

ANALYSIS OF CONTENT OF SELECTED CRITICAL ELEMENTS IN FLY ASH

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Abstract

Pursuant to the new mineral policy of the European Union, searching for new sources of raw materials is required. Coal fly ash has long been considered as a potential source of a number of critical elements. Therefore, it is important to monitor the contents of the critical elements in fly ash from coal combustion. The paper presents the results of examinations of the contents of selected elements, i.e. beryllium, cobalt, chromium and germanium in fly ash from Polish power plants. The results of the conducted investigations indicate that the examined ash samples from bituminous coal combustion cannot be treated as a potential source of the analysed critical elements. The content of these elements in ash, though slightly higher than their average content in the sedimentary rocks, is, however, not high enough to make their recovery technologically and economically justified at this moment.

Keywords: fly ash, critical elements, bituminous coal

1 INTRODUCTION

Ensuring the supply of raw materials has become one of the main tasks of the European Union Commission for the past several years, as a result of dwindling mineral resources and a growing dependence of the European industry on supplies from China, the USA, Russia and Brazil. In order to assess the situation of the European mineral mining industry, identify raw materials needed for the further development of European countries, and initiate a new mineral policy, the EU Commission formed an Ad hoc Working Group on defining critical raw materials [5, 17]. A list of critical raw materials was created for the EU. The latest list includes the following elements: antimony, beryllium, chromium, cobalt, indium, gallium, germanium, magnesium, niobium, tungsten, silicon, platinum group metals (platinum, palladium, iridium, rhodium, ruthenium, osmium), and rare earth elements (yttrium, scandium and the lanthanides). The critical elements are mainly characterized by a high supply risk, a low rate of recovery from secondary sources, a limited scale of substitution, and a great importance for the development of the world economy (especially for electronics, telecommunications, and automotive industries) at the same time.

About 90% of global raw material supplies originate from extra-EU sources. The biggest producer of critical raw materials is China, but several other countries have major supplies of specific raw materials for example the USA (beryllium), Brazil (niobium), Democratic Republic of Congo (cobalt), South Africa (PGM). Due to developing supply risk for raw elements along with the menace to the competitiveness of the EU economy, it has become necessary to search for new sources of such materials. The issue of critical materials, in relation to the Polish national mineral resources, has been the subject of several studies [3, 16, 20].

Coal as a heterogeneous organic sedimentary rock contains practically all the elements of the Periodic Table. As a result of coal combustion, the coal mineral material transforms to an incombustible residue (fly and bottom ash) enriched in a number of trace elements. For example, the average content of germanium in coal ash is 18 mg/kg [10], but as some research showed [9], it can reach 420 mg/kg. It was also specified [10] that the coalphile elements are: Ni, Hf, Sn, La, Co, Ba, Sc, Nb, Sr, Th, Ga, Cu, REE, Zn, W, Au, In, Pb, U, B, Be, while those highly coalphile are: Ag, Sb, Tl, As, Mo, Ge, Hg, Bi, Se. Therefore, coal ashes have long been regarded as a potential source of critical elements [4, 12, 13, 15, 19]. Furthermore, in recent years, intensive studies have been conducted on recovery of germanium, gallium, and vanadium from ashes formed in the industrial plant for coal gasification IGCC Puertollano [8, 9]. Additionally, a pilot plant was built for the recovery of aluminium and gallium from fly ashes resulted from a coal-fired power plant in 2011 in China [18].

The European energy sector is largely based on fossil fuels; in Poland almost the whole production of electricity (81%) is obtained from coal (hard and lignite) combustion [7]. Therefore, the amount of combustion waste (products) is very large. Fly ash is the main solid product (representing almost 66%) from coal combustion [6]. In Poland, fly ash production reaches 4.5 million tonnes [1], while in Europe exceeds 124 million tonnes annually [6].

The aim of this study was preliminary to assess the content of selected critical elements such as beryllium, cobalt, chromium, and germanium in samples of fly ashes from bituminous coal combustion. The study was performed to establish whether the examined fly ash from Polish power plants can be regarded as a potential source of critical elements such as Be, Co, Cr, and Ge.

2 MATERIALS AND METHODS

The subject of this study was four samples of fly ash from three Polish power plants (labelled A-C). The sample specification is provided in Table 1. All ash samples were collected from pulverized fuel furnaces fed with bituminous coals mainly from the Upper Silesian Coal Basin. The sample C2 was obtained from combustion of coal from the Lublin Coal Basin.

Table 1: Samples specification

Sample ID	Power plant	Coal origin
A1	A (South Poland)	Upper Silesian Coal Basin
B1	B (South Poland)	Upper Silesian Coal Basin
C1	C (Central Poland)	Upper Silesian Coal Basin
C2	C (Central Poland)	Lublin Coal Basin

The samples were firstly dried at 105 °C and then digested in a closed microwave system. For the sample digestion, a concentrated nitric acid and hydrofluoric acid were used (in a ratio of 3:1). In order to carry out the complexation of the fluoride, a saturated boric acid was added. The obtained clear solution was analysed using the Hitachi Z-2000 atomic absorption spectrometer with Zeeman background correction. As the source of radiation, hollow cathode lamps were used. The determination of the contents of beryllium, cobalt, and chromium was performed using flame atomization, while as for germanium – electrothermal atomization. The parameters of each analytical method are shown in Table 2.

For the general characterization of the analysed ash samples, the content of main components was determined. The determination of the contents of the main constituents of ash (oxide of silicon, aluminium, calcium, iron, magnesium, sodium, and potassium) was also performed using flame atomic absorption spectrometry.

Table 2: Parameters of analytical methods of analysed elements

Parameter	<i>Beryllium</i>	<i>Cobalt</i>	<i>Chromium</i>	<i>Germanium</i>
Analytical line [µm]	234.9	240.7	359.3	265.2
Atomizer	High-temperature burner	Standard burner	Standard burner	Graphite furnace
Gas	C ₂ H ₂ + N ₂ O ₂	C ₂ H ₂ + air	C ₂ H ₂ + air	Ar
Modifier	-	-	-	Pd-Mg, Na
Detection limit [mg/kg]	0.52	4.8	5.4	0.12
Relative standard deviation [%]	3.7	6.4	5.0	9.6

3 RESULTS AND DISCUSSIONS

Chemical composition of examined fly ash is presented in Figure 1. All tested samples have similar content of main compounds, typical for bituminous coal fly ash. The content of oxides of silicon and aluminium is more than wt. 70%, in a ratio of 2:1 respectively. The ash contains only a few percent of the calcium and magnesium oxides, and 6-9% of iron oxide. The sample C2 (ash from combustion of coal from the Lublin Coal Basin) has the lowest content of alkali and oxides of calcium, magnesium, and iron.

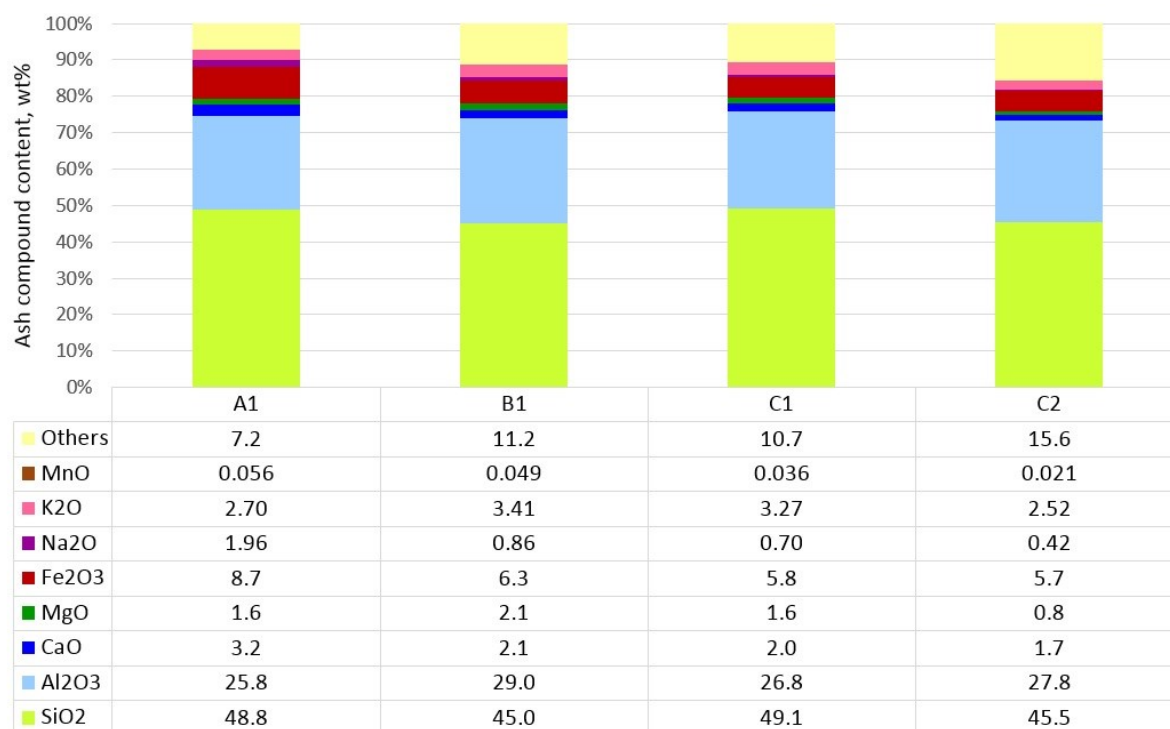


Figure 1: Main compounds of examined ashes

The contents of the analysed elements (beryllium, cobalt, chromium and germanium) in the ash samples are presented in Figure 2. The chromium content is much greater compared to the other elements and ranges from 126 to 156 mg/kg. The average concentration of cobalt for the examined samples equals 48.0 mg/kg, with the lowest content in the *A1* sample (38.7 mg/kg), and the highest in the *C2* sample (53.6 mg/kg). In case of beryllium concentration, the sample *A1* significantly differs from the other samples. The content of Be in this sample equals 36.8 mg/kg, which is three times higher compared to the others. Germanium has the lowest concentration (4.5–9.7 mg/kg) in the examined ash samples. The fact that the samples *C1* and *C2* have almost identical contents of the analysed elements and similar chemical composition deserves special attention, particularly due to the origin of the combusted coal. The previous publications [11, 14] suggest that coal from the Lublin Coal Basin can be enriched in trace elements, including critical elements.

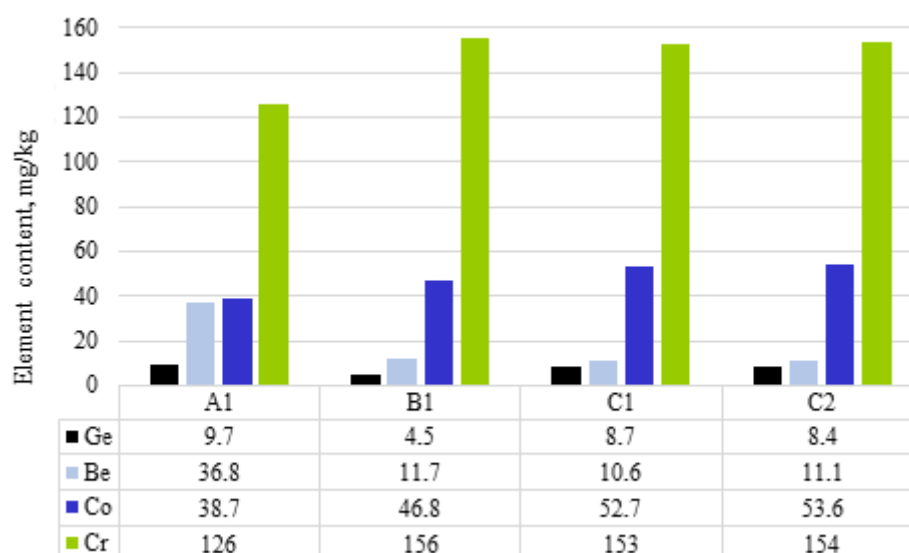


Figure 2: Content of selected critical elements in examined ashes

In order to define the suitability of the tested ashes as potential materials for critical elements recovery, the enrichment factor EF was estimated [2] (excluding reference element) according to the equation (1):

$$EF = \frac{A_e}{A_c} \quad (1)$$

where:

A_e – content of element in sample [mg/kg],

A_c – Clark value of element [mg/kg]

The Clark value is meant an average value of a concerned element in the earth's crust or specific type of rock.

For this purpose, the average content of analysed elements in the tested samples was summarized with the average content of this element in fly ashes from bituminous coal combustion and the average content from sedimentary rocks (Table 3) according to [10]. Additionally, EF was compared with a Coal Affinity Index (CAI), defined as a ratio of the average content of element in the ashes from bituminous coal and lignite to its average concentration in sedimentary rocks.

Table 3: The suitability of tested ashes as a potential material for critical elements recovery [10].

Element	Average value [mg/kg]			Factors [-]					
	Bituminous coal fly ash	Clark value for sedimentary rocks	Polish examined fly ashes	CAI	EF				
					AI	BI	CI	C2	Average
Beryllium	12 ±1	1.9	17.6	6.3	19.4	6.2	5.6	5.8	9.3
Cobalt	37 ±2	14	48	2.6	2.8	3.3	3.8	3.8	3.4
Chromium	120 ±5	58	147	2.1	2.2	2.7	2.6	2.7	2.5
Germanium	18 ±1	1.4	7.8	12.9	6.9	3.2	6.2	6.0	5.9

The average content of Be in the examined ash samples is a bit higher than its average content in the total fly ash. However, if the sample AI (which overestimates the value) is excluded, the average content will be 11.1 mg/kg and the EF equal to 5.8 (similar to CAI). Even so, the content of beryllium in the examined ashes is at least six times higher compared to its average content in sedimentary rock. In the case of cobalt and chromium, their average contents in the Polish ash samples are also higher than their contents in the total fly ash, but not more than 30%. Therefore, EF for both elements is close to their CAI and shows that their concentration in the examined samples is threefold higher than the Clark value. Only the germanium content is twice less in the tested samples compared to the average content in the fly ashes. Nonetheless, EF at the level of 5.9 shows a greater Ge enrichment in the samples.

The comparison of the obtained results with previous studies [21] on determining the content of critical elements in waste from coal cleaning processes shows that fly ashes are characterized by a substantial enrichment of the critical elements. The beryllium EF for waste from coal cleaning was 1.6 and the cobalt EF was 1.0. For one sample of coal from the Lublin Coal Basin, the beryllium and cobalt EFs for its ash was very high: for Be it was 40.6 and for Co – 11.7.

Even so, the contents of Co, Cr, Ge, and Be in the examined samples are similar to average contents in typical fly ashes. Therefore, the tested fly ashes will not be interesting for the industrial recovery of these metals. Only the AI sample contains a high amount of beryllium, nonetheless this ash would be regarded as beryllium-poor source of this metal.

4 CONCLUSION

Summing up the average content of the analysed elements in the examined Polish fly ash is similar to the typical content of the elements in total fly ash and the values: 17.6 mg Be/kg, 48 mg Co/kg, 147 mg Cr/kg, and 7.8 mg Ge/kg. The critical element enrichment in the tested samples is noticeable. Although the EFs of the analysed elements significantly exceed 1, their concentrations are insufficient in order to consider the examined fly ash as a potential source of the critical elements at the present day. However, monitoring the critical elements contents in fly ashes from both bituminous coal and lignite combustion should be further continued. Furthermore, the ashes should be stored separately to be able to use them in the future.

ACKNOWLEDGEMENTS

This work was supported by the AGH grant No. 15.11.210.311.

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