**Membrane and Water Treatment**, *Vol. 15, No. 4 (2024) 193-202*
https://doi.org/10.12989/mwt.2024.15.4.193

# Rare earth element recovery from coal ash and leaching wastewaters by ecofriendly sequential extraction

Siyu Chen[1a], Jae Wan Choe[2b] and Han S. Kim*[1]

[1]*Civil and Environmental Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea*
[2]*Department of Civil Engineering, Gwangju University, 277 Hyodeok-ro, Nam-gu, Gwangju 61743*

*(Received September 13, 2024, Revised September 29, 2024, Accepted October 8, 2024)*

**Abstract.** It has been reported that rare earth elements (REEs) are considerably present in coal ash. In this study, an ecofriendly sequential extraction method was developed for the effective REE recovery from coal ash and leaching wastewaters. Citrate, a weak and environmentally benign solvent that replaces acetate employed in the existing sequential extraction methods (e.g., European community bureau of reference (BCR) and Tessier methods), was found to be highly effective in leaching REEs from coal ash. Microwave-assisted thermal digestion improved the REE extraction efficiency even further, with an overall leaching rate of 70%, which is 2.54 and 3.76 times higher than the values achieved by the conventional BCR and Tessier methods, respectively. It was also confirmed that the majority of REEs was strongly bound to CaO, $Al_2O_3$, $Fe_2O_3$, and $P_2O_5$, not to $SiO_2$. The sequential extraction method developed in this study is expected to be used as an effective and simple recovery procedure for REEs from coal ash and remaining leaching wastewaters.

**Keywords:** coal ash and leaching waters; environmentally benign solvent; microwave-assisted thermal digestion; rare earth element; sequential extraction

## 1. Introduction

Coal has been considered a major natural resource for electric power generation worldwide; however, it produces substantial amounts of residual coal ash wastes (600–800 million tons) and wastewaters (Jayaranjan *et al*. 2014). Coal ash comprises fly ash (FA, 85–95%, w/w) and bottom ash (BA, 5–15%, w/w), which are collected in the dust collector and from the inside wall or bottom of the furnaces after combustion, respectively (Suh and Maeng 2015, Wang *et al*. 2005). In Korea, large amounts (more than 8,000,000 tons) of coal ash are produced annually from 11 coal-fired thermal power plants (TPPs; Maeng *et al*. 2014). FA and BA can be recycled as additives for cement, concrete, and structural fillers, but the remainder (approximately 20%) is dumped into landfill sites located near the TPPs without proper treatment (Cho *et al*. 2017, Rodwihok *et al*. 2023). In Korea landfill disposal of coal ash becomes unfavored due to the additional physical and chemical pretreatment, substantial disposal costs, and confined landfill areas, thereby limiting the cost-effective and performance-efficient treatment of coal ash (Um and Jeon 2021).

The main components of coal ash are metal oxides, including silicon oxide ($SiO_2$), aluminum oxide ($Al_2O_3$), iron oxide ($Fe_2O_3$), calcium oxide (CaO), magnesium oxide (MgO), potassium oxide ($K_2O$), and unburned carbon residues (Hower *et al*. 2017). Recently, it has been demonstrated that significant amounts of rare earth elements (REEs) are present in coal ash (Baba and Usmen 2006, Taggart *et al*. 2016). Hence, the recovery of REEs from coal ash has attracted significant attention with the aim of using coal ash as valuable and critical resources (Franus *et al*. 2015, Joshi *et al*. 2016, Mutlu *et al*. 2018, Yao *et al*. 2015). Currently, a number of industries, devices, and materials rely on REEs, including electronic devices, semiconductors, automotive catalytic converters, petroleum refining catalysts, metallurgical additives and alloys, permanent magnets, rechargeable batteries, fluorescent materials, glass polishing, ceramics, and medical equipment, clean and green energy devices, and so forth (Hower *et al*. 2016, Kim *et al*. 2023, Weber and Reisman 2012, Wu *et al*. 2018). REEs are represented by a group of 17 elements, which include 15 lanthanoid series elements from lanthanum ($^{57}$La) to lutetium ($^{71}$Lu) and transition metal elements of scandium ($^{21}$Sc) and yttrium ($^{39}$Y). REEs are usually grouped into light and heavy REEs (LREEs and HREEs, respectively), depending on their electronic configuration (Binnemans *et al*. 2013, Resende and Morais 2010). LREEs comprise 8 elements from La to gadolinium ($^{64}$Gd), possessing an ever-increasing number of unpaired electrons. HREEs include 8 elements from terbium ($^{65}$Tb) to Lu. Owing to the similar ionic radius and chemical property of Y, this element is also included in the HREE group. Promethium ($^{61}$Pm) is the rarest element in nature. Additionally, critical REEs (CREEs) are characterized by their crucial role in clean energy production and supply (Chu 2011). Currently, dysprosium ($^{66}$Dy), Tb, europium ($^{63}$Eu), neodymium ($^{60}$Nd), and Y are included in CREEs based on their market demands. Among the CREEs, the demand for Nd and Dy are increasing as they are essential

---

*Corresponding author, Ph.D., Professor,
E-mail: hankim@konkuk.ac.kr
[a] Ph.D. Student
[b] Ph.D., Professor

http://www.techno-press.org/?journal=mwt&subpage=7

ISSN: 2005-8624 (Print), 2092-7037 (Online)

components required for clean energy production (Alonso *et al*. 2012, Wamea *et al*. 2022); in contrast, the demands for Eu, Tb, and Y are slightly decreasing in Europe.

Sequential extraction has been employed to identify the association characteristics of metals present in geomaterials such as soils and sediments (Rauret *et al*. 1999, Tessier *et al*. 1979). The most commonly used sequential extraction procedures are the Tessier and European community bureau of reference (BCR) methods (Pueyo *et al*. 2008, Tessier *et al*. 1979). However, extraction of REEs using these methods is time-, chemical-, and energy-consuming and the leaching efficiency is unpredictable depending on the type and amount of acidic solutions and the target materials (Bordas and Bourg 1998, Quevauviller *et al*. 1994). In contrast to geomaterials, combusted coal ash contains almost no unburned carbon or organic matter, metals exist in the form of free ions in part. When the BCR sequential extraction method is used for the REE extraction, a weak acid (acetate) is used in the first step to separate the elements from the sample. Instead, organic weak acids have been employed as a substitute for acetate (Marguí *et al*. 2004). The operational stability of the weak acids for efficient REE extraction has been reported as follows: citrate exhibits the highest extraction efficiency, followed by malic, tartaric, and acetates (Shan *et al*. 2002). It has been demonstrated that citrate is highly reactive with Nd, which is the most valuable REE among the CREEs (Gergoric *et al*. 2018). Recently, it has been found that the microwave-assisted thermal digestion can enhance the REEs recovery from coal ash in the conventional sequential extraction procedures significantly (Park *et al*. 2021). This technique has advantages of rapid temperature tunability, high accuracy, controllable environmental conditions, sufficient dissolution of samples, and low reagent consumption (Li *et al*. 2019). According to Park *et al*. (2021), the most significant challenge for the REE extraction from coal ash is overcoming the adverse environmental impacts associated with strong inorganic acids. Hence, the use of ecofriendly solvents such as organic weak acids in the REE leaching from coal ash has been reported in several previous studies (Banerjee *et al*. 2021, Gergoric *et al*. 2018, Prihutami *et al*. 2021), but they employed them in a single extraction step procedure.

Similarly, most prior attempts to analyze the REE content in coal ash have focused on the quantification of total REEs and their recovery using strong and inorganic chemicals (acids and bases), which result in undesirable environmental impacts (Keshavarz *et al*. 2022, Lim *et al*. 2018). Consequently, the distribution and association of REEs in coal ash were presumably based on the concepts of the conventional sequential extraction procedures designed for geomaterials using inorganic acids and bases. In addition, the extraction efficiencies reported so far are not sufficient for the practical application of REE recovery from coal ash (Banerjee *et al*. 2021, Prihutami *et al*. 2021). Hence, in this study, a simple and efficient sequential extraction procedure was developed to recover REEs from coal ash using environmentally benign solvents and microwave-assisted thermal treatment. Using this sequential extraction procedure, the leaching efficiency of REEs from coal ash was evaluated systematically, and their association characteristics in the coal ash were revealed. The results of this study are expected to contribute to the cost-effective, performance-efficient, and ecofriendly recovery of REEs from coal ash and leaching wastewaters.

## 2. Materials and methods

### 2.1 Materials

The coal ash used in this study was collected from the Yeongheung TPP, which is located on the southern coast of Korea. The coal used in Yeongheung TPP is mainly supplied as mixtures of bituminous coals from Russia, Australia, and Indonesia. The coal ash samples (FA and BA which were collected in the dust collector and from the bottom of the furnaces of TPPs) were filtered using a sieve (2 mm) and dried at 25 °C for 48 h. Prior to analyzing the coal sample, moisture was removed by drying at 105 °C for 5 h. Hydrofluoric acid (HF, 49–52% purity), nitric acid ($HNO_3$, 60–62%), and boric acid ($H_2B_4O_7$, 99.5%) were provided by Sigma Aldrich (St. Louis, MO, USA) used for the analysis of the total REEs in the coal ash. Acetate ($CH_3COOH$, 99%, Duksan, Anyang, Korea), citrate ($C_6H_8O_7$, 99%, Sigma Aldrich), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, 97%, Duksan), hydrogen peroxide ($H_2O_2$, 34.5%, Duksan), ammonium acetate ($NH_4CH_3CO_2$, 97%, Samchun, Seoul, Korea), hydrochloric acid (HCl, 37%, Junsei, Tokyo, Japan), sodium acetate ($CH_3COONa$, 98.5%, Sigma Aldrich), phosphoric acid ($H_3PO_4$, 85%, Sigma Aldrich), sulfuric acid ($H_2SO_4$, 99.9%, Sigma Aldrich), potassium hydroxide (KOH, 85%, Duksan).

### 2.2 Total REE content analysis

A coal ash sample (0.1 g) was mixed with 2 mL of HF and 5 mL of $HNO_3$ in a 100 mL Teflon vessel. The sample mixtures were digested at 240 °C for 60 min using a microwave system (MARS 6, CEM Corporation, Matthews, NC, USA). After cooling to 70°C, the acidic gas was removed and 2 mL of $H_2B_4O_7$ was added to prevent the complex formation of dissolved REEs. The solid residues were removed with a 0.45 μm syringe filter (Millipore, Burlington, MA, USA), and then the solution was analyzed for total REE contents.

### 2.3 Sequential extraction of REEs from coal ash

A coal ash sample (1 g) was air-dried overnight and then added to a 50 mL Teflon tube. The REEs were sequentially extracted using three following procedures, namely, the Tessier, BCR, and new extraction procedures.

#### 2.3.1 Tessier sequential extraction method

The Tessier sequential extraction method, which comprises 5 steps (Rauret *et al*. 1999, Tessier *et al*. 1979) and slightly modified by Park *et al*. (2021), was employed to extract the REEs, which are exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic matter-bound, and residual fractions, presumably associated with coal ash.

Table 1 REE contents in FA and BA

| Element | FA (mg/kg) | BA (mg/kg) |
|---|---|---|
| Sc | 49.66 ± 5.48[a] | 66.54 ± 1.58 |
| Y | 12.78 ± 2.32 | 8.84 ± 0.35 |
| La | 7.00 ± 1.38 | 5.90 ± 0.12 |
| Ce | 19.32 ± 2.16 | 23.40 ± 0.27 |
| Pr | 2.06 ± 0.38 | 1.70 ± 0.03 |
| Nd | 8.39 ± 1.49 | 7.11 ± 0.07 |
| Sm | 2.24 ± 0.39 | 1.87 ± 0.07 |
| Eu | 0.56 ± 0.15 | 0.49 ± 0.03 |
| Gd | 2.49 ± 0.42 | 2.15 ± 0.07 |
| Tb | 0.42 ± 0.14 | 0.31 ± 0.01 |
| Dy | 2.63 ± 0.39 | 1.88 ± 0.06 |
| Ho | 0.58 ± 0.14 | 0.39 ± 0.01 |
| Er | 1.81 ± 0.30 | 1.17 ± 0.04 |
| Tm | 0.30 ± 0.10 | 0.17 ± 0.01 |
| Yb | 1.93 ± 0.28 | 1.11 ± 0.02 |
| Lu | 0.31 ± 0.10 | 0.17 ± 0.00 |
| Total | 112.50 ±15.62 | 123.21 ±2.77 |

[a]mean ± standard deviation (n = 3)

### 2.3.2 BCR sequential extraction method

The BCR sequential extraction method (Petit and Rucandio 1999, Pueyo *et al*. 2008), consisting of 4 steps and slightly modified by Park *et al*. (2021), was applied to extract the REEs, which are exchangeable, reducible, oxidizable, and residual fractions, presumably associated with coal ash.

### 2.3.3 Sequential extraction procedure developed in this study

Step 1

Herein, 2 M citrate (40 mL) was mixed with coal ash (1 g) and the resulting suspension was stirred vigorously on a shaker table operated at 30 strokes/min at 22 ± 5°C for 20 h. The solid was separated by centrifugation at 3000 *g* for 20 min, and then the supernatant was acidified with 1 M HCl. The concentrations of REEs in the solution were analyzed (exchangeable and CaO-bound fraction presumably associated with CaO of coal ash). The residue was washed with 20 mL Milli-Q water by stirring for 15 min. The coal ash was recovered by centrifugation at 3000 *g* for 20 min and the supernatant was discarded.

Step 2

The coal ash collected from Step 1 was mixed with 4 M KOH (40 mL) and stirred vigorously as described in Step 1. Then, the solid was separated by centrifugation at 3000 *g* for 20 min. The concentrations of REEs in the supernatants were analyzed ($SiO_2$-bound fraction presumably associated with $SiO_2$ of coal ash). The residual coal ash was washed with Milli-Q water and recovered as described in Step 1.

Step 3

The coal ash (0.2 g) collected from Step 2 was added to a 100 mL Teflon tube, and mixed with 3 mL of $H_2SO_4$, 3 mL of $H_3PO_4$, 2 mL of HF, and 4 mL of Milli-Q water. The resulting suspension was stirred vigorously as described in Step 1, followed by microwave-assisted thermal digestion as described in Section 2.2. The solid was separated by centrifugation at 3000 *g* for 20 min. The concentrations of REEs in the supernatants were determined (Al-Fe oxide-bound fraction presumably associated with $Al_2O_3$ and $Fe_2O_3$ of coal ash). The residual coal ash was washed with Milli-Q water and recovered as described in Step 1.

Step 4

The coal ash recovered in Step 3 was mixed with 2 mL HF and 5 mL $HNO_3$, followed by microwave-assisted thermal digestion as described in Section 2.2. After centrifugation at 3,000 *g* for 5 min, the concentrations of REEs in the supernatant were analyzed (residual fraction).

Step 5

The leaching aqueous solutions (acidic and basic wastewaters) used in Steps 1–4 were collected and passed through a ceramic membrane (TAMI 0.2 μm, Sterlitech, Auburn, WA, USA) to remove debris of the previous steps. Then, the solution was digested as described in Step 4. The concentration of REEs in the solution were analyzed (leaching wastewater fraction).

### 2.4 Analytical methods

Inductively coupled plasma-mass spectrometry (ICP-MS, PlasmaQuant MS Elite, Analytik Jena, Jena, Germany) was used to determine the REE concentrations. Field-emission scanning electron microscopy (FE-SEM, SUPRA 55VP, Carl Zeiss, Oberkochen, Germany) was employed to characterize the surface morphology of coal ash. X-ray fluorescence (XRF, PW2404, Philips, Amsterdam, Nederland) was employed to analyze the composition of coal ash. X-ray diffraction (XRD, D8 Advance, Bruker, Billerica, MA, USA) analysis was performed in the 2θ range of 20–50° to characterize the mineral composition and structure of coal ash. The leaching rate was calculated based on the amount of REEs leached from each step of the sequential extraction procedures compared with the amount of total REEs present in the coal ash samples.

## 3. Results and discussion

### 3.1 Total REEs in coal ash

Table 1 lists the total amounts of REEs present in FA and BA and their concentrations in FA and BA were determined as 112.50 and 123.21 mg/kg, respectively. Among 16 REEs, Sc, Ce, Y, Nd, and La were determined to be the major REEs of coal ash, which were equivalent to 86.36% and 90.73% (w/w) of the total REEs present in FA and BA, respectively. The fractional compositions of REEs in FA and BA were similar except Sc and Ce, which were at higher levels in FA than in BA. The LREE contents in both FA and BA (37.39% and 34.59%, respectively) were significantly higher than the HREE contents (7.09% and 4.22% in FA and BA, respectively). FA and BA contained significant amounts of HREEs such as Dy, Er, and Yb. The

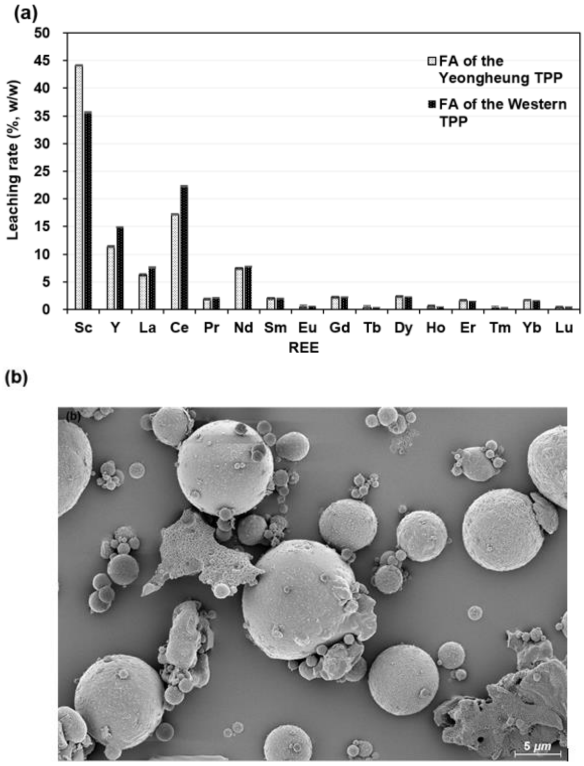

Fig. 1 (a) Comparison of REE contents in FA collected from the Yeongheung and Western TPPs. Data for the Western TPP were adapted from Park et al. (2021). Error bars denote standard deviation (n = 3). (b) FE-SEM images of FA of the Yeongheung TPP

Table 2 XRF analysis of FA remaining in each step of the new sequential extraction procedure

| Mineral component | Raw FA (%, w/w) | Step 1 (%, w/w) | Step 2 (%, w/w) | Step 3 (%, w/w) |
|---|---|---|---|---|
| $SiO_2$ | 64.12 | 64.12 | 28.40 | 0.02 |
| $Al_2O_3$ | 17.34 | 15.56 | 14.05 | 14.05 |
| $Fe_2O_3$ | 6.81 | 5.93 | 5.93 | 0.09 |
| CaO | 5.46 | 1.47 | 1.34 | 0.58 |
| $TiO_2$ | 1.23 | 1.14 | 0.99 | 0.02 |
| $P_2O_5$ | 1.20 | 0.40 | 0.33 | 5.68 |
| $K_2O$ | 1.03 | 0.97 | 1.21 | 0.84 |
| MgO | 0.96 | 0.63 | 0.53 | 0.62 |
| $Na_2O$ | 0.85 | 0.63 | 0.51 | - |
| $SO_3$ | 0.81 | 0.11 | 0.09 | 6.36 |
| Others | 0.20 | - | - | - |
| Overall | 100.00 | 90.95 | 53.36 | 28.24 |

concentrations of Y and Nd, which are representative CREEs, were higher than those of other CREEs such as Eu, Tb, and Dy in FA and BA.

The total REE contents found in this study were compared with the values reported previously by Park *et al*. (2021) as presented in Fig. 1 (a). Although the original sources of coal ash were different, the distribution of REEs in the coal ash samples exhibited a similar trend, that is, Sc, Ce, Y, La, and Nd constituted approximately 86.36% and 88.16% of the total REEs in the FA samples collected from the Yeongheung and Western TPPs, respectively. There was almost no difference in the remaining REE fractional compositions. The Sc content in the FA from the Yeongheung TPP (44.14%) was significantly higher than that from the Western TPP (35.66%). Except for Y, La, and Ce, the fractional compositions of the remaining elements in the FA samples collected from both TPPs were similar. Interestingly, the amount of Y was slightly higher in the FA of the Western TPP (14.89%) than that for the Yeongheung TPP (11.36%), whereas the other CREEs were present at similar levels.

The surface morphology of FA was examined by FE-SEM, as shown in Fig. 1 (b). The FA was characterized by smooth spherical-shaped particles with a diameter range of 0.67–14.30 μm. The composition of minerals comprising the FA was characterized using XRF as summarized in Table 2. $SiO_2$ (64.12%, w/w) was the major constituent of FA, followed by $Al_2O_3$, $Fe_2O_3$, and CaO. These 4 mineral oxides accounted for 93.73% of the total FA mass. Similarly, Park *et al*. (2021) demonstrated that FA collected from the Western TPP consisted of these 4 major mineral components, which accounted for 88.6% of the total FA mass; however, the mineral oxide compositions were significantly different, that is, $SiO_2$ (37.7%), $Fe_2O_3$ (24.5%), $Al_2O_3$ (16.7%), and CaO (9.7%). The $Al_2O_3$ content in the FA samples in both studies were approximately the same, but the $SiO_2$ content in the FA collected from the Yeongheung TPP in this study was notably higher than that for the Western TPP. The amount of total REEs in the FA in this study was lower than that for the Western TPP. Thus, it can be inferred that the REEs are not associated mainly with $SiO_2$ but are bound relatively more to other mineral parts, such as $Fe_2O_3$ and CaO. Meanwhile, the LREEs accounted for 84.02% and 89.10% of total REEs present in the FA and BA from the Yeongheung TPP, respectively, which were similar to the values reported by Park *et al*. (2021).

### *3.2 REE leaching from coal ash using the Tessier and BCR sequential extraction methods*

The leaching efficiency for REEs from FA and BA was examined using the Tessier and BCR sequential extraction methods. Figs. 2 (a) and (b) show the REE leaching rates from FA and BA, respectively. In Step 1 (exchangeable fraction), low leaching rates (approximately 2.51% or lower) from both FA and BA were observed. Tb and Tm were extracted from FA at the rates of 2.92% and 3.78%, respectively, whereas the REEs extracted from BA were insignificant (< 1%). Similar to Step 1, the carbonate-bound fraction in FA and BA found in Step 2 exhibited low REE leaching rates (approximately 3.05% or lower), indicating that the fraction of REEs loosely bound to the coal ash, which can be relatively easily recovered by changes in the aqueous solution conditions (such as pH, ionic strength, etc.), was not significant. The Fe-Mn oxide-bound fraction of REEs was extracted at higher leaching rates from both FA and BA using weak acid (acetate) in Step 3, as

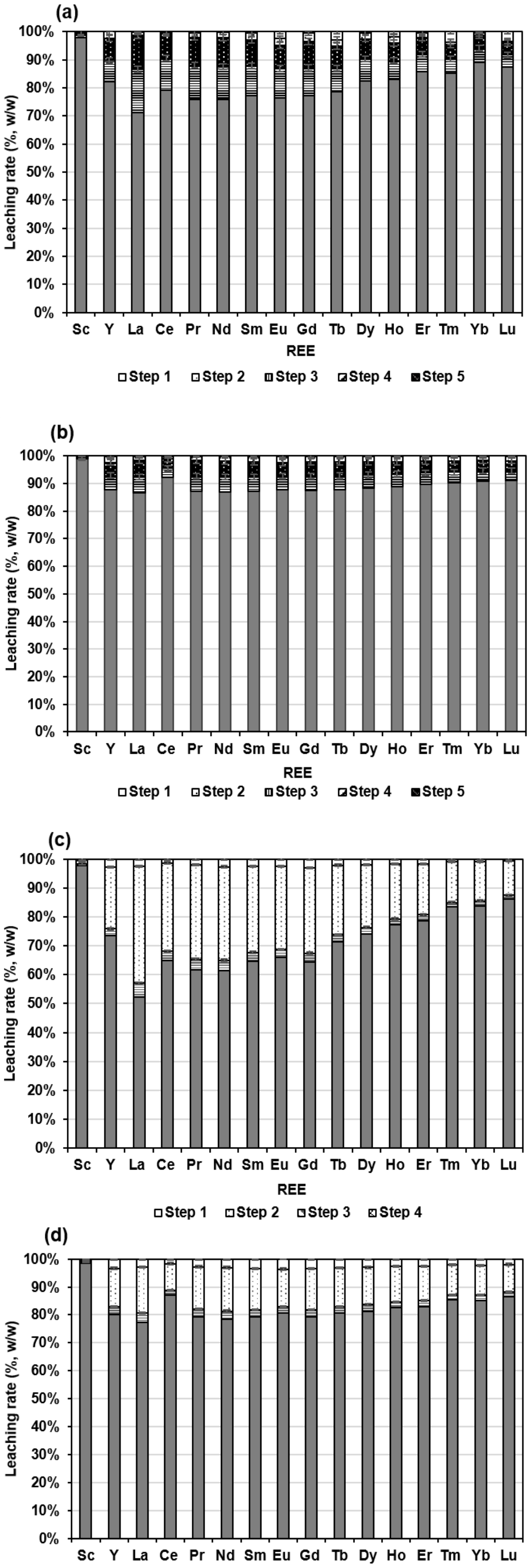

Fig. 2 REE leaching from (a) FA and (b) BA using the Tessier sequential extraction procedure and from (c) FA and (d) BA using the BCR sequential extraction procedure. Error bars denote standard deviation (*n* = 3)

compared to those obtained in Steps 1 and 2. In particular, 12.07% of La was extracted from FA, followed by Nd and Pr at 10.30% and 9.98%, respectively. The leaching rate of La from BA reached 6.08%. Note that the REEs extracted from FA (15.33% or lower) were almost twice of those extracted from BA (6.08% or lower, respectively). In Step 4, where strong chemicals were used to extract the REEs from the organic matter-bound fraction, the leaching rates of all REEs from FA were higher than those in Step 3, whereas no significant improvement was observed in the extraction of REEs from the BA in Step 4. In Step 5, the highest leaching rates (71.22% or more) were obtained from the residual fractions of FA and BA. These results also supported the idea that the majority of REEs are present in the fraction strongly associated with coal ash, and therefore, extreme conditions, such as strong chemicals and/or high temperature/pressure digestion, may be necessary to effectively recover the REEs from coal ash. Note that the REE concentrations in the extracts from FA were almost twice of that for BA.

Figs. 2 (c) and (d) show the REE leaching rates from FA and BA, respectively, using the BCR sequential extraction method. A relatively low amount of REEs (< 4%) was extracted in Steps 1 and 3, whereas a larger amount of REEs (> 10%) was extracted in Steps 2 and 4. Additionally, Y, La, Nd, Sm, and Gd were extracted from FA in Step 1with a leaching rate higher than 2.5%, which is ascribed to the exchangeable REE fraction, that is, easily releasable fraction. In contrast, Y, Nd, Sm, Eu, Gd, Tb, and Dy were extracted from BA with a leaching rate higher than 3%. Gd was extracted from FA at a maximum leaching rate of 3.06%, whereas Sm and Eu were extracted from BA at rates of 3.42% and 3.61%, respectively. In Step 2, more REEs were extracted from FA rather than from BA. Y through Dy were extracted from FA at rates higher than 20%, and La was extracted significantly. In contrast, the leaching rates from BA were 16.50% or lower. In Step 3, except for Sc, the REEs were extracted from both the FA and BA at rates of approximately 1.33% or more. Moreover, in Step 4, the residual fraction REEs were extracted at higher rates compared to those in Steps 1, 2, and 3. This indicated that most REEs are strongly associated with the components of coal ash and the REE fraction that can be easily recovered from coal ash was not significant, as also confirmed in the Tessier sequential extraction. As previously found, 10% more REEs were extracted from FA compared to those from BA in the BCR sequential extraction. This implied that more REEs are strongly bound to the components of BA relative to the case of FA, as similarly observed in the case of the Tessier extraction method. Likewise, 37.82% of LREEs were extracted from FA, while 19.74% of LREEs were extracted from BA in Step 2. In the meantime, the difference in the HREE leaching efficiencies for FA and BA was not marked; 20.73% and 16.45% of HREEs were extracted from FA and BA, respectively. CREEs were extracted from FA and BA at rates of 30.73% and 19.65%, respectively, which was similar to the case of total REEs.

As shown in Table 3, except for Sc, the REE leaching rates using the Tessier extraction method were higher for the Yeongheung TPP coal ash than those for the Western TPP coal ash, with average values of 18.50% and 12.76%,

Table 3 REE leaching from FA by the Tessier and BCR sequential extraction procedures

| REE | REE leaching rate (%, w/w) by the Tessier sequential extraction procedure | | REE leaching rate (%, w/w) by the BCR sequential extraction procedure | |
|---|---|---|---|---|
| | Yeongheung TPP | Western TPP | Yeongheung TPP | Western TPP |
| Sc | 2.25 | 3.79 | 2.17 | 5.59 |
| Y | 17.87 | 12.38 | 26.57 | 30.47 |
| La | 28.78 | 26.01 | 47.77 | 59.92 |
| Ce | 20.9 | 20.54 | 35.16 | 44.81 |
| Pr | 24.18 | 15.8 | 38.4 | 34.16 |
| Nd | 24.26 | 9.28 | 38.6 | 48.95 |
| Sm | 22.91 | 17.6 | 35.32 | 37.67 |
| Eu | 23.68 | 16.17 | 33.95 | 37.23 |
| Gd | 22.9 | 17.28 | 35.56 | 33.91 |
| Tb | 21.41 | 12.84 | 28.5 | 25.88 |
| Dy | 17.14 | 11.88 | 26.03 | 24.25 |
| Ho | 17.09 | 10.39 | 22.78 | 21.4 |
| Er | 14.21 | 9.74 | 21.25 | 20.11 |
| Tm | 14.9 | 7.4 | 16.53 | 15.59 |
| Yb | 10.86 | 7.23 | 16.12 | 15.23 |
| Lu | 12.63 | 5.78 | 13.9 | 12.45 |

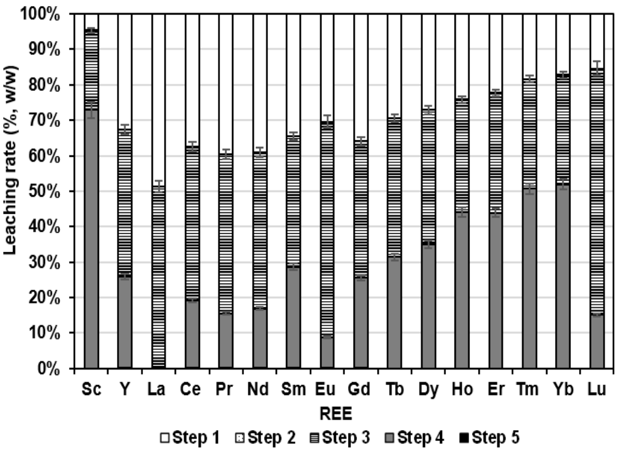

Fig. 3 REE leaching from FA using the new sequential extraction procedure. Error bars denote standard deviation (*n* = 3)

respectively. Compared with the Tessier extraction method, the overall extraction capability from the Yeongheung and Western TPP coal ash samples using the BCR extraction method was higher by 8.91% and 16.47%, respectively. The leaching rate of LREEs, except for Pr and Gd, from the coal ash of the Western TPP using the BCR extraction method was higher than those from the coal ash of the Yeongheung TPP. The average leaching rate of HREEs for the Yeongheung TPP coal ash was slightly higher than that for the Western TPP coal ash. The average leaching rate of REEs from the Yeongheung TPP coal ash was 27.41%, which was slightly lower than that for the Western TPP coal ash (29.23%). In addition, the CREE leaching rates achieved using the BCR extraction method were higher than the values obtained by the Tessier extraction method. The leaching rates of CREEs from the Western TPP coal ash using Tessier extraction method was markedly higher than those from the Yeongheung TPP coal ash. In the case of Nd, the difference in the leaching rates for the Yeongheung and Western TPP coal ash samples was as high as approximately 15%. Tb and Dy were more effectively extracted from the Yeongheung TPP coal ash by the BCR extraction method, whereas Y, Nd, and Eu exhibited leaching rates of only 3.9%, 10.35%, and 3.28%, respectively, from the Western TPP coal ash.

### *3.3 REE leaching from coal ash using the new sequential extraction procedure*

Instead of acetate used in Step 1 of the BCR extraction method, citrate was employed as an environmentally benign organic solvent in Step 1 of the new sequential extraction procedure developed in this study. Citrate has been frequently used in soil washing processes as an ecofriendly solvent for the remediation of soils contaminated with heavy metals (Gavrilescu *et al*. 2009, Ma *et al*. 2015). The REE leaching test was performed by varying the concentration of citrate (0.1–3M) and reaction time (4–24 h). As the citrate concentration increased, the REE leaching continued to increase up to 12 h, followed by a gradual leveling-off. At reaction times greater than 16 h, the leaching increased again, reaching a maximum value at 20 h. Fig. 3 shows that, the average of the leaching rates for 16 REEs was 28.56%. Except for Sc, which was resistant to be extracted, the leaching rates of 8 elements (Y, La, Ce, Pr, Nd, Sm, Eu, and Gd) were higher than 30%, and La was the most significant with a leaching rate of 48.64%. Note that the overall mass of FA was decreased by 9.05% in Step 1 (Table 2). While no change in the $SiO_2$ mass was observed, the masses of CaO, $Al_2O_3$, $Fe_2O_3$, and $P_2O_5$ decreased by 3.99, 1.78, 0.88, and 0.80g, respectively, suggesting that the REEs associated with these minerals of coal ash were released via dissociation of these minerals by citrate.

In Step 2, a strong base was employed to facilitate the leaching of REEs associated with the major mineral component of coal ash, which is $SiO_2$, in this study. Park *et al.* (2021) observed that most REEs are strongly associated with $SiO_2$ and $Al_2O_3$. KOH was found to be slightly more effective than NaOH for the dissolution of $SiO_2$ of coal ash (data not presented). Similarly, Simonsen and Søgaard (2009) reported that KOH can dissolve $SiO_2$ more efficiently than NaOH. The overall mass of FA was decreased by 37.59% in this step (Table 2). The mass of $SiO_2$ was decreased by 35.72%, which accounted for 95% of the overall coal ash mass reduction in this step. However, the REEs extracted in this step were almost negligible, indicating that the REEs are not mainly associated with $SiO_2$. Other metal oxides, such as $Al_2O_3$ and $Fe_2O_3$, were not dissociated in this step, suggesting that the REEs are more likely bound to these mineral oxides of coal ash, as proposed by Park *et al*. (2021).

In Step 3, microwave-assisted thermal digestion was employed to stimulate the dissociation of the remaining $SiO_2$, $Al_2O_3$, and $Fe_2O_3$. A large amount of REEs was

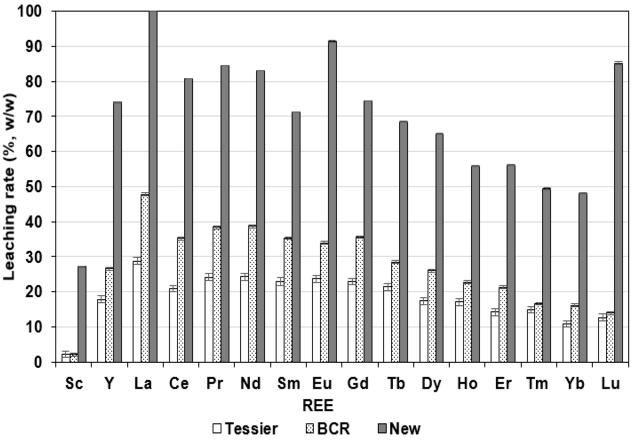

Fig. 4 Comparison of REE leaching by the Tessier, BCR, and new sequential extraction procedures. Error bars denote standard deviation (*n* = 3)

extracted in this step, reaching an average leaching rate of 41.07%. The leaching rates of La and Eu were 51.36% and 60.83%, respectively. However, Sc and Lu, which are difficult to be extracted in the Tessier and BCR extraction methods, also exhibited high leaching rates of 22.47% and 69.52%, respectively. $SiO_2$ and $Fe_2O_3$ were almost completely dissolved by microwave-assisted thermal digestion (Table 2). The $Al_2O_3$ content did not change while the overall mass decreased by 25.12% in this step. It was previously confirmed that REEs are not associated with $SiO_2$, and therefore, REEs leached in this step were presumably ascribed to the dissociation of $Fe_2O_3$ and the residual CaO (5.84% and 0.76% reduction in $Fe_2O_3$ and CaO masses, respectively). La was completely extracted, followed by Eu and Lu, reaching leaching rates of 91.24% and 84.91%, respectively, with an overall REE leaching rate of 69.63%.

In Step 4, the remaining $Al_2O_3$ and $P_2O_5$ were completely dissolved, and as a result, 30.36% of REEs were extracted. LREEs and HREEs accounted for 16.39% and 38.90%, respectively, since most LREEs were already extracted in the previous steps. The CREEs, such as Dy and Tb, were extracted by 34.97% and 31.50%, respectively, indicating that the leaching of these elements was slightly lower than those of other CREEs in the previous steps.

In Step 5, the amount of REEs remaining in the leaching aqueous solutions used in the sequential extraction procedure (e.g., acidic and basic wastewaters) was found to be insignificant. The average leaching rates of 16 REEs varied from 0.7 to 1.2%. This supports the REE leaching effectiveness of the new sequential extraction method developed in this study.

Fig. 4 shows the comparison of the extraction efficiencies analyzed with the 3 sequential extraction procedures. The leaching rates for the REEs excluding residual fractions (Step 5 of the Tessier and Step 4 of the BCE extraction methods), which can be readily obtained by chemical extraction, were only 18.52% and 27.41% of the total REEs present in FA, respectively. Moreover, the average leaching rates for the LREEs, HREEs, and CREEs in the case of the Steps 1–4 of the Tessier extraction method were 23.95%, 15.50%, and 20.93%, respectively, and 37.82%, 20.73%, and 30.73%, respectively, in the case of the Steps 1–3 of the BCR extraction method. The BCR extraction method exhibited higher leaching rates compared to the Tessier extraction method. In particular, the LREE extraction by the BCR extraction method was even 58% higher than the value obtained by the Tessier extraction method. The new sequential extraction procedure exhibited a significant improvement (69.63%) in REE leaching in the Steps 1–3, which is equivalent to 2.54 to 3.76-fold increases in extraction efficiency in comparison with the values obtained by the BCR and Tessier extraction methods, respectively. The HREE leaching rate (61.10%) obtained by the new extraction procedure was 2.95 times higher than that obtained by the BCR extraction method. The LREE leaching was improved far more substantially, with the leaching rate reaching 83.61%. In addition, the CREE leaching (76.37%) was 2.48 times higher than that achieved by the BCR extraction method, and the leaching rates of Y and Eu were increased significantly, that is, 2.79 and 2.69 times higher, respectively, than the average leaching rates for other CREEs. Although the extraction of Sc and Lu using the Tessier and BCR extraction methods was negligible, their leaching rates were increased markedly to 27.13% and 84.91%, respectively, when the new extraction procedure was employed. Note that it is highly desirable to achieve a significant improvement in the recovery of Sc, which is an extremely valuable CREE in the relevant industry.

### 3.4 Composition and structural changes in coal ash in the new sequential extraction procedure

The mass changes in FA components during each step of the new sequential extraction procedure are summarized in Table 2, including the four major oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$, and CaO) and minor constituents ($TiO_2$, $P_2O_5$, $K_2O$, MgO, $Na_2O$, and $SO_3$). Citrate did not strongly affect the composition of FA in Step 1. The mass fractions of $SiO_2$, $Fe_2O_3$, and $Al_2O_3$, which are the main components of FA, were not notably altered by citrate. As discussed earlier, only a small amount of REEs was extracted in this step, even if citrate was found to be more effective than acetate used in the Tessier and BCR extraction methods. On the contrary, after citrate treatment, CaO was removed significantly, indicating that the REEs recovered in Step 1 were bound to CaO. A notable amount of the $SiO_2$ remaining in the coal ash residue was removed by KOH in Step 2, whereas the other oxides (e.g., CaO, $Al_2O_3$, and $Fe_2O_3$,) were not dissociated. A small amount of REEs was extracted during this process, suggesting that the REEs were not bound to $SiO_2$ but to other components of coal ash. It was also observed in Step 3 that $Al_2O_3$ was not removed by KOH even by microwave-assisted thermal digestion, while the $Fe_2O_3$ was almost dissolved. The REE extraction rate was increased, indicating that the REEs recovered in this step were bound to $Fe_2O_3$. The slight increases in $P_2O_5$ and $SO_3$ were not released from coal ash because their increases were attributed to the addition of $H_2SO_4$ and $H_3PO_4$ during the microwave-assisted thermal digestion.

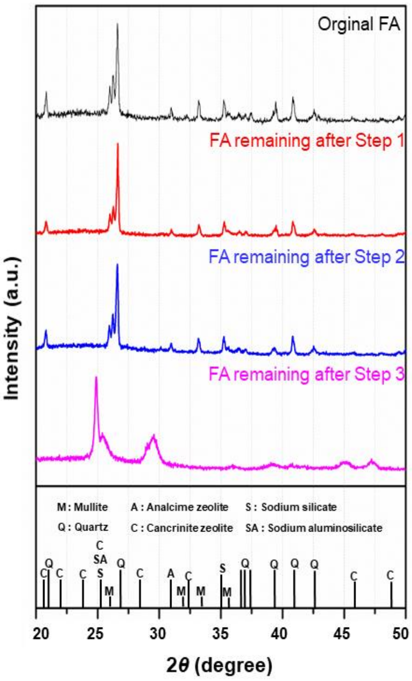

Fig. 5 XRD analysis of FA

$Al_2O_3$, a major component of FA, remained unchanged even after all other coal ash components were removed, resulting in residual REEs, which can be considered as a strongly bound and unextractable fraction of REEs in coal ash.

Fig. 5 shows the mineral composition and structure changes in FA components during each step of the new sequential extraction procedure. The original coal ash was mainly composed of quartz (JCPDS #5-490) and mullite (JCPDS #15-776) along with various minor constituents, including cancrinite and analcime zeolites. After the citrate treatment in Step 1, the various minor component peaks became insignificant but the major components remained, because these minor constituents can be dissolved by weak acids such as acetate or citrate (Sholkovitz *et al.* 1994). There were no significant effects on the coal ash structure. Following the KOH treatment in Step 2, the characteristic diffraction pattern was similar to that of the coal ash remaining in Step 1. This change was attributed to the surface structure changes, including increased porosity (Han *et al.* 2019). However, citrate and KOH did not strongly affect the coal ash crystal structure. After the microwave-assisted thermal digestion, the diffraction pattern of the coal ash remaining in Step 3 indicated significant changes in its structure. New crystal phases were observed at 24.88° and 29.25°, corresponding to cancrinite zeolite, sodium silicate, and sodium aluminosilicate, respectively, indicating zeolite formation in FA after the thermal digestion. This supported an idea that valuable materials such as zeolites for environmental applications as chemical and biochemical catalysts can be recovered during the new sequential extraction procedure from coal ash in addition to the REE recovery as demonstrated in a number of previous studies (Lim *et al.* 2019, Park *et al.* 2021, Rodwihok *et al.* 2021, Tran *et al.* 2019, Wen *et al.* 2018).

## 4. Conclusions

In this study, REEs present in coal ash collected from a coal-fired TPP in Korea were quantified, and their extractabilities were examined using the conventional Tessier and BCR sequential extraction methods, which are used in geomaterial-associated metal analysis. Additionally, a new sequential extraction procedure was developed to improve the leaching efficiency of REEs from coal ash using an environmentally benign solvent and microwave-assisted thermal digestion. It was found that 112.5 and 123.21 mg/kg of REEs are present in the FA and BA of the Yeongheung TPP, respectively. The REE leaching efficiency and patterns using the conventional sequential extraction methods were similar to those previously reported for the Western TPP coal ash. Y and Nd were the CREEs most notably extracted from FA. The leaching efficiency of REEs from coal ash was enhanced markedly by the new sequential extraction procedure. The overall extraction rate of REEs reached 70%, which was 2.54 and 3.76 times higher than the values achieved by the BCR and Tessier extraction methods, respectively. The REEs weakly bound to FA were recovered effectively using citrate. It was confirmed that the large portion of REEs is primarily associated with CaO, Al2O3, Fe2O3, and P2O5, not with SiO2 of the coal ash, and these REEs can be extracted effectively in a stepwise manner. The results of this study contribute to the development of a simple, effective, and ecofriendly procedure for the REE recovery from coal ash and leaching wastewaters.

## Acknowledgments

This work was financially supported by the Korean National Research Foundation (2022R1I1A1A01056866) and the Konkuk University Research Fund in 2020.

## References

Alonso, E., Sherman, A.M., Wallington, T.J., Everson, M.P., Field, F.R., Roth, R. and Kirchain, R.E. (2012), “Evaluating rare earth element availability: A case with revolutionary demand from clean technologies”, *Environ. Sci. Technol.*, **46**, 3406- 3414. https://doi.org/10.1021/es203518d.

Baba, A. and Usmen, M.A. (2006), “Effects of fly ash from coal-burning electrical utilities on ecosystem and utilization of fly ash”, *Groundwater Ecosyst.* Springer Netherlands, Dordrecht, 15-31. https://doi.org/10.1007/1-4020-4738-X_2.

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. https://doi.org/10.1016/j.hydromet.2021.105575.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A. and Buchert, M. (2013), “Recycling of rare earths: A critical review”, *J. Clean. Prod.*, **51**, 1-22. https://doi.org/10.1016/j.jclepro.2012.12.037.

Binnemans, K., Jones, P.T., Müller, T. and Yurramendi, L. (2018), “Rare earths and the balance problem: How to deal with changing markets?” *J. Sust. Metall.*, **4**, 126–146. https://doi.org/10.1007/s40831-018-0162-8.

Bordas, F. and Bourg, A.C.M. (1998), "A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load", *Water, Air Soil Pollut*., **103**, 137-149. https://doi.org/10.1023/A:1004952608950.

Cho, H., Maeng, J.H. and Kim, E. (2017), "Studies on expanding application for the recycling of coal ash in domestic", *J. Environ. Impact Assess*., **26**, 563-573. https://doi.org/10.14249/eia.2017.26.6.563.

Chu, S. (2011), "*Critical materials strategy*", DIANE publishing.

Franus, W., Wiatros-Motyka, M.M. and Wdowin, M. (2015), "Coal fly ash as a resource for rare earth elements", *Environ. Sci. Pollut. Res*., **22**, 9464-9474. https://doi.org/10.1007/s11356-015-4111-9.

Gavrilescu, M., Pavel, L.V. and Cretescu, I. (2009), "Characterization and remediation of soils contaminated with uranium", *J. Hazard. Mater*., **163**, 475-510. https://doi.org/10.1016/j.jhazmat.2008.07.103.

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). https://doi.org/10.3390/met8090721.

Han, L., Ren, W., Wang, B., He, X., Ma, L., Huo, Q., Wang, J., Bao, W. and Chang, L. (2019), "Extraction of SiO2 and Al2O3 from coal gangue activated by supercritical water", *Fuel*, **253**, 1184-1192. https://doi.org/10.1016/j.fuel.2019.05.118.

Hower, J.C., Evan J. Granite, Mayfield, D.B., Lewis, A.S. and Finkelman, R.B. (2016), "Notes on contributions to the science of rare earth element enrichment in coal and coal combustion byproducts", *Minerals*, **6**(2). https://doi.org/10.3390/min6020032.

Hower, J.C., Groppo, J.G., Graham, U.M., Ward, C.R., Kostova, I.J., Maroto-Valer, M.M. and Dai, S. (2017), "Coal-derived unburned carbons in fly ash: A review", *Int. J. Coal Geol*., **179**, 11-27. https://doi.org/10.1016/j.coal.2017.05.007.

Jayaranjan, M.L.D., van Hullebusch, E.D. and Annachhatre, A.P. (2014), "Reuse options for coal fired power plant bottom ash and fly ash", *Rev. Environ. Sci. Bio/Technol*., **13**, 467-486. https://doi.org/10.1007/s11157-014-9336-4.

Joshi, P.B., Preda, D.V., Skyler, D.A., Scherer, A., Green, B.D. and Marinelli, W.J. (2016), "Recovery of rare earth elements and compounds from coal ash", U.S. Patent No. 9,394,586, U.S. Patent and Trademark Office, Washington, DC, U.S.A.

Keshavarz, F., Kavun, V., van der Veen, M.A., Repo, E. and Barbiellini, B. (2022), "Molecular-level understanding of highly selective heavy rare earth element uptake by organophosphorus modified MIL-101(Cr)", *Chem. Eng. J*., **440**, 135905. https://doi.org/https://doi.org/10.1016/j.cej.2022.135905.

Kim, H., Purev, O., Myung, E., Cho, K. and Choi, N. (2023), "Characteristic of alumina-based microfiltration ceramic membrane", *Membr. Water Treat*., **14**(1), 11. https://doi.org/10.12989/mwt.2023.14.1.011.

Li, F.K., Gong, A.J., Qiu, L.N., Zhang, W.W., Li, J.R., Liu, Y., Li, J.D., Gao, G. and Yuan, X.T. (2019), "Determination of trace rare earth elements in fruits by microwave digestion coupled with inductively coupled plasma optical emission spectrometry", *Microchem. J*., **147**, 93-101. https://doi.org/10.1016/j.microc.2019.02.060.

Lim, J.M., Park, J., Park, J.T. and Bae, S. (2019), "Preparation of quasi-solid-state electrolytes using a coal fly ash derived zeolite-X and -A for dye-sensitized solar cells", *J. Ind. Eng. Chem*., **71**, 378-386. https://doi.org/10.1016/j.jiec.2018.11.049.

Lim, H., Park, S., Yang, J.W., Cho, W., Lim, Y., Park, Y.G., Kwon, D. and Kim, H.S. (2018), "Remediation of heavy metal-contaminated soils using eco-friendly nano-scale chelators", *Membr. Water Treat*., **9**(3), 137-146. https://doi.org/10.12989/mwt.2018.9.3.137.

Ma, F., Peng, C., Hou, D., Wu, B., Zhang, Q., Li, F. and Gu, Q. (2015), "Citric acid facilitated thermal treatment: An innovative method for the remediation of mercury contaminated soil", *J. Hazard. Mater*., **300**, 546-552. https://doi.org/10.1016/j.jhazmat.2015.07.055.

Maeng, J.H., Kim, T.Y. and Suh, D.H. (2014), "Minimizing environmental impact in accordance with the thermal power plant ash management (I)", *Korea Environ. Inst*., **24**(5), 472-486.

Marguí, E., Salvadó, V., Queralt, I. and Hidalgo, M. (2004), "Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes", *Analytica Chimica Acta*, **524**, 151-159. https://doi.org/10.1016/j.aca.2004.05.043.

Mutlu, B.K., Cantoni, B., Turolla, A., Antonelli, M., Hsu-Kim, H. and Wiesner, M.R. (2018), "Application of nanofiltration for rare earth elements recovery from coal fly ash leachate: Performance and cost evaluation", *Chem. Eng. J*., **349**, 309-317. https://doi.org/https://doi.org/10.1016/j.cej.2018.05.080.

Park, S., Kim, M., Lim, Y., Yu, J., Chen, S., Woo, S.W., Yoon, S., Bae, S. and Kim, H.S. (2021), "Characterization of rare earth elements present in coal ash by sequential extraction", *J. Hazard. Mater*., **402**, 123760. https://doi.org/10.1016/j.jhazmat.2020.123760.

Petit, M.D. and Rucandio, M.I. (1999), "Sequential extractions for determination of cadmium distribution in coal fly ash, soil and sediment samples", *Analytica Chimica Acta*, **401**, 283-291. https://doi.org/10.1016/S0003-2670(99)00487-0.

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. Sust. Metall*., **7**, 1241-1253. https://doi.org/10.1007/s40831-021-00414-7.

Pueyo, M., Mateu, J., Rigol, A., Vidal, M., López-Sánchez, J.F. and Rauret, G. (2008), "Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils", *Environ. Pollut*., **152**, 330-341. https://doi.org/10.1016/j.envpol.2007.06.020.

Quevauviller, P., Rauret, G., Muntau, H., Ure, A.M., Rubio, R., López-Sánchez, J.F., Fiedler, H.D. and Griepink, B. (1994), "Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments", *Fresenius' J. Anal. Chem*., **349**, 808-814. https://doi.org/10.1007/BF00323110.

Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, P. (1999), "Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials", *J. Environ. Monit*., **1**(1), 57-61. https://doi.org/10.1039/A807854H.

Resende, L.V. and Morais, C.A. (2010), "Study of the recovery of rare earth elements from computer monitor scraps - Leaching experiments", *Minerals Eng*., **23**(3), 277-280. https://doi.org/10.1016/j.mineng.2009.12.012.

Rodwihok, C., Suwannakeaw, M., Charoensri, K., Wongratanaphisan, D., Woo, S. and Kim, H.S. (2021), "Alkali/zinc-activated fly ash nanocomposites for dye removal and antibacterial applications", *Bioresour. Technol*., **331**, 125060. https://doi.org/10.1016/j.biortech.2021.125060.

Rodwihok, C., Suwannakaew, M., Han, S.W., Chen, S., Wongratanaphisan, D. and Kim, H.S. (2023), "Selective removal of cationic dye pollutants using coal ash-derived zeolite/zinc adsorbents", *Membr. Water Treat*., **14**(3), 121-128. https://doi.org/10.12989/mwt.2023.14.3.121.

Rollat, A., Guyonnet, D., Planchon, M. and Tuduri, J. (2016), "Prospective analysis of the flows of certain rare earths in Europe at the 2020 horizon", *Waste Manag*., **49**, 427-436. https://doi.org/10.1016/j.wasman.2016.01.011.

Shan, X., Lian, J. and Wen, B. (2002), “Effect of organic acids on adsorption and desorption of rare earth elements”, *Chemosphere*, **47**(7), 701-710. https://doi.org/10.1016/S0045-6535(02)00032-2.

Sholkovitz, E.R., Landing, W.M. and Lewis, B.L. (1994), “Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater”, *Geochimica et Cosmochimica Acta*, **58**(6), 1567-1579. https://doi.org/10.1016/0016-7037(94)90559-2.

Simonsen, M.E. and Søgaard, E.G. (2009), “ESI-MS investigation of the polymerization of inorganic polymers”, *Int. J. Mass Spectr.*, **285**(1-2), 78-85. https://doi.org/10.1016/j.ijms.2009.04.010.

Suh, D.H. and Maeng, J.H. (2015), “A study on expanding the recycling of coal ash for minimizing environmental impact imposed by the establishment of thermal power plant ash ponds”, *J. Environ. Impact Assess.*, **24**(5), 472-486. https://doi.org/10.14249/eia.2015.24.5.472.

Taggart, R.K., Hower, J.C., Dwyer, G.S. and Hsu-Kim, H. (2016), “Trends in the rare earth element eontent of U.S.-based coal combustion fly ashes”, *Environ. Sci. Technol.*, **50**(11), 5919-5926. https://doi.org/10.1021/acs.est.6b00085.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979), “Sequential extraction procedure for the speciation of particulate trace metals”, *Anal. Chem.*, **51**(7), 844-851. https://doi.org/10.1021/ac50043a017.

Tran, Y.T., Lee, J., Kumar, P., Kim, K.H. and Lee, S.S. (2019), “Natural zeolite and its application in concrete composite production”, *Compos. Part B Eng.*, **165**, 354-364. https://doi.org/10.1016/j.compositesb.2018.12.084.

Um, N. and Jeon, T.W. (2021), “Pretreatment method for the utilization of the coal ash landfilled in ash ponds”, *Proc. Safe. Environ. Protect.*, **153**, 192-204. https://doi.org/10.1016/j.psep.2021.07.013.

Wamea, P., Pitcher, M.L., Muthami, J. and Sheikhi, A. (2022), “Nanoengineering cellulose for the selective removal of neodymium: Towards sustainable rare earth element recovery”, *Chem. Eng. J.*, **428**, 131086. https://doi.org/https://doi.org/10.1016/j.cej.2021.131086.

Wang, S., Boyjoo, Y., Choueib, A. and Zhu, Z.H. (2005), “Removal of dyes from aqueous solution using fly ash and red mud”, *Water Res.*, **39**(1), 129-138. https://doi.org/10.1016/j.watres.2004.09.011.

Weber, R.J. and David J. Reisman, (2012), “Rare earth elements: A review of production, processing, recycling, and associated environmental issues”, *US EPA Region*, **8**, 189-200.

Wen, J., Dong, H. and Zeng, G. (2018), “Application of zeolite in removing salinity/sodicity from wastewater: A review of mechanisms, challenges and opportunities”, *J. Clean. Prod.*, **197**, 1435-1446. https://doi.org/10.1016/j.jclepro.2018.06.270.

Wu, S., Wang, L., Zhao, L., Zhang, P., El-Shall, H., Moudgil, B., Huang, X. and Zhang, L. (2018), “Recovery of rare earth elements from phosphate rock by hydrometallurgical processes– A critical review”, *Chem. Eng. J.*, **335**, 774-800. https://doi.org/https://doi.org/10.1016/j.cej.2017.10.143.

Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S. and Xi, Y.Q. (2015), “A comprehensive review on the applications of coal fly ash”, *Earth Sci. Rev.*, **141**, 105-121. https://doi.org/10.1016/j.earscirev.2014.11.016.