



Investigation of rare earth elements from coal and coal byproducts

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Abstract. Rare earth elements (REE) are considered critical raw materials essential for numerous clean technologies. As the discrepancy, their supply and demand increase globally. It is conceivable to recover REEs from secondary sources in order to close the gap. The coal, fly ash, and bottom ashes are collected from Baganuur Mining, Thermal Power Plant IV, and Baganuur Thermal Plant, respectively. The TESCAN Integrated Mineral Analyzer (TIMA) and X-ray diffractometer (XRD) were used to characterize the mineralogy of coal, fly ash, and bottom ashes and further investigation of REE associations and its mineral. It was demonstrated that rare earth minerals still exist in coal fly ash and are associated with metal oxides. The quantity of REEs in the coal sample was determined by using the inductively coupled plasm-mass spectrometry (ICP-MS) technique. The quantitative analysis result shows that the total REEs content in the coal ash was 414 parts per million (ppm). It was revealed that REEs are concentrated in fine non-magnetic particle size, and the froth flotation process is most effective at a pH=10. Using the physical separation method, the REEs in the coal fly ash was slightly enriched from 414 to 456.44 ppm. Thus, hydrometallurgical leaching is advised to evaluate the possibility of REEs recovery from secondary sources.

Keywords: Rare Earth Elements, Secondary resource, Fly ash, Coal combustion by-products

1 Introduction

Several international agencies and national governments have designated rare earth elements (REEs), which encompass the 15 lanthanides alongside yttrium and scandium, as vital commodities. This recognition stems from their indispensable contributions to clean energy, high technology, and national defense sectors [1]. Due to the uneven distribution of rare earth resources among a small number of countries, the supply of these resources is affected by economic conditions and political circumstances [2].

As the global need for energy continues to rise, coal is being viewed as a dependable and stable energy resource. As a result, the production of coal fly ash worldwide is growing, creating an urgent requirement for its recycling and utilization [3]. The primary difficulties in recovering rare earth elements from coal and coal byproducts revolve around the substantial amount of material that needs to be processed in order to extract the REEs [4]. In recent years, there has been significant research conducted on the extraction of rare earth elements (REEs) from various coal-related materials. These materials include coal itself, coal waste, coal combustion ash, and acid coal mine drainage [5,6]. Various techniques, including size fractionation, density separation, magnetic separation, and froth flotation, have been employed to concentrate rare earth elements (REEs) from coal, coal refuse, and coal combustion ash [7–11]. By implementing size fractionation and magnetic separation techniques, the concentration of rare earth elements in a fly ash sample increased from 782 mg/kg to 1025mg/kg [8].

As a result, the utilization of physical methods proves to be successful in pre-concentrating REEs, allowing for the production of a higher-grade feedstock. This higher-grade feedstock is then utilized in subsequent recovery and purification processes. Hydrometallurgical techniques, including leaching methods using salt, roasting additives, acid, and alkaline solution, have been utilized to extract REEs from materials associated with coal fly ash [12–17].

This study represents one of the initial investigations into the utilization of physical beneficiation methods for estimating REEs from coal fly ash. It also highlights the significance of experimental conditions in order to maximize the recovery of REEs.

2 Materials and Methods

The coal fly ash was collected from the hopper of the electrostatic precipitators at Thermal Power Plant IV. The coal, and bottom ashes are collected from Baganuur Mining, and Baganuur Thermal Plant, respectively. A total of 1 kg of the fly ash sample was utilized for particle size separation using a standard sample screen. The sample was divided into five different fractions based on their size ranges: 150 μm , 106 μm , 78 μm , 38 μm , and 20 μm . After the separation, each component was carefully screened, weighed, and placed in individual bags. In addition, the original fly ash sample underwent magnetic separation at two different interests, namely 0.5 Tesla and 0.16 Tesla. Gravity separation was accomplished using a shaking table and a Knelson concentrator. The single-stage flotation tests on fly ash were conducted using a D12 flotation machine provided by METSO. The tests were carried out at various pulp pH levels ranging from 12 to 8. The impeller speed was adjusted between 659 and 800 rpm, while the air flow rate varied from 0.1m³/h to 0.3m³/h. In order to aid the flotation process, specific reagents were utilized: Sodium Oleate (C₁₈H₃₃NaO₂) as a collector reagent at a dosage of 1000 g/t, Sodium silicate as a depressant at a dosage of 500g/t MIBC 50g/t a frother, hydrochloric acid to regulate the pH levels. X-ray fluorescence (XRF) analysis was employed to measure the concentration of major element oxides present in the coal ashes. Furthermore, the mineral composition was examined using x-ray diffraction (XRD) D8 Advance, Bruker. The TESCAN Integrated Mineral Analyzer (TIMA) was

used alongside an energy-dispersive spectrometer (SEM-EDS) to examine morphology and microstructure that contain REEs. The level of various elements was determined using a technique called Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

3 Results and Discussion

The minerals in the coal fly ash sample were detected and measured using X-ray diffraction (XRD) by the Rietveld method. The primary components in the samples were determined to be microcline (61.92%), quartz (13.83%), and mullite (12.74%) as listed in Table 2. These minerals are primarily formed through the heating of clay minerals (specifically, kaolinite and illite) found in coal at varying temperatures during the combustion process.

Table 1. Main chemical components coal ashes (in wt%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	K ₂ O	MgO	Na ₂ O	SO ₃	P ₂ O ₅
BN	28.0	11.02	46.04	6.36	0.37	0.99	1.58	0.47	3.9	0.05
*	5								7	
BA	58.3	18.84	10.52	5.70	0.60	2.26	1.20	0.27	1.2	0.11
*	3								2	
FA*	49.3	16.61	8.43	17.2	0.54	1.32	3.28	0.51	1.3	0.08
	9			2					5	

*BN (Baganuur coal), BA (Bottom ash), FA (fly ash)

A minor amount of siderite, magnetite, hematite, and periclase was also present in the sample, as indicated in Table 2. These findings were supported by the results obtained from XRF analysis as listed in Table 1. The predominant components of the sample were silica and aluminum oxides, which accounted for approximately 66 % of the sample. Despite the relatively high iron oxide content (8.5%), some of the iron-bearing minerals were trapped in the amorphous phase. The calcium content in the fly ash is likely combined with various minerals to form calcium-bearing minerals phases, such as anhydride and lime, which have been previously reported as carriers of REEs.

	Quartz	Siderite	Magnetite	Microcline	Hematite	Kaolinite	Mullite	Periclase
FA	13.83	2.53	2.27	61.91	3.59	0	12.74	2.93
B								
A	43.70	0	0.76	21.56	10.79	0	9.24	0
B								
N	36.06	0.61	0	17.98	0	15.66	0	0

Table 2. Phase composition sample (wt.%), quantified by XRD analysis

The elemental composition of coal ashes was analyzed using ICP-OES, as outlined in Table 3. The analysis revealed that the sample contained 416 ($\mu\text{g} \cdot \text{g}^{-1}$) of REE. To assess the market value and potential of REE-bearing ores, the outlook coefficient (C_{outl}) was employed. C_{outl} represents the ratio of critical REE (Nd, Eu, Tb, Dy, and Er) to excessive (Ce, Ho, Tm, Yb and Lu). A higher C_{outl} which indicates greater profitability of the resources was determined to be 0.35 [18]. This significant C_{outl} value, coupled with the absence of mining costs associated with coal fly ash, suggests that recovery of REE from coal ashes could potentially be economically feasible.

Table 3. REEs elements in coal ashes ($\mu\text{g} \cdot \text{g}^{-1}$)

	BN	BA	FA
La	37.34	35.08	85.16
Ce	73.32	80.23	162.1
Pr	5.06	8.1	14.39
Nd	25.46	32.12	52.44
Sm	3.74	6.92	8.8
Eu	1	1	1.53
Gd	2	2.16	13.55
Tb	3.84	2	2
Dy	12.1	7.55	10.74
Er	3.26	2.87	4.51
Tm	15.23	4.03	2.95
Yb	24.24	31.13	50.32
Lu	6.94	2.5	2.31
Y	7.14	4.75	5.9
Total	220.67	220.44	416.7

To investigate the distribution of REEs in different size fractions, a wet sieve analysis was performed. The size fractions examined 150 μm , 106 μm , 75 μm , 38 μm and 20 μm . The figure 1 illustrates the concentration, distribution, and mass yield of REEs in each particle size fraction. The findings demonstrated that the as the particle size decreased, the REEs content increased from 312 to 449 $\mu\text{g} \cdot \text{g}^{-1}$, with the highest concentration observed in the below 20 μm .

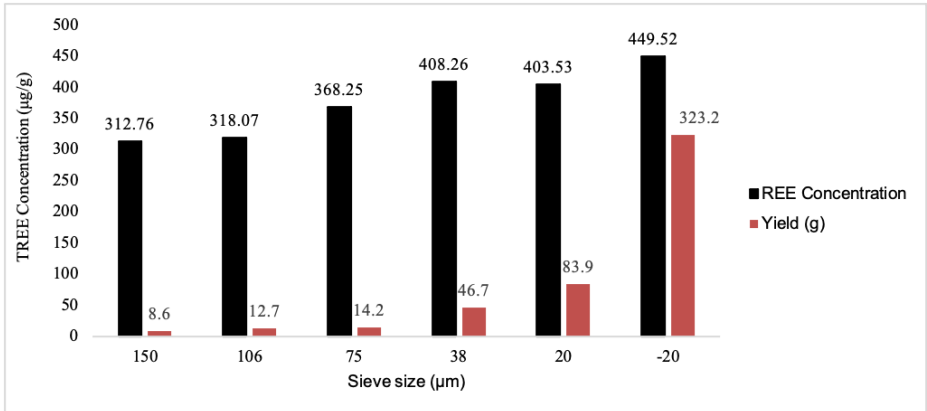


Fig. 1. Total REE content and mass yield in particle size fraction

In Figure 2, it is evident that the prominent REEs like Ce, La, Nd, and Y exhibit higher concentrations in the non-magnetic fractions. Conversely, Sm demonstrates a higher concentration in the weak-magnetic fractions due to its elevated magnetic susceptibility.

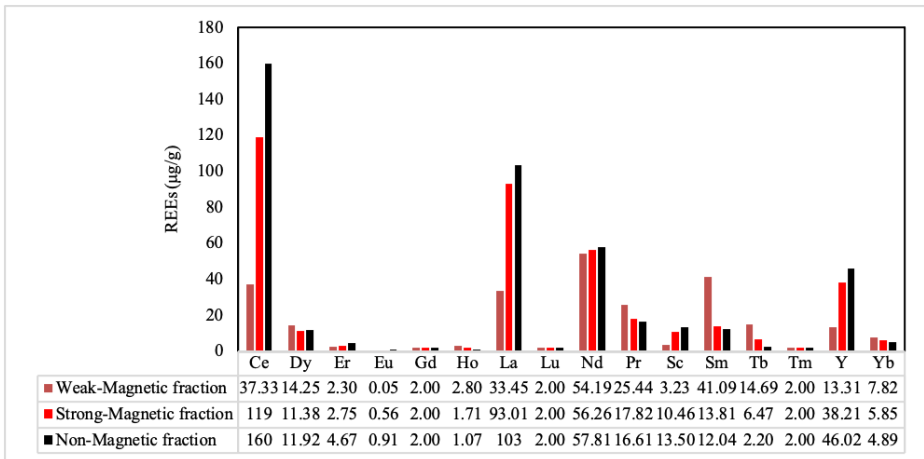


Fig. 2. REE content and different magnetic fractions

Figure 3 depicts the findings indicating that lowering the pulp pH from 12 to 8 led to a substantial decline in the recovery of REEs, from 72 % to 13 %, accompanied by an increase in REE grade from 360 to 456 $\mu\text{g} \cdot \text{g}^{-1}$. These results suggest that the extraction and enrichment of REEs from coal fly ash are influenced by the pH of the pulp.

The highest REE recovery was observed at a pulp pH of 12, whereas the best REE grade was achieved at a pulp pH of 10.

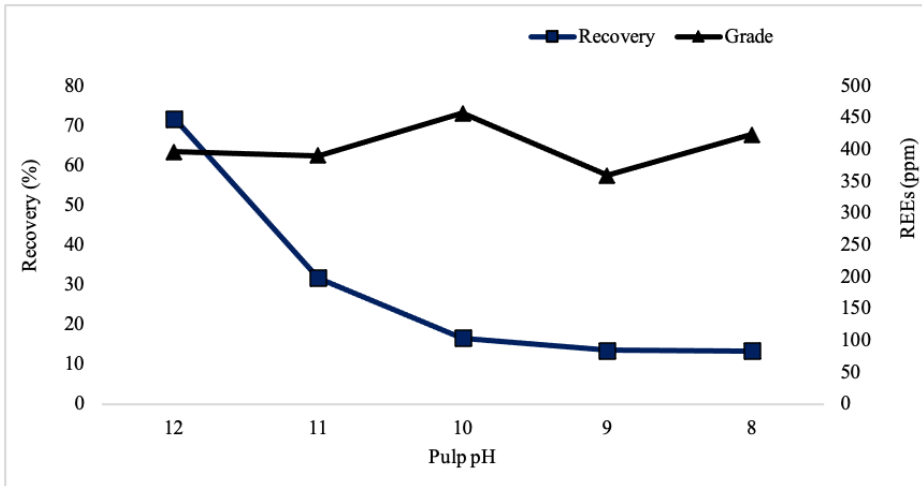


Fig. 3. Froth flotation grade and recovery with a different pH

4 Conclusion

This study has emphasized the potential of coal-fired power plant by-products, especially coal fly ash, as valuable secondary sources of REEs. These by-products possess substantial reserves that can be explored and beneficiated in the future. The elemental analysis of coal fly ash demonstrated a total concentration of $416.7 \mu\text{g} \cdot \text{g}^{-1}$ for REEs. The majority of the REEs were found to be concentrated in the fraction $449 \mu\text{g} \cdot \text{g}^{-1}$ below $20 \mu\text{m}$. The experiment conducted on magnetic separation revealed that as the magnetic intensity increased, the concentration of REEs also increased. However, this was accompanied by lower recovery rates. It was observed that the majority of the REEs were concentrated in the non-magnetic fraction. Sodium oleate flotation generated a concentrate with a slightly higher grade of REEs compared to the tailings. The pulp's pH influenced the recovery and upgrading of REEs, with pH=12 yielding the highest recovery and pH=10 leading to the slightly higher grade of REEs. When magnetic and flotation processes were combined, a slightly higher REEs grade was achieved at pH=10. In summary, Further research will focus on exploring hydrometallurgical techniques for REE extraction and processing from coal fly ash.

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