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GEOCHEMICAL CHARACTERISTICS OF RARE EARTH ELEMENT DISTRIBUTION IN COAL COMBUSTION PRODUCTS

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Abstract. The study presents an integrated morphological and geochemical characterization of coal combustion products from the Prydniprovska Thermal Power Plant, with the aim of assessing their potential as secondary sources of rare earth elements (REEs). The samples of fly ash, boiler slag, and bottom ash were examined using scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) and inductively coupled plasma mass spectrometry (ICP-MS). SEM-EDS results revealed that the investigated materials are mainly composed of amorphous and cryptocrystalline aluminosilicates, glassy phases, and numerous cenospheres containing mineral inclusions and agglomerates. Such microstructural features indicate rapid cooling of the molten material and provide favorable conditions for REE accumulation within the fine-grained aluminosilicate matrix.

The ICP-MS data show significant differences in REE concentrations among the analyzed products. The highest total REE contents were detected in fly ash (Ce – 150.6 ppm, Nd – 77.4 ppm, La – 64.9 ppm, Y – 50.7 ppm), followed by lower values in boiler slag and bottom ash. Chondrite-normalized REE distribution patterns exhibit a pronounced enrichment in light REEs (LREE/HREE = 2.48–2.60) and high $(La/Yb)_N$ ratios (6.23–7.56), indicating strong fractionation between light and heavy elements. All samples display a negative Eu anomaly (Eu/Eu* = 0.64–0.72), most distinct in the bottom ash, which is likely related to the incorporation of Eu^{2+} into feldspar-group minerals during high-temperature combustion.

The integration of SEM-EDS and ICP-MS results demonstrates consistent morphological and geochemical trends, highlighting fly ash and boiler slag as the most promising fractions for REE recovery. These findings emphasize the importance of coal combustion residues as a valuable source of critical raw materials and contribute to the development of sustainable strategies for waste utilization and resource diversification in Ukraine's post-war energy sector. The obtained data can serve as a sustainable basis for the development of effective technological solutions for processing coal combustion products, taking into account economic and environmental feasibility.

Keywords: thermal power plant, solid wastes, rare earth elements, critical raw materials, recycling of by-products.

1. Introduction

With the rapid advancement of technology, there has been a steady increase in global demand for rare earth elements (REEs), which are indispensable components in the production of electronics, renewable energy systems, energy storage technologies, defense applications, and advanced materials. The wide range of their applications renders REEs strategically important for most countries, which classify them as critical raw materials [1]. It is important to note that mineral resources are considered critical when they serve specific industrial applications, lack viable substitutes at the current stage of technological development, and their supply is dominated by one or a few producers. In other words, such mineral resources are of high economic significance, while the stability of their supply is associated with a considerable degree of risk [2]. Since China is currently the primary supplier of rare earth elements, many countries are seeking to diversify their markets by developing alternative sources of extraction.

One of the most promising directions in this context is the utilization of technogenic wastes, particularly coal combustion products generated at thermal power plants (TPP). These residues are produced in large volumes and have traditionally

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been considered as environmentally hazardous materials, contributing to waste accumulation and environmental pollution. Nevertheless, numerous studies over the last decades have demonstrated that coal ash and slag may contain significant concentrations of REEs, in some cases comparable to or even exceeding those in natural deposits [3–7].

In Ukraine, coal combustion products constitute a significant technogenic resource. According to various estimates, more than 15 million tonnes are generated annually, while the cumulative volume accumulated in disposal sites exceeds 250–300 million tonnes, covering an area of over 20,000 hectares. From the perspective of their utilization as an alternative source of critical raw materials, these deposits exhibit several advantages. Being the by-products of previous industrial activities, they do not require additional geological exploration or large-scale infrastructural development, which considerably reduces the associated costs. Furthermore, their processing contributes to mitigating anthropogenic pressure on the environment, facilitating the reclamation of contaminated territories, and advancing the principles of the circular economy. Thus, the recycling of such waste deposits is justified not only in terms of resource efficiency but also from an environmental standpoint.

Thus, this article proposes to consider the prospects of processing coal combustion products as an alternative source of REEs using the example of one of the Ukrainian thermal power plants (Prydniprovska TPP).

The main aim of this study is to determine the concentrations of rare earth elements in coal combustion products from the Prydniprovska TPP (fly ash, boiler slag, bottom ash) and to analyze the geochemical patterns of their distribution and fractionation, including chondrite-normalized spectra, light-to-heavy REE ratios, and characteristic anomalies (e.g., Eu).

2. Methods

For the purposes of this study, samples of fly ash, boiler slag, and bottom ash were collected from the dumps of the Prydniprovska TPP by specialists of the M.S. Poliakov Institute of Geotechnical Mechanics of the NAS of Ukraine. These materials represent the combustion products of bituminous coal and anthracite. The samples were preliminarily prepared (dried and crushed) in the Laboratory for the Study of Structural Changes in Rocks at the aforementioned institute.

The REE content in the samples was determined using ICP-MS (Thermo Element 2, Thermo Scientific, Germany) at the Laboratory of Trace Element and Isotope Analyses, M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the NAS of Ukraine. One of the advantages of the ICP-MS analysis method is its ability to obtain quantitative concentrations of almost all lanthanides. Preliminary acid digestion was performed in a microwave system (ETHOS, Milestone, Italy) using a mixture of HNO_3, HF, and HCl, following a standard procedure [8]. Calibration was carried out with a multi-element standard solution (Inorganic Ventures CMS-1), and indium (10 ppb) was used as an internal standard. For quality control, the certified reference material JG-1a [9] was analyzed, and the obtained results were consistent with the certified values. The REE concentrations in the samples were normalized to CI-chondrite values for graphical representation of distribution patterns [10]. Europium anomalies (*Eu/Eu**) were calculated using the formula:

$$Eu/Eu^{*} = \frac{Eu_N}{(Sm_N \times Gd_N)^{1/2}}$$

where subscript N denotes chondrite-normalized concentrations.

Eu anomalies (Eu/Eu*) reflect deviations of europium from the expected trend of neighboring rare earth elements (Sm and Gd). Positive or negative Eu anomalies provide insights into fractionation processes occurring during coal combustion and mineral phase transformations.

To comprehensively investigate the coal combustion products, scanning electron microscopy combined with energy-dispersive spectroscopy (SEM-EDS) was additionally used. This method enables a detailed examination of particle morphology and a preliminary identification of their chemical composition. The analysis was performed in the Division of Applied Geochemistry and Environmental Engineering of the Mineral and Energy Economy Research Institute, Polish Academy of Sciences. For the SEM-EDS analysis, the samples were placed on a conductive double-sided adhesive tape, which had been previously fixed to the microscope sample holder. Since coal combustion products are non-conductive materials, their electrical and thermal conductivity was ensured by coating the surface with an ultrathin carbon film using the Safematic CCU-010HV vacuum coating system. To ensure maximum sample stability, a carbon layer approximately 10 nm thick was applied to the surface. Both morphological imaging and elemental mapping were carried out using a Secondary Electron (SE) detector, which provided high-resolution surface topography and detailed element distribution maps.

The integration of the above-mentioned approaches provides a reliable basis for assessing the mineral resource potential of coal combustion products as an alternative source of critical raw materials.

3. Results

SEM-EDS analysis revealed that the fly ash, bottom ash and boiler slag samples from the Prydniprovska TPP are composed mainly of amorphous and cryptocrystalline aluminosilicates, represented predominantly by irregularly shaped particles (Fig. 1). A considerable number of cenospheres and fractured spheres containing mineral intergrowths and agglomerates inside them were also observed.

Most ash fragments are characterized by a glassy surface texture, indicating the rapid cooling of molten material during the combustion process. The presence of cenospheres and hollow spherical particles suggests the intensive melting and gas release that occurred under high-temperature conditions within the boiler. The size of spherical particles ranges from several micrometers up to 60–80 μm, with the finer fraction being more abundant in fly ash samples.

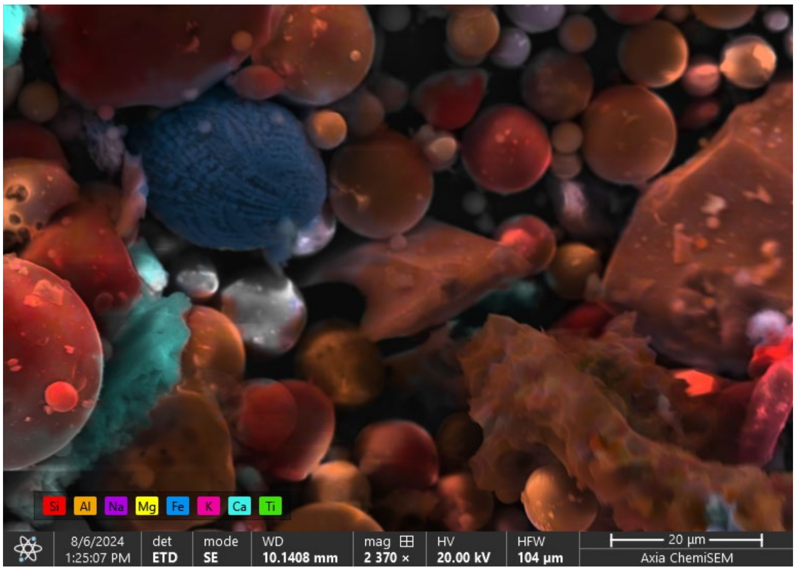

Figure 1 – Microphotograph of boiler slag (sample No. 5308) showing morphological and elemental composition determined by the SEM-EDS method

Regarding the determination of the elemental composition, the SEM-EDS method is effective and the result is reliable only for elements whose mass fraction in the sample exceeds 0.5%, and thus the obtained spectra primarily reflect the major and minor components of the analyzed materials (Tab.1).

Table 1 – Elemental composition of coal combustion products (CCPs) of Prydniprovska TPP according to SEM-EDS data

Type of coal combustion product	Elemental composition (in wt.%)							
	Si	Al	Fe	Ca	K	Mg	Ti	Na
Boiler slag	48.2	18.4	16.4	8.2	4.5	1.4	1.4	1.5
Bottom ash	12.4	6.8	5.8	1.3	1.8	0.8	0.5	0.6
Fly ash	16.8	8.4	9.0	1.5	1.6	0.6	2.0	0.7

The Table 1 shows clear compositional differences among the studied coal combustion products. Boiler slag is dominated by Si, Al, and Fe, indicating the prevalence of aluminosilicate and iron-bearing phases formed under high-temperature conditions. Bottom ash contains lower contents of major oxides, reflecting a less intensive melting process, while fly ash is slightly enriched in Ti (2.0 wt%), which may indicate the presence of Ti-bearing phases such as ilmenite or rutile.

As a result of the ICP-MS analysis, the content of rare earth elements in the samples of boiler slag, bottom ash, and fly ash from the Prydniprovska Thermal Power Plant was determined. The highest REE concentrations are characteristic of fly ash, with maximum values for Ce (150.6 ppm), Nd (77.4 ppm), La (64.9 ppm), and Y (50.7 ppm). This indicates intensive accumulation of REEs in fine-grained particles that are effectively retained by the filters. Slightly lower concentrations were observed in the boiler slag (Ce – 113.4 ppm, Nd – 59.0 ppm, La – 55.2 ppm), while the lowest values were recorded in the bottom ash (Ce – 72.7 ppm, Nd – 37.7 ppm, La – 44.6 ppm).

The chondrite-normalized REE distribution patterns for all types of coal combustion products show a clear enrichment in light rare earth elements. The highest REE concentrations occur in the fly ash. A common feature of all samples is a negative Eu anomaly, reflecting specific mineralogical and geochemical processes that take place during coal combustion (Fig. 2).

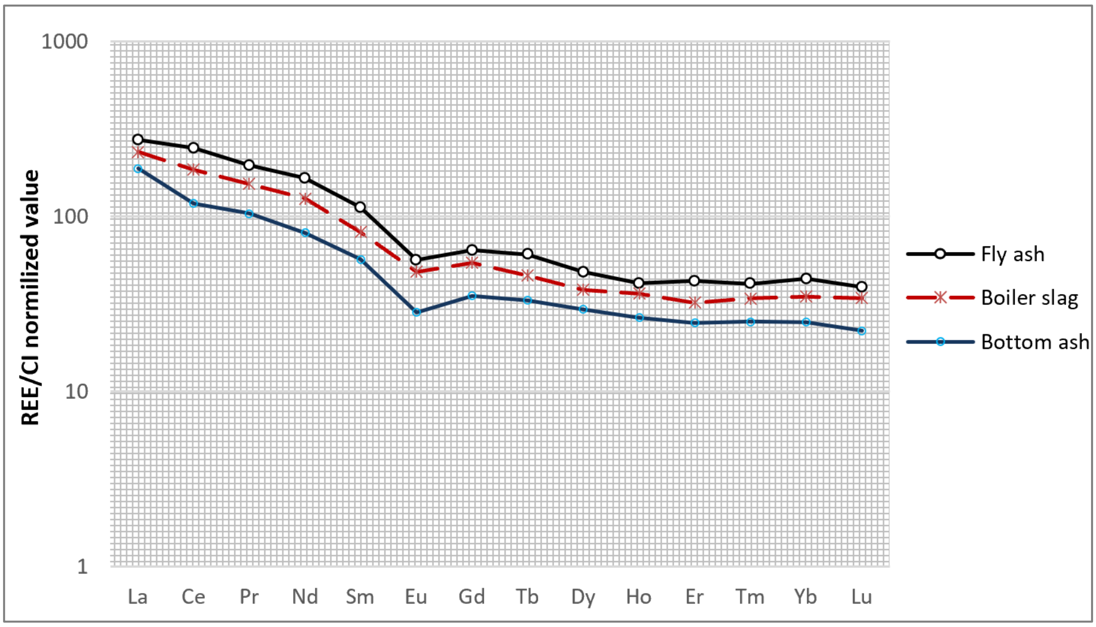

Figure 2 – REE distribution patterns in the coal combustion products from the Prydniprovska TPP normalized to CI-chondrite

The chondrite-normalized parameters of REE distribution in the coal combustion products from the Prydniprovska Thermal Power Plant show distinct variations depending on their type (Table 2). The highest total concentrations of light (ΣLREE_N = 994.64) and heavy (ΣHREE_N = 382.71) REEs were recorded in the fly ash, indicating that this fraction is the most promising potential source of REEs. For boiler slag, the respective values are lower (ΣLREE_N = 779.67; ΣHREE_N = 309.77), while the lowest ones are observed in bottom ash (ΣLREE_N = 548.11; ΣHREE_N = 220.98). The LREE/HREE ratios in all combustion products range from 2.48 to 2.60, confirming the dominance of light REEs over heavy ones. The high (La/Yb)_N values (6.23–7.56) indicate pronounced fractionation between light and heavy REEs.

Table 2 – Chondrite-normalized REE parameters in the coal combustion products from the Prydniprovska TPP

Type of coal combustion product	∑LREE_N	∑HREE_N	LREE/ HREE	(La/Yb)_N	Eu/Eu*
Fly ash	994.64	382.71	2.60	6.23	0.67
Boiler slag	779.67	309.77	2.52	6.67	0.72
Bottom ash	548.11	220.98	2.48	7.56	0.64

All samples exhibit a negative Eu anomaly (Eu/Eu* = 0.64–0.72), most pronounced in the bottom ash, which may be related to the incorporation of Eu^{2+} into the crystal lattices of feldspar-group minerals during high-temperature combustion processes [11, 12].

The microstructural and morphological observations obtained by SEM-EDS support these findings, revealing the presence of aluminosilicate matrices, glassy phases, and accessory mineral inclusions that serve as hosts for REE accumulation [13]. Overall, the integration of SEM-EDS and ICP-MS results demonstrates consistent geochemical trends, emphasizing the significant potential of coal combustion residues, particularly fly ash and boiler slag, as secondary sources of rare earth elements.

4. Results and Discussion

The results obtained in this study enable a comparison with data reported by other researchers. According to [14], the concentrations of the REEs in the bottom ash of the one of the Polish TPP range from 199 to 286 ppm. Comparable concentrations were determined for the bottom ash of the Prydniprovska TPP, where the total REE content is 244 ppm. The authors of [14] also noted that the industrial potential of bottom ash may be comparable to that of fly ash, provided that both materials originate from the same combustion process. In the present study, boiler slag demonstrated the highest REE concentration after fly ash (∑REE = 365 ppm), supporting its consideration as a potential secondary source of REEs.

When assessing the potential of coal combustion products as a source of REEs, it is also important to consider the rank of the coal being burned. Bituminous coal ash typically contains higher concentrations of REEs than anthracite and sub-bituminous coal ash [15]. This observation underscores the influence of coal rank on the distribution and concentration of REEs in combustion products. At the Prydniprovska TPP, separate disposal sites are available for the combustion residues of bituminous and anthracitic coal. Samples from these sites have already been collected, and preliminary ICP–MS analyses have been performed. In future research, these data will be compared to evaluate whether similar trends can be observed for the ash generated at the Prydniprovska TPP.

When developing technological solutions for the extraction of REEs from coal combustion products, it is essential to consider the specific fractions in which these elements tend to accumulate. According to [13], extraction from the aluminosilicate glass fraction of coal ash can recover a significant portion of the total REE content; therefore, this fraction should be prioritized in future recovery efforts.

5. Conclusions

The conducted SEM–EDS and ICP–MS analyses of coal combustion products from the Prydniprovska Thermal Power Plant revealed consistent morphological and geochemical patterns that determine the potential of these residues as a secondary source of rare earth elements. The examined samples of fly ash, bottom ash, and boiler slag are primarily composed of amorphous and cryptocrystalline aluminosilicates, glassy phases, and cenospheres containing mineral inclusions, which provide favorable conditions for REE accumulation.

Quantitative ICP–MS data indicate a distinct enrichment of light REEs over heavy ones in all types of combustion products, with the highest total concentrations of both LREEs and HREEs recorded in fly ash. The chondrite-normalized ratios confirm significant fractionation between light and heavy REEs, while the negative Eu anomaly reflects high-temperature processes that influenced mineral phase transformations during coal combustion.

Overall, the integration of microstructural and geochemical data demonstrates that fly ash and boiler slag are the most promising fractions for further REE recovery. Considering that REE distribution is also affected by coal rank, future comparative analyses of the bituminous and anthracitic residues from the Prydniprovska TPP will provide additional insights into the accumulation behavior of REEs in different combustion products. These findings emphasize the potential of coal combustion products as valuable raw materials for critical element recovery and support the development of sustainable strategies for waste valorization and resource diversification within Ukraine's energy sector. Nevertheless, the practical implementation of such initiatives requires the development of suitable technological solutions and assessment of their economic and environmental feasibility.

Conflict of interest

Authors state no conflict of interest.

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ГЕОХІМІЧНІ ОСОБЛИВОСТІ РОЗПОДІЛУ РІДКІСНОЗЕМЕЛЬНИХ ЕЛЕМЕНТІВ В ПРОДУКТАХ ЗГОРЯННЯ ВУГІЛЛЯ

Антіпович Я., Швайка І., Кунєцкі П.

Анотація. У дослідженні представлено комплексну морфологічну та геохімічну характеристику продуктів згоряння вугілля Придніпровської теплоелектростанції (ТЕС) з метою оцінки їхнього потенціалу як вторинних джерел рідкісноземельних елементів (РЗЕ). Зразки золи фільтра, котельного шлаку та залишкової золи були досліджені за допомогою скануючої електронної мікроскопії з енергодисперсійною спектроскопією (SEM-EDS) та мас-спектрометрії з індуктивно-зв’язаною плазмою (ICP-MS). Результати SEM-EDS показали, що зразки продуктів згоряння вугілля Придніпровської ТЕС переважно складаються з аморфних і криптокристалічних алюмосилікатів, склоподібних фаз і численних ценосфер, які містять мінеральні включення та агломерати. Такі мікроструктурні особливості вказують на швидке охолодження розплавленого матеріалу, що створює сприятливі умови для накопичення РЗЕ у дрібнозернистій алюмосилікатній матриці.

Дані ICP-MS виявили суттєві відмінності у вмісті РЗЕ між різними видами відходів. Найвищі сумарні концентрації РЗЕ зафіксовано у золі фільтра (Ce – 150,6 ppm, Nd – 77,4 ppm, La – 64,9 ppm, Y – 50,7 ppm), тоді як нижчі значення характерні для котельного шлаку та залишкової золи. Хондрит-нормовані профілі розподілу РЗЕ демонструють чітке збагачення легкими рідкісноземельними елементами (LREE/HREE = 2,48–2,60) та високі значення (La/Yb)_N (6,23–7,56), що свідчить про значне фракціонування між легкими та важкими елементами. У всіх зразках спостерігається негативна аномалія Eu (Eu/Eu* = 0,64–0,72), найбільш виражена в залишковій золі, що, ймовірно, пов’язано з включенням Eu^{2+} у мінерали групи польових шпатів під час високотемпературного горіння.

Інтеграція результатів SEM-EDS та ICP-MS виявила певні морфологічні та геохімічні тенденції, що визначають золу фільтра та котельний шлак як найбільш перспективну сировину для вилучення РЗЕ. Отримані результати підкреслюють перспективність твердих відходів ТЕС як цінного джерела критичної мінеральної сировини та сприяють формуванню сталих підходів до утилізації відходів і диверсифікації енергетичної бази України в післявоєнний період. Представлені дані можуть стати науковою основою для розроблення ефективних технологічних рішень з переробки продуктів згоряння вугілля з урахуванням економічної доцільності та екологічної безпеки.

Ключові слова: теплова електростанція, тверді відходи, рідкісноземельні елементи, критична сировина, переробка відходів.