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Fly ash characterisation for rare earth elements (REEs) beneficiation in Türkiye

Türkiye'deki uçucu küllerden nadir toprak elementlerinin (NTE) zenginleştirilmesi için karakterizasyonu

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Fly Ash Characterization for Rare Earth Elements (REEs) Beneficiation in Türkiye

Highlights

- *Türkiye's fly ashes as a secondary source for REE recovery was determined.*
- *Characterization analyses of six different fly ashes were carried out.*
- *For the recovery, the biological leaching approach appears to be crucial.*

Graphical Abstract

Information on REE reserves worldwide has been provided. The enrichment of REEs in fly ash as a secondary source has been investigated.

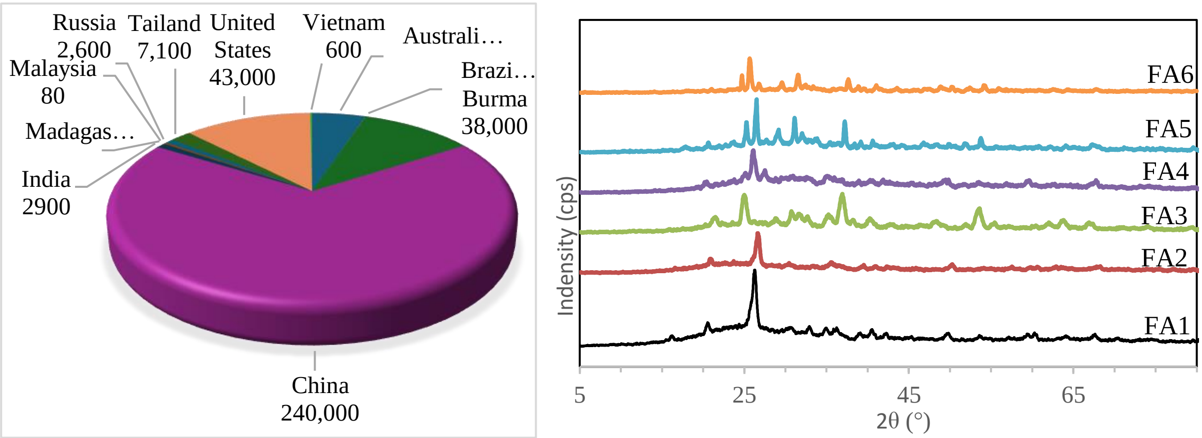

Figure 1. Worldwide production of rare earth elements in 2023 and XRD patterns for fly ash samples

Aim

In this study, the enrichment of REEs in fly ash as a secondary resource was investigated. Coal fly ash waste from several Turkish power plants was utilized in this research. Initially, the physical, chemical, mineralogical, and morphological properties of the fly ash samples were analysed. Subsequently the, concentrations of REEs within the fly ash were determined, providing insights into their potential as a valuable secondary source of these critical elements.

Design & Methodology

In this context, fly ash from Türkiye is concluded to have significant potential for REE recovery, and this method can contribute to the sustainable use of existing resources. This study also validates its findings by comparing them with literature.

Originality

Rare earth elements (REEs) are of strategic importance and present a significant challenge for countries lacking primary sources. This study will contribute to the efforts to find solutions to the resource shortages in our country.

Findings

The enrichment potential of REEs in two selected fly ashes was examined. Total REE values were found to be 168.9 and 244.9 ppm. The results indicate that fly ashes can be utilized as a secondary source of REEs.

Conclusion

Fly ash from Türkiye is concluded to have significant potential for REE recovery.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Fly Ash Characterisation for Rare Earth Elements (REEs) Beneficiation in Türkiye

Research Article

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ABSTRACT

The rapid advancement of technology is continuously increasing the need for rare earth elements (REEs). These strategically important metals are mainly sourced from primary resources, and then secondary resources are explored. Despite the significant issues caused by post products, fly ash generated from coal-fired power plants can be considered a secondary source due to its high REE content. This study conducted characterization analyses of six fly ash samples from power plants in Türkiye and investigated the potential for REE enrichment. The fly ashes were analysed using atomic absorption spectrophotometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and X-ray diffraction (XRD) methods. The enrichment potential of REEs in two selected fly ashes was examined. Total REE values were found to be 168.9 and 244.9 ppm. The findings suggest that fly ash could serve as a potential secondary source of REEs. Moreover, the application of bioleaching for the enrichment of REEs from fly ash is considered both an economically viable and environmentally friendly alternative. In this context, fly ash from Türkiye is concluded to have significant potential for REE recovery, and this method can contribute to the sustainable use of existing resources. This study also validates its findings by comparing them with literature.

Keywords: Coal fly ash, rare earth elements, mineral processing, waste management, biomining.

Türkiye'deki Uçucu Küllerden Nadir Toprak Elementlerinin (NTE) Zenginleştirilmesi için Karakterizasyonu

ÖZ

Teknolojinin hızla gelişmesi, nadir toprak elementlerine (NTE) olan talebi her geçen gün artırmaktadır. Stratejik öneme sahip bu metaller, ülkelerin ihtiyaçlarını karşılamak için birincil kaynaklardan temin edilmekte, bu kaynaklar yetersiz kaldığında ise ikincil kaynaklar araştırılmaktadır. Üretim sonrası ortaya çıkan atık ürünleri önemli sorunlara yol açsa da kömür yakıtlı termik santral uçucu külü içerdiği yüksek miktarda NTE nedeniyle ikincil kaynak olarak değerlendirilebilir. Bu çalışmada, Türkiye'deki termik santrallerden çıkan altı uçucu külün karakterizasyon analizleri gerçekleştirilmiş ve tespit edilen NTE'lerin zenginleştirme olasılıkları araştırılmıştır. Uçucu küller, atomik absorpsiyon spektrofotometresi (AAS), indüktif eşleşmiş plazma kütle spektrometrisi (ICP-MS), X-ışını floresansı (XRF) ve X-ışını kırınımı (XRD) yöntemleri kullanılarak analiz edilmiştir. Seçilen iki uçucu külde NTE'lerin zenginleştirme potansiyeli incelenmiştir. Toplam NTE değerlerinin 168.9 ve 244.9 ppm olduğu tespit edilmiştir. Elde edilen sonuçlar, uçucu küllerin ikincil NTE kaynağı olarak kullanılabilirliğini ortaya koymaktadır. Ayrıca, biyoliç yönteminin uçucu küllerden NTE zenginleştirilmesinde uygulanmasının ekonomik ve çevre dostu bir alternatif sunacağı düşünülmektedir. Bu bağlamda, Türkiye'den elde edilen uçucu külün, NTE'nin geri kazanımı için önemli bir potansiyele sahip olduğu ve bu yöntemin, mevcut kaynakların sürdürülebilir kullanımına katkı sağlayacağı sonucuna varılmıştır. Bu çalışma, geçmişte yapılan çalışmalarla da karşılaştırılarak elde edilen bulguların doğruluğunu pekiştirmektedir.

Anahtar Kelimeler: Uçucu kül, nadir toprak elementi, cevher zenginleştirme, atık yönetimi, biyomadencilik.

1. INTRODUCTION

Energy is an indispensable component of our daily life as well as the infrastructure of industrialisation. Coal ranks as the world's second-largest energy source, contributing approximately 30% of non-renewable energy. Power plants play a crucial role in national energy production and have significant implications for the global energy landscape [1]. With the energy crisis that emerged after the war between Russia and Ukraine, currently, the need for coal is increasing day by day. Türkiye's electricity consumption fell by 1.2% to 328.9 TWh in 2022 compared to the previous year, while electricity generation fell by 2.5% to 326.2 TWh, according to data from the Ministry of Energy and Natural Resources. Türkiye's National Energy Plan results indicate that the country's energy usage is projected to be 510.5 TWh in 2035 [2]. This data clearly demonstrates a trend of increasing energy consumption over time. The most important energy production methods to meet the energy demand in Türkiye are thermal and hydraulic methods

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[3]. This is followed by other energy production methods that are open to development. In 2023, the top three most utilized sources of electricity generation were coal (36.3%), natural gas (21.4%) and hydropower (19.6%). Besides these, 10.4% from wind, 5.7% from solar, 3.4% from geothermal and 3.2% from other sources. Based on data from 2023, Türkiye's installed capacity was 107,271 MW. Based on available resources, current capacity is split as follows: natural gas (23.7%), coal (20.3%), wind (11,1) and solar (11%), geothermal energy (1.6%), hydraulic energy (29.8%), and other resources (2.5%) [2]. These values underscore the continued significance of coal in Turkey's energy production (Fig. 1). However, coal-fired power plants produce a significant amount of waste and fly ash called under-boiler slag during their operation. Toxic trace elements in this waste can be washed with rainwater and contaminated with surface water and groundwater. Major economic and ecological issues arise when incineration ashes are improperly managed [4].

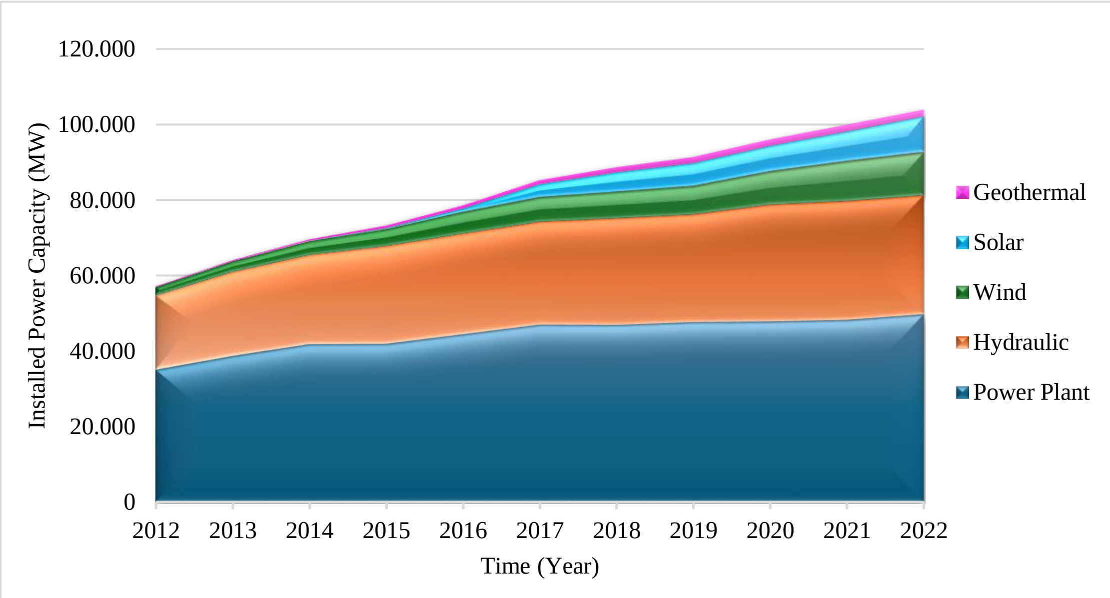


Figure 1. Changes in Turkey's installed power capacity in electricity generation by energy sources [3]

Of the nearly 600 million tons of coal ash produced every year worldwide, fly ash makes up about 500 million tons or 75–80% of it. It is used in various ways in proportions that vary from 3% to 57%; however, the median global ash utilisation is only 16% of the total ash produced [5]. In the US, 111.3 million tons of coal ash was produced in 2017, of which 64% or 71.8 million tonnes were recycled. In addition to the large reserves at old disposal sites, approximately 40 million tonnes of newly produced fly ash each year constitutes a very large industrial waste [6,7]. In 2009, Türkiye produced an average of 13 million tons of fly ash annually from 11 power plants. However, these figures fluctuate due to the commissioning of natural gas power plants and changing energy demands. Therefore, it is estimated that annual amounts of fly ash will increase more in the future [8] In Türkiye, the amount of fly ash utilisation remains at very low values compared to developed countries. It is primarily utilized in the manufacturing of construction materials and concrete. Upon the need arising in this field, there are many national and international studies to gain economic value of fly ashes and at the same time to prevent the effects on the environment. These studies predominantly focus on the determination of physical, chemical, mineralogical, and morphological properties of the fly ashes, their classification and determination of their usage areas [8–11].

Additionally, the environmental and social challenges associated with fly ash utilization, along with possible solutions, have been thoroughly investigated [12]. Literature reviews reveal a wide range of applications for fly ash, extending beyond the construction industry to include sectors such as paint, plastics, agriculture, and environmental management, depending on its properties [13–17]. Extensive research has been carried out on obtaining cenospheres with economic methods and determining its characteristic properties [18–23]. Fly ash is extensively used in the production of cement and concrete, bricks, aerated concrete, road stabilization, and lightweight aggregates. Furthermore, numerous studies have explored its potential as a raw material in brick production, yielding promising results [24–30]. In addition to these, hydrothermal methods, commonly used in the synthesis of zeolites, particularly enable the production of Na-P1 zeolites with outstanding features including a high ability for cation exchange. and a regular pore structure [31–34]. Similarly, geopolymers, formed through alkaline activation into three-dimensional polymeric networks, stand out as sustainable construction materials due to their superior compressive performance and low carbon footprint [35–37].

It is also known that ashes from the combustion of lignite for energy production contain metals of strategic importance, semi-metals, and REEs. The distinctive physicochemical properties of REEs have led to increased demand in the global market because of their use in technology, industrial, medical, and agricultural applications. The periodic table contains 15 elements with atomic numbers ranging from 57 to 71 and chemically similar characteristics [38,39]. Due to their small atomic diameters and similar ionic diameters, yttrium (Y) and scandium (Sc) are included in the REE group [40].

REEs are utilized in various applications, the manufacturing of ceramics and glass, metallurgy, magnets, lasers, and catalysts. Additionally, hybrid cars, wind turbines, solar panels, MRI machines, computers, cell phones, and electronic circuits are just a few of the many applications of rare earth elements [41–43]. In addition, REEs, which are used as raw materials in defence industry, are strategic raw materials due to these usage areas. As illustrated in Fig. 2, China has approximately one - third of the world's REE reserves and is the only country with substantial control in world REE production, utilisation, export and most importantly REE technology [41,44]. Based on the report prepared on this subject and the analysis of three critical factors, it is stated that REEs rank highest with a criticality level score of 29 [45]. The aggregate of each of the scores for every item in the most current critical materials reviews conducted in the USA, EU, UK, Japan, and South Korea was used to compute this score, which is mentioned in this document [38,45].

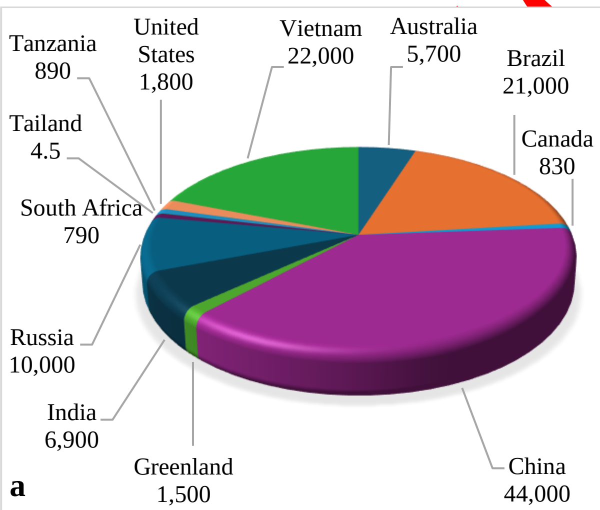


Figure 2. (a) Worldwide reserves (in 1,000 metric tons REO) and mine production

Studies have indicated that fly ash could serve as a viable source of metals needed in industrial production. Initially, it was not possible to carry out studies on the enrichment of metals in lignite and hard coal ashes for economic reasons. In addition to economic reasons, inadequate equipment and technological deficiencies can be counted among these reasons.

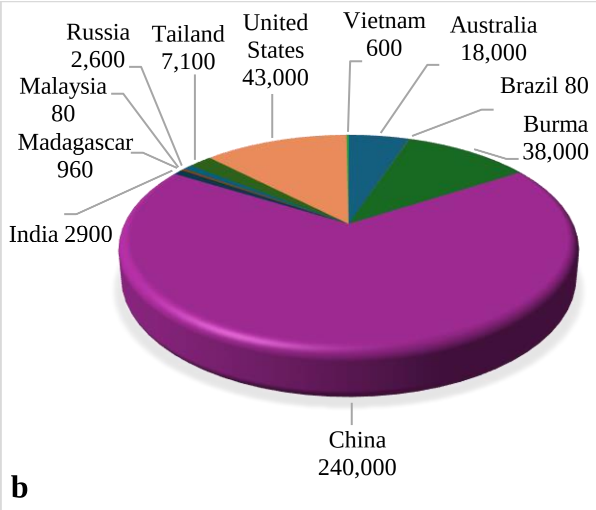


Figure 2. (b) of rare earth elements in 2023 [46]

Nevertheless, studies have been carried out on the recovery of Ge, Ga, Be, Mo, Fe elements from fly ash [47]. In a similar study conducted with fly ash from Yeniköy power plant, similar trace elements were determined and analysed in terms of limit values [48,49]. Because fly ashes from burning coal to generate electricity contain metalloids, rare earth elements, and strategic metals, they may be a potential source of metals that are needed in industry.

The enrichment of REEs in fly ash as a secondary resource was investigated. Coal fly ash waste from six Turkish power plants was used. Initially, the physical, mineralogical, chemical, and morphological properties of the fly ash samples were analysed. Subsequently, the concentrations of REEs within the fly ash were determined, providing insights into their potential as a valuable secondary source of these critical elements.

2. MATERIAL and METHOD

2.1. Material

In this study, fly ash from six different power plants in Türkiye was used. The selection of these plants was based on specific criteria: their use of coal as fuel, high energy production capacity, and the fact that the coal used was produced in Türkiye. The representative sample quantities were approximately 20 kg for each power plant. The fly ash samples were homogenously mixed, representative samples were taken by the coning/quadrupling method, and the remaining portions were packaged as witness samples (archive) and stored in sealed containers. For sampling, fly ash was categorized and coded as follows: FA1 (Black Sea region), FA2 (Central Anatolia), FA3 (Marmara region), FA4 and FA5 (Aegean region), and FA6 (Mediterranean region).

2.2. Methods

Characterisation study of the fly ash obtained from power plants was carried out using the laboratories of Çukurova

University, Alparslan Türkeş Science and Technology University, Çukurova University Central Research Laboratory and General Directorate of Mineral Research and Exploration (MTA) in Türkiye. Malvern Mastersizer 3000 was used as the device and measurements were taken by wet method for grain size analyses of the fly ash samples. SEM analyses were conducted at the Advanced Technology Application and Research Center laboratory of Pamukkale University. Morphological analysis was performed using the Quanta 150RS Field Emission SEM. Pycnometer method was applied for density measurements of the fly ashes. The density measurement using a pycnometer relies on determining the volume of solid particles within a liquid, utilizing the relationship between mass and volume. The density is calculated by finding the difference between the weight of the empty pycnometer and the weight of the pycnometer filled with the liquid and solid. Mineralogical analysis of these samples was carried out between 2-70 □□degrees theta using the Malvern Panalytical X' Pert Powder brand XRD spectroscopy device. The X-ray pattern containing mineral peaks was obtained by tableting the material without the need for grinding. The test samples were tableted, and the chemical analysis of the sample was carried out by Thermo ARL brand XRF device in accordance with the standard. Chemical methods, such as hydrofluoric acid digestion and measurement using Perkin Elmer 900 H atomic absorption spectrophotometry (AAS), were used to analyse the fly ash chemically. For the loss on ignition (LOI) test, pre-weighed dry samples were initially heated in an oven at 105°C, then cooled in a desiccator, and subsequently heated to 600°C for two hours. The carbon and organic sulphur levels in the ashes were then measured. An inductively coupled Perkin Elmer Nexion 2000 P brand ICP-MS apparatus was used to perform REEs studies.

3. RESULTS

3.1. Characterisation of fly ash samples

As depicted in Fig. 3, FA2 have the highest grain size with only 40% by weight less than 100 µm where it was around 70% by weight for FA5 and FA6. The finest fly ashes were FA1 and FA3.

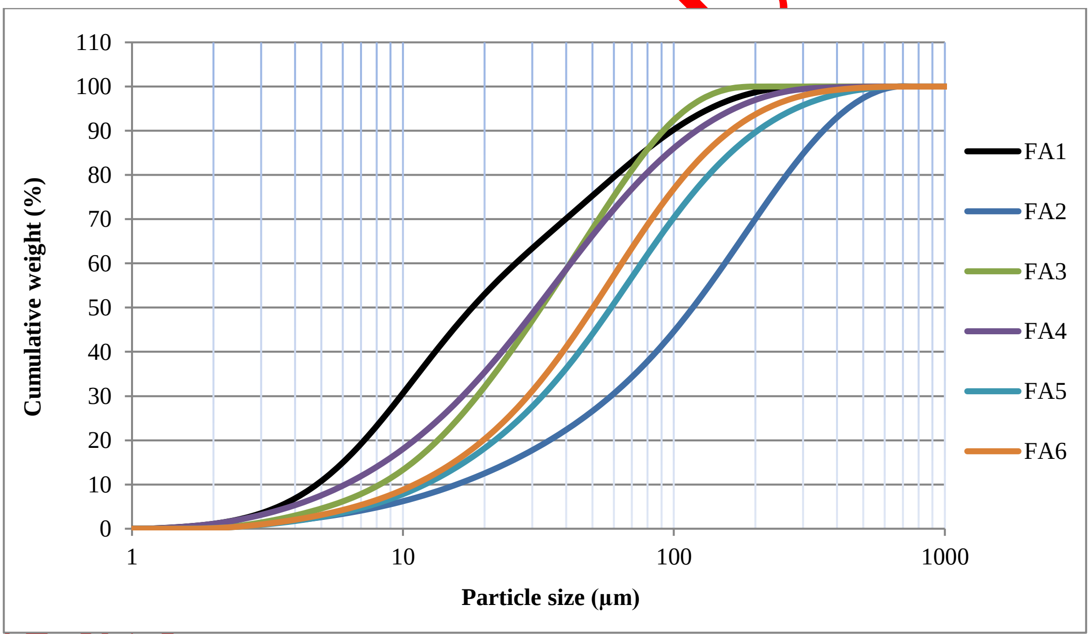


Figure 3. Particle size distribution of the fly ash samples

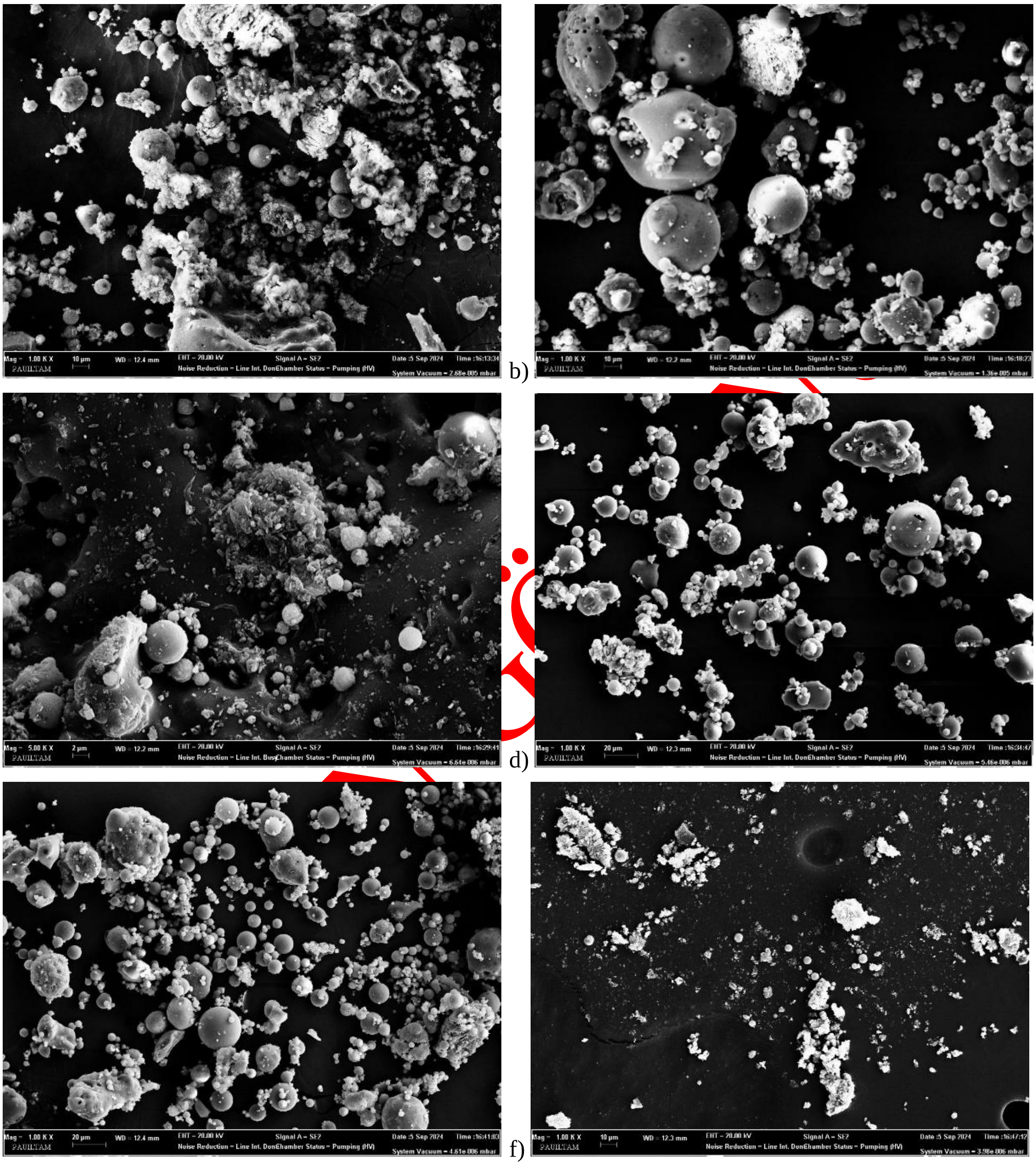
It is observed that the densities of the fly ashes were between 1.77 and 2.45 g/cm^3 as given in Table 2 and FA5 had the highest value, and FA2 has the lowest value of 1.77 g/cm^3. Morphological analysis was conducted using a Quanta 150RS

Field Emission SEM. The examined images reveal spherical structures of varying sizes and shapes (Fig. 4). The samples basically consist of quartz (SiO_2), Anhydrite ($CaAl_2(SiO_4)_2$), mullite ($Al_{4}.8$ $Si_{1}.2$ $O_{9}.6$), hematite (Fe_2O_3), Calcium Oxide (CaO) and Lime (CaO) phases (Fig. 5)

XRF analysis results are given in Table 1. As shown, all fly ashes contain a significant amount of SiO_2 and Al_2O_3. This indicates the presence of quartz and clay containing minerals. The presence of SO_3 indicates the sulphur content and Fe_2O_3 content indicates pyrite mineral.

While classifying fly ashes, total values of SiO_2, Al_2O_3 and Fe_2O_3 are considered. In addition, CaO value is also an important parameter for determination. The classifications of fly ashes used in the study according to TS EN 197-1 and ASTM C16 standards are given in Table 2 [50,51]. According to the ASTM C 618-15 standard, fly ashes are categorized into Class F and Class C. These ashes from bituminous coal are categorized as

F if their proportion of SiO_2, Al_2O_3, and Fe_2O_3 combined is higher than 70%. Which are also referred to as low calcareous since the amount of CaO in them is less than 10%. Fly ashes from the F class contain pozzolanic qualities. Class C fly ashes are made from semi-bituminous coal or lignite and contain more than SiO_2, Al_2O_3 and Fe_2O_3. These ashes are also known as high calcareous fly ashes since CaO is greater than 10% in Class C fly ashes. Fly ashes from class C exhibit pozzolanic and binding characteristics [8,51].



a) b) c) d) e) f)

Figure 4. Images of fly ash SEM (a: FA1, b: FA2, c: FA3, d: FA4, e: FA5, f: FA6)

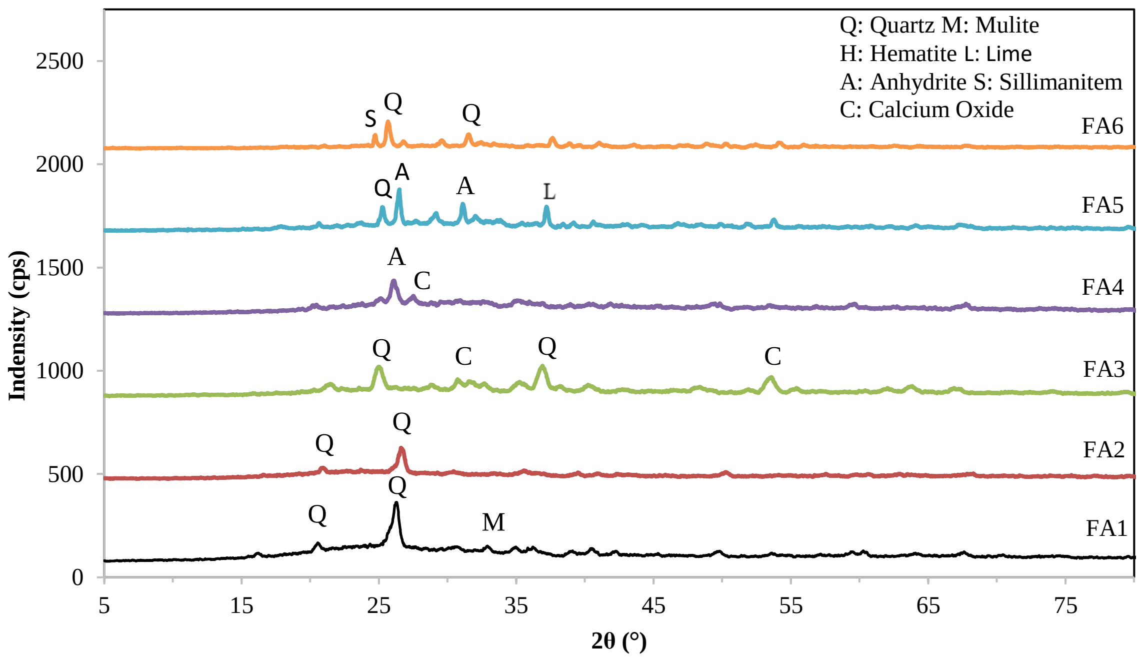


Figure 5. XRD patterns for fly ash samples

Table 1. The elemental composition of the fly ash (wt%)

Component	Fly Ash					
	FA1	FA2	FA3	FA4	FA5	FA6
Al_2O_3	25.00	19.20	18.00	19.60	16.20	9.90
SiO_2	56.70	58.90	33.40	48.00	32.00	25.2
Fe_2O_3	6.30	9.60	9.10	8.3	5.40	6.80
CaO	1.60	2.70	24.90	15.1	34.5	38.7
SO_3	1.10	0.90	11.30	2.10	5.50	15.00
K_2O	3.80	1.60	0.30	2.20	1.70	0.60
MgO	2.70	4.30	0.80	2.60	2.20	1.90
Na_2O	1.30	0.80	1.10	0.90	0.90	0.40
P_2O_5	0.10	0.20	0.10	0.20	0.30	0.30
TiO_2	0.90	0.80	0.50	0.70	0.70	0.50
MnO	0.10	0.20	0.10	0.00	0.10	0.10
V_2O_5	0.09	0.07	0.08	0.07	0.08	0.08
ZnO	0.04	0.03	0.01	0.03	0.02	0.02
SrO	0.09	0.11	0.08	0.13	0.27	0.13
$SiO_2 + Al_2O_3 + Fe_2O_3$	88	87.7	60.5	75,9	53.6	41.7

Fly ashes are classified into two types, siliceous (V) and calcareous (W), in accordance with TS EN 197-1. The majority of the ash is made up of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3), with the remainder consisting of iron oxide and other materials. Reactive lime (CaO) should make up less than 10% of these ashes, while reactive silica should make up more than 25%. Class V fly ashes are a fine powder that predominantly consists of spherical particles with pozzolanic capabilities. Reactive lime (CaO), reactive silica (SiO_2), and reactive aluminium oxide (Al_2O_3) make up the majority of Class W ashes, which also contain iron oxide (Fe_2O_3) and other materials. Reactive lime (CaO) should make up more than 10% of these ashes, and reactive silica should make up more than. Class W ashes have hydraulic or pozzolanic capabilities [8,52].

When the fly ash samples were analysed, the fly ash with the highest CaO value was FA6, followed by FA3 and FA5 while the lower CaO contents were found to belong to FA1 and FA2. It is predicted that the high CaO values in fly ash will cause significant deviations in pH values. When metal enrichment is desired to be made by applying leaching methods, it will significantly affect the costs for acid balancing. CaO compound which creates a basic environment is therefore important. Otherwise, acid consumption increases. For this reason, in this study, REE content was analysed in FA1 and FA2 samples with low CaO values. Carbon values also were determined. FA4 and FA5 were found to have the lowest carbon values while FA6 has the highest carbon value. Organic sulphur contents were found to be quite low (Table 2). It is thought that the concentration differences observed between samples may be the result of variations in their geological provenance and methods of processing/firing.

Table 2. Loss on ignition and organic sulphur values of the fly ashes

Fly Ash	Loss on ignition (wt%)	Organic sulphur (wt%)	Density (g/cm³)	TS EN 197-1	ASTM C618
FA1	1.09	0.007	2.01	V	F
FA2	0.50	0.1271	1.77	V	F
FA3	2.99	0.008	2.38	W	F
FA4	0.18	0.02	2.30	W	F
FA5	4.34	0.001	2.45	W	C
FA6	5.78	0.002	1.98	W	C

It is possible to observe trace amounts of elements in the solution at ppm level. The distribution of REEs in the gathered CFA samples is displayed in Table 3. It is evident from the table that Ce has values of 72.2 and 53.6 µg/g. With concentration values ranging from 39 µg/g to 24.3 µg/g, the element La was found to have the second highest concentration. The lowest concentration among REEs was observed to be Lu element, with concentration values of 0.5 µg/g and 0.4 µg/g in two samples. Among the analysed samples, FA2 had the highest concentration for all REEs.

4. DISCUSSION

The study aimed to evaluate Turkish fly ashes as an alternative and efficient secondary source for REEs, which are important for technological development. As a result of intensive experimental studies, it was determined that the grain sizes of all the fly ashes studied were below 200 microns, except for FA2 ash, which had a higher grain size. The diverse fly ash collecting techniques utilized in the power plants, like bag filters, cyclones, or electrostatic precipitation, are likely to be to blame for this variance in size distribution [10]. This may be an important parameter for the enrichment method to be applied.

Generally, quartz, mullite and hematite were observed in all type of the fly ashes but only FA5 fly ash was observed to be different from the other ashes having anhydrite, sillimanite, quartz, free lime and mullite. Risdanareni et al. (2017) obtained similar results in their study about Japanese and Australian fly ashes [53]. They categorized Australian, Indonesian, and Japanese fly ashes as class F. The two fly ashes examined in this study had respective total REE contents of 168.9 and 244.9 ppm.

A table was created base on the literature review to determine the REE values in fly ash from different countries and power plants. When the results are compared, it is seen that the REE content is average compared to other data. It is thought to be an important factor in beneficiation selection (Table 3). In modern pyro-hydrometallurgical processes, a significant amount of cerium enters leaching solution, resulting in increased operational and capital costs during the solvent extraction step, which is used to separate individual rare earth elements. As a less valuable element, cerium acts as a penalty element in the separation process, further complicating and raising costs in purification [54,55]. The analysis reveals that the cerium concentration in the two fly ashes studied is lower than that found in various other materials documented in the literature. Therefore, this feature is likely to offer a significant advantage for the fly ashes being examined.

Table 3. REE values of the fly ashes obtained in different studies (ppm)

REE	FA1 Türkiye in this study	FA2 Türkiye in this study	Sandeep et al., 2023 India [56]	Lin et al., 2017 USA [57]	Wang et al., 2019 China [58]	Ketris et al., 2009 World Coal Ash [59]
Ce	53.5	72.2	88.2-218	246	266.4	130
Dy	4	6.3	6.9-12.2	20	20.4	14
Er	2.3	3.5	3.6-5.7	14	12,0	5,5
Eu	1,3	2	1,6-2,8	4	4,1	2,5
Gd	4,7	7,7	7-,12,7	25	22,9	16
Ho	0,9	1,8	1,1-2,0	5	2,9	4
La	29	39	28,9-92,7	115	134,44	69
Lu	0,4	0,5	0,5-0,8	2	1,6	1,2
Nd	24.3	36	29.2-66	113	114.7	67
Pr	3.9	5.5	8-19.9	29	29.8	20
Sc	15.9	25.5	21.8-27.7	83	25.9	23
Sm	5	8	8.9-17.2	24	21.9	13
Tb	0.8	1.1	1.1-2	4	3.37	2.1
Tm	0.4	0.5	0.5-0.8	2	1.6	2
Y	20.4	32	22.8-48.3	132	105.2	51
Yb	2	3.3	3.7-5.4	13	11.0	6.2

The sum of light rare earth elements (ΣLREE) includes the elements La, Ce, Pr, Nd, Sm, Eu in Table 4. The sum of heavy rare earth elements (ΣHREE) includes the elements Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y. Total REE's (ΣREE) is the sum of ΣLREE and ΣHREE. If Sc and Y are added to the total REE content, the ΣREY content is obtained [56,60].

The overall classification of REEs in fly ash is displayed in Table 4. The findings show that LREYs are more prevalent in CFA samples than ΣHREEs. It can be observed that the total REE and REY values of FA2 fly ash are higher than FA1 values in this classification as light and heavy.

Table 4. Total Amount of REEs in Fly Ash (ppm)

	ΣLREE	**ΣHREE**	**ΣREE**	**ΣREY**
FA 1	117	35.9	152.9	168.8
FA 2	162.7	56.7	219.4	244.9

In their work, Wang et al. (2019) used fly samples from China's Luzhou coal-fired power plant to investigate concentration, characterization, and optimal extraction. As a result of their analysis, they determined that the fly ash was in class F and they also concluded that the fly ash consists of mineral phases such as amorphous glass above 70% and mineral phases such as blolite, quartz and iron oxide below 30%. After application of NaOH and HCL leaching enrichment, they obtained 39.43% REY and 88.15% REY results, respectively [58].

Sandeep et al. (2013) reported in their study that there is a large amount of coal ash in India. Coal ash from eight power plants was analysed and the most suitable ashes for recovery were identified. The sum of all rare earth contents in the analysed samples ranged from 234 μg/g to 533 μg/g, they found that some of the analysed samples could be used as secondary sources for the extraction of REEs. The main purpose of determining the REE contents obtained is to determine the possibility of using secondary sources [56]. It will only be possible to learn this by applying beneficiation methods. Cao et al. (2018), the research utilized fly ash samples obtained from China, revealing a REE content of 489 ppm. The three REEs with the highest content in the ash sample cerium, lanthanum and neodymium were considered. A thorough investigation was conducted into the impact of different factors on hydrochloric acid leaching efficiency. With the exception of a tiny effect from stirring speed, the results indicated that acid concentration, temperature, reaction time and liquid-solid ratio significantly affected the recovery of REEs [61]. Peiravi et al. (2017) examined a total of 14 coal samples and used the ash of anthracite coal with the highest rare earth element value (700 ppm). D2EHPA was identified as the most effective extractant in the solvent extraction tests, achieving an REE recovery rate of approximately 99% [62].

Acidithiobacillus ferrooxidans and *Acidithiobacillus thiooxidans* bacteria are widely used in metal beneficiation from sulphide ores or materials. It is understood that they can be used in the enrichment of metals contained in power plant fly ash [63,64]. The bioleaching mechanism occurs in two main ways: direct and indirect. In this method, microorganisms attach to the mineral surface and dissolve the metal through direct oxidation or reduction. In this process, bacteria directly oxidize the mineral, making it soluble, as seen in 1 and 2. For example, bacteria like *Acidithiobacillus ferrooxidans* directly oxidize iron sulfide (FeS_2), converting it into iron and sulfate ions [65]. *Acidithiobacillus ferrooxidans*, which are effective in the removal of pyritic sulfur, perform the following reactions during this oxidation process [66].

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{\text{Bacteria}} 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$4FeSO_4 + 02 + 2H_2SO_4 \xrightarrow{\text{Bacteria}} 2Fe_2(SO_4)_3 + 2H_2O \quad (1)$$

In the indirect mechanism, microorganisms produce chemical intermediaries to dissolve minerals. These intermediaries react on the mineral surface, making the metal soluble. For example, some bacteria can oxidize sulfide minerals by producing ferric iron (Fe^{3+}). In this process, bacteria reduce ferric iron to ferrous iron (Fe^{2+}), which is then re-oxidized by the bacteria [66,67].

$$FeS_2 + Fe_2(SO_4)_3 \xrightarrow{\text{Bacteria}} 3FeSO_4 + 2S^\circ \quad (2)$$

Here, elemental sulfur is oxidized by the bacteria into sulfuric acid.

$$2S^\circ + 3O_2 + H_2O \xrightarrow{\text{Bacteria}} 2H_2SO_4^\circ \quad (3)$$

According to the studies examined, it is possible to enrich REE in fly ashes and bring them into the economy. This situation is also valid for the fly ashes we analysed. It is believed that the enrichment methods that can be applied will gain results because of detailed research and experimental studies.

5. CONCLUSION

Increasing energy demand and solid waste generation have led to an alarming rise in fly ash production worldwide. In addition to their environmental side effects, fly ashes also occupy otherwise usable land. This situation poses significant problems for businesses, local people, and the environment. This study aims to provide solutions to these problems. It is believed that understanding fly ash's chemical and physical features is crucial for spotting and averting issues with its impact on the environment and human health. Inert fly ash can be used in different sectors even if the area of use is glazed. First, the possibility of enrichment of the metals contained in it should be considered. It is thought that the possibilities of obtaining REEs with economic and high efficiency methods should be investigated and will provide economic value. Obtaining REEs, which are of critical importance for the future of Türkiye and seen as the main raw material of technology, from fly ashes as a secondary source will provide a significant economic contribution. As a result of the analysis obtained, it is thought that it would be appropriate to enrich the REEs from fly ashes. It is possible to enrich REEs by chemical leaching method. In the same way, it is thought that it is possible to make environmentally friendly enrichment by applying the bioleaching method. Considering the CaO content and the content of REEs among the fly ashes we examined in our study, FA1 ash is more suitable for enrichment. Further research on Turkish coal fly ashes is needed for the recovery of REEs as a secondary resource.

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Yasin ÇİNÇİN: Performed the experiments and analyse the results. Wrote the manuscript and checked the accuracy of the results. Guidance and manuscript finalization.

Oktay BAYAT: He wrote the manuscript and checked the accuracy of the results. Guidance and manuscript finalization.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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