Indones. J. Chem., 2025, 25 (4), 1028 - 1037

Preliminary Study on Leaching Capacity of Rare Earth Elements from Coal Fly Ash by Using Citric Acid Solution

Gilbert Winoto[1], Panut Mulyono[1], Suyanti Suyanti[2], and Agus Prasetya[1*]

[1]*Sustainable Mineral Processing Research Group, Department of Chemical Engineering, Faculty of Engineering,*
Universitas Gadjah Mada, Jl. Grafika No. 2, Yogyakarta 55281, Indonesia

[2]*Research Center of Mining Technology, National Research and Innovation Agency (BRIN),*
Jl. Ir. Sutami Km. 15, Tanjung Bintang, Lampung Selatan 35361, Indonesia

** **Corresponding author:***

email: aguspras@ugm.ac.id

Received: September 9, 2024
Accepted: March 25, 2025

DOI: 10.22146/ijc.99763

Abstract: *Rare earth elements (REEs) are chemical elements in the III B and lanthanide groups on the chemical periodic table. Extracting REEs from secondary resources (such as coal fly ash) could be environmentally friendlier than extracting REEs from primary resources. Coal fly ash was chosen because of its attractive REE availability and to minimize the pollution problem created by coal fly ash dumping. Citric acid is used as the leaching agent because of its biodegradability, relatively safe vis-à-vis mineral acid commonly used in the REE leaching, and its non-damaging nature to coal fly ash's properties as construction material. The leaching experiment was conducted at temperature variations of 30, 50, and 85 °C, with liquid-solid ratio (L/S) of 5, 10, and 15 mL/g in 50 mL of 0.01 mol/L citric acid solution. The leaching experiments were conducted in a water bath shaker. It was found that increasing L/S and temperature mainly contributed to increasing cerium leaching capacity.*

Keywords: *rare earth elements; citric acid; coal fly ash; leaching; leaching capacity*

■ INTRODUCTION

Rare earth elements (REEs), consist of lanthanide elements — lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, plus scandium and yttrium [1]. End-use demand for REEs in 2020 can be seen in Table 1, showing that REEs were mainly used as magnets, followed by catalysts and polishing agents in 2020. Moreover, the 'magnets' category shown in Table 1 could be further differentiated into several end uses in Table 2. Tables 1 and 2 show that REEs are used in various applications, from their application as components in consumer electronics to their use as catalysts in the manufacturing sector. REEs also play an influential role in transition efforts toward renewable energy, such as the application of praseodymium, neodymium, terbium, and dysprosium as permanent magnets to be used in electric vehicles and wind turbines [2-3]. About 91% of the global REE market value is related to clean energy technology [3].

Table 1. Share of demand for REEs' by end-use in 2020 from Gielen and Lyons [2]

End-use	Share of end-use demand (%)
Magnets	29.0
Catalysts	20.0
Polishing agents	13.0
Others	9.0
Metallurgy	9.0
Batteries	8.0
Glass	8.0
Ceramics	3.0
Phosphors	1.0
Pigments	0.4

REEs are not rare as they are more abundant in the earth's crust than other common metals such as silver, mercury, zinc, and copper [3-4]. Regardless of their relative abundance to more common metals, the distribution of REEs is not evenly spread, with the plurality of their total global reserves (totaling around 115.82 million tons) located in China (38%), and another

Table 2. Share of REEs' demand by end-use as magnets in 2020 from IRENA [2]

End-use	Share of magnetics end-use demand (%)
Others consumer electronics	5.80
Drivetrain (xEV)	
Wind turbines	4.00
Other automotive	2.50
Air conditioning	2.25
	1.75
Acoustic transducer	1.00
HDD	1.00
E-bikes	0.80
Electric power steering	0.50
Robotics	0.50
Others	8.50
Total	28.60

two-fifths of them equally divided by Brazil and Vietnam holding [2]. Almost all of the global REE production comes from less ten REE–bearing minerals, such as apatite, monazite, xenotime, allanite, and bastnaesite [5].

While responding to the disparity in global REE resources can be done through opening or searching for new mines, which might be an answer, mining REEs–related minerals and processing the minerals also pose pollution risks [6]. Aside from pollution risks processing REEs requires large amounts of water, energy, and chemical consumption. Moreover, land allocation for REE–mineral mining and processing is another pressing issue [7]. Zapp et al. [8] concluded that there were radioactive elements (such as uranium and thorium) that exist in commonly mined REEs–bearing minerals such as bastnaesite and monazite, with relatively low concentrations of radioactive elements found in eudialyte and ion adsorption clay.

Bearing in mind the rising demand for REEs, potential alternative REE sources such as coal and its combustion products (including coal fly ash) has been increasingly studied for REE sources [5]. In investigating coal ash chemical content from coal fly ash samples from several power plants in Java, besides the REEs, coal fly ash also have silicon, aluminum, iron, calcium, magnesium, sodium, potassium, chromium, titanium, manganese, phosphorous, strontium, and barium [9]. Coal fly ash for REE resources is one of the ways to utilize coal fly ash that can relieve the pollution problems caused by its overproduction. Wang et al. [10] stated that the world produced between 600–800 million tons of coal fly ash per year and coal fly ash commonly stored in landfills, ponds, or stacked. Due to the storing practice and its leachability, radioactivity, and toxicity, coal fly ash becomes pollutant for soil, natural water sources, and air.

Coal fly ash consists of organic and inorganic components. The organic component in coal fly ash is the remaining part of the combustible part of coal that has not combusted, thus, 'unburned coal'. Both coal fly ashes and bottom ashes from eight different powerplants across Java (from which one of them was used in this research) contained unburned coal, which was less in fly ashes than in bottom ashes. The glass, mullite, Fe–oxide minerals, quartz, and spinel form the inorganic component of coal fly ash. Glass is formed during the high temperature resulting from the combustion process, and as a result the coal's clay component transforms into glass. Quartz is the part of coal fly ash that is from the part of coal that is not melted due to its high melting temperature (1700 °C versus 1400–1500 °C temperature in a combustion boiler). Melted and crystallized clay minerals produce mullite. Fe–oxide minerals are possibly formed by pyrite in coal feed during the combustion process. The spinel part of coal fly ashes is derived from coal that contains high iron [9].

Determination of the elemental components in coal fly as could be done with various instrumentations, like inducted coupled plasma–optical emission spectroscopy (ICP–OES) and X–ray fluorescence (XRF). ICP–OES can detect major, minor, or trace chemical elements in coal fly ash (and in other environmental samples) very precisely and sensitively (capable to detect an element in ppb order), while also requiring rigorous and time consuming sample preparation. XRF method does not need rigorous sample preparation, thus it is more time and cost effective than ICP–OES, while it also has disadvantages, such as being influenced by the sample matrix and standard, and different excitation sources analyzing some elements [11].

According to Liu et al. [12], in place of its contents, coal fly ash could be divided into two classes, class C and class F coal fly ashes. Class C coal fly ashes have a total content of SiO_2, Al_2O_3, and Fe_2O_3 between 50 and 70%, while class F has a total content of components of more than 70%. Besari et al. [9] found that the combustion process of coal enriches the content of REEs in its fly ash products around 10–15 times relative to REEs content in coal. From their analysis, it could be concluded that REEs are more concentrated in fly ash samples (average value 207.07 ppm) than in bottom ash (average value 171.21 ppm) and coal samples (average value 9.21 ppm).

Determining the mode of occurrence of REEs in raw material is important before deciding the best extraction method to extract REEs out of it. Besari et al. [9] stated that yttrium does not occur in the organic part of fly ash, while yttrium exists in the inorganic part of fly ash, the amorphous glass, and correlated with Si and O elements. On the other hand, Rybak and Rybak [13] also reported that REE oxides strongly correlated with Al oxides. REEs can also possibly be found in iron-, calcium- enriched aluminosilicates, and iron- enriched areas of coal fly ash [14]. It should be remembered that while using alternative resources is possibly helpful in preventing the relatively negative environmental impact of mining REEs-related resources and their processing, the need to use less hazardous materials, less water use, and fewer energy inputs is still urgent. As an example, extracting REEs from unused products generates large amounts of waste of strong acid and wastewater [7].

Citric acid was chosen over the other acids because citric acid is less hazardous than inorganic acid used in REE extraction from coal fly ash. The use of mineral acids also destroys the chemical structures of coal ash, making it unsuitable for further use as construction materials. Inorganic acids can leach both transition metals and REEs less selectively than organic acids do [15]. Citric acid is biodegradable and naturally occurring (in both animal and plant kingdoms, including in citrus fruit) and could be synthesized with renewable resources (e.g., from agricultural products and wastes through fermenting glucose or sucrose with *Aspergillus* sp.) [16-17]. Moreover, using citric acid avoids the production of harmful side products (such as toxic gases) and prevents polluting acid leakage [18]. There are four reversible chemical reactions in the leaching of REE from coal fly ash with citric acid according to Prihutami et al. [19], with citric acid dissociation in Eq. (1–3), and REEs complexation with hydrogen and citric ions in Eq. (4).

$$H_3C_6H_5O_7 \leftrightarrow H^+ + H_2C_6H_5O_7^- \tag{1}$$

$$H_2C_6H_5O_7^{-2} \leftrightarrow H^+ + HC_6H_5O_7^{-2} \tag{2}$$

$$HC_6H_5O_7^{-2} \leftrightarrow H^+ + C_6H_5O_7^{-3} \tag{3}$$

$$REE^{+3} + jH^+ + kC_6H_5O_7^{-3} \leftrightarrow REEH_j\left(C_6H_5O_7\right)_k^{3+j-3k} \tag{4}$$

Leaching (in this context) is also a solid-liquid non-catalytic reaction involving solid-liquid mass transfer – like most solid-liquid non-catalytic reactions, follows the shrinking core model. The shrinking core model consists of five steps: (1) diffusion of fluid from the surrounding to the particle through the film, (2) diffusion of fluid through the ash layer of the particle, (3) reaction of the fluid with the reactive parts of the particle, (4) diffusion of the reaction products through the particle's ash layer, and (5) diffusion of the reaction products through the film [20].

Much research about the REE leaching from coal fly ash has been conducted. Temperature and liquid–solid ratio (or L/S) influences will be discussed in this paper. Elevated temperature increases the amount of REEs extracted as the probability of interaction between the citric, hydrogen, and REE ions represented in Eq. (4) rises. The probability increases as the elevated temperature increases the molecular kinetic energy, thus inter–molecular collisions become more frequent [19]. Increased frequency of inter–molecular collisions also contributes positively to solid–liquid interaction, as solid-liquid diffusivity increases [18]. At the same time, in the same concentration, an elevated L/S ratio means that less solids (coal fly ash), hence more acid (hydrogen and possibly in this case, citric ions) would be available to interact with the coal fly ash, thus increasing the diffusivity between the solid and the liquid involved [21]. Moreover, due to the reversible nature of the Eq. (4) reaction, more hydrogen and forms of citric ions may increase the possibility to react with REE ions, as a result, more REE can be possibly extracted from coal fly ash.

■ EXPERIMENTAL SECTION

Materials

Coal fly ash from PT PJB UP Paiton Unit 2 Power Plant in Paiton, East Java (taken on 28 January 2021) was used. Citric acid monohydrate was manufactured (CAS number 5949–29–1) by Merck KGaA Darmstadt Germany of 99.5–100.5% purity. A 0.01 M citric acid solution used in this research was made by diluting the crystals. Distilled water and reverse osmosis water prepared in the Energy Conservation and Pollution Prevention Laboratory, Chemical Engineering Department, Universitas Gadjah Mada, Yogyakarta. OneMed WaterOne water (the latter was manufactured by PT. Jayamas Medica Industri Tbk., Sidoarjo, East Java, Indonesia) was used in the experiment. For ICP–OES instrumentation, TraceCERT mixed REEs standard that contains scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium each at 50 mg/L concentration at 2% nitric acid (weight basis) produced by Sigma–Aldrich Co. LLC (number 67349–100 mL) was used to provide standard solution.

Instrumentation

The sieving operation was done in a closed (with a lid) 400–mesh sieving pan supported with a bottom pan (to store part of the particle that passed the mesh), and the sieving operation was done by shaking the sieving pan with Wstyler RX–29–10 Serial 17370 shaker. The leaching operation was done in a Memmert WTB 15 water bath. The WTB 15 water bath used a Memmert SV1524 shaker. Centrifugation operation was done in a Thermo Fisher Scientific Heraeus Labofuge 200 centrifuge. For elemental analysis, the experiment used two instrumentation devices –XRF to quantify major elements in the coal fly ash and ICP–OES. The XRF instrumentation process was conducted in the Yogyakarta Radiation Laboratory, National Research and Innovation Agency, with EDXRF Malvern PANalytical Epsilon 4 instrument, and for ICP–OES instrumentation process in the Analysis and Instrumentation Laboratory, Department of Chemical Engineering, Faculty Engineering, Universitas Gadjah Mada with Perkin Elmer Optima 8000 ICP–OES instrument.

Procedure

Sieving

Coal fly ash taken from the Paiton II power plant in East Java in January 2021 and stocked in the laboratory. The restocked coal fly ash sample was sieved through shaking. Coal fly ash that passed the 400–mesh sieve–screen was stocked afterward to be used in the next step of this research. Elemental analysis had been done with XRF.

Leaching capacity study

Partly inspired by Prihutami et al. [18] with several modifications, about 3.333; 5.000; or 10.000 g (or L/S of 15, 10, and 5 mL/g) of coal fly ash that had passed the 400–mesh screening was later added into 250 mL Erlenmeyer flasks after 50 mL of 0.01 mol/L citric acid solution had been added into each of the flasks. After the ash and the acid had been added, each of the flasks' lids was closed with aluminum foil, and the leaching process was undergone for 24 h at temperatures of 30, 50, and 85 °C, according to the temperature shown on the water bath's monitor. After the shaking (and heating) process stopped, the solid–liquid mixture from each of the flasks used was taken into a centrifugation vial to be centrifuged. The supernatant from the centrifugation was sampled and diluted ten times with WaterOne water prepared in the laboratory. Sampling for the dilution process was done with 1 mL of Onemed disposable syringes manufactured by PT. Jayamas Medica Industri Tbk., Sidoarjo, East Java, Indonesia, took 1 mL of sample into a 10 mL volumetric flask. The diluted supernatant was later analyzed with ICP–OES to quantify its REE content. From the leaching capacity study, the leaching capacity (LC, in percentage) could be calculated with Eq. (5);

$$LC = \frac{\left(C_{Ce,supernatant} - C_{Ce,aquadest}\right) \cdot V_{supernatant}}{C_{Ce,fly\ ash} \cdot m_{fly\ ash}} \times 100\% \quad (5)$$

with the $C_{Ce,aquadest}$ is 0.031 mL/g, $C_{Ce,\ supernatant}$ is the concentration of cerium in the supernatant (in mL/g), $V_{supernatant}$ is the volume of citric acid used, 0.05 mL, $C_{Ce,fly\ ash}$ is the concentration of cerium in the fly ash

(83 mg/kg), and the mass of fly ash used is represented as $m_{\text{fly ash}}$ (in kg).

To analyze the trends of cerium leaching capacity versus L/S and temperature, linear curves are made with Microsoft Excel Software (along with the leaching capacity data calculation). Linear curves represent linear equations with the form shown in Eq. (6);

$$y = ax + b \tag{6}$$

with y represents the cerium leaching capacity (in %), x represents the L/S value (in mL/g) or temperature value (in °C), a represents the slope, and b represents the intercept. With the Chart Design tool of Microsoft Excel, a and b values could be determined. One linear curve represents cerium leaching capacity data versus L/S in a temperature variable (or cerium leaching capacity data versus temperature in an L/S variable). The data are available in the supplementary materials.

■ RESULTS AND DISCUSSION

Coal Fly Ash Analysis

Coal fly ash that was taken from PT PJB UP Paiton II power plant in Paiton, East Java, was sieved through the 400–mesh sieving pan through shaking. The result of the XRF analysis is shown in Table 3 (in terms of the oxide of major elements). The total amount of ferric, silicon, and aluminum oxides is between 50–70%; thus, the coal ash concerned falls into class C. Table 4 concludes that REEs were present in the coal fly ash used with XRF. While XRF can detect REEs, it is less sensitive than ICP-OES and ICP-MS in detecting REEs [1]. Acknowledging the detection limit and accuracy of XRF measurement of coal fly ash used, there is a need to compare the data shown in Table 4 with more accurate secondary sources to analyze REE content with rare earth composition. The sources utilized the ICP–MS method to quantify REE content in their coal fly ashes. Table 5 shows the amount of REEs in the coal fly ash from the Paiton 2 power plant and the data from the Indramayu power plant that passed the 400–mesh sieve [9,22]. In comparing Tables 4 and 5, it could be concluded that from all of the REEs analyzed, only the rare earth element of cerium has the nearest fit (83.0 ppm vs 66.1 and 75.9 ppm) compared to other rare earth elements found in the researchers' raw material, thus the discussion is limited only to cerium extraction.

While cerium has the nearest fit relative to other REEs in the coal fly ash used, the cerium value in XRF and ICP–MS readings has around a 26% difference [9] and a 9.35% difference [22]. The differences are probably caused by the difference in the way of solid preparation (e.g. collection and quartering) before preparing the samples for instrumentation, as Besari et al. [9] did not

Table 3. Oxides of major elements in the coal fly ash used

Oxide of major element	Amount (%)
Fe_2O_3	35.45
SiO_2	22.10
Al_2O_3	8.53
CaO	14.52
Na_2O	1.03
SO_3	1.58
K_2O	1.61
TiO_2	1.29
P_2O_5	0.49
MgO	0.92
MnO	0.39
SrO	0.23
BaO	0.36

Table 4. XRF data of rare earth elements in the coal fly ash sample used in the research

REEs	Amount (ppm)
La	Undetected
Ce	83.0
Pr	Undetected
Nd	Undetected
Sm	Undetected
Eu	1240.0
Gd	957.0
Tb	5000.0
Dy	Undetected
Y	95.8
Ho	488.2
Er	524.7
Tm	Undetected
Yb	Undetected
Lu	34.7

Table 5. Data of REE content in the coal fly ash

Element	Data from Besari et al. (ppm) [9]	Data from Rosita et al. (ppm) [22]
La	31.30	38.70
Ce	66.10	75.90
Pr	7.60	9.20
Nd	29.60	36.40
Sm	6.22	8.00
Eu	1.38	1.70
Gd	6.03	8.20
Tb	0.96	1.30
Dy	5.56	8.10
Y	34.20	47.80
Ho	1.20	1.70
Er	3.60	5.10
Tm	0.51	0.80
Yb	3.22	5.40
Lu	0.51	0.80

report size separation processes in their report (size reduction also contributes in the enrichment of REEs as according to Rosita et al. [22]), and difference in the instrumentation tools that were used (XRF and ICP–MS). The difference in coal burning operation in the source power plant can also possibly affect the chemical components in the coal ash. We chose XRF because of its relative ease in preparing the samples compared to the ICP methods. Furthermore, the investigation of REE content in the researchers' coal fly ash with ICP–MS must be conducted.

Leaching Capacity

As mentioned before, leaching capacity study runs were done in different L/S and temperature conditions with citric acid concentration of 0.01 M. The concentration amount was chosen based on the REE leaching study made by Liu et al. [12], and also near the lowest value of citric acid concentration in Banerjee et al. [15] that nears 0% citric acid concentration as a stepping stone for the researcher's next step (as this study is preliminary). In regard to temperature conditions, the choice of 30, 60, and 85 °C temperatures were because of the need to investigate the leaching trends from low to high temperatures, and as mentioned before, the temperature is crucial in the leaching process. L/S ratios of 5, 10, and 15 mL/g were chosen because of the relatively low liquid–to–solid ratio to consider water conservation efforts.

The leaching capacity of cerium as a function of L/S and temperature is investigated in this research. The leaching capacity of cerium as a function of L/S can be seen in Fig. 1. The data points shown in Fig. 1 are further linearized to produce three linear curves (represented with the form shown in Eq. (6)) with the slope values shown in Table 6. From Fig. 1, it could be concluded that cerium leaching capacity is positively rising as L/S rises at each temperature trend point (30, 50, or 85 °C). The rising cerium capacity along with the rising L/S has also been reported by Banerjee et al. [15] which investigated

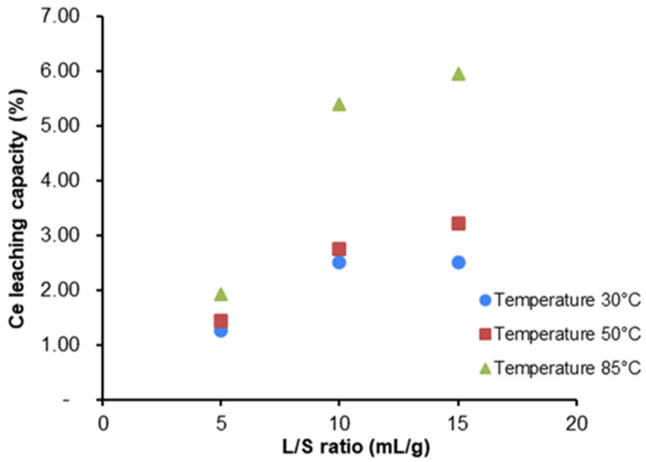

Fig 1. Cerium leaching capacity as a L/S function

Table 6. Slopes of cerium leaching capacity vs L/S ratio in different temperatures

Temperature (°C)	a (%/(mL/g))
30	0.1255
50	0.1785
85	0.4020

leaching capacity at L/S range of 25–200 mL/g with tartaric acid and Zhang et al. [23] in their REE leaching from coal fly ash with citric acid by column leaching at coal fly ash with mass variations of 10, 20, and 30 g. Should L/S rise, more acid is available to react with the solid; thus, the possibility of contact between cerium and related ions (such as hydrogen and citric ions, as represented in Eq. (4), also rises. To analyze the phenomenon in Fig. 1, three linear curves modeled after Eq. (6) are drawn upon the three datasets representing a temperature value.

In Table 6, the highest temperature value that gives the steepest cerium leaching capacity vs L/S ratio curve is 85 °C. The slope values increase along with rising temperature, so the curve is much steeper at higher temperature variables. The steepening of the curves could also be explained by the spreading of the datasets in respective L/S values. As the L/S value rises, the spread of the cerium leaching capacity data points also increases (at L/S 5 mL/g, the distance between the highest and lowest data points is 0.66% while at L/S 15 mL/g, the distance is 3.43%). Other than the acid availability vis–à–vis the solids, the solid concentration in the leaching samples could answer the data spread per L/S values. Thicker solid concentration means more effort to suspend the solids in the leaching sample, while the shaking velocity was fixed for different L/S values.

The leaching capacity of cerium as a function of temperature at three different L/S conditions is represented in Fig. 2. The 5 and 10 mL/g L/S conditions show that increasing temperature positively contributes to increasing cerium leaching capacity; thus, it could be concluded that increasing temperature at each of the L/S conditions means increasing the cerium leaching capacity. This phenomenon has also been reported by Banerjee et al. [15] and Prihutami et al. [18]. If the temperature is higher, more cerium (or REEs in general) is extracted from the coal fly ash, because as the temperature rises, the kinetic energy of each of the molecules in the reaction increases, thus making inter–molecular interaction for complexation reaction represented in Eq. (4) more possible. Moreover, higher molecular kinetic energy means lower mass transfer resistance. As a result, more cerium is likely to be extracted from the ash [18]. To analyze Fig. 2 further, three linear curves modeled after Eq. (6) are made upon the three datasets representing cerium leaching capacity in an L/S variation.

In Table 7, the highest L/S ratio that gives the sharpest cerium leaching capacity vs temperature curve is 15 mL/g. Regarding the factor of L/S, the cerium leaching capacity data spread in each of the L/S values is shown in Fig. 2, as the L/S ratio rises, the spread of cerium leaching capacity data also rises (the distance between the highest and the lowest data points at 30 °C is 1.25%, and at 85 °C is 4.02%). The sharpening of the curve resulting from the increasing L/S ratio could be attributed to the effect of the rising temperature explained in the previous paragraph. From Fig. 1 and 2,

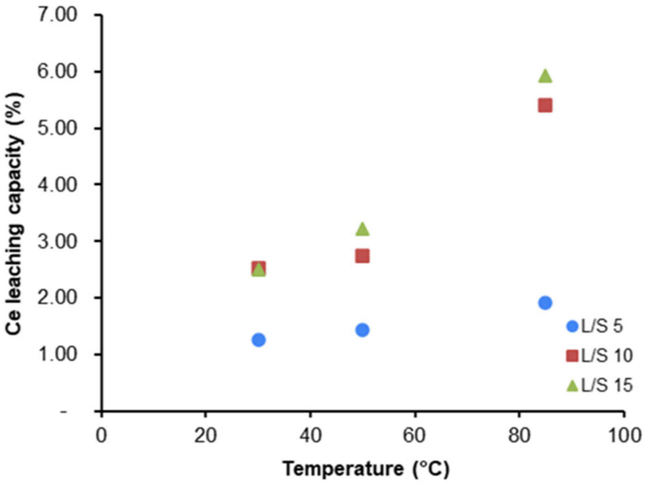

Fig 2. Cerium leaching capacity as a function of temperature

Table 7. Slopes of cerium leaching capacity vs temperature in different L/S ratios

L/S ratio (mL/g)	a (%/°C)
5	0.0122
10	0.0550
15	0.0640

it could also be concluded that the leaching operation of cerium is possible in a diluted citrate concentration of 0.01 M. Liu et al. [12] had leached REEs from different types of coal fly ash (types C and F) with citrate concentrations of 10, 50, and 100 mmol/L, with L/S of 50, 100, and 200 mL/g, at room temperature with pH adjustment at pH 2, 4, and 7 with periodic addition of dilute sodium hydroxide or hydrochloric acid solutions, and reported (in the supporting information of their publication), that REEs leaching with 0.01 M citrate condition was possible at L/S of 200 mL/g in both of the coal fly ash types they used and in all of the pH condition. In that L/S and citrate condition with class F coal fly ash, the cerium leaching efficiency was below 10% to below 5%, and the amount of cerium leached rose as the pH decreased. Still, for class C coal fly ash, the amount of cerium leached was near 70 to 10%, with the same trend (concerned with pH values) as class F ash.

From Tables 6 and 7, it could be concluded that the effects of temperature and L/S ratio positively contribute to the cerium leaching capacity vs L/S ratio curve and cerium leaching capacity vs temperature curve, respectively. All six slopes' values shown in Tables 6 and 7 show positive values, which means that the combination of the rising L/S ratio and temperature increases the amount of cerium extracted from the ash. Aside from the rising L/S ratio, temperature, and the type of coal ash used, cerium leaching capacity could be increased by increasing citric acid concentration, albeit with limitations, as citric acid dissociation reactions are reversible [19]. Pretreating the coal fly ash with a hot and concentrated alkali can possibly improve the amount of cerium (and possibly other REEs) extracted compared to without pretreatment [24-25]. Another alternative is using of ethylenediaminetetraacetate acid (EDTA) as a leaching agent in place of citric acid, as EDTA could possibly leach more REEs than citrate leaching agents [26].

■ CONCLUSION

The research concludes that cerium leaching with a very dilute citric acid concentration of 0.01 M is possible. The increase in temperature and L/S values positively contribute to rising cerium leaching capacity. As the temperature rises, there is an increase in inter-molecular interaction due to kinetic energy rise. Moreover, the increase in interaction also positively affects solid-liquid diffusivity. The increase in L/S (within the same concentration range) provides more acid vis-à-vis than the ash, thus providing more citric and hydrogen ions to the leaching reaction. As the L/S and temperature increase, cerium leaching capacity data points become more divergent.

■ ACKNOWLEDGMENTS

The researchers acknowledge Yunus Hidayat for analyzing the samples with ICP–OES. The researchers also acknowledge Pandu Satya Permana and Wisnu Suprapta as the laboratory officers of the Analysis and Instrumentation Laboratory and Energy Conservation and Pollution Prevention Laboratory, Department of Chemical Engineering, Universitas Gadjah Mada respectively.

■ CONFLICT OF INTEREST

There is no conflict of interest.

■ AUTHOR CONTRIBUTIONS

Gilbert Winoto did the experiments, processed the data, and wrote the article draft. Agus Prasetya and Panut Mulyono provided guidance on the experiments, data processing, and draft writing. Suyanti helped with the XRF analysis of the raw materials used in this experiment.

■ REFERENCES

[1] Balaram, V., 2019, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, *Geosci. Front.*, 10 (4), 1285–1303.

[2] Gielen, D., and Lyons, M., 2022, *Critical materials for the energy transition: Rare earth elements*, International Renewable Energy Agency, Abu Dhabi.

[3] Liu, S.L., Fan, H.R., Liu, X., Meng, J., Butcher, A.R., Yann, L., Yang, K.F., and Li, X.C., 2023, Global rare earth elements projects: New developments and supply chains, *Ore Geol. Rev.*, 157, 105428.

[4] Depraiter, L., and Goutte, S., 2023, The role and challenges of rare earths in the energy transition, *Resour. Policy*, 86 (Part B), 104137.

[5] Balaram, V., 2023, Potential future alternative resources for rare earth elements: Opportunities and challenges, *Minerals*, 13 (3), 425.

[6] Yin, X., Martineau, C., Demers, I., Basiliko, N., and Fenton, N.J., 2021, The potential environmental risks associated with the development of rare earth element production in Canada, *Environ. Rev.*, 29 (3), 354–377.

[7] Charalampides, G., Vatalis, K., Karayannis, V., and Baklavaridis, A., 2016, Environmental defects and economic impact on global market of rare earth metals, *IOP Conf. Ser.: Mater. Sci. Eng.*, 161 (1), 012069.

[8] Zapp, P., Schreiber, A., Marx, J., and Kuckshinrichs, W., 2022, Environmental impacts of rare earth production, *MRS Bull.*, 47 (3), 267–275.

[9] Besari, D.A.A., Anggara, F., Rosita, W., and Petrus, H.T.B.M., 2022, Characterization and mode of occurrence of rare earth elements and yttrium in fly and bottom ash from coal-fired power plants in Java, Indonesia, *Int. J. Coal Sci. Technol.*, 9 (1), 20.

[10] Wang, N., Sun, X., Zhao, Q., Yang, Y., and Wang, P., 2020, Leachability and adverse effects of coal fly ash: A review, *J. Hazard. Mater.*, 396, 122725.

[11] Taftazani, A., Roto, R., Ananda, N.R., and Murniasih, S., 2017, Comparison of NAA XRF and ICP-OES methods on analysis of heavy metals in coals and combustion residues, *Indones. J. Chem.*, 17 (2), 228–237.

[12] Liu, P., Zhao, S., Xie, N., Yang, L., Wang, Q., Wen, Y., Chen, H., and Tang, Y., 2023, Green approach for rare earth element (REE) recovery from coal fly ash, *Environ. Sci. Technol.*, 57 (13), 5414–5423.

[13] Rybak, A., and Rybak, A., 2021, Characteristics of some selected methods of rare earth elements recovery from coal fly ashes, *Metals*, 11 (1), 142.

[14] Kolker, A., Scott, C., Hower, J.C., Vazquez, J.A., Lopano, C.L., and Dai, S., 2017, Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe, *Int. J. Coal Geol.*, 184, 1–10.

[15] Banerjee, R., Mohanty, A., Chakravarty, S., Chakladar, S., and Biswas, P., 2021, A single-step process to leach out rare earth elements from coal ash using organic carboxylic acids, *Hydrometallurgy*, 201, 105575.

[16] Astuti, W., Hirajima, T., Sasaki, K., and Okibe, N., 2016, Comparison of atmospheric citric acid leaching kinetics of nickel from different Indonesian saprolitic ores, *Hydrometallurgy*, 161, 138–151.

[17] Gergoric, M., Ravaux, C., Steenari, B.M., Espegren, F., and Retegan, T., 2018, Leaching and recovery of rare-earth elements from neodymium magnet waste using organic acids, *Metals*, 8 (9), 721.

[18] Prihutami, P., Sediawan, W.B., Prasetya, A., and Petrus, H.T.B.M., 2022, A product diffusion model for the extraction of cerium and yttrium from magnetic coal fly ash using citric acid solution, *Int. J. Technol.*, 13 (4), 921–930.

[19] Prihutami, P., Prasetya, A., Sediawan, W.B., Petrus, H.T.B.M., and Anggara, F., 2021, Study on rare earth elements leaching from magnetic coal fly ash by citric acid, *J. Sustainable Metall.*, 7 (3), 1241–1253.

[20] Levenspiel, O., 1999, *Chemical Reaction Engineering*, 3rd Ed., John Wiley & Sons, New York, US.

[21] Cao, S., Zhou, C., Pan, J., Liu, C., Tang, M., Ji, W., Hu, T., and Zhang, N., 2018, Study on influence factors of leaching of rare earth elements from coal fly ash, *Energy Fuels*, 32 (7), 8000–8005.

[22] Rosita, W., Bendiyasa, I.M., Perdana, I., and Anggara, F., 2020, Sequential particle-size and magnetic separation for enrichment of rare-earth elements and yttrium in Indonesia coal fly ash, *J. Environ. Chem. Eng.*, 8 (1), 103575.

[23] Zhang, L., Chen, H., Pan, J., Yang, F., Long, X., Yang, Y., and Zhou, C., 2025, Rare earth elements recovery and mechanisms from coal fly ash by column leaching using citric acid, *Sep. Purif. Technol.*, 353 (Part B), 128471.

[24] Pan, J., Zhang, L., Wen, Z., Nie, T., Zhang, N., and Zhou, C., 2023, The mechanism study on the integrated process of NaOH treatment and citric acid leaching for rare earth elements recovery from coal fly ash, *J. Environ. Chem. Eng.*, 11 (3), 109921.

[25] Rosita, W., Perdana, I., Bendiyasa, I.M., Anggara, F., Petrus, H.T.B.M., Prasetya, A., and Rodliyah, I., 2024, Sequential alkaline-organic acid leaching process to enhance the recovery of rare earth elements from Indonesian coal fly ash, *J. Rare Earths*, 42 (7), 1366–1374.

[26] Yang, J., Montross, S., and Verba, C., 2021, Assessing the extractability of rare earth elements from coal preparation fines refuse using an organic acid lixiviant, *Min., Metall., Explor.*, 38 (4), 1701–1709.