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Critical raw material in mineral elements found in fly ashes from the Czech Republic power plant

Author(s) ORCID Identifier:
Agnieszka Klupa: 0000-0002-6703-1085

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Critical raw material in mineral elements found in fly ashes from the Czech Republic power plant

Abstract

The economic development of EU countries is limited due to limited access to a number of mineral raw materials, which necessitates actions aimed at securing the supply of CRM. For this reason, CRMs constitute elements of particular importance for the EU. The aim of the study was to assess the content of CRMs as a potential source of REY in fly ash resulting from the coal combustion in one of the power plants in the Czech Republic. In the tested ash the main phases are: glassy phase, mullite and quartz. The chemical composition of the tested fly ashes showed dominance of SiO2 and Al2O3. The CRM included Co, Sb, W, Be, Nb, Ga, lanthanides and Y, as well as Cr and In. Light elements have the largest share among REE, while heavy elements have the smallest share. In the tested fly ash, the share of critical elements, the content of uncritical elements and the content of excessive elements in the total REY content were also determined. Based on the analyzed results, the value of the Coutl prospective coefficient was calculated, which assesses the profitability of obtaining CRM from fly ash as an alternative source of these metals.

Keywords

critical raw materials; fly ash; power plants; mineral element; coal

RESEARCH ARTICLE

Critical raw material in mineral elements found in fly ashes from the Czech Republic power plant

Agnieszka Klupa

Central Mining Institute, National Research Institute, Department of Environmental Monitoring, Poland

Abstract

Critical raw materials are elements of particular importance for the European Union, which necessitates taking actions to secure the supply of these raw materials. The aim of the research was to assess the content of critical raw materials as a potential source of rare earth elements and Y in fly ash resulting from coal combustion in one of the power plants in the Czech Republic. The main phases in the ash tested are: glassy phase, mullite and quartz. The chemical composition of the tested fly ashes was dominated by SiO_2 and Al_2O_3. The critical raw materials included Co, Sb, W, Be, Nb, Ga, lanthanides, Y, Cr, and In. Light elements have the largest share among rare earth elements. The content of critical elements, the content of non-critical elements and the content of excessive elements in the total content of rare earth elements were also determined in the tested fly ashes. Based on the analyzed results, the value of Coutl's prospective coefficient was calculated, which assesses the profitability of obtaining critical raw materials from fly ash as an alternative source of these metals.

Keywords: critical raw materials, fly ash, power plants, mineral element, coal

1. Introduction

Over the centuries, the intensively developing industries and economy of Europe required vast amounts of natural resources. With the discovery of new mineral resources, technologies for their processing, including metals, were implemented. New metal recovery technologies are still being developed to meet contemporary needs, both qualitatively and quantitatively, as well as environmental protection [1–3]. The economic development of European Union (EU) countries is limited due to the restricted access to a range of mineral resources, prompting actions to secure the supply of Critical Raw Materials (CRM). The EU's raw materials policy aims to reduce dependence on supplies from China, Russia, Turkey, and Brazil. Consequently, the EC has established a list of CRM for the EU. This list is regularly updated. In 2010, 41 CRMs were identified, in 2013–54, in 2016–78, and in 2019–83. The resulting lists of CRMs for the European Commission (EC) included 14, 20, 27, 30, and 34 raw materials in 2011, 2014, 2017, 2020, and 2023, respectively [4]. CRMs combine resources with high added value and high supply risk. Out of the 34 identified critical raw materials, 16 are strategic raw materials (SRM) (Table 1). This list includes elements such as Sb, Be, Co, In, Ga, Ge, Mg, Nb, Ta, W, platinum metals (Pt, Pd, Ir), Rh, Ru, Os), and rare earth elements – REE (Y, Sc and lanthanides, especially Nd and Dy). Critical elements are primarily characterized by limited resources and a lack of substitutes despite their significant importance for the global economy, especially in the electronics, telecommunications, and automotive industries [5]. In November 2023, the EU reached a temporary agreement on the European Critical Raw Materials Act, as the demand for rare earth metals is expected to grow in the coming years exponentially. CRM are resources of great economic importance to the EU, whose supply is likely to be disrupted due to source concentration and the lack of good, affordable substitutes. This act aims to increase and diversify the supply of CRM in the EU, strengthen the closed loop, including recycling, and support research and innovation in resource efficiency and substitutes. The new regulations will also enhance Europe's strategic autonomy [6].

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E-mail address: aklupa@gig.eu.

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Table 1. List of CRM for the EU [6].

Critical and strategic raw materials				
Antimony	Cobalt	Hafnium	Natural Graphite	Silicon metal
Arsenic	Coking Coal	Helium	Nickel − battery grade	Strontium
Aluminium/Bauxite	Copper	Heavy Rare Earth Elements	Niobium	Tantalum
Baryte	Feldspar	Light Rare Earth Elements	Phosphate rock	Titanium metal
Beryllium	Fluorspar	Lithium	Phosphorus	Tungsten
Bismuth	Gallium	Magnesium	Platinum Group Metals	Vanadium
Boron	Germanium	Manganese	Scandium	

The industry and economy of the EU depend on international markets for access to many critical raw materials, which are produced and sourced from third countries. Many critical raw materials are highly concentrated. For instance, China supplies 100% of the EU's heavy rare earth elements (HREE), Turkey provides 99% of the EU's demand for boron, South Africa delivers 71% of the EU's platinum needs, and an even higher percentage of platinum group metals (Ir, Rh, and Ru). The concentration of production is exacerbated by low substitution rates and low recycling rates [5].

The article presents the results of research on the content of critical raw materials in fly ashes from a coal power plant located in the Czech Republic, as a potential source of rare earth elements and yttrium (REY). The Czech Republic, like Poland, China, and Turkey, is one of the countries where electric power is generated from coal. The combustion of coal produces fly ash, a so-called "by-product". These products are used, among other things, in reclamation, in the cement industry, for the production of building materials, fertilizers, synthesis of zeolites, etc. [7−10].

As indicated by literature studies, ashes resulting from coal combustion serve as a source of critical raw materials [11,12], despite the fact that bituminous coal is not classified as a critical raw material. Research by Seredin and Finkelman [12] shows that concentrations of rare earth elements in some coals and in coal combustion products are comparable or even higher than in REE ore deposits. In recent years, much attention has been given to research on the assessment of the potential and recovery of REE from coals and ashes [13−23]. Seredin and Dai [19] proposed a division of REE considering the cost-effectiveness of extracting rare earth metals from secondary raw materials. This division takes into account the diverse demand for individual metals and their availability on the market:

- critical − Nd, Eu, Tb, Y, Er,
- uncritical − La, Pr, Sm, Gd,
- excessive − Ce, Ho, Tm, Yb, Lu.

The above division of rare earth metals served the authors in developing the prospective index (C_{outl}) to assess the profitability of extracting them from fly ashes as an alternative source of these metals. This coefficient considers the proportions of critical and excessive elements and is expressed in the following manner:

$$C_{outl} = \frac{(Nd + Eu + Tb + Dy + Er + Y)}{Ce + Ho + Tm + Yb + Lu} \quad (1)$$

The Prospective Index (C_{outl}) is generally applied to assess ashes resulting from coal combustion. The higher its value, the more profitable the recovery of REE from ashes is considered. According to Seredin and Dai [19], the recovery of rare earth metals from fly ashes is economically viable when their content exceeds 1000 ppm. Worldwide research is ongoing to determine the quantity and methods of recovering critical raw materials from coal combustion ashes [24−33].

The mean concentration of rare earth oxides (REO) in fly ashes is 485 ppm, a level comparable to the REO content found in certain deposits abundant in REY. Therefore, if the concentration of REO in coal ash is slightly more than twice the average REO content, waste from coal combustion can be deemed a potential source of these metals, and their recovery can be economically viable [18,20].

Given the substantial demand for critical elements, ash has the potential to emerge as a valuable resource for extracting these elements, prompting the need for additional research in this field.

2. Materials and methods

To perform the determination of the chemical composition and phase composition of fly ash from one of the power plants in the Czech Republic, studies were conducted using the following methods:

- X-ray fluorescence spectrometry (XRF),
- inductively coupled plasma mass spectrometry (FUS-ICP),
- X-ray diffractometry (XRD),
- scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS).

Chemical analyses using inductively coupled plasma mass spectrometry FUS-ICP (fusion – inductively coupled plasma) were carried out at Activation Laboratories – ACTALBS in Ancaster (Ontario, Canada).

The primary chemical constituents of the fly ash samples were identified through X-ray fluorescence spectrometry (XRF) utilizing a Philips PW 2400 spectrometer and SuperQ software. The outcomes were presented as percentages of the major oxides of the elements.

X-ray diffraction studies were conducted using the powder X-ray diffraction method with a PANalytical Empyrean diffractometer employing Co Kα radiation. The Rietveld method was employed to ascertain the quantitative distribution of individual phase components.

The fly ashes were characterized using a scanning electron microscope (SEM) in conjunction with X-ray microanalysis. This characterization involved determining the morphology and size of grains, as well as the elemental and mineral composition based on observations of grain surfaces and X-ray microanalysis. SEM/EDS analysis was conducted with a Hitachi SU3500 variable-pressure scanning electron microscope coupled with an energy-dispersive X-ray spectrometer (EDS) UltraDry Detector from ThermoFisher Scientific. The X-ray microanalysis was carried out under the following parameters: accelerating voltage – 15 keV, working distance (WD) – 10 mm, pressure – 30 Pa, vacuum – variable. An electron backscattered (BSE) detector was utilized for the analysis due to its ability to highlight the contrast in the composition of multiphase samples, and the analyses were performed on a polished cross-sectional surface. The obtained images illustrated the qualitative phase/chemical diversity of the surfaces of the examined fly ashes. Approximately 10 measurements of the chemical composition in a micro-area were conducted on each ash particle, and the final result represented the average of these measurements.

Table 2. Composition of phases in fly ash resulting from coal combustion (% by mass).

Q	Mu	Ah	Li	He	Mgt	Mgh	Pe	Am	Total
11.07	20.12	0.20	0.30	0.40	0.20	0.80	0.50	66.41	100.00

3. Results and discussion

According to the findings from mineralogical investigations in the sample (Table 2), the prevalent component was the glassy phase (Am), constituting 66.5% by mass. The second most prevalent phase was mullite (Mu), comprising 20.12% by mass, and the third significant component in terms of quantity was quartz (Q), accounting for 11.07% by mass. All three phases (Am, Mu, Q) together constituted over 97% by mass in the examined fly ashes, suggesting a practically insignificant presence of other components, such as anhydrite, hematite, lime, maghemite, periclase, and magnetite. The presence of all these components was confirmed by micro-area chemical composition analysis using SEM/EDS. Crystalline components and unburned carbon typically coexisted with the glassy phase in the form of precipitates, occasionally forming individual grains (mainly unburned carbon). It is noteworthy that larger-sized grains are often multiphase, while smaller-sized grains exhibit the presence of a single phase (Fig. 1).

The chemical composition of the investigated fly ash revealed that the predominant components were SiO_2 and Al_2O_3 (Table 3), exhibiting relatively low concentrations, with SiO_2 at 52.20% by mass and Al_2O_3 at 24.67% by mass. Together, these two components accounted for over 76% by mass.

Chemical components present in amounts of a few mass percent included: Fe_2O_3 (6.78% by mass),

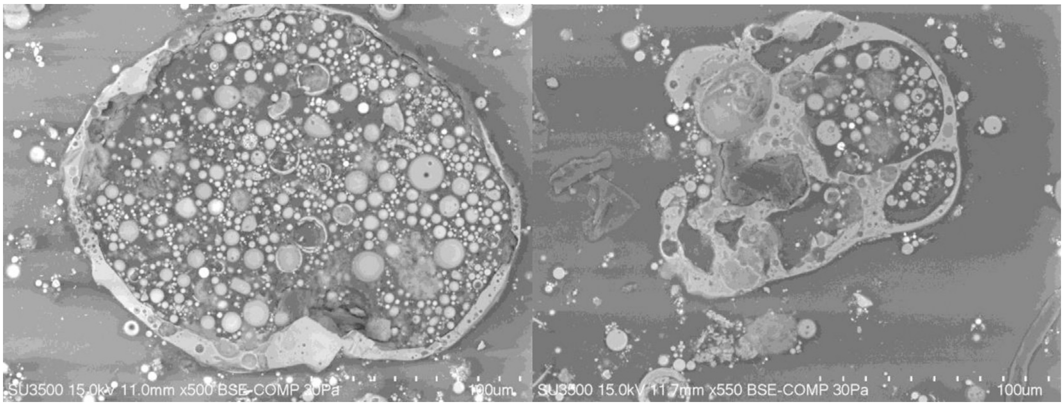

Fig. 1. Example SEM images of multiphase grains in fly ash.

Table 3. Contents of major chemical components in the investigated fly ashes from coal combustion (% by mass).

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI	Total
52.20	1.06	24.67	6.78	0.12	2.55	3.62	0.79	3.30	0.43	0.36	4.12	100.00

CaO (3.62% by mass), K_2O (3.30% by mass), MgO (2.55% by mass), Na_2O (0.79% by mass), and TiO_2 (1.06% by mass). The average content of the remaining chemical components (Mn_3O_4, P_2O_5, and SO_3) did not exceed 1% by mass.

Among the critical raw materials, the following elements were identified: cobalt, antimony, tungsten, beryllium, niobium, gallium, as well as lanthanides and yttrium (rare earth elements), as well as chromium and indium.

The results of the analysis of selected critical metallic raw materials in the fly ashes from the power plants in the Czech Republic are presented in Table 4.

Table 4. Content of selected critical metallic raw materials in fly ashes from the combustion of coal, including chromium and indium.

Be	Co	Ga	Nb	Sb	W	Cr	In
ppm							
7.0	40.4	40.01	19.4	7.79	9.3	168	0.18

The cobalt content in the examined fly ash was 40.4 ppm. The cobalt content did not show a positive correlation with any of the identified phases, except for the quartz content, which exhibited a negative correlation with cobalt (−0.68), as also reflected in the case of SiO_2 (−0.50). Positive correlations with cobalt content were also found for TiO_2 (0.63), Al_2O_3 (0.69), and P_2O_5 (0.53).

The antimony content in the examined fly ash was 7.79 ppm. Antimony content correlated with anhydrite (0.70), hematite (0.56), and periclase (0.69), as well as negatively correlated with quartz (−0.52). These correlations were also observed with the main chemical components of these phases: SO_3 (0.69) and CaO (0.78) for anhydrite, Fe_2O_3 (0.49) for hematite, MgO (0.63) for periclase, and SiO_2 (−0.80) for

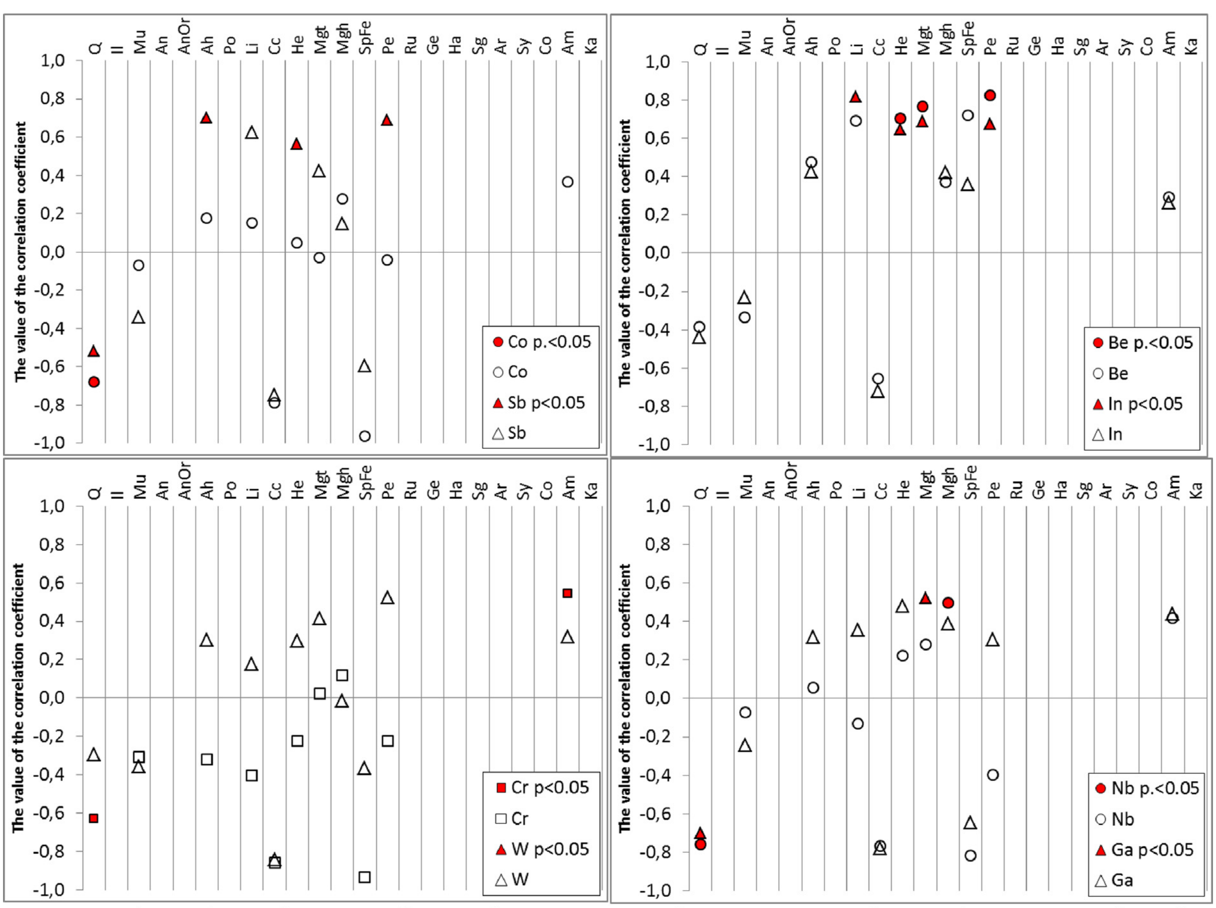

Fig. 2. Values of correlation coefficients between mineral components and critical raw materials in fly ash from the Czech power plant. Significant correlations are marked in red ($p < 0.05$).

quartz. A high correlation with Na_2O (0.83) was also noted.

The tungsten content in the examined fly ash was 9.3 ppm. The tungsten content did not show a correlation with the identified mineral phases in the fly ash. However, a positive correlation was observed with CaO (0.51), SO_3 (0.51), and Fe_2O_3 (0.53).

The beryllium content in the examined fly ash was 7.0 ppm. For beryllium, correlations were found with periclase (0.82), hematite (0.71), and magnetite (0.77). The correlation with iron-containing minerals was confirmed by a high correlation with Fe_2O_3 (0.90). Positive correlations were also observed for beryllium content with CaO (0.61), SO_3 (0.82), Na_2O (0.63), and negative correlations with SiO_2 (−0.58) and K_2O (−0.55).

The niobium content in the examined fly ashes was 19.4 ppm. Niobium content showed a positive correlation with maghemite (0.50), a negative correlation with quartz (−0.76), and Mn_3O_4 (−0.77). Positive correlations were observed for niobium with TiO_2 (0.82), Al_2O_3 (0.85), P_2O_5 (0.52), and SO_3 (0.50).

The gallium content in the examined fly ash was 40.01 ppm. Gallium content showed a negative correlation with quartz (−0.70) and SiO_2 (−0.66). Simultaneously, positive correlations were noted for gallium content with magnetite (0.52) and Fe_2O_3 (0.65), as well as TiO_2 (0.63), Al_2O_3 (0.71), CaO (0.48), Na_2O (0.49), and SO_3 (0.68).

The chromium content in the examined fly ash was 168 ppm. Chromium content showed a positive correlation with the glassy phase (0.55) and a negative correlation with quartz (−0.63). The positive correlation of chromium content with Al_2O_3 (0.53) and TiO_2 (0.60) supports the association of chromium with glassy phase. The correlation of chromium content and Al_2O_3 may be related to the ability of Cr^3+ ions to replace Al^{3+} or Fe^{3+} ions in aluminosilicates. A negative correlation was also observed with ignition loss (−0.48).

The indium content in the examined fly ash was 0.18 ppm. Indium content showed a correlation with hematite (0.65), magnetite (0.69) and, consequently, with Fe_2O_3 (0.81). Correlation was also observed with periclase (0.67), lime (0.80), as well as with CaO

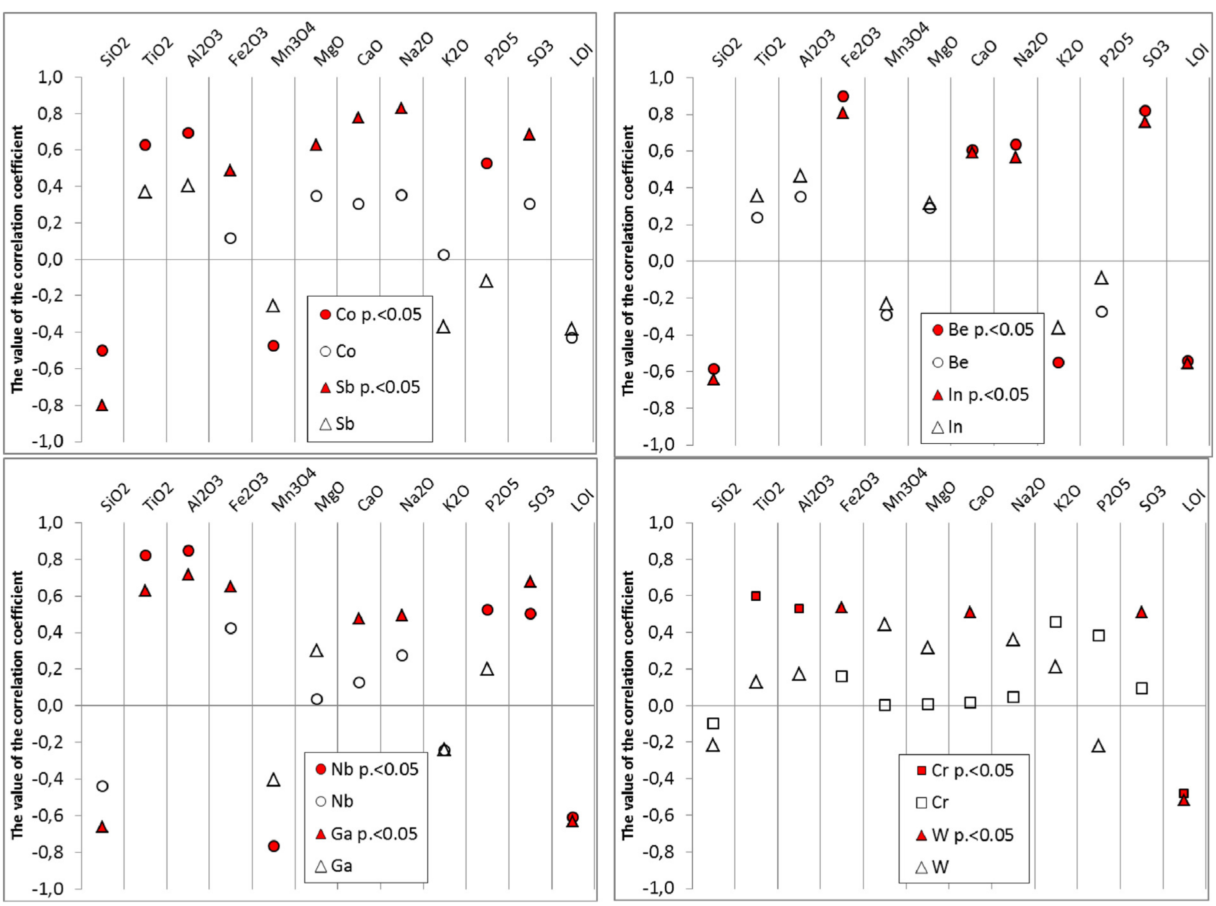

Fig. 3. Correlation coefficients between the primary chemical components and critical raw materials in fly ash from the Czech power plant. Significant correlations are marked in red (p < 0.05).

Table 5. Rare earth element content in the investigated fly ash sample from the Czech power plant.

Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ppm														
39.9	37.8	85.6	10.7	39.3	8.7	2.0	9.2	1.3	7.8	1.6	4.1	0.7	4.3	0.6

Table 6. Rare earth element content in the investigated fly ash sample from the Czech power plant.

REY	LREY	HREY	LREY	MREY	HREY	CE	UNC	EE	CE	UNC	EE	C_{outl}	ΣREO
ppm			%			ppm			%				ppm
253.61	182.11	11.30	72	24	4	94.40	66.40	92.81	37	26	37	1.02	300.01

(0.59) and SO_3 (0.76). A negative correlation was noted with SiO_2 (−0.64) and a positive correlation with Na_2O (0.57).

Figures 2 and 3 depict positive and negative correlation coefficient values between individual mineral components and the aforementioned elements, as well as the main chemical components.

3.1. Rare earth elements content in ash

The concentration of rare earth elements and yttrium (REY) in fly ash samples obtained from a Czech power plant measured 253 ppm. When converted to oxides, the REO content is 300 ppm. Among the REE, the highest share, amounting to 182.11 ppm,

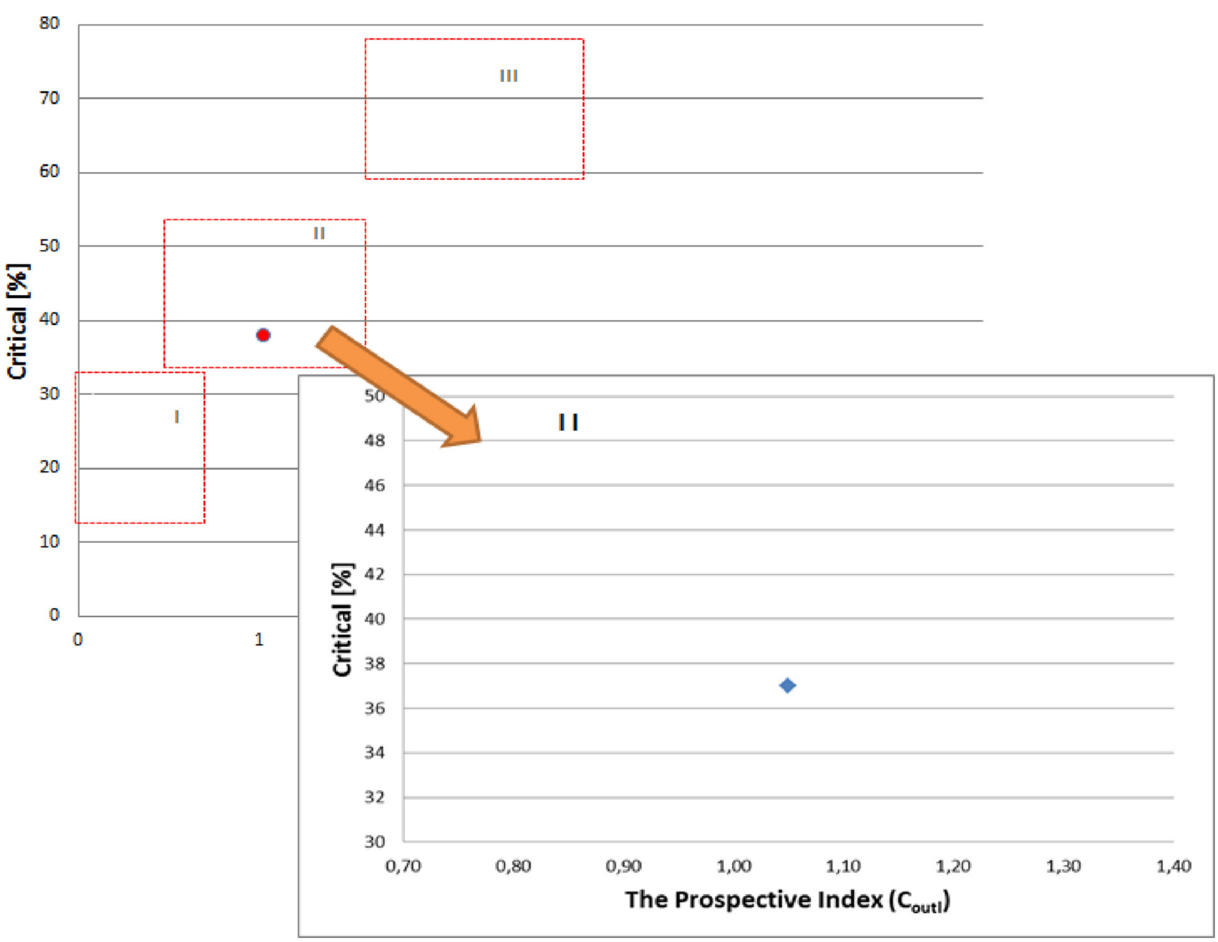

Fig. 4. The correlation between the critical content of rare earth elements and the outlook coefficient C_{outl} [26]. The classification scheme for REY sources is as follows: Category I – unpromising, Category II – promising, and Category III – highly promising.

is attributed to light rare earth elements (LREY). The heavy rare earth elements (HREY) exhibit the smallest share at 11.30 ppm (Tables 5 and 6). The contribution of critical elements (CE) to the total REY content in the examined fly ash was 94.40 ppm. The concentration of uncritical elements (UNC) within the overall REY content in the analyzed sample was 66.40 ppm, whereas the presence of excessive elements (EE) in the total REY content amounted to 92.81 ppm. To evaluate the analyzed fly ash samples as a prospective rare earth elements and Y (REY) source, the perspective coefficient (C_{outl}) was computed, considering the levels of critical and surplus elements (refer to Tables 5 and 6; see Fig. 4).

3.2. Correlations of REY with phase composition

Table 7 provides a summary of correlation coefficients (r values) for different relationships involving the content of rare earth elements, LREY, HREY, medium rare earth elements (MREY), CRM and minerals in the analyzed sample, including anhydrite and quartz. The correlation coefficients (r) and their characteristics are provided in the context of the examined relationships. The term "Significant" is used to indicate statistically significant correlations.

Mullite, commonly found in fly ash samples, manifests predominantly as a component dispersed within the amorphous glaze. As such, has been examined the associations between the content of rare earth elements and the cumulative shares of mullite and amorphous glaze. The following Table 8 presents the results of the analysis concerning the relationship between mullite and the content of rare earth elements, particularly in the context of the mullite and amorphous glaze share. There was no notable correlation identified between the content of rare earth elements and the proportion of other mineral phases. The correlation coefficient values (r) are included, as well as the statistical significance of the correlation and the type of correlation.

Table 7. Correlations of REY with phase composition in the investigated fly ash sample from the Czech power plant.

Correlations (r)	LREY	MREY	HREY	CRM
REY content and anhydrite	−0.50			
LREY content and anhydrite	Significant			
Absolute values of correlation coefficients (LREY to HREY)	Decrease			
CRM content and anhydrite	No significant correlation			
MREY Content and quartz		−0.72		
HREY content and quartz			−0.80	
REY content and quartz	No significant correlation			
LREY content and quartz	No significant correlation			
Absolute values of correlation coefficients (LREY to HREY)	Increase			
Critical elements content and quartz				−0.58

Table 8. Correlation between REY content and mullite and amorphous glaze in the fly ash sample from the Czech power plant.

Correlation	r
REY Content vs. mullite & amorphous gaze	
- correlation coefficient	0.51
- correlation significance	Significant
- correlation type	Positive
Correlation coefficients for the above relationship	
- LREY vs. mullite & amorphous glaze (r value)	
- MREY vs. mullite & amorphous glaze (r value)	Significant
- HREY vs. mullite & amorphous glaze (r value)	Significant
Absolute values of correlation coefficients (LREY to HREY)	Increase
CRM content vs. mullite & amorphous glaze share	
- correlation coefficient (r)	0.64
- correlation significance	Significant
- correlation type	Positive
REY content vs. other mineral phases share	
- correlation coefficient (r)	No significant correlation

3.3. Correlations of REY with chemical components

Table 9 presents the results of the correlation analysis between the content of rare earth elements,

Table 9. Correlations between the contents of REY with the major chemical components of the fly ash sample from the Czech power plant.

Correlation (r)	REY	LREY	HREY	CRM
REY content vs. TiO_2	0.62	0.47 to 0.89		
REY content vs. Al_2O_3	0.51	0.35 to 0.88		
Values of correlation coefficients (LREY to HREY)		Increase		
TiO_2 vs. CRM				0.77
Al_2O_3 vs. CRM				0.71
REY content vs. P_2O_5	0.75	0.72 to 0.61		
Values of correlation coefficients (LREY to HREY)		Decrease		
CRM vs. P_2O_5				0.74
REY content vs. Mn_3O_4	−0.70	−0.60 to −0.75		
Values of correlation coefficients (LREY to HREY)		Increase		
REY vs. Mn_3O_4	−0.60	−0.60 to −0.75		
Absolute values of correlation coefficients (LREY to HREY)		Increase		
CRM vs. Mn_3O_4	−0.78			
REY vs. MgO	−0.58			
REY vs. CaO	−0.59			
LREY vs. MgO		−0.68		
LREY vs. CaO		−0.71		

LREY, HREY, and the proportion of critical elements with the major chemical components of fly ash samples. The involvement of medium rare earth elements was not observed. No significant correlation was detected between the rare earth elements content and the proportion of other mineral phases such as SiO_2, Fe_2O_3, SO_3, Na_2O, and K_2O. The correlation coefficient values (*r*) and their ranges have been included, and the presence of significant correlations has been indicated.

4. Conclusions

In the examined ash from the Czech power plant, the main phases are: glassy phase (Am), constituting 66.5% by mass, mullite (Mu) (20.12% by mass), and quartz (Q), with a share of 11.07% by mass. All three phases (Am, Mu, Q) together account for over 97% by mass in the investigated ashes, indicating a practically insignificant contribution of other components, such as anhydrite, lime, hematite, magnetite, maghemite, and periclase. The chemical composition of the examined fly ash revealed that SiO_2 and Al_2O_3 were the dominant components. Together, these two components accounted for over 76% by mass. Among the critical raw materials, cobalt, antimony, tungsten, beryl, niobium, gallium, as well as lanthanides and yttrium (rare earth elements), were identified, along with chromium and indium. The content of rare earth elements (REY) in the fly ash sample from the power plant was 253 ppm (REO is 300 ppm). The light rare earth elements (LREY) had the highest share among the rare earth elements, at 182.11 ppm, while the heavy rare earth elements (HREY) had the smallest share at 11.30 ppm. The share of critical elements in the total REY content in the fly ash was 94.40 ppm, while the content of non-critical elements in the total REY content in the examined sample was 66.40 ppm, and the content of excessive elements in the total REY content was 92.81 ppm. Based on the analyzed research results, it can be concluded that the examined ash could be a potential source of some raw materials. The calculated prospective coefficient value $C_{outl} > 1.02$ allows considering the examined ash from the Czech power plant as a promising REY resource. Therefore, conducting further research on the content of critical elements in coal combustion ashes to estimate their potential resources is of great importance.

Ethical statement

The authors state that the research was conducted according to ethical standards.

Funding body

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Conflicts of interest

The author declares no conflict of interest.

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