Leaching characteristics of cerium and yttrium from non-magnetic coal fly ash after silicate digestion using acetic acid

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Abstract

The leaching kinetics of cerium (Ce) and yttrium (Y) in sodium-hydroxide-digested non-magnetic coal fly ash using acetic acid were investigated. The variables analysed were pH, solid-to-liquid ratio (S/L), and temperature. The results show that cerium and yttrium's maximum recovery was 57.33% and 58.36%, respectively, under leaching temperature of 90°C for Ce and 60°C for Y at pH of 1,74 and 10 g/mL solid-liquid ratio in 240 minutes. Increasing the leaching time to more than 120 minutes did not significantly improve the results. After the magnetic separation process, the ICP-OES analysis shows a slight increase in the concentration of cerium and yttrium on non-magnetic components. The XRD and ICP-OES analysis for the sample before and after silicate digestion shows that 40% silicate was dissolved. The calculation of apparent activation energies of leaching using the Arrhenius law for the leaching of cerium and yttrium gives 22.72 kJ/mol and 35.84 kJ/mol, respectively. The kinetic leaching model of cerium and yttrium all fit Dickinson's new shrinking core model. The calculation results show that the leaching reaction is controlled by combining interface transfer and diffusion across the product layer.

Keywords
coal fly ash, cerium, yttrium, kinetics, recovery

Introduction

In recent years, rare earth elements (REE) have become essential due to increasing demand in many industries. The exploration of alternative sources of rare earth elements has been conducted on materials such as red mud, coal, spent catalyst, tailing zircon, and coal fly ash (Aung and Ting, 2005; Abhilash et al., 2014; Borra et al., 2015; Anggara et al., 2018; Prameswara et al., 2020; Rosita et al., 2020).

The importance of recovering rare earth elements (REE), such as cerium and yttrium, from coal fly ash lies in their growing demand across various high-tech industries, including renewable energy, electronics, and defense. Traditional sources of REE are becoming increasingly scarce and challenging to mine, making alternative sources, such as industrial waste, essential. Coal fly ash, a by-product of coal combustion, offers a promising opportunity for REE extraction. Zhou et al. (2017) predicted that the demand for lanthanum, cerium, neodymium, europium, terbium, yttrium, and dysprosium oxide will rise to 33,600 ton by 2025 and reach 51,900 ton in 2030. The global demand for rare earth oxides is projected to increase from 208,250 metric tons in 2019 to 304,678 metric tons by 2025 (Zhou et al., 2017). This surge in demand underscores the need for sustainable extraction methods. However, current literature often focus on inorganic acids for REE recovery, leaving a gap in exploring the efficiency of organic acids such as acetic acid. This study addresses that gap by investigating the leaching kinetics of cerium and yttrium from non-magnetic coal fly ash using acetic acid, contributing to sustainable resource management. The findings are expected to offer new insights into optimizing extraction processes, reducing chemical waste, and improving the viability of coal fly ash as a secondary source of critical REE.

Coal fly ash is one of the alternative sources of rare earth elements (REE), listed as solid waste from coal power plants (Peramaki, 2014; Anggara et al., 2018). In Indonesia, 50% of energy is produced by coal-fired power plants (Edi, 2017). According to data from 2019, the demand for coal increased annually. The byproduct of coal combustion, fly ash and bottom ash, reached production of 19.92 million tons in 2019 (Energy and Mineral Resources Ministry, 2016). Anggara et al. (2018) recently reported that fly ash and bottom ash (FABA) from the coal power plant in Java are promising raw materials for rare earth element extraction. Kashiwakura et al. (2013) also reported that the rare earth elements and yttrium (REY) concentration increased by ten times after the combustion process in coal fly ash in amorphous phases, such as quartz (SiO_2) and mullite (Al_2O_3). Because REE were accumulated in amorphous silicate, it can be enriched in the non-magnetic component of coal fly ash (Blissett et al., 2014; Rosita et al., 2020).

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Rare earth elements include lanthanides and scandium groups, with atomic numbers ranging from 57 to 71. The components of the rare earth elements include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y. These elements are highly electropositive and have good conductivity, making them valuable for various industrial applications, including renewable and clean energy technologies (Nagaiyar and Gupta, 2016; Rosita et al., 2024).

There are some requirements to estimate the prospect of REE extraction from coal fly ash, such as the possibility of beneficiation, metal resources, simplicity, and hydrometallurgical recovery (Seredin and Dai, 2012). Seredin (2010) reported that the minimum cut of REE grade should be higher than 1,000 ppm, such as in monazite, xenotime, and bastnasite. However, due to the increasing price, this criterion is not the main requirement for REE extraction. The present criterion for REE extractions from coal fly ash is based on the individual concentration of the elements. They have been divided into three classifications: critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu)(Seredin, 2010). The amount of critical is essential to identify the viability of REE extraction. Mathematically, the equation is presented as

$$C_{outlook} = \frac{((Nd + Eu + Tb + Dy + Er + Y)/\sum REY)}{((Ce + Hp + Tm + Yb + Lu)/\sum REY)} \qquad [1]$$

The $C_{outlook}$ is the index used to identify the viability of REE extraction, in which the minimum $C_{outlook}$ should be higher than 0.7 ($C_{out} > 0.7$) - the more promising material for extracting REE, the higher the C_{out} value.

Hydrometallurgy is one of the most efficient extraction methods for extracting metal in low concentrations because this method consumes little energy but has high recovery. Leaching is a hydrometallurgy method where acid is used as a solvent to leach the valuable metal from a solid to a liquid. Inorganic acid is widely used as a leaching agent, including fluoride, hydrochloric, sulfuric, and nitric acids (Kashiwakura et al., 2013). However, inorganic acid produces harmful byproducts in gas and liquid form. In recent years, organic acids such as acetic, oxalic, nitric, and citric acid as leaching agents have been investigated to substitute inorganic acids. (Behera and Parhi, 2016; Lazo et al., 2017; Sari et al., 2018; Sekar et al., 2018; Anggraeni et al., 2023; Prameswara et al., 2024).

This study investigates acetic acid as a leaching agent for extracting rare earth elements from non-magnetic coal fly ash. Two elements are the focus of this study: cerium and yttrium, where cerium is in the excessive group, and yttrium is in the critical group. The usage of acetic acid as a leaching agent has been demonstrated by Parhi for leaching neodymium from the scrub magnet and Setiawan et al. for leaching lithium and cobalt from spent lithium-ion batteries (Behera and Parhi, 2016). The magnetic separator wet method was applied to obtain the non-magnetic coal fly ash. Silicate digestion was conducted to decrease and break the amorphous silicate content. The effect of pH levels, solid-to-liquid ratio, and temperature on the leaching process of cerium and yttrium was investigated in this study. The leaching kinetic models of cerium and yttrium are formulized by analysing the influence of temperature using the existing model, whereafter the apparent activation energies were calculated.

The focus on rare earth elements (REE) extraction from coal fly ash in Indonesia holds significant global relevance due to the increasing demand for REE in various industries worldwide. While the samples for this study were collected in Indonesia, the methodologies and findings are applicable across different geographical regions, including South Africa, which also has substantial coal power production. The techniques and results presented in this paper contribute to the broader understanding and potential applications of REE recovery, making the research valuable for a global audience. This research addresses universally pertinent issues in mining and metallurgy, providing insights that can be adapted and utilized by researchers and industries in Africa and beyond (Cornelius et al., 2021; Uysal, 2022).

Experimental method

The characterization of coal fly ash

Coal fly ash (CFA) samples were collected from the Tuban coal powered plant (PLTU-Tuban) in East Java province, Indonesia. The samples were collected continuously during regular operating hours over one week to ensure a representative sample of typical operations. The power plant operates under standard conditions for coal-fired facilities with combustion temperatures typically ranging from 1,200°C to 1,500°C. The plant has a capacity of 2 x 330 MW and primarily uses sub-bituminous coal, influencing the composition of the fly ash produced. The fly ash is collected from electrostatic precipitators, ensuring the consistency and quality of the samples used in this study.

The samples were then separated based on particle size using a sieve, with raw material particles smaller than 38 μm (-400 mesh) being selected for further analysis. To obtain the magnetic and non-magnetic components of coal fly ash, a wet magnetic separator was applied at the Centre for Research and Technology Development of Mineral and Coal (PUSLITBANG Teknologi Mineral dan Batubara) in Bandung, West Java province, Indonesia. The XRD analysis of raw material and magnetic and non-magnetic coal fly ash, was performed using the XRD X'Pert 3 Powder instrument (Figure 1). XRF analyses were conducted to determine the raw material's primary and minor components and magnetic and non-magnetic coal fly ash. Additionally, the non-magnetic coal fly ash was analysed using ICP-OES at the ALS Global-Geochemistry Analytical Laboratory in North Vancouver, British Columbia, to quantify the concentration of rare earth elements and yttrium. All measurements were conducted in triplicate to ensure data accuracy and reproducibility.

Coal fly ash was characterized using XRF, XRD, and the ICP-OES instrument. Material characterization aims to identify the raw material composition, phase (crystalline or amorphous), and concentration of rare earth elements. The XRF analysis results show that non-magnetic components of coal fly ash contain SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO as major minerals, and K_2O, Cr_2O_3, TiO_2, MnO, P_2O_5, SrO, and BaO as minor minerals (Figure 2). Generally, SiO_2 is the main mineral in non-magnetic coal fly ash (Figure 1).

The benefit of the magnetic separation step is that it concentrates rare earth elements (REE) by segregating magnetic and non-magnetic components. Although REE are present in both fractions, magnetic separation can simplify subsequent chemical processes by reducing the volume of material to be processed and potentially increasing the concentration of REE in the non-magnetic fraction. This step is beneficial when processing large quantities of fly ash. However, the data indicates that REE are hosted in magnetic and non-magnetic components, and their concentration is not significantly different from the raw fly ash, suggesting that further refinement in the separation process or additional steps may be necessary to enhance the REE recovery.

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The separation process of the magnetic and non-magnetic components using a wet magnetic separator was conducted based on literature, which indicate that rare earth elements accumulate and enrich in the glass phase after melting during the combustion process (Jorjani and Shahbazi, 2016). Kashiwakura et al. reported that, due to the high temperature of the combustion process, rare earth elements melted, distributed, and slightly enriched the amorph phase, such as quartz and mullite (Kashiwakura et al., 2013).

Figure 3 shows that a wet magnetic separator slightly enriches rare earth elements and yttrium after physical separation. It presents the concentration of each rare earth element in raw material, magnetic, and non-magnetic components. Equation [1] is used to compute the Coutlook, a metric determining the feasibility of rare earth element extraction. The Coutlook value is 1.08 (> 0.7), indicating that rare earth elements in non-magnetic coal fly ash are promising for extraction.

Silicate digestion using sodium hydroxide

The non-magnetic coal fly ash was digested using 8M sodium hydroxide (NaOH, pro-analysis grade, Merck Inc.) to break down the silicate structures. The digestion was conducted in a 500 mL three-necked flask fitted with a reflux condenser, temperature probe, and mechanical stirrer (500 rpm). The setup was placed in a water bath, maintained at a constant temperature of 90°C using a PID temperature controller.

A fixed mass of 62.5 mg CFA was combined with 250 mL NaOH solution (8M), resulting in a 25% mass-to-liquid ratio to maximize the reaction. Digestion was performed for 120 minutes under atmospheric pressure, with continuous stirring to prevent sedimentation and ensure homogeneous contact between solid and liquid phases. After digestion, the resulting solids were filtered using Whatman filter paper (pore size: 0.45 μm) and washed with distilled water until a constant dry sample weight was achieved, indicating the complete removal of sodium silicate residues ($NaSiO_3$). The solids were then dried at 110°C for 5 hours in an oven. XRD analysis was performed post-digestion to assess structural changes and confirm the dissolution of amorphous silicates.

Acid selection

The acid selection process was conducted to assess the efficiency and selectivity of various acids in extracting rare earth elements (REE). Two organic acids (acetic and oxalic acids) and one inorganic acid (sulfuric acid) were tested. Each acid was prepared to a pH of 1.7 and used under identical conditions: a temperature of 90°C, agitation speed of 500 rpm, and a leaching duration of 120 minutes.
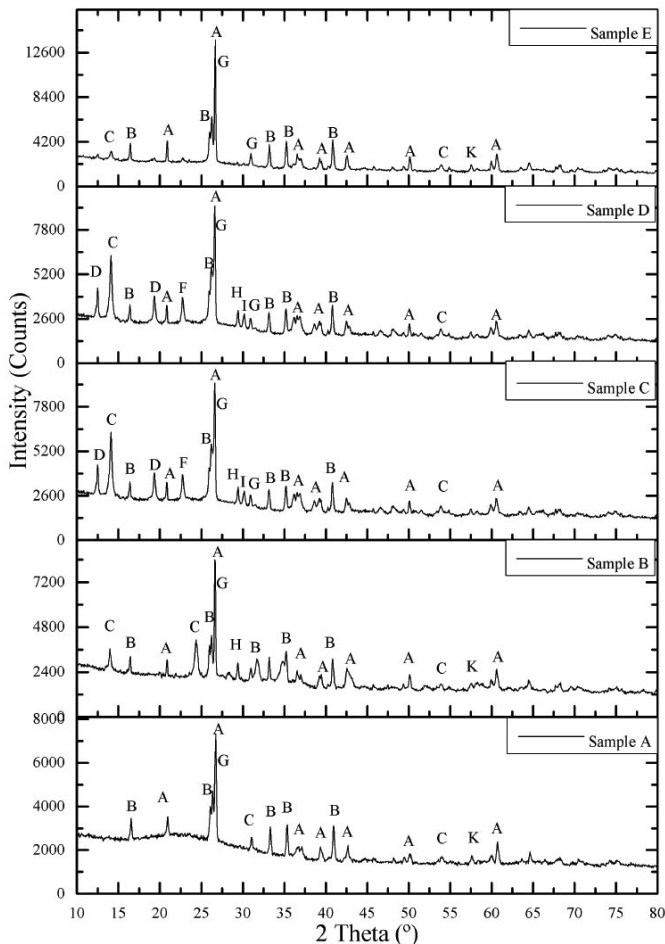

Figure 1—XRD analysis pattern for coal fly ash (Sample A: raw material, Sample B: after silicate digestion, Sample C: acid leaching at 90°C, Sample D: acid leaching at 60°C, and Sample E: acid leaching at 30°C (Note: A: SiO_2, B: $3Al_2O_3.2SiO_2$, C: Fe_2O_3, D: $(Fe^{2+}, Mg)_5Al(AlSi_3O_{10})(OH)_8$, E: $Ca(OH)_2$, F: $SiO_2.(Na_2O.K_2O)$, G: $Ca(Al_2Si_{14}O_{12}).12H_2O$, H: $CaCO_3$, I: Fe_3O_4, K: Al_2O_3)
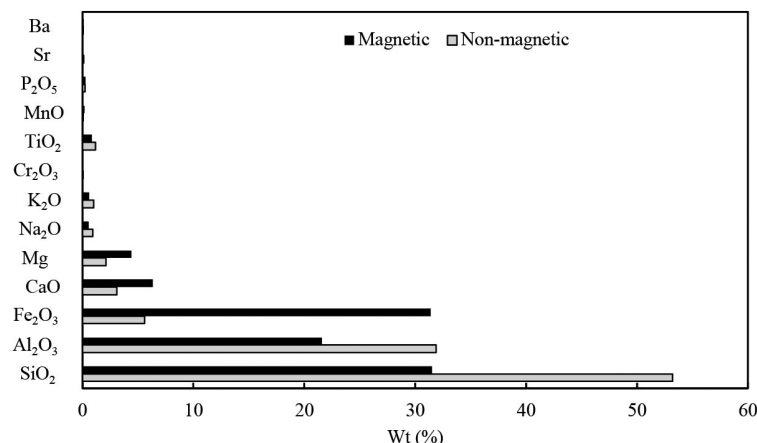

Figure 2—Coal fly ash characterization for a magnetic and non-magnetic component using XRF

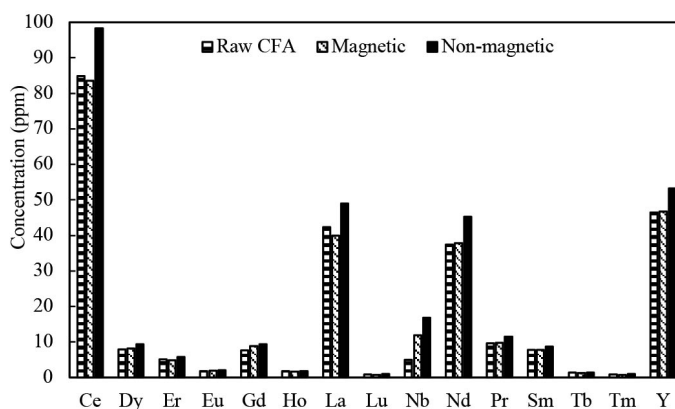# Leaching characteristics of cerium and yttrium from non-magnetic coal fly ash after silicate digestion using acetic acid

Figure 3—Rare earth elements and yttrium concentration in raw material, magnetic coal fly ash, and non-magnetic coal fly ash

Table I

Summary of Experimental Conditions for Leaching

Condition	Parameters
Solid-to-liquid ratio (w/v)	5%, 10%, 15%
Temperature	30°C, 70°C, 90°C
pH Levels	1.72, 2.4, 2.9
Equipment	Three-necked flask, reflux condenser, thermometer, heating mantle with temperature controller
Agitation	External agitator, stirring rate of 500 rpm
Leaching duration	4 hours
Sample collection intervals	0, 1, 2, 3, 5, 8, 15, 30, 60, 180, 240 minutes

After leaching, 2 mL of the sample was collected at 10-minute intervals using a pipette fitted with a microfilter (0.22 μm) to avoid contamination from suspended solids. The collected samples were analysed using ICP-OES (Perkin Elmer Optima 8000) to determine the concentration of critical metals (e.g., Y) and excessive group metals (e.g., Ce). Selectivity for each acid was calculated based on the Y/Ce ratio to assess which acid provided optimal separation.

Leaching

The leaching reagent was acetic acid (100% vol) pro-analytical produced by Merck Inc. The metal leaching experiment was carried out under various conditions, summarized in Table I.

The leaching process was conducted in a three-necked flask equipped with a reflux condenser and thermometer on a heating mantle with a temperature controller. The solution was agitated using an external agitator with a stirring rate of 500 rpm. The solution was leached over 4 hours to dissolve the rare earth elements and yttrium from non-magnetic coal fly ash. Samples of 2 mL were collected at specified intervals during the experiment to examine the kinetics of the leaching reaction.

Analysis ICP-OES

The samples for ICP-OES analysis were prepared by diluting 1 mL of each leached sample into 20 mL using deionized water (20 x dilution) to achieve optimal detection. The diluted samples were filtered through a microfilter (0.22 μm) to remove suspended particles that could interfere with the optical emission spectrometry. All measurements were performed in triplicate, and the standard deviation was reported to ensure data accuracy.

The prepared filtrate was analysed using inductive coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8000) at the Instrumental Analyst Laboratory, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Special Region of Yogyakarta province, Indonesia. The instrument was calibrated using certified standards to ensure reliable quantification of rare earth elements, with the detection limit set at 0.01 ppm.

Results and discussion

Silicate digestion

The characterization of coal fly ash shows that silicious and glass minerals were the most abundant. The dissolving silicious component becomes a critical material to remove. Generally, silicious removal can be achieved using alkaline fusion or alkaline leaching. This study used sodium hydroxide (NaOH) 8 M as a reagent to dissolve and break the silicious bounding. The XRF results show that 20% - 40% of silicious components were dissolved. The general reaction for silicate digestion can be described as the equation below.

$$2SiO_2REY_{(s)} + 4NaOH_{(aq)} + 4H_2O_{(aq)} \rightarrow \qquad [2]$$
$$2Na_2SiO_{3(aq)} + 2REY(OH)_{3(s)} + 3H_{2(g)}$$
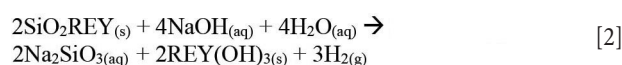
SiO_2REY, as a silicious component, is transformed into sodium silicate salt based on Equation [2]. Besides that, sodium hydroxide also changes the REY bound to form $REY(OH)_3$, where the silicate component replaced O.H.- from sodium hydroxide (Nagaiyar and Gupta, 2016). After silicate digestion, some filtrates were analysed

using ICP-OES to identify the amount of rare earth and yttrium (REY) in the solution. The ICP results show that only a tiny amount of REY was leached, and the recovery was not more than 5.6% for all elements of REY. Gupta et al. (2016) also reported that alkaline fusion is applied to recover rare earth elements from monazite (CePO$_4$) to remove phosphate as a pretreatment before acid leaching.

Acid selection

The acid selection was conducted to determine the impact of various organic and inorganic acids at pH 1.7, at a temperature of 90°C for 120 minutes. They were oxalic acid and acetic acid as organic acids, and sulfuric acid as inorganic acid. Four elements were selected for comparison to determine the impact of various acids (Figure 4a).

Figure 4(a) illustrates that sulfuric acid has a higher recovery than other organic acids, oxalic acid, and acetic acid. The recoveries were 74.51% and 33.07%, respectively, for cerium and yttrium for sulfuric acid, and 44.44% and 57.01% for acetic acid. However, acetic acid can dissolve higher than sulfuric acid for metals like La and Yb. Of the four elements, oxalic acid has the lowest recovery. The general reaction for each acid with rare earth elements is shown in Equations [2]–[4] (Feng et al., 2013; Jorjani and Shahbazi, 2016):

$$2REE(OH)_3 + 3C_2H_2O_4 \rightarrow REE_2(C_2O_4)_3 + 6H_2O \qquad [3]$$

$$2REE(OH)_3 + 3H_2SO_4 \rightarrow REE_2(SO_4)_3 + 6H_2O \qquad [4]$$

$$REE(OH)_3 + 3CH_3COOH \rightarrow REE(CH_3COO)_3 + 3H_2O \qquad [5]$$
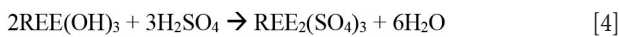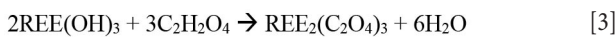
Figure 4(b) indicates that acetic acid has the highest ratio for metal selectivity. Based on this data, we can conclude that acetic acid has a high selectivity for rare earth elements. Thus, acetic acid was selected as a reagent for rare earth leaching.

Acid leaching using acetic acid

Acid leaching was conducted using acetic acid to leach at various leaching conditions. As explained in the aforementioned, acetic acid was selected as a leaching reagent based on the high selectivity of acetic acid compared to oxalic acid and sulfuric acid. The results indicate that acetic acid efficiently extracts rare earth elements (REE) from non-magnetic coal fly ash, achieving a recovery rate of 44.44% for cerium and 57.01% for yttrium, respectively. While sulfuric acid exhibits higher recovery for some elements, such as cerium, with a recovery rate of 74.51%, acetic acid presents distinct advantages. Acetic acid is more environmentally friendly, producing fewer hazardous byproducts than inorganic acids like sulfuric

acid, and it is also biodegradable and safer to handle in industrial applications. This statement makes it an appealing choice for processes that minimize environmental impact.

Furthermore, acetic acid offers comparable selectivity for critical elements such as yttrium, achieving a selectivity ratio (Y/Ce) of 0.96. As essential in renewable energy technologies, yttrium makes the use of acetic acid particularly beneficial in applications related to sustainable industries. These findings highlight the potential for integrating acetic acid into eco-friendly industrial processes, especially with strict environmental regulations. Additionally, achieving high recovery rates without relying on aggressive inorganic acids opens new possibilities for future REE recovery processes, potentially reducing operational costs and simplifying waste management. The mildness of acetic acid also reduces equipment corrosion, which can prolong the operational lifespan of processing plants, leading to further cost savings. Future studies could explore scaling up the process and integrating acetic acid leaching with other beneficiation methods to enhance overall recovery efficiency.

The influence of pH on metal recovery

Acid-leaching experiments were carried out by varying the pH level at the same temperature and solid-to-liquid ratio, as presented in Figure 5. Figure 5a shows that the pH levels influenced the extraction of cerium. The potential of hydrogen (pH) had a significant effect on the one-minute leaching of cerium. The recovery of cerium was 21.16%, 35.75%, and 41.30%, respectively, for pH 2.90, 2.40, and 1.72. The recovery of cerium steadily increases during the first 60 minutes of leaching, but beyond this point, the rate of increase becomes minimal.

Figure 5b shows that pH levels strongly influence the yttrium extraction, increasing yttrium recovery. The equilibrium of yttrium was achieved at 5 minutes of leaching for each pH level. After 5 minutes, Yttrium recovery was relatively constant, as shown in Figure 5b. The final recovery of yttrium after leaching of 240 minutes was 38.29%, 51.00%, and 57.63%, respectively, for pH 2.90, pH 2.40, and pH 1.72. The complexation of Ce^{3+} and Y^{3+} can be explained as REE^{3+}. More H+ ions will be released with a lower pH level, generating a complex REE(CH$_3$COO)$_3$ ion. This complexation has a significant effect on REE leaching.

The influence of temperature on REE recovery

The experiments regarding the effect of temperature on rare earth elements recovery were conducted at various temperatures, as shown in Figure 6, with a pH of 1.72. The extraction of cerium
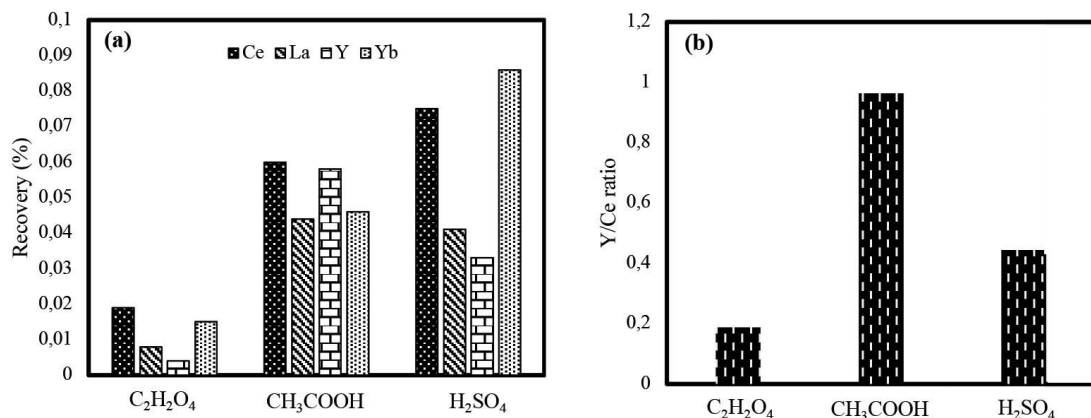

Figure 4—(a)Recovery of Ce, La, Y, and Yb at various leached agents (oxalic. acid, acetic acid, and sulfuric acid) and (b) Selectivity of oxalic acid, acetic acid, and sulfuric acid for Y/Ce ratio
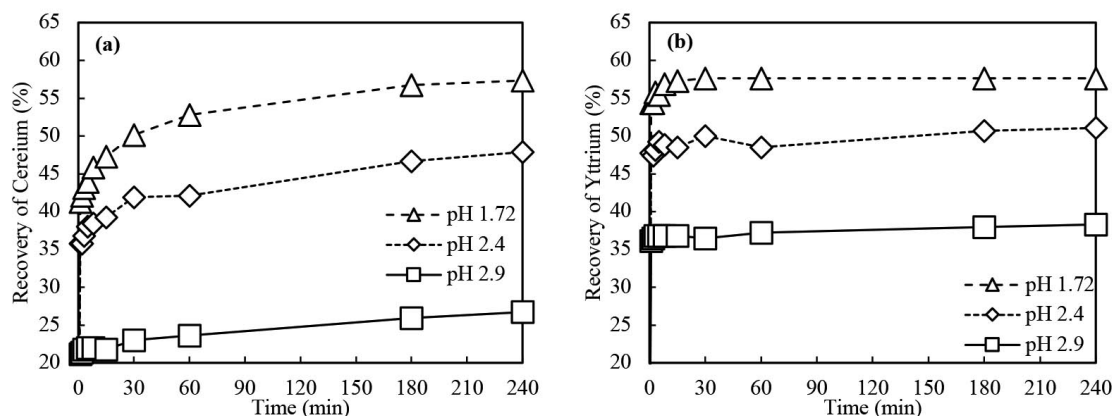
Figure 5—The influence of pH levels on recovery of (a) cerium and (b)yttrium
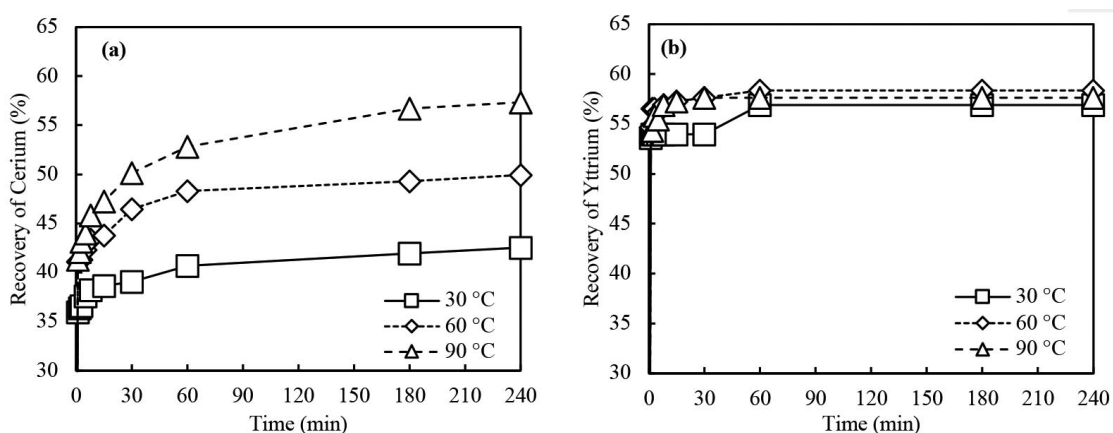

Figure 6—The influence of temperature on (a) cerium and (b) yttrium recovery

increased gradually for all temperatures from 1 to 60 minutes of leaching. The high reaction temperature increases the cerium recovery. When the temperature increases from 30°C to 60°C and 90°C, the extracted cerium rises from 40% to 48% and 52%, respectively (Figure 6a). After 60 minutes of leaching, the leaching rate becomes almost constant. This phenomenon is consistent with the Arrhenius rate law, which states that increasing the reaction temperature by 10°C will increase the reaction rate twice (Levenspiel, 1999; Fogler, 2005).

The extraction of yttrium increases significantly after one-minute leaching at all temperatures (Figure 6b). They are 53.60%, 54.70%, and 54.30%, respectively, for 30°C, 60°C, and 90°C. Increasing the temperature from 30°C to 90°C only increases the recovery slightly. Increasing the leaching time to 240 minutes does not increase the recovery. It can be inferred that Y^{3+} quickly diffuses to the liquid body. Therefore, the temperature does not influence the yttrium extraction but significantly influences the cerium extraction. The ion radius of both elements could influence this. The ion radius of yttrium is smaller than cerium, with an ion radius of 0.9 Å and 1.01 Å, respectively (Hartman and Chan, 1993).

The influence of solid-to-liquid ratio on metal recovery

The experiments were conducted by varying the solid-to-liquid ratio at the same condition (pH 1.72 and temperature 90°C), as shown in Figure 7. The recovery of cerium (Figure 7a) achieved 59% after 180 minutes for a solid-to-liquid ratio of 10% (w/v). The decreasing solid-to-liquid ratio from 15% to 5% slightly increased the recovery. The recoveries were 54.25%, 57.33%, and 59.59% for solid-to-liquid ratios of 15%, 10% and 5%, respectively. It is well known that, the

lower the liquid ratio, the more surface contact between particle and reagent. Besides that, a higher solid-to-liquid ratio can increase the viscosity of the slurry. From the result of cerium extraction, it can be inferred that the cerium leaching process is controlled by diffusion. The extraction of yttrium (Figure 7b) achieved 57.60% after 15 minutes for a solid-to-liquid ratio of 10%. There was no significant effect of varying solid-to-liquid ratios.

Leaching kinetics study

The leaching kinetics study of rare earth elements from non-magnetic coal fly ash was analysed by using the shrinking core model for spherical particles of constant size (Levenspiel, 1999). The selection of the shrinking core model in this application is driven by its effectiveness in describing the reaction kinetics of solid-fluid systems. This model is particularly suitable for processes involving the leaching or dissolution of solid particles, where the reaction occurs at the interface between the solid and the fluid (Maulidia et al., 2023). The shrinking core model simplifies the complex process by assuming that the unreacted core of the solid shrinks over time while the product layer grows outward. This model allows for a clear and quantifiable description of the reaction rate and extent, making it easier to predict the system's behaviour under various conditions.

Moreover, the model aligns well with the physical and chemical characteristics of the rare earth elements extraction process from coal fly ash, where the reactants and products exhibit distinct phases and interfaces. Its ability to account for factors such as diffusion through the product layer and chemical reaction at the surface, makes the shrinking core model a robust choice for this application, facilitating accurate and reliable analysis (Supriadi et al., 2023). The
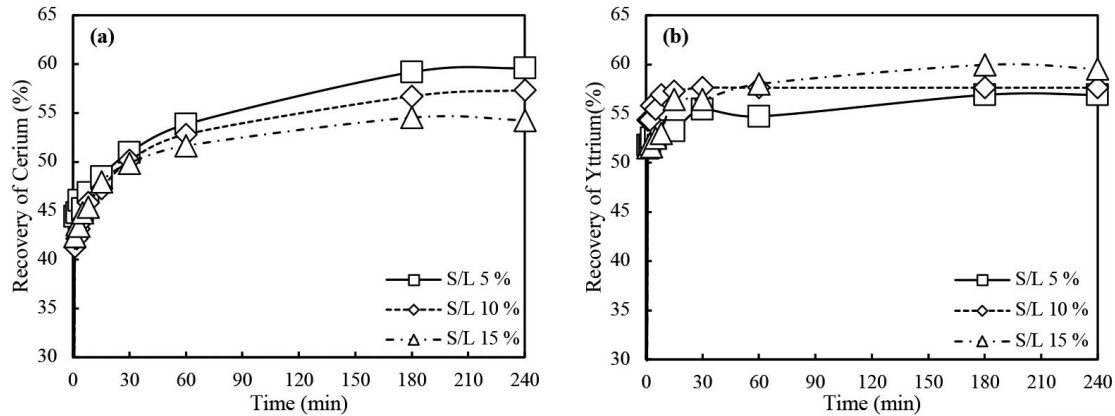
Figure 7—The influence of solid-to-liquid ratio on recovery (a) for cerium and (b) for yttrium

existing model was validated against the experiment data using the linearization method to determine the kinetic parameters. The existing model is described in Equations [5]–[7].

Chemical reaction control

$$1 - (1-\alpha)^{1/3} = k_1\, t \qquad [5]$$

Inner diffusion control

$$1 - (2/3)\alpha - (1-\alpha)^{2/3} = k_2\, t \qquad [6]$$

Ash diffusion control

$$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = k_3\, t \qquad [7]$$

where α is rare earth elements conversion (cerium and yttrium), k is equilibrium reaction constant (min-1), and t is time (minute/s). The kinetic equation can be determined by fitting all the experimental data in different temperatures with different kinetics models in various rate-controlling mechanisms.

The experimental data shown in Figure 6 was substituted into Equations [5], [6], and [7] and then plotted as model vs. time. After plotting model vs. time, the straight line's correlation coefficient (R^2) values were calculated after linearization using the regression method, as shown in Tables II and III. The result indicates that the leaching process did not agree with a chemical reaction or ash diffusion control due to the R^2 value being below 0.95 for cerium and 0.85 for yttrium. Subsequently, the new modification model for the shrinking core model suggested by Dickinson and Heal was tested to fit the kinetic data. The equation was expressed as Equation [8] below.

$$\left(\frac{1}{(1-\alpha)^{1/3}} - 1\right) + \frac{1}{3}\ln(1-\alpha) = k_4\, t \qquad [8]$$

The result of this model was presented in Table I for cerium and Table II for yttrium. The results show that the R^2 for both metals was higher using the last model by Dickinson and Heal. The correlation coefficient for cerium were 0.74, 0.96, and 0.95, respectively, for temperatures 30°C, 60°C, and 90°C. As for cerium, Dickinson and Heal's models were also fitted to test the experimental data, as shown in Table II. The results show that the last model presented a higher correlation coefficient (R^2) than other models, although the correlation coefficient was not higher than 0.95. These kinetic models indicate that the leaching of rare earth elements from non-magnetic coal fly is controlled by chemical reaction and diffusion control. However, the correlation coefficient at a temperature of 30°C in cerium and yttrium kinetic models was very low. They were 0.74 and 0.49, for cerium and yttrium, respectively. The experimental data in Figure 6 shows that it only slightly increases the recovery of cerium and yttrium.

Activation energy must be provided to a chemical reaction or phenomenon. The activation energy is often calculated using the Arrhenius equation. The equation of Arrhenius is represented as:

$$k = A\exp[-E/(RT)] \qquad [9]$$

where k is the reaction rate constant, A is the pre-exponential factor, E is the apparent activation energy, R is the mole gas constant, and T is the reaction temperature (K). Model vs. time was plotted to calculate the activation energy to obtain the intercept and slope (as a k-value) using the regression method (y=a+bx). This plot should be straight to get the slope, as presented in Figure 8. After the k-value is obtained, Equation [9] is modified to become a linear trendline as:

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad [10]$$

Table II

Linear fitting parameter equations for various leaching kinetic models of cerium

T (°C)	1-(1-α)^{1/3}			1-(2/3)α-(1-α)^{(2/3)}			1-3(1-α)^{(2/3)}+2(1-α)			((1-α)^{-1/3}-1)+(1/3)ln(1-α)		
	k	b	R^2	k	b	R^2	k	b	R^2	k	b	R^2
30	0.0005	0.1408	0.7322	0.0001	0.0180	0.7396	0.0003	0.0539	0.7396	0.00009	0.0121	0.7441
60	0.0009	0.1619	0.9605	0.0003	0.0233	0.9651	0.0008	0.0700	0.9651	0.0002	0.0165	0.9683
90	0.0015	0.1668	0.9274	0.0004	0.0246	0.9407	0.0013	0.0739	0.9407	0.0004	0.0176	0.9513

Table IIII

Linear fitting parameter equations for various leaching kinetic models of yttrium

T (°C)	$1-(1-\alpha)^{1/3}$			$1-(2/3)\alpha-(1-\alpha)^{(2/3)}$			$1-3(1-\alpha)^{(2/3)}+2(1-\alpha)$			$((1-\alpha)^{-1/3}-1)+(1/3)\ln(1-\alpha)$		
	k	b	R2	k	b	R2	k	b	R2	k	b	R2
30	0.0001	0.226	0.497	0.0001	0.0436	0.497	0.0001	0.130	0.497	0.0001	0.036	0.497
60	0.0010	0.233	0.825	0.0004	0.0461	0.828	0.0011	0.138	0.828	0.0004	0.038	0.833
90	0.0012	0.230	0.853	0.0004	0.0450	0.855	0.0013	0.135	0.855	0.0005	0.037	0.858
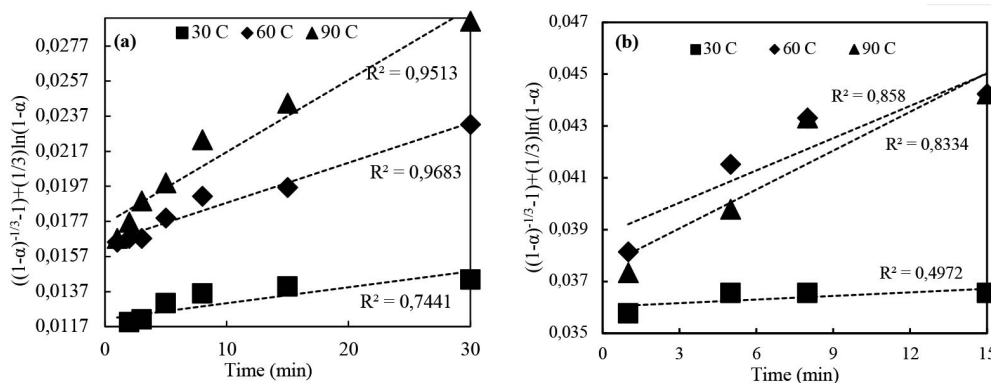
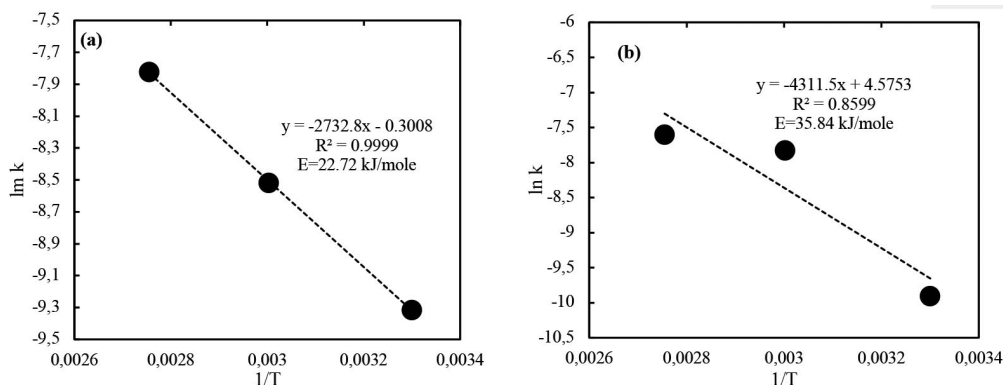**Figure 8—Model vs. time (a) cerium and (b) for yttrium**

Figure 9—Plot ln k vs 1/T (a) cerium and (b) for yttrium

where ln k is ordinate, and 1/T is absis. From Figure 8, the k-value was obtained as a slope. The ln k vs. 1/T should be plotted as a straight line to calculate the apparent activation energy, as presented in Figure 9.

Figure 9 shows a correlation between ln k vs. 1/T. This figure indicates that the apparent rate constant (k) can be calculated. Thus, the apparent activation energy of the overall reaction for cerium and yttrium is 22.72 kJ/mole and 35.84 kJ/mole, respectively. These energy activation values indicate that the leaching of cerium and yttrium from non-magnetic coal fly ash after silicate digestion using acetic acid is controlled by combining interface transfer and diffusion across the product layer. The silicate digestion step involved treating the non-magnetic coal fly ash with sodium hydroxide to break down and dissolve siliceous components, which was crucial in preparing the sample for effective leaching. The same digested sample was used for subsequent leaching experiments to ensure consistency. Feng et al. (2013) reported that the activation energy of the diffusion-controlled process is less than 13 kJ/mol,

while for the chemical reaction-controlled process, it is usually greater than 43 kJ/mol. The activation energy in the 13 kJ/mol-43 kJ/mol range is controlled by mixed processes such as chemical reaction and ash diffusion-controlled, and/or chemical reaction control and inner diffusion. This statement is also similar to Huang et al. (2017), which reported that leaching rare earth elements and fluoride from mixed rare earth element concentrate after roasting with calcium hydroxide, was controlled by both interfacial transfer and diffusion through the product layer affected by the reaction with activation energy in the range of 13 kJ/mol – 43 kJ/mol. Therefore, the results from this study align with existing literature, further validating the mechanism of leaching involving a combination of interface transfer and diffusion processes.

Conclusion

This study shows that physical separation using a magnetic separator slightly increases the cerium and yttrium concentration in non-magnetic coal fly ash. Acetic acid has a higher selectivity

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for Ce/Y than oxalic acid and sulfuric acid. The main factors influencing the leaching of cerium and yttrium were temperature and pH levels. Increasing the S/L ratio did not provide any significant improvement. The highest recovery of cerium and yttrium was 57.33% and 58.36%, respectively, under different temperatures, i.e., 90°C for Ce and 60°C for Y at pH 1.74 and 10 g/mL solid-liquid ratio in 240 minutes. However, extending the leaching time to 240 minutes does not appear to be necessary as the recovery becomes relatively constant after 60 minutes.

The apparent activation energies were 22.72 kJ/mol and 35.84 kJ/mol for cerium and yttrium, respectively. The kinetic data of leaching cerium and yttrium were fitted using a new shrinking core model by Dickinson and Heal. The calculation results show that the leaching reaction is controlled by combining interface transfer and diffusion across the product layer. This understanding can be applied in optimizing industrial processes for rare earth elements extraction from coal fly ash, reducing energy consumption, and improving efficiency by focusing on the most effective leaching conditions identified, such as appropriate temperatures, pH levels, and shorter leaching durations.

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Conflict of Interest

The corresponding author states that there is no conflict of interest on behalf of all authors.

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