Effect of Temperature on Rare Earth Elements Recovery from Coal Fly Ash Using Citric Acid

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Abstract. Production of fly ash as a solid waste of coal combustion rises as the need of electricity in Indonesia increases. In 2020, the amount of fly ash produced is estimated to reach 9.72 million tons. Utilization of coal fly ash is still limited while poor handling on abundant amount of this material can cause air, soil and water pollution. This research aims to recover rare earth elements contained in coal fly ash. In this study, the recovery of La, Ce, Nd, Dy and Y was done using citric acid. Magnetic phase of fly ash with particle size less than 38 µm from PLTU Tanjung Awar-awar Tuban was leached with 300 mL citric acid of 0.5 M using solid/liquid ratio of 1:10. The experiment was carried out in various temperature of 26ºC and 45ºC. Liquid samples were taken at 2, 5, 10, 15, 30, 60, 90, 120 and 240 minutes to be analyzed. The five elements recovered was found to rise until the end of the leaching period. Value of relative recovery also increases along with leaching temperature. The greatest recovery value is reached by yttrium that are 51.00% for leaching at 26ºC and 83.35% at 45ºC.

1. Introduction

Indonesia is a country who meets 58.1% its need of electricity using coal as its source of energy [1]. The utilization of coal is predicted to increase every year due to government’s electricity supply business plan [2]. However, the combustion of coal produces fly ash which considered as solid waste with still limited utilization [3]. Total production of the waste is estimated to reach 9.72 million tons in 2020 [4], [5]. Poor handling on fly ash can cause air, soil and water pollution due to its ability to generate dust and heavy metal composition [6].

Aside from containing heavy metal, fly ash also contains rare earth elements [7], [8], [9]. Rare earth elements consist of 15 lanthanides, yttrium and scandium in which all have similar properties except for promethium which is a radioactive [10]. The demand for these elements rises 5.3% every year since its unique catalytic, magnetic and phosphorescent properties are critical for modern technology [11], [12], [13]. In general, world’s coal fly ash is foreseen to have 445 ppm rare earth elements and is potential to be source of rare earth elements when the amount is comparable to conventional ore [7].

One of the method that can be used in order to recover rare earth elements from its source is leaching method using acid [14], [15], [16]. Organic acid can be used to replace inorganic acid which may produce dangerous gasses as well as harm ecosystem when penetrates into soil and water [17], [18]. In this study, the acid used is citric acid which is one of the common acid produced from metabolism.
activity in living being including microbes [19]. Leaching activity in different temperature was done to observe its effect on rare earth elements recovery from coal fly ash.

2. Materials and Methods

2.1. Materials
Coal fly ash was obtained from PLTU Awar-awar Tuban, Jawa Timur, Indonesia. Fly ash has been screened on sieve trays to get raw material with particle size of less than 38 µm. The raw material has been separated using magnetic separator via wet method to obtain magnetic phase of fly ash that later was used in the study. Citric acid monohydrate (C₆H₈O₇·H₂O) used as leachant was of analytical grade bought from Merck with CAS number of 5949-29-1 and was prepared using distilled water.

2.2. Coal fly ash preparation
Coal fly ash was dried in oven at 125°C for an hour.

2.3. Citric acid leaching
As much as 300 mL of citric acid 0.5 M was put into a three neck flask placed on waterbath. Fly ash of 30 gram was then added. The mixture was stirred using glass stirrer of 400 rpm for 4 hours. Samples of 3 mL were drawn using syringe at 2, 5, 10, 15, 30, 60, 90, 120 and 240 minutes. Solid and liquid phase were later separated using centrifuge at 4,000 rpm for one minute. The experiment was repeated for temperature of 45°C. Three neck flask filled with 300 mL of citric acid 0.5 M was heated to experiment temperature before fly ash was added and the temperature was kept constant using waterbath.

2.4. Liquid sample preparation
Liquid sample was filtered using microfilter. As much as 1 mL of sample was then drawn and diluted using distilled water to produce 10-fold dilution before analyzed using ICP-EOS PQ 9000 Elite.

3. Result and discussion
Relative recovery of rare earth elements is described as the amount of element leached into liquid body at every sampling time compared to maximum amount of element that can be leached by the system. The value of relative recovery is calculated using Equation (1).

\[
\text{Recovery} = \frac{C_t}{C_{\text{max}}} \times 100\% \tag{1}
\]

where Recovery is relative recovery in percent (%), \(C_t\) is concentration of rare earth element at every sampling time (mg/L), \(C_{\text{max}}\) is maximum concentration of rare earth element that can be leached into citric acid solution (mg/L).
Figure 1. Recovery of (a) Lanthanum, (b) Cerium, (c) Dysprosium, (d) Neodymium and (e) Yttrium Using Citric Acid Solution

Figure 1 showed that recovery of five rare earth elements studied increase as leaching time increases. The longer the leaching process, the longer contact time between citric acid and fly ash that enables more rare earth elements to be leached out. The recovery of rare earth elements is shown to be rapid at earlier time and later becomes comparably slow. Citric acid having 3 carboxyl group and 1 hydroxyl group leaches rare earth elements out of fly ash by forming soluble metal-ligand complex. This chemical reaction can only happen when the reactants undergo effective collision. At first, the amount of citric acid is still abundant. The amount becomes less as it leaches out rare earth elements as well as other leachable elements. As consequence, the number of collisions between reactants decreases making the leaching rate to become slower with time.
Figure 1 also showed that the recovery of lanthanum, cerium, dysprosium, neodymium and yttrium are all greater at 45°C compared to room temperature leaching. Heating the system to 45°C increases kinetic energy of the reactants, allows them to collide and react faster with citric acid molecules. Therefore, this results in faster leaching rate.

Table 1. Recovery for Every Leaching Temperature at 240 Minutes

| Elements | 26°C  | 45°C  |
|----------|-------|-------|
| La       | 49.06 | 75.95 |
| Ce       | 45.10 | 72.36 |
| Dy       | 48.78 | 75.05 |
| Nd       | 47.93 | 78.47 |
| Y        | 51.00 | 83.35 |

Among five elements studied, yttrium gives greatest recovery values. At room temperature leaching, 51.00% of yttrium can be recovered. The value goes even higher for leaching at 45°C and reaches 83.35% after 240 minutes. This is due to the small ionic radii of yttrium compared to the rest of the elements. Ion of Y³⁺ has ionic radii of 0.9 Å while La³⁺, Ce³⁺, Dy³⁺ and Nd³⁺ have radii of 1.032 Å, 1.01 Å, 0.983 Å and 0.912 Å, respectively [20]. Small radii results in smaller size of yttrium-ligand complex formed after reaction thus makes it possible to diffuse more easily into liquid body. Bigger ionic radii will produce immense complex with citric acid resulting in slower diffusion and smaller amount of elements leached into liquid body.

Leaching kinetics of rare earth elements from the solid surface to liquid body is also studied. \( C_{\text{max}} \) is defined as concentration of rare earth element in liquid film that is always in equilibrium with its concentration in solid. Meanwhile, \( C_t \) is rare earth element concentration in liquid body at any given time. The difference between \( C_{\text{max}} \) and \( C_t \) is the driving force for rare earth element leaching.

\[
\frac{dC_t}{dt} = k_{\text{app}} (C_{\text{max}} - C_t) V \tag{2}
\]

where \( V \) is liquid volume (L), \( C_t \) is rare earth element concentration in liquid body at any time \( t \) (mg/L), \( t \) is leaching time (min), \( k_{\text{app}} \) is the apparent leaching rate constant (min⁻¹) and \( C_{\text{max}} \) is maximum concentration of rare earth element in liquid (mg/L).
Equation (2) can be written in relative recovery form to obtain Equation (3).

\[ \frac{dx}{dt} = k_{\text{app}}(1 - x) \]  

(3)

where \( x \) is relative recovery as described by Equation (1).

The solution for Equation (3) results in linear equation.

\[ -\ln(1 - x) = k_{\text{app}}t + c \]  

(4)

where \( x \) is the value of relative recovery, \( k_{\text{app}} \) is leaching rate constant (min\(^{-1}\)), \( t \) is leaching time (min) and \( c \) is intercept.

**Figure 3.** Leaching Kinetics of (a) Lanthanum, (b) Cerium, (c) Dysprosium, (d) Neodymium and (e) Yttrium into Citric Acid Solutions
As shown by Figure 3 (a) to (e), the leaching kinetics for all rare earth elements investigated fit well with the first order mass transfer kinetics model.

The apparent leaching rate constant ($k_{\text{app}}$) is assumed to follow the form of Arrhenius equation [21].

$$k_{\text{app}} = A' e^{-\frac{E}{RT}}$$  

(5)

where $A'$ describes the relative intensity of interactions between rare earth element and citric-acid molecules, $E$ describes ‘energy barrier’ for leaching process, $R$ is gas constant and $T$ is absolute leaching temperature. The value of $A'$ as well as $E$ can be calculated using Equation (5).

| Element | $k_{\text{app}}$ (min$^{-1}$) | $26^\circ$C (x10$^3$) | $45^\circ$C (x10$^3$) | A | E/R (K) |
|---------|-------------------------------|------------------------|------------------------|---|---------|
| La      | 2.31                          | 2.31                   | 4.55                   | 196.78 | 3,396.31 |
| Ce      | 1.73                          | 1.73                   | 4.16                   | 4,238.58 | 4,401.61 |
| Dy      | 1.94                          | 1.94                   | 4.67                   | 4,798.55 | 4,403.81 |
| Nd      | 1.94                          | 1.94                   | 5.34                   | 45,397.37 | 5,076.45 |
| Y       | 2.12                          | 2.12                   | 6.21                   | 142,630.26 | 5,392.52 |

The value of $k_{\text{app}}$ for different temperature show some differences. Leaching at 45°C causes the value of $k_{\text{app}}$ to become 2 to 3 times higher than the ones at room temperature. The differences among $k_{\text{app}}$ value of all rare earth elements at room temperature are practically not significant. Meanwhile, the distinction of the leaching rate constant for each element is noteworthy at elevated temperature. It differs from 4.16x10$^{-3}$ to 6.21x10$^{-3}$ min$^{-1}$ with yttrium having the highest leaching rate constant. This corresponds with earlier data where recovery of yttrium is the highest at the same given time. The small size of yttrium ion makes it collide more frequently and it is enough to overcome its high activation energy.

4. Conclusions

Recovery of five rare earth elements from coal fly ash using citric acid was studied. The results of the present study showed that citric acid had a promising potential as leachant for rare earth elements. The amount of rare earth elements leached increases with time. Elevated temperature has positive effect on leaching La, Ce, Dy, Nd as well as Y shown by the escalation of recovery value. The leaching rate of each element is faster as the temperature becomes higher. At 26°C, leaching rates of the rare earth elements practically have no significant differences but at 45°C the leaching rates turn to be more varied. The highest value of recovery is achieved by yttrium which has the smallest ionic radii with a value of 83.35% at 45°C after 240 minutes of leaching.

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