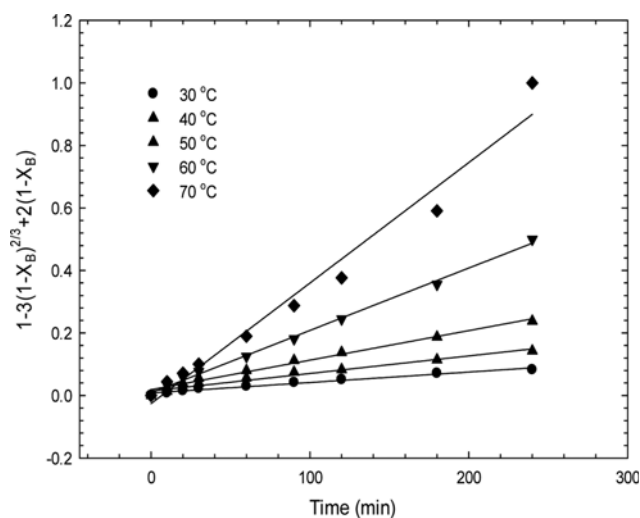Fig. 8. The relationship of $1-3(1-X_B)^{2/3}+2(1-X_B)$ vs. time during the ash layer diffusion stage in 2.5 M H_2SO_4.

Fig. 10. The relationship of $1-3(1-X_B)^{2/3}+2(1-X_B)$ vs. time during the ash layer diffusion stage in 3.0 M H_2SO_4.
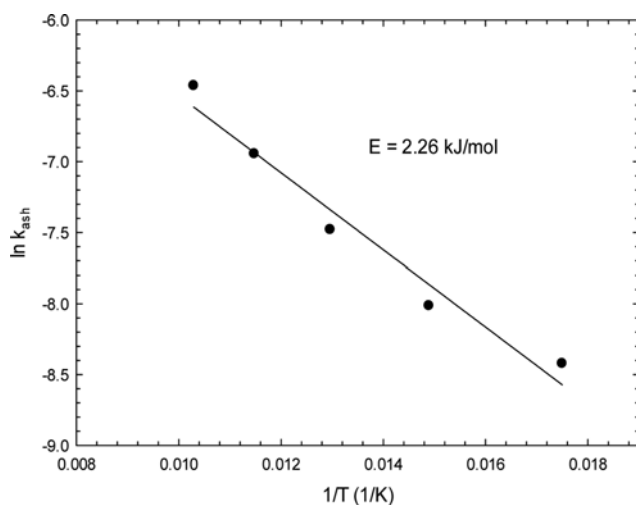

Fig. 9. Arrhenius plot of ash layer diffusion stage in 2.5 M H_2SO_4.
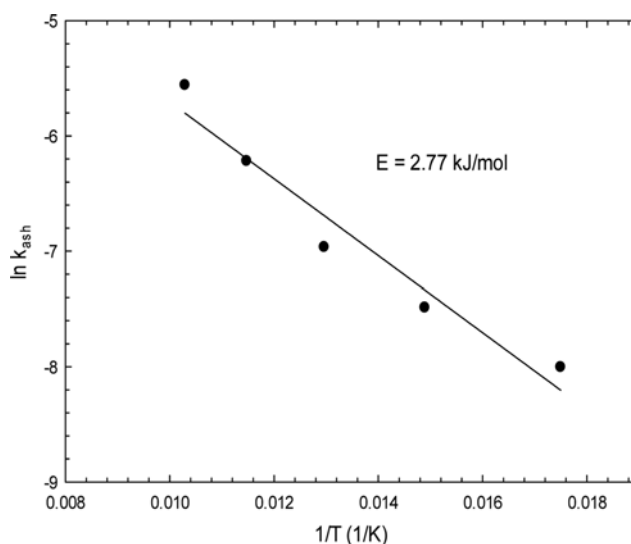

Fig. 11. Arrhenius plot of ash layer diffusion stage in 3.0 M H_2SO_4.

the reaction rate constant is proportional to initial acid concentration, as described in Eq. (3). Accordingly, k_{ash} becomes higher when the initial acid concentration is higher, and the increase of the reaction rate constant increases the reaction rate at the same reaction time. Therefore, the leaching yield of neodymium for 3.0 M H_2SO_4

solution is higher than that for 2.5 M.

The activation energy values were found to be 2.26 kJmol^{-1} at 2.5 M H_2SO_4 and 2.77 kJmol^{-1} at 3.0 M H_2SO_4. These small val-

Table 2. Parameter searching data obtained from the regression for ash layer diffusion determining step in 2.5 M H_2SO_4

Parameter	30 °C	40 °C	50 °C	60 °C	70 °C
k_{ash}	2.199×10^{-4}	3.308×10^{-4}	5.641×10^{-4}	9.642×10^{-4}	1.559×10^{-3}
y_o	7.716×10^{-3}	1.117×10^{-2}	2.264×10^{-2}	2.853×10^{-2}	3.071×10^{-2}
R^2	0.944	0.964	0.961	0.974	0.987

Table 3. Parameter searching data obtained from the regression for ash layer diffusion determining step in 3.0 M H_2SO_4

Parameter	30 °C	40 °C	50 °C	60 °C	70 °C
k_{ash}	3.348×10^{-4}	5.606×10^{-4}	9.440×10^{-4}	1.995×10^{-3}	3.854×10^{-3}
y_o	8.126×10^{-3}	1.457×10^{-2}	1.880×10^{-2}	8.608×10^{-3}	-2.556×10^{-2}
R^2	0.973	0.969	0.987	0.997	0.972

Table 4. Summary of leaching kinetics of neodymium from E-scrap powders of NdFeB permanent magnet

Pulp density (g/L)	H$_2$SO$_4$ conc. (mol/L)	Unreacted ash layer controlling step					Activation energy (kJ/mol)
		k_{ash} (1/min), Leaching yield (%)					
		30	40	50	60	70	
110.8	2.5	2.199×10^{-4}	3.308×10^{-4}	5.641×10^{-4}	9.642×10^{-4}	1.559×10^{-3}	2.26
		38	46	59	71	82	
110.8	3.0	3.348×10^{-4}	5.606×10^{-4}	9.440×10^{-4}	1.995×10^{-3}	3.854×10^{-3}	2.77
		45	56	69	88	~100	

ues were caused by the ash layer diffusion being more insensitive than other mechanisms like the chemical reaction and the film layer diffusion. Furthermore, the solubility of rare earth elements such as neodymium is generally decreased with the increase of temperatures [13].

CONCLUSIONS

A leaching mechanism for neodymium in E-scrap powders of NdFeB permanent magnets in H$_2$SO$_4$ was proposed by a shrinking core model with constant size. The neodymium content (Nd, Nd$_2$O$_3$) in E-scrap powder was completely converted into an Nd$_2$(SO$_4$)$_3$ solution phase within 4 h with a pulp density of 110.8 g/L in 3.0 M H$_2$SO$_4$. Through this kinetic study, the leaching reaction was determined by the ash layer diffusion stage.

1. The leaching kinetics followed a shrinking core model with the ash layer diffusion as the first rate-determining step. At this time, the activation energy values were found to be 2.26 kJmol^{-1} in 2.5 M H$_2$SO$_4$ and 2.77 kJmol^{-1} in 3.0 M H$_2$SO$_4$. These small values are caused by the mechanism by ash layer diffusion and the decrease of solubility of neodymium according to the increase of temperature. The dependence of temperature change of the leaching of neodymium was very low.

The optimum condition for the recovery of neodymium from E-scrap of NdFeB permanent magnets was proposed to be a leaching time of 4 h with a pulp density of 110.8 g/L, with a temperature of 70 °C in 3.0 M H$_2$SO$_4$.

ACKNOWLEDGEMENTS

NOMENCLATURE

C_{A0} : initial concentration of H$_2$SO$_4$ reactant [molL^{-1}]

E : apparent activation energy for ash layer diffusion [kJmol^{-1}]
k_{ash} : apparent rate constant for ash layer diffusion [s^{-1}]
r_c : radius of E-scrap [m]
R : radius of initial E-scrap [m]
X_B : fractional conversion of neodymium in E-scrap
D_e : effective diffusion coefficient of H$_2$SO$_4$ reactant

Greek Letter
ρ_B : molar density of neodymium in E-scrap [molL^{-1}]

REFERENCES

1. A. Ermete and P. Joelma, *Int. J. Hydrog. Energy*, **36**, 15752 (2011).
2. C. Jirang and Z. Lifeng, *J. Hazard. Mater.*, **158**, 228 (2008).
3. M. Kul, Y. Topkaya and I. Karakaya, *Hydrometallurgy*, **93**, 129 (2008).
4. J.-C. Lee, H. T. Song and J.-M. Yoo, *Conserv. Recycl.*, **50**, 380 (2007).
5. H. Park, J. Lee, S. Cho and J. Kim, *J. Korean Inst. Res. Recycl.*, **21**, 73 (2012).
6. A. Tuncuk, V. Stazi, A. Akcil, E. Y. Yazici and H. Deveci, *Miner. Eng.*, **25**, 28 (2012).
7. I. C. Nnorom and O. Osibanjo, *Conserv. Recycl.*, **52**, 843 (2008).
8. Massari Stefania, Ruberti Marcello, *Rare earth elements as critical raw materials: Focus on international markets and future strategies*, Resources Policy (2012), DOI : http://dx.doi.org/10.1016/j.resourpol.2012.07.001.
9. C. F. Dickinson and G. R. Heal, *Thermochim. Acta*, **340-341**, 89 (1999).
10. J. J. M. Órfão and F. G. Martins: *Thermochim. Acta*, **390**, 195 (2002).
11. O. Levenspiel, *Chemical reaction engineering*, 3rd Ed., Wiley, New York, 566 (2003).
12. L. D. Schmidt, *The engineering of chemical reactions*, 2nd Ed., Oxford University Press, UK, 357 (2005).
13. J. G. Speight, *Lange's handbook of chemistry*, 16th Ed., McGraw-Hill, New York, 1323 (2005).