

The Effect of HNO_3 Concentration Variations on the Recovery of REEs from Coal Fly Ash Through Hydrometallurgical Processes

Tri Wahyuningsih, Yasmina Amalia*, Mahendra Ivan Fahrezi, Farhan Putra,

Zikra Fitri Kasih, Ahmad Alfarizi, Rinaldi Zainun Syah

Universitas Pembangunan Nasional Veteran Yogyakarta, Indonesia

Received : Sept 16, 2025

Revised : Sept 17, 2025

Accepted : Sept 17, 2025

Online : October 14, 2025

Abstract

In this study, coal fly ash was used as the primary material for analysis and extraction of REEs contained therein. Coal fly ash is a waste product from coal combustion, commonly used in the power generation sector, which is typically disposed of without further processing. Therefore, this study was conducted to utilize this waste, which contains a significant amount of REEs, for use in the metallurgy industry as strategic additives in material engineering. The rare earth metal recovery process involved leaching with strong acid HNO_3 at concentrations of 0.6 M, 0.8 M, and 1 M. Analysis using the ICP-OES method on the three variations yielded very low dissolution of REEs. Characterization with XRD of the leaching results showed that the leaching process effectively mobilized and reformed REEs into various new crystalline phases.

Keywords: Fly Ash, REEs, HNO_3

INTRODUCTION

Rare Earth Elements (commonly referred to as REEs) consist of 17 elements: the 15 elements in the lanthanide series, in addition to Scandium and Yttrium. These elements include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc. In nature, REEs are found as complex phosphate and carbonate compounds, typically occurring as accessory minerals associated with primary minerals such as copper, gold, silver, tin, and others.

Over the past decade, rare earth elements (REEs) have garnered significant attention in the international market due to their widespread use in various industries and technologies. Although the demand for rare earth elements (REEs) has experienced a significant surge, commercial or large-scale production is still limited to a few countries. Rare earth elements (REEs) are considered as one of the most important and strategic elements due to the high risk of supply and growing demand around the world, especially in the defense, energy, electronics, and automotive sectors. Examples of its applications include a decisive material for hybrid vehicles, medical diagnostic devices (such as MRI, X-rays, scanners, and contrast agents), LCDs, computer hard drives, wind power generation facilities, green technologies, high-precision equipment, night vision devices, radar systems, and military hardware (Abaka-Wood et al., 2019; Blissett et al., 2014; Liu et al., 2019).

Rare earth elements (REEs), including the lanthanide elements and yttrium, are widely used in a broad range of high-tech applications. Due to increasing demand and vulnerability to supply disruptions, REEs have been designated as critical minerals by the United States. Their applications include permanent magnets, phosphors, catalysts, and rechargeable batteries. Consequently, there is growing interest in exploring alternative REE resources, including recovery from industrial wastes such as coal fly ash (CFA).

Copyright Holder:

© Tri, Yasmina, Mahendra, Farhan, Zikra, Ahmad, & Rinaldi. (2025)

Corresponding author's email: yasminaamalia@upnyk.ac.id

This Article is Licensed Under:



The following data presents the total REE production in various countries and their estimated reserves (Abaka-Wood, 2022). China dominates most of the REE resources as well as production, accounting for about 58-60% of the total global production during 2019-2020. Meanwhile, the United States and Australia produced about 15-18% and 7-15% of rare earth oxides (REOs) worldwide, respectively. The information also indicates that China has 41 Mt, which is equivalent to about 37% of the economically proven REE resources, followed by Brazil and Vietnam, each with 21 Mt (18%), Australia (4.1 Mt, about 3%), and the United States (1.5 Mt, 1.2%).

In the search for alternative REE sources, attention has shifted toward industrial waste, one of which is fly ash—a solid residue produced from coal combustion in coal-fired power plants (PLTU). Previously classified as hazardous waste (B3), fly ash has been found to contain several REE elements, such as cerium (Ce), neodymium (Nd), and lanthanum (La), in concentrations that are considered promising for extraction. Several studies have reported that fly ash can contain up to 80 ppm of REEs (Suganal et al., 2018).

Coal ash residue from mine-mouth power plants is produced in large volumes but has not been optimally utilized. This ash originates from the combustion of coal, which is used as boiler fuel to generate steam that subsequently drives turbines for electricity production. The solid waste produced from this process consists of 25% bottom ash and 75% fly ash. The combustion residue that is carried along with the flue gas is referred to as fly ash, while the residue that settles and is discharged from the bottom of the furnace is known as bottom ash. The process of coal ash formation, including both fly ash and bottom ash in an industrial setting, is illustrated in the schematic provided in Figure 1.

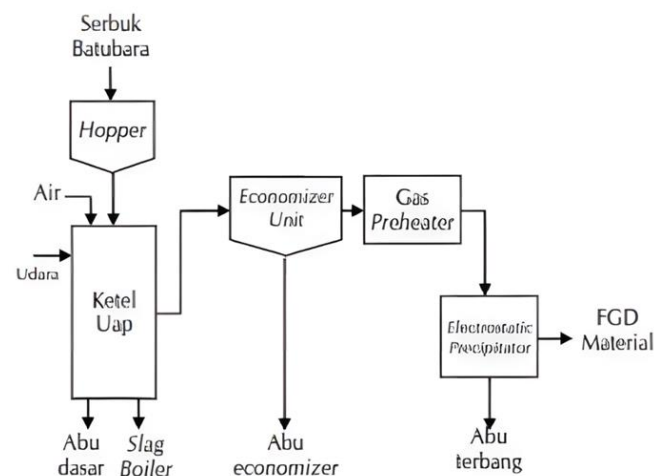


Figure 1. Schematic of Coal Ash Formation in a Coal-Fired Power Plant (PLTU)

The extraction of REEs from fly ash requires a precise approach to ensure the process is both efficient and economically viable. One of the most promising methods is hydrometallurgy, particularly the leaching process using acidic solutions. Among the various leaching agents, nitric acid (HNO_3) is widely utilized due to its high ability to dissolve REEs. However, the effectiveness of the leaching process is highly influenced by the acid's molarity (Purbasari et al., 2023; Sahidi et al., 2020). Therefore, it is essential to investigate the effect of varying HNO_3 concentrations on the optimal extraction of REEs from coal fly ash (Sahidi et al., 2020).

The processing of rare earth elements (REEs) from fly ash requires an appropriate approach to ensure that the process is both efficient and economical. One of the most promising methods is hydrometallurgy, particularly the leaching process using acidic solvents. Among various types of

solvents, nitric acid (HNO_3) is widely used due to its high ability to dissolve rare earth elements. However, the effectiveness of the leaching process is strongly influenced by the concentration of the solution used. Therefore, it is important to investigate the effect of varying HNO_3 molarity on the optimal extraction of REEs from coal fly ash.

In the national context, the utilization of fly ash as a source of REEs holds strategic value. As one of the world's largest coal producers, Indonesia generates millions of tons of fly ash annually, most of which remains underutilized. This approach not only supports the principles of circular economy and the reduction of hazardous waste but also opens new opportunities for supplying high-tech industries with valuable raw materials. Accordingly, this study aims to isolate lanthanum from coal combustion waste in the form of fly ash. The separation process is carried out using a hydrometallurgical method with nitric acid (HNO_3) as the leaching agent, employing various molarities as experimental parameters. This method is chosen for its effectiveness in enhancing the purity level of the recovered REEs. The final product of this process is expected to be REEs oxide, which has economic value and potential applications in various industrial sectors.

LITERATURE REVIEW

RESEARCH METHOD

Materials and Methods

The samples used in this study were coal ash residues from the Pelabuhan Ratu coal-fired power plant in Sukabumi, West Java. In this study, only fly ash (FA) was used as a sample. The equipment used in this study included a magnetic stirrer, beaker, digital scale, Erlenmeyer flask, funnel, measuring cup, stirrer, and the tests conducted included Inductively Coupled Plasma (ICP) analysis, and X-ray diffraction (XRD) analysis. The materials used in this study were fly ash, HNO_3 , oxalic acid, ammonia, filter paper, and distilled water.

Fly ash has great potential as a secondary material in various industrial applications, including geopolymers, adsorbents, and as a source of rare earth elements (REEs). To optimize the measurement process for fine particles (200 mesh; $75\ \mu\text{m}$), sample preparation using the cone and quartering method was performed for homogenization, followed by sieving to standardize the size distribution. Before further investigation, the initial characteristics of the fly ash must be determined. Initial analysis is required to obtain baseline data that can be used as a reference after the extraction process is completed. In this case, two main characterization methods were initially used: ICP-MS testing with the ICAP-RQ instrument and the ASX-560 autosampler. The ICP analysis results also serve as a reference for comparing changes in chemical composition after extraction treatment, enabling the effectiveness of the target element separation process to be evaluated quantitatively. The second method used X-Ray Diffraction (XRD) with the MELVERN PANALYTICAL EMPYREAN SERIES 3 instrument. Testing of coal fly ash samples using X-Ray Diffraction (XRD) was conducted to identify the crystalline phases contained within it and to determine the primary mineralogical structure of the material. The XRD was performed using a PHILIPS X'Pert MPD diffractometer with a Theta/Theta goniometer configuration. The following are the results of ICP analysis followed by XRD analysis for coal fly ash. These can be seen in Table 1 and Figure 2.

Tabel 1 ICP Test Results on Coal Fly Ash Samples

Element REEs	Average Concentration (ppb)
La (Lanthanum)	-1,143
Ce (Cerium)	-4,108

Pr (Praseodymium)	-0,308
Nd (Neodymium)	-0,666
Sm (Samarium)	-0,276
Eu (Europium)	-0,266
Gd (Gadolinium)	-0,569
Tb (Terbium)	-0,162
Dy (Dysprosium)	-0,290
Ho (Holmium)	-0,161
Er (Erbium)	-0,243
Tm (Tulium)	-0,159
Yb (Ytterbium)	-0,354
Lu (Lutetium)	-0,160
Sc (Scandium)	-24,397
Y (Itrium)	-0,632

Based on the test results using the Inductively Coupled Plasma (ICP) instrument as shown in Table.1, the presence of various rare earth elements (REE) was identified in the coal fly ash samples, although most were recorded at relatively low concentrations in parts per billion (ppb). Some elements such as Lanthanum (La), Cerium (Ce), and Scandium (Sc) showed negative concentrations, which may indicate values below the instrument's detection limit or matrix interference during the measurement process. Nevertheless, the detection of elements such as Neodymium (Nd), Praseodymium (Pr), Samarium (Sm), and Europium (Eu) still indicates that coal fly ash contains strategically valuable REE components. The presence of these REEs reinforces the potential of fly ash as a secondary source of rare earth metals, especially given the increasing global demand for REEs in various high-tech sectors such as electronics, renewable energy, and defense. However, the low concentrations and variations among the elements also indicate the need for optimization of extraction and purification techniques to enhance the efficiency of separating REEs from the ash. These values will be considered after the extraction process is completed.

The X-ray source used a copper (Cu) anode with a wavelength of $K\alpha = 1.5406 \text{ \AA}$. Data was acquired in the 2θ angle range between 5° and 90° . The following are the results of ICP analysis followed by XRD analysis for coal fly ash.

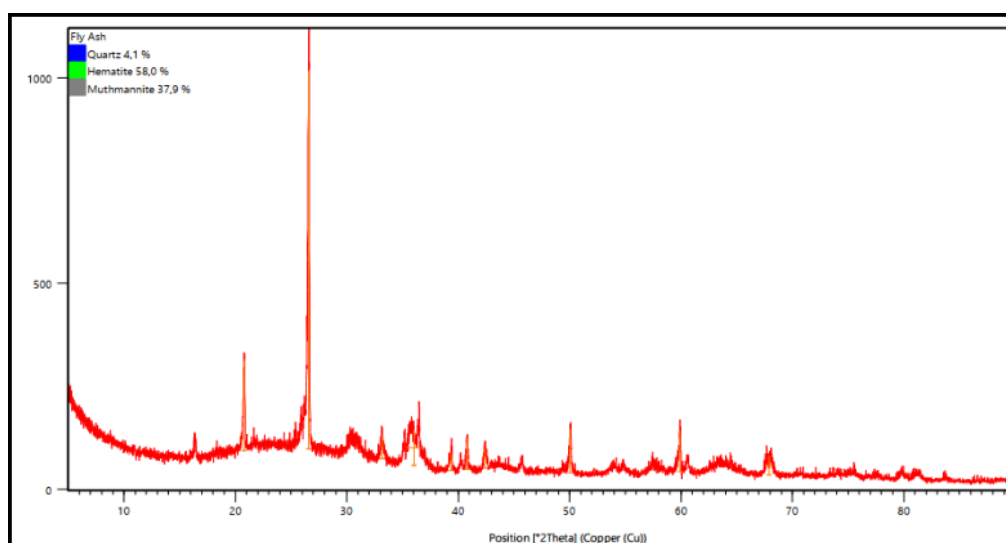


Figure 2. XRD Fly Ash Analysis Results.

Based on pattern matching results against the PDF (Powder Diffraction File) database, three main crystalline phases were identified in the fly ash sample, as shown in Table 2 below.

Tabel 2. XRD Test Results on Coal Fly Ash Samples

Crystalline Phase	Chemical Formula	Percentage
Quartz	SiO_2	4.1%
Hematite	Fe_2O_3	58.0%
Muthmannite	AgAuTe_2	37.9%

Quartz (SiO_2) was identified as a minor phase but had the highest match score in the XRD analysis, marked by a peak of maximum intensity at an angle of $2\theta = 26.56^\circ$, which is the characteristic position of the quartz crystalline structure. Meanwhile, hematite (Fe_2O_3), despite showing a low match score (19), appears as the dominant phase in a semi-quantitative analysis, likely due to its high intensity in the 33° – 35° angle range, which may also overlap with other crystalline phases.

FINDINGS AND DISCUSSION

The results of the XRD analysis on the samples, which were treated with varying HNO_3 concentrations of 0.6 M, 0.8 M, and 1 M, are shown in Figures 3, 4, and 5.

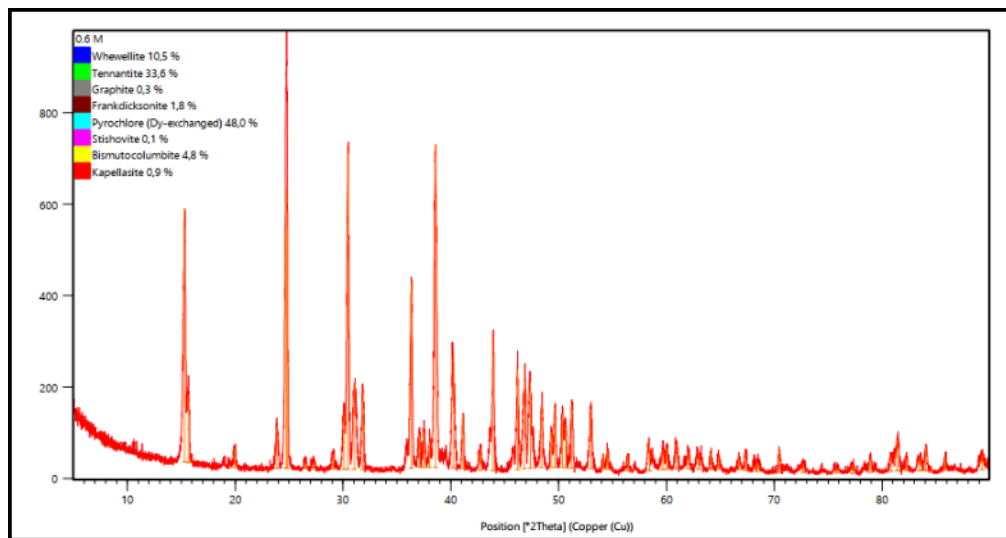


Figure 3. XRD Analysis Results for the 0.6 M HNO_3 Concentration

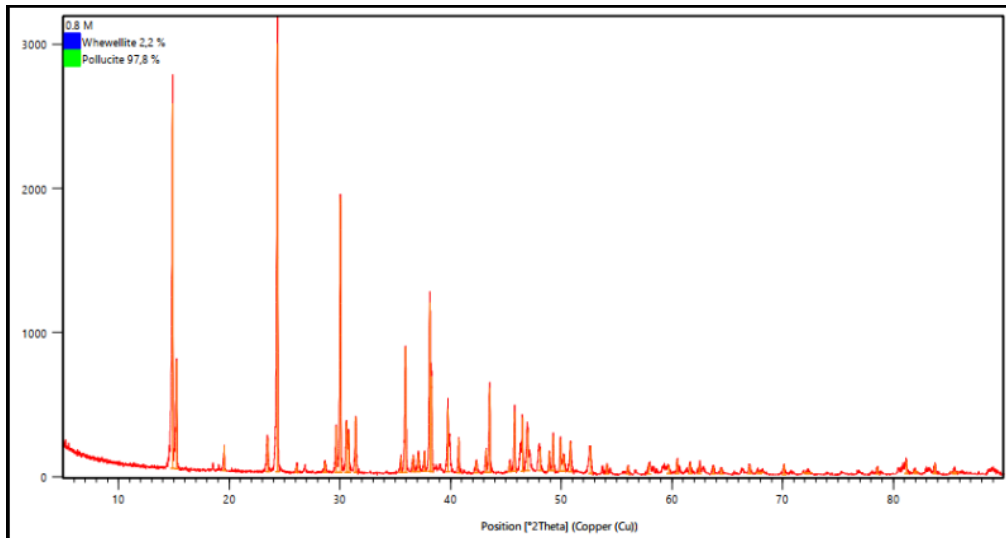


Figure 4. XRD Analysis Results for the 0.8 M HNO₃ Concentration

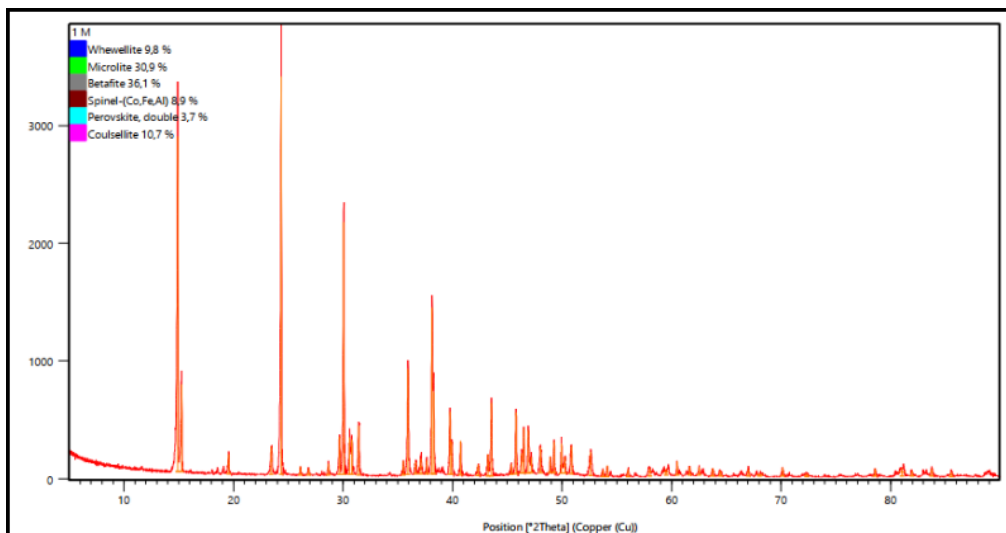


Figure 5. XRD Analysis Results for the 1 M HNO₃ Concentration

Based on the results of the XRD characterization, variations in HNO₃ concentration had a significant effect on the mineral transformation of post-leaching fly ash, both in terms of the types of crystalline phases formed and the indication of Rare Earth Elements (REEs) presence.

During leaching with 0.6 M HNO₃, most of the initial minerals, such as hematite and quartz, showed a decrease in peak intensity or even disappeared. They were replaced by the formation of a new Pyrochlore (Dy-exchanged) phase, with a dominant content of approximately 48%. The presence of this phase indicates that Dy³⁺ was successfully mobilized from the fly ash matrix and bound within a complex oxide structure. Additionally, Bismutocolumbite (BiNbTaO₄) was detected, which, despite not being a primary REE carrier, has a crystal structure capable of accommodating other REE ions like Ce or Nd. This finding indicates that at low to medium concentrations, leaching can directly facilitate the formation of crystalline REE compounds.

At a 0.8 M HNO₃ concentration, the XRD pattern showed a more selective mineral transformation, where almost all initial phases changed into Pollucite (CsNaAlSi₆O₁₂) with a dominance of ~97.8%, as well as Whewellite (CaC₂O₄·H₂O) as a minor phase. The large porous structure of Pollucite has a high potential to adsorb REE ions through isomorphic substitution or ion-exchange mechanisms, even though no pure crystalline REE phase was detected. This condition indicates that at this concentration, REEs tend to be trapped within secondary mineral structures

or amorphous parts, rather than forming pure REE minerals that are detectable by XRD.

In leaching with 1 M HNO_3 , the dissolution process was more aggressive, breaking down almost all of the initial mineral structures and forming complex oxide phases that directly contain REEs. The dominant phases detected were Betafite (36.1%) containing Ce, Microlite (30.9%) which has the potential to accommodate La^{3+} or Nd^{3+} , and Double Perovskite ($\text{Ba}_2\text{GdNbO}_6$) at 3.7%, which clearly contains Gd as a Heavy Rare Earth Element (HREE). The presence of these minerals indicates that at high concentrations, HNO_3 is not only effective at dissolving REE-bearing minerals but also promotes the reformation of stable crystalline REE compounds.

Overall, the observed trend indicates that an increase in HNO_3 concentration enhances the degree of initial mineral dissolution and affects the REE fixation mechanism. This proves that the HNO_3 concentration is a key parameter determining whether REEs will appear as a pure crystalline phase, be trapped in secondary minerals, or be refixed within stable complex oxide structures.

In addition to using XRD for analysis, an ICP was also utilized to identify the elements that dissolved from the various HNO_3 concentrations. The resulting ICP data is as follows:

Table 3. ICP Test Results for Fly Ash at 0.6 M Concentration

Elements REEs	Average Concentration (ppb)
La (Lanthanum)	-0,576
Ce (Cerium)	-2,189
Pr (Praseodymium)	0,075
Nd (Neodymium)	-0,003
Sm (Samarium)	0,199
Eu (Europium)	0,059
Gd (Gadolinium)	-0,231
Tb (Terbium)	0,080
Dy (Dysprosium)	0,014
Ho (Holmium)	0,083
Er (Erbium)	0,119
Tm (Tulium)	0,153
Yb (Ytterbium)	-0,005
Lu (Lutetium)	0,053
Sc (Skandium)	-23,496
Y (Itrium)	-0,357

An ICP-OES test on fly ash with a 0.6M HNO_3 concentration revealed that most rare-earth elements (REEs) were present at extremely low concentration levels. Several elements, such as Ce (-2.189 ppb), La (-0.576ppb), and Sc (-23.496ppb), were even recorded as negative, indicating that their content was below the instrument's detection limit. Only a small fraction of the elements, including Sm (0.199ppb), Er (0.119ppb), Tm (0.153ppb), Pr (0.075ppb), and Tb (0.080ppb), were detected with positive but still very low values. This result suggests that at a moderate acid concentration, the dissolution of REEs from fly ash is limited, likely only dissolving elements located on the surface or those weakly bound within the mineral matrix.

Table 4. ICP Test Results for Fly Ash at 0.8 M Concentration

Elements REEs	Average Concentration (ppb)
La (Lanthanum)	-0,546
Ce (Cerium)	-2,388
Pr (Praseodymium)	0,028
Nd (Neodymium)	-0,204
Sm (Samarium)	0,072
Eu (Europium)	0,081
Gd (Gadolinium)	-0,084
Tb (Terbium)	0,198
Dy (Dysprosium)	0,047
Ho (Holmium)	0,188
Er (Erbium)	0,148
Tm (Thulium)	0,214
Yb (Ytterbium)	-0,068
Lu (Lutetium)	0,117
Sc (Scandium)	-24,034
Y (Itrium)	-0,240

At an HNO_3 concentration of 0.8 M, several elements experienced a slight increase; for instance, Er rose to 0.148 ppb and Lu to 0.117 ppb, while Sm decreased to 0.072 ppb compared to the 0.6 M concentration. Elements that previously exhibited negative values, such as Ce (-2.388 ppb) and Sc (-24.034 ppb), remained difficult to detect. This indicates that increasing the acid concentration does not consistently have a positive effect on all elements. Overall, the change from 0.6 M to 0.8 M only resulted in a marginal increase for some elements, whereas others tended to remain stagnant or decrease.

Table 5. ICP Test Results for Fly Ash at 1 M Concentration

Elements REEs	Average Concentration (ppb)
La (Lanthanum)	-0,724
Ce (Cerium)	-3,098
Pr (Praseodymium)	-0,031
Nd (Neodymium)	-0,262
Sm (Samarium)	0,041
Eu (Europium)	0,007
Gd (Gadolinium)	-0,289
Tb (Terbium)	0,037
Dy (Dysprosium)	-0,083
Ho (Holmium)	0,083

Er (Erbium)	0,027
Tm (Tulium)	0,046
Yb (Ytterbium)	0,022
Lu (Lutetium)	0,040
Sc (Skandium)	-23,672
Y (Itrium)	-0,181

The use of 1 M HNO₃ also did not yield significant improvement. In fact, some elements that were previously positive experienced a decrease, such as Sm falling to 0.041 ppb and Er to 0.027 ppb. The value for Ce declined even further to -3.098 ppb, and Sc remained in the negative range (-23.672 ppb), indicating that these elements are still difficult to extract despite the stronger acidic conditions. This phenomenon suggests that mineralogical factors and the stability of Rare Earth Element (REE) compounds in fly ash play a dominant role in their low solubility, rather than being solely influenced by the HNO₃ concentration.

Overall, the results from all three variations demonstrate that increasing the HNO₃ concentration from 0.6 M to 1 M was not able to significantly enhance the dissolution of REEs from fly ash. This limitation is attributed to the presence of highly stable mineral phases, such as monazite, zircon, and aluminosilicates, which require more aggressive leaching conditions to decompose. Referring to previous research findings, an increase in REE extraction efficiency can be achieved through the use of concentrated acids, high temperatures and pressures, or the addition of complexing agents like EDTA and DTPA. Therefore, the leaching method using dilute HNO₃ only provides limited results and requires further optimization to maximize the potential for REE extraction from fly ash.

CONCLUSIONS

The results of the post-leaching XRD analysis with varying concentrations of HNO₃ showed significant changes in the mineral phases, indicating the mobilization and recrystallization of REEs into new structures. At a concentration of 0.6 M, a Pyrochlore phase (Dy_{1.5}Na_{0.5}SbTiO₇) was formed, indicating the specific release of the element Dy. A concentration of 0.8 M resulted in the dominance of a Pollucite phase (97.8%) with a zeolitic structure that has the potential to adsorb REEs, although this adsorption property may limit their re-release into the solution. At the highest concentration of 1 M, complex phases such as Betafite (Ce-bearing), Microlite, and Double Perovskite (Gd-bearing) emerged. This indicates that concentrated acid leaching not only dissolves REEs but also facilitates the formation of new, more stable phases. Thus, varying the HNO₃ concentration is proven to influence the REE recrystallization pathway, with the 1 M condition showing the most effective tendency to produce more thermodynamically stable REE-bearing phases.

REFERENCES

- Abaka-Wood, G. B., Zanin, M., Addai-Mensah, J., & Skinner, W. (2019). Recovery of Rare Earth Elements Minerals from Iron Oxide–Silicate Rich Tailings – Part 1: Magnetic Separation. *Minerals Engineering*, 136, 50–61. <https://doi.org/10.1016/j.mineng.2019.02.026>
- Abaka-Wood, G. B., Addai-Mensah, J., & Skinner, W. (2022). The Concentration of Rare Earth Elements from Coal Fly Ash. *Journal of the Southern African Institute of Mining and Metallurgy*, 122(1), 21–28. <https://doi.org/10.17159/2411-9717/1654/2022>
- Blissett, R. S., Smalley, N., & Rowson, N. A. (2014). An Investigation Into Six Coal Fly Ashes from the

- United Kingdom and Poland to Evaluate Rare Earth Element Content. *Fuel*, 119, 236–239. <https://doi.org/10.1016/j.fuel.2013.11.053>
- Liu, P., Huang, R., & Tang, Y. (2019). Comprehensive Understandings of Rare Earth Element (REE) Speciation in Coal Fly Ashes and Implication for REE Extractability. *Environmental Science & Technology*, 53(9), 5369–5377. <https://doi.org/10.1021/acs.est.9b00005>
- Purbasari, D., Pebrianto, R., & Harsiga, E. (2023). Potensi logam tanah jarang di dalam abu batubara. *MINERAL*, 8(2), 1–7. <https://doi.org/10.30591/mineral.v8i2.4364>
- Sahidi, A. A., Senen, A. M., & Madjid, S. B. M. (2020). Pemanfaatan Limbah Abu Batubara Sebagai Sumber Logam Tanah Jarang. *Jurnal GEOMining*, 1(2), 72–78.
- Suganal, Umar, D. F., & Mamby, H. E. (2018). Identifikasi Keterdapatan Unsur Logam Tanah Jarang dalam Abu Batubara Pusat Listrik Tenaga Uap Ombilin, Sumatera Barat. *Jurnal Teknologi Mineral dan Batubara*, 14(2), 111–125. <https://doi.org/10.30556/jtmb.Vol14.No2.2018.395>