

K.W. CHUNG*, C.-J. KIM*, H.-S. YOON*[‡]

NOVEL EXTRACTION PROCESS OF RARE EARTH ELEMENTS FROM NdFeB POWDERS VIA ALKALINE TREATMENT

NOWY SPOSÓB EKSTRAKCJI PIERWIASTKÓW ZIEM RZADKICH Z PROSZKÓW NdFeB W ROZTWORACH ALKALICZNYCH

The alkaline treatment of NdFeB powders in NaOH solution at various equivalent amounts of NaOH at 100°C was performed. The resultant powders were then leached in 0.5M H₂SO₄ solution at 25°C for 2 minutes. At 5 equivalents of NaOH, neodymium in NdFeB powders was partially transformed to neodymium hydroxide. The transformation of neodymium to neodymium hydroxide actually occurred at 10 equivalents of NaOH and was facilitated by increasing the equivalent of NaOH from 10 to 30. In addition, iron was partially transformed to magnetite during the alkaline treatment, which was also promoted at a higher equivalent of NaOH. The leaching yield of neodymium from alkaline-treated powders was increased with an increasing equivalent of NaOH up to 10; however, it slightly decreased with the equivalent NaOH of over 10. The leaching yield of iron was inversely proportional to that of rare earth elements. NdFeB powders treated at 10 equivalents of NaOH showed a maximum leaching yield of neodymium and dysprosium of 91.6% and 94.6%, respectively, and the lowest leaching yield of iron of 24.2%, resulting in the highest selective leaching efficiency of 69.4%.

Keywords: recycling, NdFeB magnet, alkaline treatment, leaching, selective leaching efficiency

1. Introduction

NdFeB magnets were first developed in 1984, and since then their use has become widespread in IT devices, automobiles, wind turbine systems, etc. Their demand and subsequently their production has considerably increased [1-4]. The markedly growing use of NdFeB magnets has induced the correspondingly increasing generation of scrap materials, because about 25% of the input amount is discharged as waste scrap during the manufacturing process [5]. Additionally, an abundance of waste magnets has been gradually released from end-of-life devices and systems. The drastic increase in the number of waste magnets and manufacturing scraps has inevitably induced interest in their recycling to preserve the natural environment. Discarded NdFeB magnets and scrap can release boron upon contact with an acidic medium, subsequently damaging the environment. In addition, recycling of NdFeB magnets and scrap can provide alternative material sources, thus preserving the natural resources. Lately, the sustainability of the raw material supply chain has been threatened worldwide, also inducing the need for recycling. The recovery of rare earth elements (REEs) from waste NdFeB magnets and scrap has traditionally been attempted using a hydrometallurgical process [6]. The process steps include leaching in strong acid, the selective precipitation of REEs as double sulfates, oxalates or fluorides, REEs purification processes, and the synthesis of REEs compounds and metals [7]. Saito et al. investigated the complete dissolution of NdFeB alloy

and selective precipitation of sodium neodymium sulfates [8]. Itakura et al. reported the hydrothermal treatment of Ni-coated NdFeB magnets in a mixture of HCl and oxalic acid solutions at 110°, where neodymium can be selectively recovered as oxalate compound in a one-step process [9]. In these works, NdFeB alloys were reported to be easily and quickly leached up to almost 100% in acidic solution. However, the simultaneous dissolution of iron and REEs induces large consumption of chemicals and discharges large amounts of waste solution containing dissolved iron. Ideally, the selective leaching of REEs from NdFeB alloy is essential in terms of commercial and environmental sustainability. In the 1990s, the thermal oxidation of NdFeB alloy was applied prior to the leaching step [10, 11]. The formation of relatively refractory iron oxides (Fe₂O₃) and easily soluble neodymium oxide (Nd₂O₃) was attempted to suppress the leaching of iron in acidic solution. However, the oxidation roasting of NdFeB powders yields the formation of neodymium-iron mixed oxide (NdFeO₃), which causes insufficient separation efficiency due to the simultaneous leaching of neodymium and iron from mixed oxide. It also requires a strong acidic medium for leaching. J. W. Lyman et al. investigated the selective oxidation of REEs and the leaching of resultant products. Even though the selective oxidation of REEs was successful with iron remaining in the metallic state, the selective leaching of REEs in diluted acid solution was ineffective [12]. M. Itoh et al. suggested a new recovery process for REEs using selective chlorination of REEs and leaching of resultant products in distilled water, where a

* KOREA INSTITUTE OF GEOSCIENCE AND MINERAL RESOURCES, DAEJEON, KOREA

[‡] Corresponding author: hsyoon@kigam.re.kr

chlorination process requires relatively high temperatures and long reaction times [13].

Although various methods have been developed for the hydrometallurgical recycling of NdFeB magnets, the problems associated with the hydrometallurgical process (leaching with strong acid and generation of large amounts of acidic waste solution) has yet to be solved. In this study, a new approach for recovering REEs from NdFeB scraps through alkaline treatment and leaching was proposed. Alkaline treatment has been traditionally applied for the hydrometallurgical process of monazite ores to convert REEs phosphates to soluble REEs hydroxides [14]. Alkaline treatment can be performed at a relatively low temperature of around 100°C and an ambient pressure without any special equipment. In addition, REEs hydroxides are easily and quickly dissolved in weakly acidic solution. Therefore, the present work applied alkaline treatment to the recycling process of NdFeB alloys and investigated not only the leaching behavior of the resultant powders but also the separation efficiency of REEs and iron.

2. Experimental

NdFeB scrap was obtained from JAHWA Electronics co., LTD, where the composition is shown in TABLE 1. First, the powders were ground into finer powders with the size of less than 100 μm using a shatter box (using a tungsten carbide barrel). For alkaline treatment, a mixture of 200 ml of NaOH solution and 20 grams of the powders were charged in a Teflon bath, heated to 100°C, and held for 5 hr (see Fig. 1). The amount of NaOH in the alkaline treatment solution is shown in TABLE 1. After alkaline treatment, the resultants were filtered and collected. Leaching of powders was conducted in a 0.5M H₂SO₄ solution of 30 ml at 25°C for 2 minutes, where the ratio of solid/liquid was 0.1 (w/v).

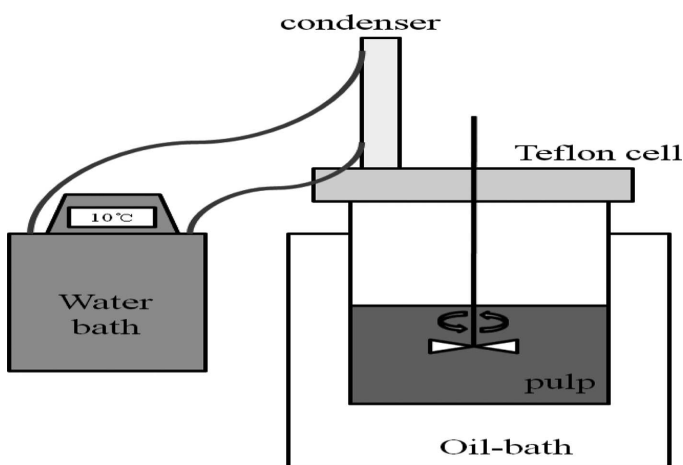
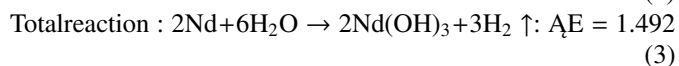
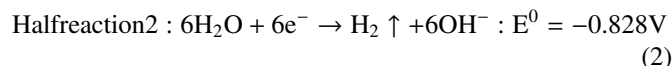
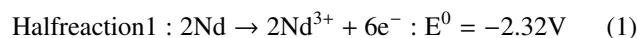


Fig. 1. Schematic diagram of apparatus for alkaline treatment

Alkaline-treated NdFeB powders were identified using X-ray diffraction analysis (XRD, D8 ADVANCE, BRUKER AXS) before and after leaching. The concentrations of neodymium, dysprosium, and iron, both in powders and leaching solutions, were analyzed using the inductively coupled plasma-atomic emission spectrometer (ICP-AES, iCAP6000, Thermo Fisher, UK).

3. Results and discussion

In alkaline treatment of NdFeB powders, neodymium is expected to be transformed to neodymium hydroxides, Nd(OH)₃, as follows [15]:



No additional OH⁻ ions are required for transformation of neodymium to neodymium hydroxide. As neodymium hydroxide is stable in the alkaline region, NdFeB powders were treated in a NaOH solution. The molar ratio of [OH⁻]/[Nd] in neodymium hydroxide, Nd(OH)₃, is 3. For the sake of convenience, in the current paper one equivalent of NaOH was defined as three times neodymium in a molar ratio, and the amount of NaOH charged in alkaline treatment solution was varied from 5 to 30 equivalents.

TABLE 1
Compositions of NdFeB powders before and after alkaline treatments

Sample Number	Equivalent of NaOH	Fe (wt%)	Nd (wt%)	Dy (wt%)
0	-	65.8	26.2	3.48
1	5	55.74	22.55	3.17
2	10	52.58	21.36	2.98
3	20	52.58	20.72	2.89
4	30	50.9	19.63	2.75

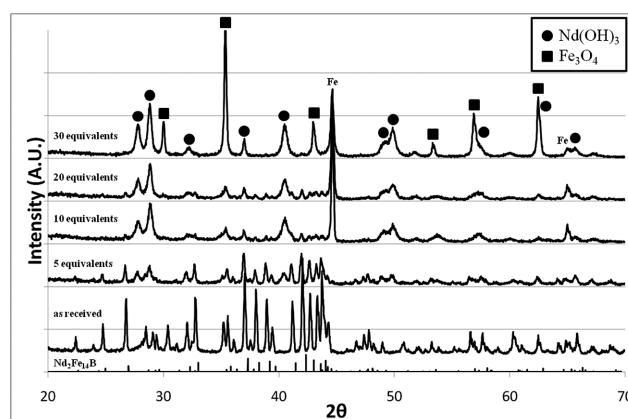


Fig. 2. XRD patterns of NdFeB powders before and after alkaline treatments at various equivalents of NaOH

XRD patterns of NdFeB powders before and after alkaline treatment are shown in Fig. 2. NdFeB powders as received reveal the X-ray diffraction pattern corresponding to Nd₂Fe₁₄B. In XRD patterns for the powders that were alkaline-treated at 5 equivalents of NaOH (sample 1), diffraction peaks typical of neodymium hydroxide are observed. However, these characteristics of Nd₂Fe₁₄B remain, which indicates that a large part of Nd₂Fe₁₄B was unreacted. With increasing the equivalent of NaOH from 10 to 30 (Samples 2-4), the diffraction peaks

typical of neodymium hydroxide become obvious. It can be seen that the reaction expressed using eq. (3) actually occurred at a higher equivalent of NaOH than 10. Notably, the diffraction peaks of magnetite, Fe_3O_4 , in addition to those of α -Fe were detected and become also noticeable with increasing the equivalent of NaOH. It indicates that α -Fe was transformed to magnetite upon alkaline treatment, which was promoted with increasing the equivalent of NaOH. The concentrations of neodymium, dysprosium, and iron in NdFeB alloys before and after alkaline treatment are shown in TABLE 1. With the increasing equivalent of NaOH, the concentrations of these elements decreased due to the increased transformation of neodymium to neodymium hydroxide and iron to magnetite.

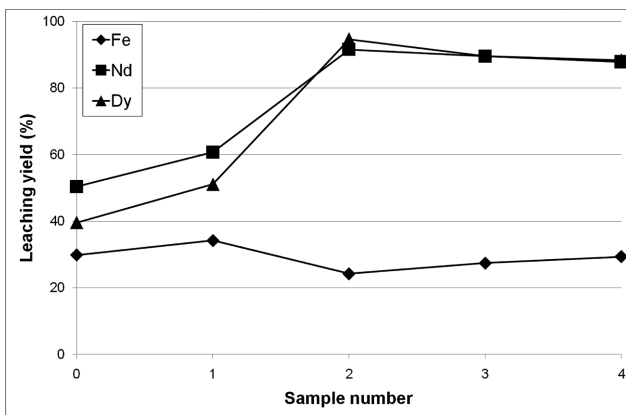


Fig. 3. Leaching yields of neodymium, dysprosium, and iron from NdFeB powders before and after alkaline treatments at various equivalents of NaOH (0.5M H_2SO_4 , 25°C, ratio of solid to liquid = 1:10, 2 minutes)

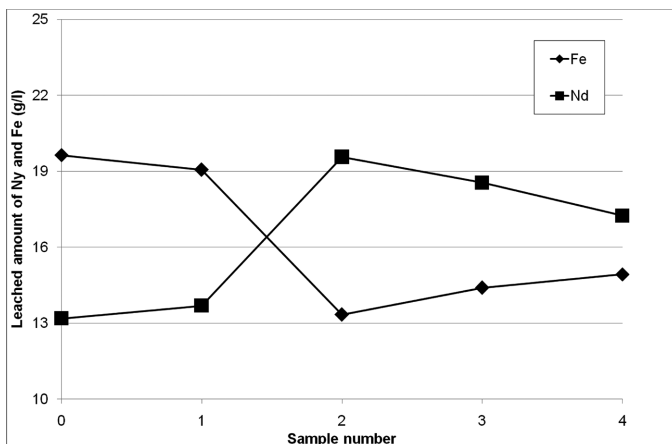


Fig. 4. Concentrations of neodymium and iron in leaching solution for NdFeB powders before and after alkaline treatments at various equivalents of NaOH (0.5M H_2SO_4 , 25°C, ratio of solid to liquid = 1:10, 2 minutes)

Figure 3 displays the leaching yields of neodymium, dysprosium, and iron from NdFeB powders before and after alkaline treatment in 0.5M H_2SO_4 solution at 25°C. Neodymium and dysprosium for sample 0 (NdFeB powder as received) is observed to dissolve only 50.3% and 39.6%, respectively, while iron was leached by 29.8%. Despite the low leaching yield of iron, the leaching amount of iron is much higher than that of REEs, as shown in Fig. 4. The slightly increased

leaching yields of REEs and iron are observed for sample 1; however, those of neodymium and dysprosium are still low. Sample 2, in which most of the neodymium was transformed to neodymium hydroxide, reveals a marked increase of the leaching yield of neodymium, 91.5%, and that of dysprosium, 94.6%. Iron shows a very low value of 24.2%. In particular, the leached amount of neodymium has much higher values than that of iron for sample 2. For samples 3 and 4, high leaching yields of ca. 89% were also observed for REEs, with those lower than 30% for iron. This indicates that REEs were leached predominantly over iron for the alkaline-treated Nd-FeB powders. It is particularly important to note that REEs were leached up to 95% in the very short time of 2 minutes at 25°C, which indicates the fast dissolution of neodymium hydroxide. Figure 5 shows the XRD patterns of leaching residue. For sample 1, in which neodymium was partially transformed to neodymium hydroxide, most of the characteristic peaks of neodymium hydroxide disappeared, while those of $\text{Nd}_2\text{Fe}_{14}\text{B}$ are still observed. This means that the dissolution of neodymium hydroxide predominantly occurred compared to that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ during leaching. It was observed that neodymium hydroxide dissolved very easily and quickly in weak acidic solution.

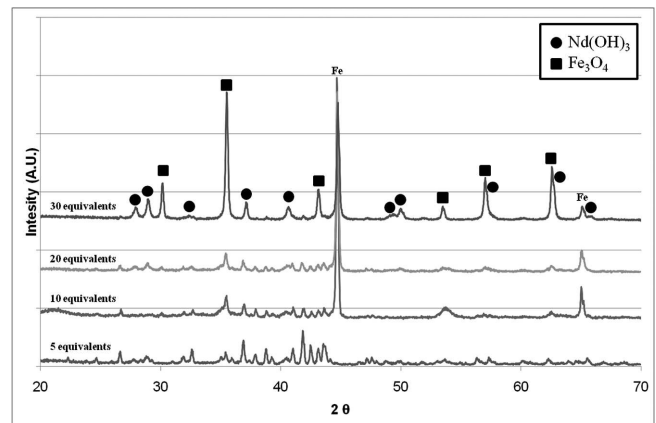


Fig. 5. XRD patterns of NdFeB powders after leaching as a function of the equivalent of NaOH for alkaline treatment

It was observed that the leaching yield of REEs became dominant over that of iron when neodymium in NdFeB alloys was actually transformed into neodymium hydroxide. However, these decreased slightly for REEs and increased slightly for iron with the increasing equivalent of NaOH for alkaline treatment from 10 to 30. In other words, less REEs were leached and more iron was leached, which may be due to the facilitated transformation of iron to magnetite with increasing equivalent of NaOH. To verify this, the phase ratio of magnetite to metallic iron in samples 2-4 was evaluated using XRD patterns before and after leaching. A comparison between Fig. 2 and Fig. 5 shows that the intensity ratios of the main peaks of α -Fe to magnetite for samples 2-4 change after leaching. Notably, the intensity ratios for samples 2-4 were meaningfully increased from 12.5, 9.4, and 0.5 to 14.5, 12.1, and 0.95, respectively after leaching. This indicates that the fraction of α -Fe over magnetite increased after leaching [16], which means that the leaching of magnetite occurred faster and higher than that of α -Fe. Increasing the concentration of NaOH for alkaline treatment facilitates the formation of mag-

netite, which induces an increase in the leaching yield of iron and subsequently a decrease in that of REEs. This suggests that facilitation of the formation of neodymium hydroxide and the suppression of the formation of magnetite are preferable to attain high leaching yields of REEs and low leaching yields of iron under the leaching condition of the present study.

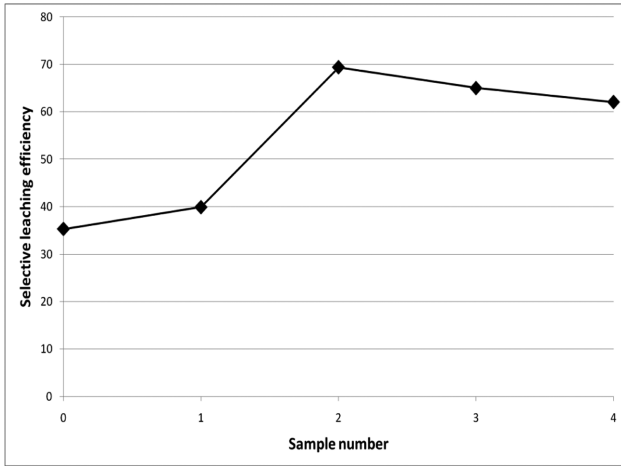


Fig. 6. Selective leaching efficiency for NdFeB powders before and after alkaline treatments at various equivalents of NaOH

TABLE 2
Selective leaching efficiency calculated using data from the previous report

Conc. of H ₂ SO ₄	Leaching yield of Nd	Leaching yield of Iron	SLE
2 M	77.8%	18.1%	63.7
3 M	82.0%	20.3%	65.4

In the works on the hydrometallurgical recycling process of waste NdFeB magnets and manufacturing scraps, selective leaching of REEs is one of the most important issues. To quantify the selective leaching efficiency of REEs, a factor of selective leaching efficiency is suggested in the present paper as follows:

$$\text{Selective leaching efficiency (SLE)} = \frac{[100 - \text{leaching yield of iron (\%)}] \times \text{leaching yield of neodymium (\%)}}{100} \quad (4)$$

In the ideal case, when no iron is leached and all neodymium is leached, SLE equals 100. Figure 6 shows SLE for samples 0-4. The SLE of sample 0 shows the very low value of 35.3. Samples obtained by alkaline treatment reveal the increased values of SLEs, and the highest SLE value of 69.4 is obtained for sample 2, which is 2 times that for sample 0. To compare SLEs for the leaching of alkaline-treated NdFeB powders and for that of thermally oxidized NdFeB powders, the latter values were calculated using data in the previous report [17] and are revealed in TABLE 2. The leaching yields of neodymium and iron are ca. 80% and ca. 20%, respectively, and SLEs are thus in the range of between 63 and 66. A higher value of SLE is obtained in the present study than those in previous works. This indicates that the alkaline treatment and leaching

process is effective in the selective leaching of REEs from NdFeB alloys and is potentially applicable for the recovery of REEs from NdFeB waste magnets and scraps.

4. Conclusion

In the present study, alkaline treatment was applied as a pretreatment of NdFeB powders for selective leaching of REEs over iron. The treatment of NdFeB powders in NaOH solution at 100°C for 5hr induced neodymium and iron transformed to neodymium hydroxide and magnetite, respectively, which were facilitated with increasing amounts of NaOH. Upon alkaline treatment at 10 equivalents of NaOH, most of neodymium was transformed to neodymium hydroxide and these alkaline-treated powders showed much higher leaching yields of REEs and lower leaching yields of iron compared with those of the untreated powders. However, leaching yields of REEs slightly decreased and that of iron slightly increased with further increasing equivalent of the NaOH up to 30. This is due to the enhanced transformation of iron to magnetite. It could be concluded that the facilitation of neodymium's transformation to neodymium hydroxide and the suppression of iron's transformation to magnetite are simultaneously required for selective leaching of REEs. For the powders obtained by alkaline treatment at 10 equivalents of NaOH, the highest leaching yields of neodymium and dysprosium were 91.6% and 94.6%, respectively, and the lowest leaching yield of iron was 24.2%, giving rise to the highest SLE value of 69.4. These results suggest that alkaline treatment and leaching process is efficient in the selective leaching of REEs over iron for waste NdFeB magnets and scraps.

Acknowledgements

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program), funded by the Ministry of Environment (Project No.: 11-A10-MR).

REFERENCES

- [1] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, Y. Matsuura. *J. Appl. Phys.* **55**, 2083 (1984).
- [2] L.Q. Yu, X.L. Zhong, Y.P. Zhang, Y.G. Yan, Y.H. Zhen, M. Zakotnik, J. Mang. *Magn. Mater.* **323**, 1152 (2011).
- [3] J.W. Kim, Y.D. Kim, *J. Kor. Powd. Met. Inst.* **20**, 169 (2013).
- [4] S. Namkung, M.W. Lee, S.J. Han, T.S. Jang, *J. Kor. Powd. Met. Inst.* **19**, 1 (2012).
- [5] K. Miura, M. Itoh, K.-I. Machida, *J. Alloys Compd.* **466**, 228 (2008).
- [6] K. Binnemans, P.T. Jones, B. Blanpain, T.V. Gerven, Y. Yang, A. Walton, M. Buchert, *J. Clean. Prod.* **51**, 1 (2013).
- [7] T.W. Ellis, F.A. Schmidt, L.L. Jones, Methods and opportunities in the recycling of rare earth based materials, in: K.C. Liddell, R.G. Bautista and R.J. Orth (Eds.), *Metals and Materials Waste Reduction, Recovery and Remediation*, The Minerals, Metals & Materials Soc., Pennsylvania 1994.
- [8] T. Saito, H. Sato, T. Motegi, *J. Alloys Compd.* **425**, 145 (2006).
- [9] T. Itakura, R. Sasai, H. Itoh, *J. Alloys Compd.* **408-412**, 1382 (2006).

- [10] J.-C. Lee, W.-B. Kim, J. Jeong, I.J. Yoon, J. Korean Inst. of Met. & Mater. (in Korean with English Abstract) **36**, 967 (1998).
- [11] M. Niinae, K. Yamaugchi, Y. Nakahiro, Shigen-to-Sozai **110**, 337 (1994).
- [12] J.W. Lyman, G.R. Palmer, Report of Investigation RI 9481, U. S. Bureau of Mines (1993).
- [13] M. Itoh, K. Miura, K.-I. Machida, J. Alloys. Comp. **477**, 484 (2009).
- [14] R. Panda, A. Kumari, M.K. Jha, J. Hait, V. Kumar, J.R. Kumar, J.Y. Lee, J. Ind. Eng. Chem. **20**, 2035 (2014).
- [15] Speight James G., Lange's Handbook of Chemistry (16th ed.), McGRAW-HILL, New York 2005.
- [16] F.H. Chung, J. Appl. Cryst. **7**, 519 (1974).
- [17] K.W. Chung, C.-J. Kim, H.-S. Yoon, Leaching and recovery of Nd from spent NdFeB magnet. 243rd American Chemical Society National Meeting & Exposition, San Diego, California, U.S.A., March 25-29, 2012, American Chemical Society.

Received: 20 November 2014.