www.czasopisma.pan.pl PAN www.journals.pan.pl
POLSKA AKADEMIA NAUK

Arch. Metall. Mater. **68** (2023), 1, 103-106

DOI: https://doi.org/10.24425/amm.2023.141480

BORAM KIM[1], DAE-WEON KIM[1*], HEE LACK CHOI[2*]

A STUDY ON RECOVERY OF CERIUM BY LEACHING SOLVENTS FROM NiMH WASTE BATTERY

In this study, a rare earth composite precipitation ($NaREE(SO_4)_2H_2O$, REE: Ce, La, Nd, Pr) powder was prepared from spent nickel hydride batteries, and cerium hydroxide was separated from its constituent rare earth elements. As $Ce(OH)_3$ can be oxidized more easily than other rare earth elements (La, Nd, and Pr), Ce^{3+} was converted to Ce^{4+} by injecting air into the leachate at 80°C for 4 h. The oxidized powder was leached using sulfuric and hydrochloric acids. Because $Ce(OH)_4$ has low solubility, it can be separated from other elements. Therefore, the pH of the leaching solution was adjusted for selective precipitation. To determine the crystalline phase, recovery, and grade of the recovered $Ce(OH)_4$, the powders were analyzed using X-ray diffraction, scanning electron microscopy, and inductively coupled plasma optical emission spectroscopy. The grade and recovery rates of the $Ce(OH)_4$ powder recovered from the rare earth composite precipitate using sulfuric acid as the solvent were 95% and 97%, respectively, whereas those of the powder recovered using hydrochloric acid were 96% and 95%, respectively.

Keywords: NiMH; Cerium recovery; rare earth composite powder

1. Introduction

Owing to the complexity of the processes for separating and refining elements from their mineral states as well as the remoteness of locations of their mines, the production of rare earth elements (REEs) is limited. According to the United States geological survey statistics, 36.67% of the world's rare earth reserves are in China, and because of the stringent policies and regulations of the government, an imbalance exists in the world's supply and demand of REEs [1].

As REEs are used in sophisticated applications, such as electric/hybrid vehicles and wind power generation, their demand is expected to increase in future [2-3]. Therefore, in countries with scarce REE resources, it is necessary to develop technologies that can efficiently recover rare earth resources from e-waste, especially batteries [4].

Nickel hybrid batteries contain nickel, cobalt, and REEs, such as cerium, lanthanum, neodymium, and praseodymium. Several studies have been conducted to efficiently recover these elements [5-10]. In particular, extensive efforts have been devoted to the recovery of nickel, cobalt, and REEs from spent nickel hydride (NiMH) batteries. Oxalic acid has been used for the recovery of REEs in the form of $NaREE(SO_4)_2 \cdot H_2O$ via a precipitation reaction [9,10]. However, rare earth composite powders in the form of $NaREE(SO_4)_2 \cdot H_2O$ cannot be used directly for industrial applications, and the research on the separation techniques for REEs is insufficient.

Therefore, we conducted a study on the separation and recovery of cerium from rare earth composite powders obtained from spent NiMH batteries. Cerium, with the highest content among the other constituents, such as lanthanum, neodymium, and praseodymium, is the principal constituent of the $NaREE(SO_4)_2 \cdot H_2O$ powders. In a previous study, we isolated $Ce(OH)_4$ from sulfuric acid-based solvents [11]. However, in industries, REEs are generally separated via solvent extraction using hydrochloric acid [12,13]. In this study, $NaREE(SO_4)_2 \cdot H_2O$ was prepared through a metathesis reaction from wasted NiMH batteries, and it was further oxidized to prepare cerium hydroxide. The characteristics of the final product obtained using different types of acid solvents, such as sulfuric acid or hydrochloric acid, were analyzed.

2. Experimental

In this study, rare earth composite precipitation ($NaREE(SO_4)_2 \cdot H_2O$, REE: La, Ce, Nd, and Pr) powder was obtained by removing cobalt and nickel from wasted nickel

---

[1] INSTITUTE FOR ADVANCED ENGINEERING, ADVANCED MATERIAL & PROCESSING CENTER, 175-28 GOAN-RO, 51 BEON-GIL, YONGIN-SI, GYEONGGI, 17180, KOREA
[2] PUKYONG NATIONAL UNIVERSITY, DEPARTMENT OF MATERIAL SCIENCE & ENGINEERING, 45, YONGSO-RO, NAM-GU, BUSAN, 48513, REPUBLIC OF KOREA

* Corresponding authors: choihr@pknu.ac.kr; mdsimul@iae.re.kr

TABLE 1

The composition and concentration of NiMH battery and the rare earth composite precipitation powder ($NaREE(SO_4)_2{\cdot}H_2O$)

Element (wt.%)	**Ni**	**Ce**	**Co**	**La**	**Mn**	**Nd**	**C**	**K**	**Zn**	**Pr**	**Al**	**Fe**
NiMH battery	45.8	10.4	8.5	6.7	3.6	3.1	2.1	1.8	1.2	0.9	0.9	0.4
$NaREE(SO_4)_2{\cdot}H_2O$	0.1	17.2	0.02	13.1	—	5.44	—	—	—	1.8	—	—

hydride batteries (NiMH battery, Model: HHR-33AH72W6, Hitachi). TABLE 1 lists the contents of the spent NiMH battery and $NaREE(SO_4)_2{\cdot}H_2O$ powder. The precipitated powder contained 17.2% Ce, 13.1% La, 5.44% Nd, and 1.8% Pr.

A metathesis reaction was performed to convert $NaREE(SO_4)_2{\cdot}H_2O$ to $REE(OH)_3$ by adding a sodium hydroxide solution to the slurry of the $NaREE(SO_4)_2{\cdot}H_2O$ powder with a solid-liquid ratio of 50 g/l. The temperature of the reaction was maintained at 70°C for 4 h using a jacketed reaction flask.

Unlike other REE hydroxides ($La(OH)_3$, $Nd(OH)_3$, and $Pr(OH)_3$, powder), cerium hydroxide ($Ce(OH)_3$, powder) can be easily oxidized. Therefore, the slurry was oxidized at a temperature of 80°C for 4 h while injecting air at a rate of 2000 cc/min. After oxidation, the slurry was separated into solid and liquid phases. The recovered powder was separately dissolved in 1 M sulfuric acid and 1 M hydrochloric acid, each having a solid-liquid ratio of 25 g/L.

Ce^{4+} has low solubility; therefore, unlike other elements (La^{3+}, Nd^{3+}, and Pr^{3+}), it can be selectively precipitated by adjusting the pH. Hence, 10 M aqueous NaOH solution was added to the leachate to adjust the pH, and the powder was selectively recovered in the form of $Ce(OH)_4$. The precipitated powder ($Ce(OH)_4$) was recovered via solid-liquid separation and dried at 80°C for 24 h.

The crystalline phase of the recovered powder was analyzed using X-ray diffraction (XRD), and the shape of the powder particles was confirmed using field emission scattering electron microscopy (FE-SEM). The recovery rate and grade of the recovered $Ce(OH)_4$ according to the type of solvent used were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES).

3. Results and discussion

We substituted the $NaREE(SO_4)_2{\cdot}H_2O$ powder with an rare earth hydroxide ($REE(OH)_3$) powder through a metathesis reaction using a sodium hydroxide solution. The metathesis reaction is given by Eq. (1). For the Ce^{4+} state, which is obtained after the oxidation of Ce^{3+} of $REE(OH)_3$, the basicity is weaker than that of other REEs (La^{3+}, Nd^{3+}, and Pr^{3+}); therefore, it is possible to separate the REEs by adjusting the pH [14]. Therefore, after the metathesis reaction, the slurry was oxidized.

$$NaREE\left(SO_4\right)_2 \cdot H_2O + 3NaOH$$
$$\rightarrow REE\left(OH\right)_3 \downarrow + 2Na_2SO_4 \qquad (1)$$

Fig. 1 shows FE-SEM images of the rare earth composite powder and $REE(OH)_3$ before and after the metathesis and oxidation reactions. As the $NaREE(SO_4)_2{\cdot}H_2O$ powder was converted to the corresponding $REE(OH)_3$ powder, a color change from white to pale yellow was observed. The particles in the $REE(OH)_3$ powder before the oxidation reaction exhibits a pointed polygonal pyramid shape, and after the oxidation, the particles possess a blunt point, and fine particles exist together.

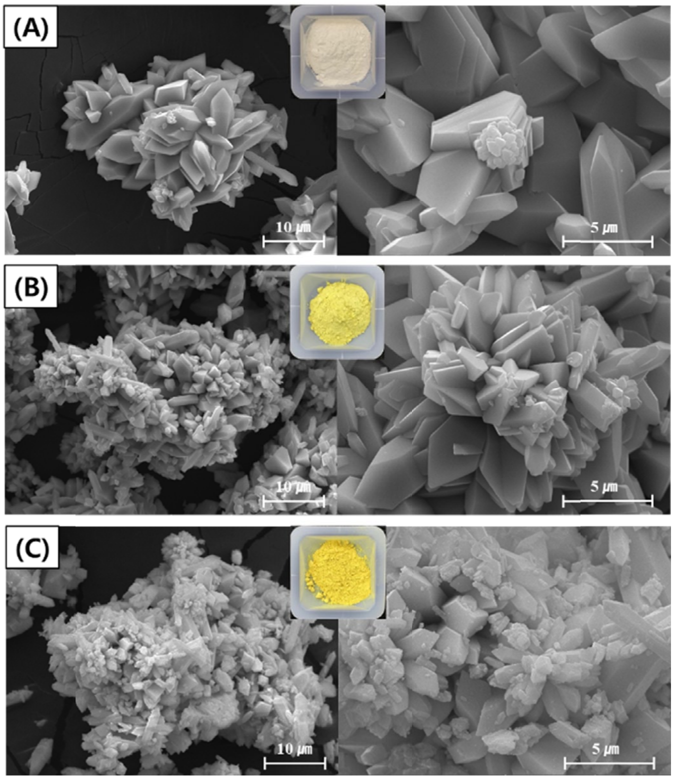

Fig. 1. FE-SEM images and digital photographs of the rare earth composite precipitation powders and hydroxide rare earth powder before and after oxidation process. (A: $NaREE(SO_4)_2{\cdot}H_2O$, B: $REE(OH)_3$ before oxidation, C: $REE(OH)_3$ after oxidation)

The oxidized powder was leached into sulfuric acid and hydrochloric acid, each at a solid-liquid ratio of 25 g/L. The leachate was analyzed according to the pH using ICP-OES for each acid type, and the leaching rate for each element is shown in Fig. 2.

Experimental results differed depending on the type of the leaching solvent used. Using sulfuric acid, the leaching rates of La, Pr, and Nd were higher than 80% at pH 2.5, whereas approximately 0.1% of Ce was leached. Therefore, the optimal condition for separating $Ce(OH)_4$ from other rare earth hydroxides (La, Nd, $Pr(OH)_3$) using sulfuric acid was pH 2.5. In addition, at pH 1, more than 90% of all REEs, including Ce, were leached.

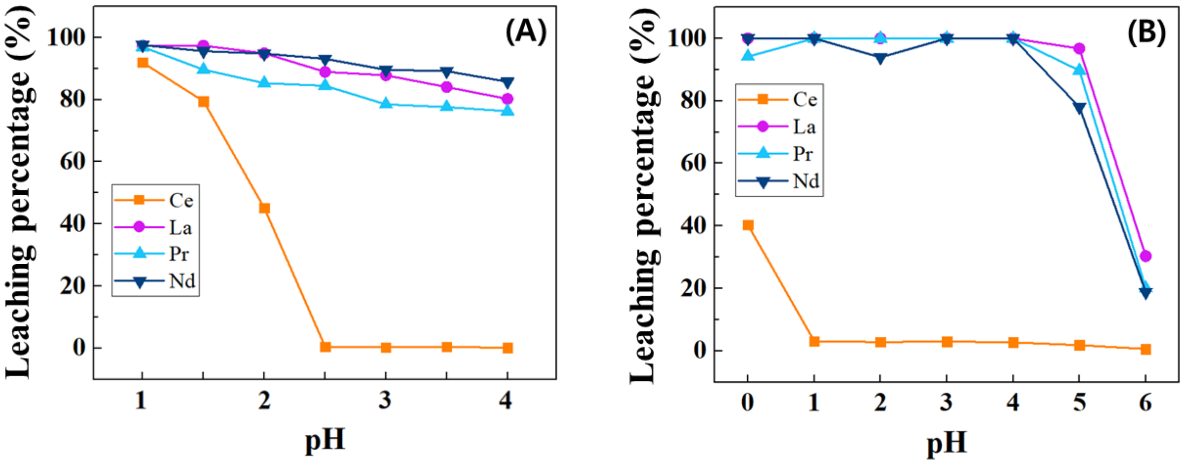

Fig. 2. Rare earth element leaching rate according to pH of rare earth hydroxide powder after oxidation process. (A: Sulfuric acid solvent, B: Hydrochloric acid solvent)

In contrast, hydrochloric acid leached 3.1% of Ce at pH 1. Under the conditions of pH 2, 3, and 4, less than approximately 3% of Ce was leached, and other REEs (La, Nd, and Pr) showed a leaching rate of more than 90%. At pH 6, the leaching rate decreased sharply for all the elements. Using hydrochloric acid is a more efficient strategy than using sulfuric acid because hydrochloric acid separates Ce at a relatively lower pH and consumes less amounts of NaOH. Based on this result, the recovered powder after oxidation (La, Nd, Pr$(OH)_3$, Ce$(OH)_4$) was leached in sulfuric acid and hydrochloric acid, and Ce$(OH)_4$ was selectively recovered by adjusting the pH to 2.5 and 1, respectively, to separate cerium from other REEs.

Fig. 3 shows the crystal phase and the SEM image of the recovered Ce$(OH)_4$ powder. The results of this study also confirmed the presence of a cubic fluorite crystal phase, consistent with the XRD pattern of Ce$(OH)_4$ reported by Ansari et al. [15]. In the XRD pattern of the Ce$(OH)_4$ powder, the powder recovered using hydrochloric acid demonstrates relatively less noise signals and a sharper peak than that recovered using sulfuric acid. The Ce$(OH)_4$ powder recovered by hydrochloric acid comprises particles of ~5 μm in size with a distinct polygonal pyramidal particle shape. However, the powder recovered by sulfuric acid agglomerated into large and small particles. This resulted in the relatively low noise of the XRD pattern of the powder obtained using the hydrochloric acid solvent. The powder recovered after sulfuric acid and hydrochloric acid leaching was dark yellow and pale greenish-yellow in color, respectively.

After recovering Ce$(OH)_4$, ICP-OES analysis was performed on the liquid and solid phases, and Fig. 4 shows the recovery and grade of Ce with respect to the contents of

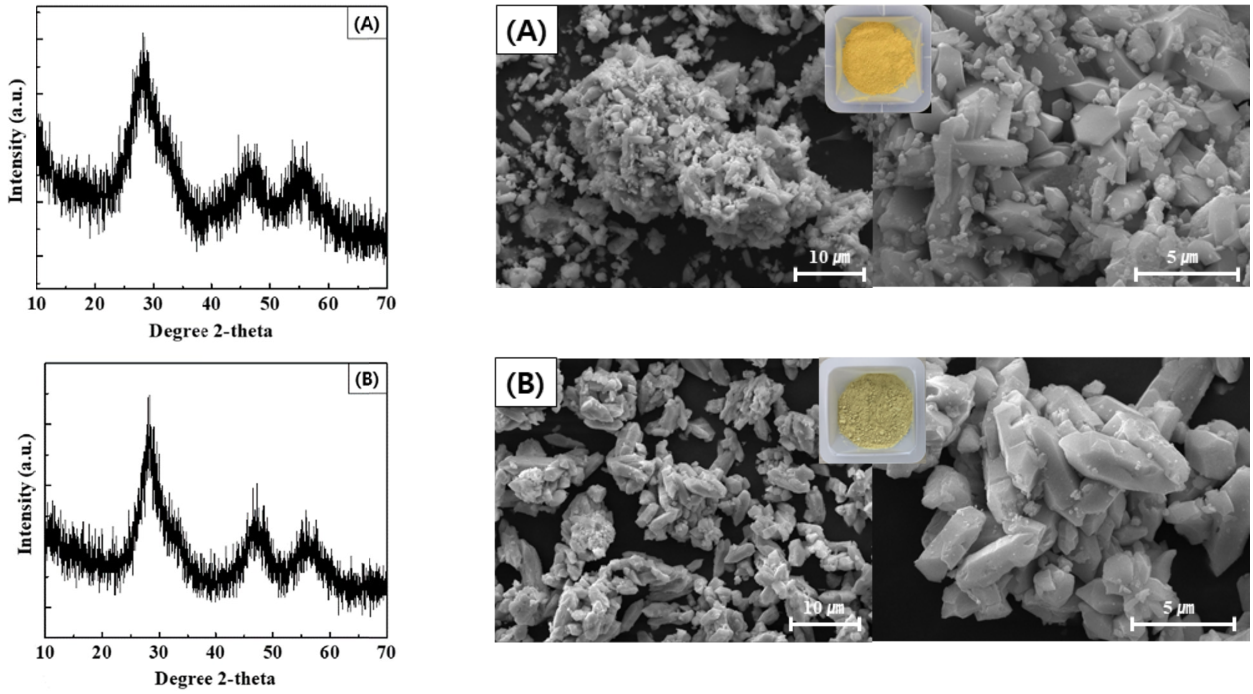

Fig. 3. XRD patterns and FE-SEM images of Ce$(OH)_4$. (A: Sulfuric acid solvent, B: Hydrochloric acid solvent)

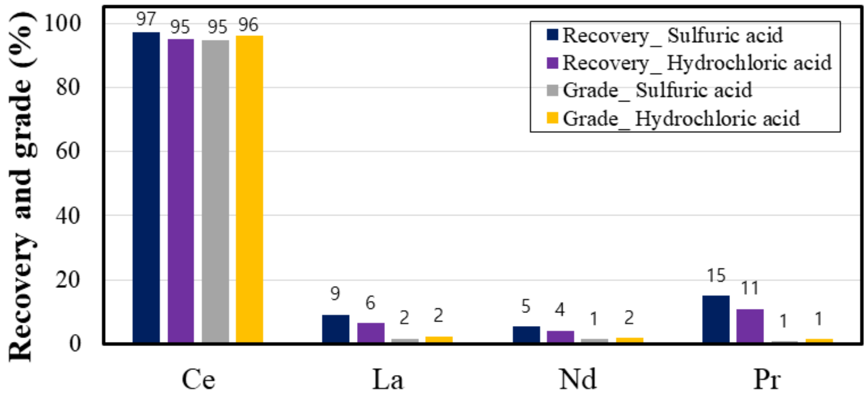

Fig. 4. Recovery rate and grade of rare earth elements by solvents

the $NaREE(SO_4)_2 \cdot H_2O$ powders. The recovery is the percentage of the amount of Ce contained in the powder finally recovered in the form of $Ce(OH)_4$ compared to the $NaREE(SO_4)_2 \cdot H_2O$ powders. The grade is the proportion of Ce, which is the main component, in Ce(OH)4 powder. The recovery rate and grade of Ce obtained using sulfuric acid as the solvent were 97% and 95%, respectively, while those obtained using hydrochloric acid were 95% and 96%, respectively. Therefore, extraction of Ce using both solvents demonstrated similar results.

4. Conclusions

A study was conducted to selectively separate cerium from $NaREE(SO_4)_2 \cdot H_2O$ powders recovered from a spent NiMH battery. The important highlights of this study are as follows:

1) After the metathesis and oxidation reactions, the recovered powder (La, Nd, $Pr(OH)_3$+$Ce(OH)_4$) was leached in sulfuric acid and hydrochloric acid, and the selective precipitation of $Ce(OH)_4$ according to the solvent used was compared.
2) The shape of $Ce(OH)_4$ particles recovered using hydrochloric acid was a polygonal pyramid, whereas the powder recovered using sulfuric acid contained small particles of various shapes, which were agglomerated.
3) After leaching, $CeOH_4$ was selectively precipitated at a pH of 2.5 in sulfuric acid, whereas it precipitated at a pH of 1 in hydrochloric acid. The recovery and grade of Ce showed a similar trend for both solvents. Considering the amount of aqueous NaOH solution used for the pH adjustments, the recovery of Ce using hydrochloric acid was economical.

Acknowledgments

This work was supported by a Research Grant of Pukyong National University (2021year)

REFERENCES

[1] https://search.usa.gov/
[2] K.M. Goodenough, F. Wall, D. Merriman, Nat. Resour. Res. **27**, 201 (2018).
[3] N.A. Mancheri, B. Sprecher, G. Bailey, J. Ge, A. Tukker, Res. Conserv. Recycl. **142**, 101 (2019).
[4] N. Swain, S. Mishra, Journal of Cleaner Production **220**, 884 (2019).
[5] V. Innocenzi, F. Veglio, J. Power Sources **211**, 184 (2012).
[6] L. Pietrelli, B. Bellomo, D. Fontana, M. Montereali, Waste Manag. **25**, 221 (2005).
[7] X.I.A. Yun, X. Liansheng, T.I.A.N. Jiying, L. Zhaoyang, Z. Li, Journal of Rare Earths **33**, 1348 (2015).
[8] F. Liu, C. Peng, A. Porvali, Z. Wang, B.P. Wilson, M. Lundström, ACS Sustain Chem. Eng. **7**, 16103 (2019).
[9] A. Fernandes, J.C. Afonso, A.J.B. Dutra, Hydrometallurgy **133**, 37 (2013).
[10] X. Yang, J. Zhang, X. Fang, J. Hazard Mater. **279**, 384 (2014).
[11] B. Kim, N.K. Ahn, S.W. Lee, D.W. Kim, JKIRR. **26**, 18 (2019).
[12] H. Wei, Y. Li, Z. Zhang, W. Liao, Hydrometallurgy **191**, 105240 (2020).
[13] Z. Zhao, Z. Qiu, J. Yang, S. Lu, L. Cao, W. Zhang, Y. Xu, Hydrometallurgy **167**, 183 (2017).
[14] H.S. Yoon, C.J. Kim, H.C. Eom, J.S. Kim, Resources Recycling **14**, 3, (2005).
[15] A.A. Ansari, A. Kaushik, Journal of Semiconductors **31**, 033001, (2010).