Analysis of the occurrence of critical elements and raw materials in Polish lignite deposits with particular emphasis on coal ashes

M Wagner¹*, B Bielowicz¹ and J Misiak¹

¹AGH University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection, Mickiewicza Av. 30, 30-059 Krakow, Poland

E-mail: wagner@geol.agh.edu.pl

Abstract. Fly ash collected from landfills at power plants using lignite from the following mines: Turów in Bogatynia, Bełchatów in Rogowiec, and Pątnów in Konin was subjected to analysis. Petrographic studies were performed using a reflected light optical microscope. The chemical composition (the presence of minor, trace, and rare elements) was determined using ICP-MS and X-ray spectroscopy. Petrographic examination using a JEOL JXA-8230 electron microprobe analyzer allowed determining critical elements in the selected minerals. Silicate and aluminosilicate enamel, mullite aggregates, magnetite-hematite iron microspheres and fine unburned carbon particles were found in the analyzed fly ash samples; in addition, small amounts of gypsum and anhydrite were also recorded. The results of oxide analyses of fly ash samples, e.g. CaO content higher than 10% wt, suggest their calcium character. In order to present interesting concentrations of the analyzed critical elements, their maximum contents were compared to their Clarke values (for sedimentary rocks and crustal rocks). The comparison to Clarke values of sedimentary rocks, based on calculation of the enrichment factor (EF), has shown that the content of majority of critical elements in lignite and its ashes is similar to the mean values for sedimentary rocks; the contents higher than Clarke value did not exceed the mentioned values and were observed in the case of tungsten (6.2 - the Turów deposit) and silver (5 to 7 in the Turów deposits). In addition, the comparison of analytical content to Clarke values of crustal rocks did not fundamentally alter these relations; the maximum contents higher than the Clarke value were recorded for tungsten (9.4) and silver (9.3) in the Turów deposit. The microanalysis of iron microspheres has revealed the presence of Ga. In the case of the platinum group, the presence of Pd, Pt, In, Nb, V, Cu, and Ti was confirmed.

1. Introduction

The mined coal and its ashes, including the so-called fly ash collected in electrostatic precipitators of professional power plants and CHPs, may be the source of some critical elements, even though coal and waste generated during its exploitation are not classified as critical elements or raw materials. This is due to the limited number of scientific studies, which, in turn, is a consequence of the low concentration of critical elements in coal that can be compared to the average content in other sedimentary rocks (the Clarke value of sedimentary rocks) even when the concentration of multiple elements is taken into account. The economically satisfactory concentration of critical elements in the mentioned raw materials is uncommon and can be observed mainly in small coal deposits formed or subjected to secondary transformation under specific conditions deviating from common models of sedimentation (e.g. epigenetic hydrothermal or exhalation mineralization, poor metamorphism, particularly during the so-called metasomatic metamorphism).

Among the many applications of critical elements and raw materials, special attention should be paid to the production of the so-called clean energy. The most important elements from this group include: Ga, In, REE, Si, Pt, Li, Co, Ge, Ru, Pd, and Se [1,2].
Some elements from this list are being searched or exploited in Poland and are currently, or were recovered in the past, during metal refining [3,4]. These include, among others, metals such as zinc, cadmium, nickel, cobalt, molybdenum, vanadium, tin, rhenium; non-metallic elements - barium, fluorine, and a group of elements with intermediate properties: arsenic, antimony, and bismuth. The mentioned critical and deficient elements and raw materials are produced or explored primarily by the KGHM Polska Miedź. The Polish demand for raw materials is mainly met by imports [5].

2. Materials and research methodology
Fly ash collected from landfills at power plants using lignite from the following mines: Turów in Bogatynia, Belchatów in Rogowiec, and Pątnów in Konin, was subjected to analysis. In order to analyze fly ash (5 samples), the following analytical methods were applied:
- Examination using a reflected light petrographic microscope, immersion oil, and an OPTON-ZEISS optical microscope,
- The determination of chemical composition (the presence of minor, trace, and rare elements) carried out at the Acme Labs (Canada). A total of 53 elements, mostly metals, including most of the critical elements according to Christmann [2] were determined using inductively coupled plasma mass spectrometry (ICP-MS) and X-ray spectroscopy.

The concentration of the most widely distributed critical elements at the selected locations was determined on the basis of petrographic examination using a JEOL JXA-8230 SuperProbe Electron Probe Microanalyzer at the (AGH UST - KGHM Polska Miedź SA Laboratory of Critical Elements) Laboratory of Critical Elements of the Faculty of Geology, Geophysics and Environmental Protection at the AGH University of Science and Technology in Kraków.

3. Research results
3.1. Chemical composition of the examined fly ash
A characteristic feature of ashes originating from the power Belchatów, Pątnów, and Turów power plants is the increased CaO content, ranging from 18.48 to 26.22 (Table 1). Given the SiO₂ content above 30% wt and the Al₂O₃ content below 30% wt, the presented chemical composition allows classifying them as, in accordance to the BN-79/6722-09 standard, calcium-dominated ashes. Compared to the literature data, the chemical composition of the fly ash has changed (from aluminum- to calcium-dominated) only in the case of the Turów power plant [6].

The main chemical components of ash include SiO₂ (32.19-60.23% wt), CaO (18.48-26.22% wt), and Al₂O₃ (6.67-24.20 % wt). Iron converted to oxide is less abundant: (Fe₂O₃ - 3.88-7.52 % wt), MgO (1.21-3.30% wt), and TiO₂ (0.93-2.33% wt). These ashes exhibit a variable, predominantly small amount of alkali, which, as the sum of the oxides (Na₂O + K₂O), is in the range from 0.25 to 2.53 % wt (Turów); ashes with the content of alkali oxides greater than 0.5% wt may have a corrosive effect. The concentration of such oxides, including P₂O₅ and MnO, is of the order of tenths and hundredths of a percent (Table 1), while their values do not differ from older ashes [7].

| Sample | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | MnO |
|--------|------|-------|-------|-----|-----|------|-----|------|------|-----|
| 11     | 50.98| 16.48 | 4.23  | 1.19| 20.23| 0.16 | 0.12| 1.57 | 0.09 | 0.03|
| 14     | 32.19| 24.20 | 3.88  | 1.97| 26.22| 1.39 | 1.14| 2.33 | 0.20 | 0.03|
| 15     | 40.28| 19.72 | 7.52  | 1.22| 25.65| 0.12 | 0.13| 1.15 | 0.13 | 0.03|
| 18     | 51.67| 17.55 | 4.01  | 1.21| 18.48| 0.12 | 0.13| 1.38 | 0.10 | 0.03|
| 19     | 60.23| 6.67  | 4.14  | 4.30| 21.06| 0.08 | 0.54| 0.93 | 0.14 | 0.23|

The numbering of ash samples: 11 - Belchatów, 14 - Turów, 15 - Belchatów, 18 - Belchatów, 19 – Pątnów.

3.2. The petrographic analysis of fly ash in reflected light and immersion oil
The examination of fly ash resulting from the combustion of lignite from the Turów, Belchatów, and Pątnów power plants has confirmed the presence of microparticles from the following groups:
aluminosilicates (quartz, mullite), iron oxides, carbonates, and unburned organic matter. The ferromagnetic grains (microspheres), found in the following concentrations in the samples examined using an electron microprobe:

- Turów (sample no. 14) – 0.20%,
- Belchatów (sample no. 18) – 0.78%,
- Pątnów (sample no. 19) – 1.19%, are promising in analyzing the occurrence of critical elements.

Iron microspheres are highly variable in terms of both size and morphology [8]. The size of cenospheres and plerospheres ranges from a few to several dozen micrometers. Cenospheres may have very thin walls (tenuisphere). The cenosphere walls can also be thicker (crassisphere), in which case they usually show secondary porosity within the walls. The spherical objects (plerospheres) can be filled with porous magnetite-hematite aggregates, where lighter hematite lamellae are clearly visible against the background of the darker magnetite. Some of the plerospheres are fully filled with magnetite containing fine (lighter) hematite lamellae. In addition, plerospheres filled with enamel (of dark gray color) containing magnetite grains in different geometrical forms have also been found. In some cases, magnetite in the enamel filling the microspheres forms various dendritic-skeletal forms. In addition, magnetite-hematite aggregates filling the gaps in the enamel have also been shown in the examined samples.

3.3. The content of critical elements in the examined fly ash

Overall, 32 elements, classified as critical, were determined out of the total mass of fly ash (Table 2). These elements are classified to all three groups due to the risk of deficiency in the coming years. In order to estimate their maximum amount in fly ash, they were compared to the Clarke value in both ortho-lignite (worldwide ortho-lignite deposits excluding Polish deposits according to [9] and the earth's crust [10]. The comparison was based on the calculation of enrichment factors (EF - Table).

When it comes to heavy rare earth elements (HREE), only gallium (Ga), and yttrium (Y) were determined. The content of Ga in fly ash from Belchatów and Turów is twice or almost twice as high the above mentioned Clarke value (Table 2); while in the case of the Pątnów power station, the mentioned content is about two times lower. The above-Clarke concentrations of yttrium (Y) were recorded in only one ash sample (Belchatów), with the EF of about 1.4. In the remaining samples, its content is close to the Clarke value; a slight deviation can be observed for the sample from the Turów power station. Yttrium, however, is a highly variable element, as indicated by a comparison of the composition of all samples.

When it comes to the second group of heavy rare earth elements (HREE) in the examined fly ash, the concentrations of lanthanum (La), cerium (Ce), and scandium (Sc) were determined. The concentrations of both Ce and La in the examined ash samples, with the exception of the Pątnów sample, are elevated and range from 1.18 to 1.69 (Belchatów) and from 1.15 to 1.64 (Belchatów), respectively.

The concentration of scandium slightly deviates from the above relationships and is lower than the Clarke value in all samples.

When it comes to the platinum group, the concentration of platinum (Pt) and palladium (Pd) was determined. The palladium enrichment factor in the samples of fly ash from Belchatów is up to 50, while special attention should be paid to the Turów sample, in which the content of this metal is <10 ppm, with a detection limit of 0.1 ppm (Table 2). This gives an enrichment factor (EF) of palladium lower than 16.6 thousand and higher than 1600; therefore, it is necessary to repeat the determination process for fly ash from the Turów power plant due to the exceptional value of this metal in numerous applications.

The platinum content (Pt) in the examined ashes is not shown or is low (Table 2). It is worth noting that the enrichment factor of the ash sample from Turów, containing 2 ppm of platinum, is 200 times higher than its Clarke value in the earth's crust.

In the vast majority of fly ash, the concentration of Beryllium (Be) is lower than its Clarke value in the earth's crust; the only exception is the sample from the Turów power plant, with the enrichment
factor of 1.10. In the discussed deposit, elevated gamma radiation levels (higher or close to 1.5 pCi/kg), measured by the "f1" condition, are observed for lignite and ash [11], which is clearly related to the content of this element.

A number of elements, including: cobalt (Co), germanium (Ge), indium (In), magnesium (Mg), niobium (Nb), antimony (Sb), wolfram (W), aluminium (Al), chromium (Cr), iron (Fe), nickel (Ni), tellurium (Te), copper (Cu), and titanium (Ti) can be found in fly ash in concentrations comparable to or slightly lower than the Clarke value in the earth's crust (Table 2), and hence they are not of interest for our study. Similar values are characteristic for manganese with the exception of fly ash from the Pątnów deposit and power plant, where the elevated presence of this element and the EF of about 1.79 can be observed.

Table 2. Summary of the occurrence of critical elements in the examined fly ash.

| Group | Power plant | Belchatów | Belchatów | Belchatów | Pątnów | Turów | The Clarke value in the earth’s crust |
|-------|-------------|-----------|-----------|-----------|--------|-------|------------------------------------|
| CE    | CE ash type | fly ash   | fly ash   | fly ash   | fly ash | fly ash |                                   |
|       | Sample no.  | 18        | 11        | 15        | 19     | 14     |                                   |
| HREE (I) | Y  ppm     | 29.87     | 32.21     | 46.54     | 27.00  | 19.76  | 33.00                              |
| LREE (I) | Ce ppm    | 78.50     | 81.10     | 112.80    | 39.60  | 84.70  | 66.50                              |
| LREE (I) | La ppm    | 44.80     | 47.10     | 64.10     | 17.70  | 50.10  | 39.00                              |
| LREE (I) | Sc ppm    | 13.90     | 15.40     | 16.80     | 8.00   | 11.20  | 22.00                              |
| I     | Ga ppm     | 22.00     | 23.70     | 24.00     | 7.30   | 20.80  | 12.00                              |
| I     | Pd ppm     | 0.03      | 0.03      | 0.02      | <0.01  | <0.002 | 0.01                               |
| I     | Pt ppm     | 0.00      | 0.00      | 0.00      | <0.002 | 2      | 0.01                               |
| I     | Be ppm     | 2.00      | 1.80      | 2.50      | 1.10   | 3.10   | 2.80                               |
| I     | Co ppm     | 11.60     | 11.00     | 17.70     | 9.20   | 15.80  | 25.00                              |
| I     | Ge ppm     | 1.10      | 1.20      | 1.10      | 0.50   | 0.40   | 6.20                               |
| I     | In ppm     | 0.10      | 0.14      | 0.15      | <0.02  | 0.06   | 0.25                               |
| I     | Mg %       | 0.54      | 0.55      | 0.60      | 1.79   | 0.78   | 2.33                               |
| I     | Nb ppm     | 0.09      | 0.07      | 0.11      | 18.00  | 0.20   | 20.00                              |
| I     | Sb ppm     | 0.24      | 0.33      | 0.19      | 0.30   | 0.62   | 1.20                               |
| I     | W ppm      | 0.30      | 0.40      | 0.60      | 0.60   | 0.50   | 1.25                               |
| II    | Al %       | 5.69      | 5.76      | 6.61      | 2.86   | 6.19   | 8.20                               |
| II    | Cr ppm     | 75.80     | 87.30     | 90.60     | 43.60  | 60.10  | 102.00                             |
| II    | Fe %       | 2.47      | 2.50      | 4.63      | 2.50   | 1.97   | 5.60                               |
| II    | Mn ppm     | 199.00    | 173.00    | 236.00    | 1701.00| 200.00 | 950.00                             |
| II    | Mo ppm     | 4.93      | 6.69      | 4.96      | 2.29   | 4.29   | 1.50                               |
| II    | Ni ppm     | 33.80     | 34.00     | 51.50     | 25.90  | 42.80  | 84.00                              |
| II    | Re ppm     | 0.03      | 0.04      | 0.05      | 0.00   | 0.00   | 0.0004                             |
| II    | Te ppm     | 0.29      | 0.38      | 0.26      | 0.18   | 0.05   | 100.00                             |
| II    | V ppm      | 132.00    | 151.00    | 169.00    | 45.00  | 146.00 | 120.00                             |
| II    | Zn ppm     | 70.00     | 65.40     | 97.20     | 22.90  | 43.40  | 70.00                              |
| III   | Ag ppm     | 0.12      | 0.14      | 0.11      | 0.06   | 0.13   | 0.12                               |
| III   | B ppm      | 55.00     | 58.00     | 69.00     | 261.00 | 69.00  | 72.00                              |
| III   | Ba ppm     | 253.30    | 316.30    | 323.10    | 775.00 | 95.00  | 425.00                             |
| III   | Ca %       | 12.07     | 12.79     | 17.28     | 13.17  | 17.34  | 3.54                               |
| III   | Cu ppm     | 35.72     | 43.91     | 42.98     | 14.28  | 40.92  | 60.00                              |
| III   | Li ppm     | 28.30     | 19.20     | 43.80     | 15.20  | 33.90  | 33.00                              |
| III   | Ti %       | 0.21      | 0.27      | 0.25      | 0.24   | 0.23   | 0.56                               |

CE – critical elements
Another interesting critical element in the examined fly ash samples is molybdenum (Mo), with the enrichment factor (EF), in relation to the Clarke value in the earth's crust, in the range from 1.52 to 4.46 (Table 2).

The presence of rhenium (Re) in the examined elements is also worth noting. This extremely rare element, though of great technical importance (Poland is the only manufacturer of this metal in Europe), which is supposed to be an accompanying element in the so-called cuboidal clays in the Belchatów deposit [12]. The concentration factor of this metal in fly ash from the Belchatów power plant is between 75 and 125. In addition, the rhenium content of the black clay rocks from the profile of the Belchatów lignite deposit should be examined in the future (the possibility of selective exploitation is indicated by the conclusions of Stryszewski [13]).

Manganese (Mn) is found in higher concentrations only in fly ash from the Pątnów power plant (EF=1.79), similarly to borium (B – 3.6) and barium (Ba – 1.8). In other examined ashes, the concentration of these elements is lower than the Clarke value in the earth's crust (Table 2).

The elevated silver (Ag) concentration in fly ash, shown by the analysis of chemical composition of lignite and its ashes, has not been confirmed. Only a slight increase in the concentration of this element has been shown for fly ash from the Belchatów and Turów power plants. This is due to the fact that the coefficient of volatility of this element is slightly higher (comparable to zinc) than in the case of other heavy element [14].

Lithium (Li) is another examined element that deserves special attention in the presented study; its above-Clarke concentrations were found in the fly ash from the Belchatów and Turów power plants (EF in the range from 1.0 to 1.3).

The summary of geochemical studies of fly ash is presented in Table 3, in which the mean, maximum and minimum values of the examined ash fly ash are summarized and compared to the Clarke value of lignite (Clarke value no. 1) and to the Clarke value in the earth's crust (Clarke value no. 2).

Compared to the Clarke value of lignite (Clarke value no. 1 in Table 3), the set of the so-called above-Clarke elements in the examined fly ash includes Y, La, In, Nb, Cr, Mn, and V. However, these values are of the same order as the Clarke value and can be compared to their content in coal. On the other hand, it should be noted that this comparison concerns coal rather than its ashes, where the concentration of micronutrients results from the combustion of carbonaceous matter with the exception of a few elements with high volatility (e.g. sulphur, mercury [13, 15]

Compared to the Clarke value in the earth's crust (Clarke value no. 2 – Table 3 ) the set of elements is more extensive and includes: Ga, La, Y, Ce, Pd, Be, Mn, Mo, Re, V, Zn, Ag, B, and Li. This summary highlights the maximum values for palladium (EF = 500) and rhenium (125) and the need for further studies in order to examine the relationship between the lithological types of rocks and the discussed concentrations.

3.4. The characteristic of critical elements in iron microspheres of the examined fly ash samples using the WDS analysis

The analysis, including determining the selected elements at the selected measurement points, was carried out on three preparations: Turów (sample no. 14) Belchatów (sample no. 18), and Pątnów (sample no. 19). In the case of sample no. 14 (Turów), a total of 12 elements were determined. Special attention should be paid to the concentration of gallium (Ga), ranging from 0 (5 measurement points) to 1,090 ppm, which is 90 times higher than its Clarke value in the earth's crust. In the case of the platinum group, the concentration of palladium (Pd) is between 0 (6 measurement points) and 290 ppm, which is 483,333 times higher than its Clarke value. The concentration of platinum ranges from 0 (in six measurement points) to 700 ppm, which is 35,000 times higher than its Clarke value. In the first group of critical minerals, the concentration of In is between 70-830 ppm (the concentration of 0 ppm was determined in one measurement point), which is 280-3,320 times higher than its Clarke value. In the case of niobium (Nb), this value ranges from 30 to 410 ppm (no niobium has been found in two measurement points), that is up to 20 times higher than the Clarke value. In the second group, the concentration of vanadium (V) ranged from 30 to 450 ppm (the concentration of 0 ppm was determined in four measurement point), which is several times higher than its Clarke value. In the
third group, the concentration of Cu ranged from 20 to 770 ppm (no Cu has been found in five measurement points), which is several times higher than its Clarke value. The concentration of Ti in the examined sample is close to its Clarke value with one exception, when it is ten times higher.

**Table 3.** The summary of the mean, maximum, and minimum values of the examined ash fly ash and their enrichment factors in relation to the maximum values.

| Group CE | CE | Mean value | Max value | Min value | Clarke value no. 1 | EF 1 | Clarke value no. 2 | EF 2 |
|----------|----|------------|-----------|-----------|-------------------|------|-------------------|------|
|         |     |            |           |           |                   |      |                   |      |
| HREE (I) | Y  ppm | 31.08  | 46.54  | 19.76  | 44  | 1.06  | 33  | 1.41  |
| LREE (I) | Ce ppm | 79.34  | 112.80 | 39.60  | 120 | 0.94  | 66.5 | 1.70  |
| LREE (I) | La ppm | 44.76  | 64.10  | 17.70  | 61  | 1.05  | 39  | 1.64  |
| LREE (I) | Sc ppm | 13.06  | 16.80  | 8.00  | 23  | 0.73  | 22  | 0.76  |
| I     | Ga ppm | 19.56  | 24.00  | 7.30  | 29  | 0.83  | 12  | 2.00  |
| I     | Pd ppm | 0.02   | 0.03   | 0.02   | 0.07 | 0.43  | 0.00006 | 500.00 |
| I     | Pt ppm | 0.00   | 0.00   | 0.00   | 0.02 | 0.00  | 0.01  | 0.00  |
| I     | Be ppm | 2.10   | 3.10   | 1.10   | 6.7  | 0.46  | 2.8   | 1.11  |
| I     | Co ppm | 13.06  | 17.70  | 9.20   | 26  | 0.68  | 25  | 0.71  |
| I     | Ge ppm | 0.86   | 1.20   | 0.40   | 11  | 0.11  | 6.2   | 0.19  |
| I     | In ppm | 0.11   | 0.15   | 0.06   | 0.11 | 1.36  | 0.25  | 0.60  |
| I     | Mg %  | 0.85   | 1.79   | 0.54   | N/A | N/A   | 2.33  | 0.77  |
| I     | Nb ppm | 3.69   | 18.00  | 0.07   | 18  | 1.00  | 20  | 0.90  |
| I     | Sb ppm | 0.34   | 0.62   | 0.19   | 5   | 0.12  | 1.2   | 0.52  |
| I     | W ppm  | 0.48   | 0.60   | 0.30   | 6   | 0.10  | 1.25  | 0.48  |
| II    | Al %  | 5.42   | 6.61   | 2.86   | N/A | N/A   | 8.2   | 0.81  |
| II    | Cr ppm | 71.48  | 90.60  | 43.60  | 82  | 1.10  | 102  | 0.89  |
| II    | Fe %  | 2.81   | 4.63   | 1.97   | N/A | N/A   | 5.6   | 0.83  |
| II    | Mn ppm | 501.80 | 1701.00 | 173.00 | 550 | 3.09  | 950  | 1.79  |
| II    | Mo ppm | 4.63   | 6.69   | 2.29   | 15  | 0.45  | 1.5   | 4.46  |
| II    | Ni ppm | 37.60  | 51.50  | 25.90  | 52  | 0.99  | 84   | 0.61  |
| II    | Re ppm | 0.03   | 0.05   | 0.00   | N/A | N/A   | 0.0004 | 125.00 |
| II    | Te ppm | 0.23   | 0.38   | 0.05   | N/A | N/A   | 100  | 0.00  |
| II    | V ppm  | 128.60 | 169.00 | 45.00  | 140 | 1.21  | 120  | 1.41  |
| II    | Zn ppm | 59.78  | 97.20  | 22.90  | 110 | 0.88  | 70   | 1.39  |
| III   | Ag ppm | 0.11   | 0.14   | 0.06   | 0.59 | 0.24  | 0.12  | 1.17  |
| III   | B ppm  | 102.40 | 261.00 | 55.00  | 410 | 0.64  | 72   | 3.63  |
| III   | Ba ppm | 352.54 | 775.00 | 95.00  | 900 | 0.86  | 425  | 1.82  |
| III   | Ca %  | 14.53  | 17.34  | 12.07  | bd  | bd    | 3.5   | 4.95  |
| III   | Cu ppm | 35.56  | 43.91  | 14.28  | 74  | 0.59  | 60   | 0.73  |
| III   | Li ppm | 28.08  | 43.80  | 15.20  | 49  | 0.89  | 33   | 1.33  |
| III   | Ti %  | 0.24   | 0.27   | 0.21   | 0.4 | 0.68  | 0.56  | 0.48  |

Explanations: the Clarke value no. 1 – the average content of the analyzed element in worldwide ortho-lignite deposits [8,9], klark 2 – average content of the analyzed element in the earth's crust [9], N/D – not available, CE – critical elements.

In the case of sample no. 18 (Belchatów), a total of 13 elements were determined. The concentration of gallium (Ga), ranges from 0 (3 measurement points) to 620 ppm, which is 51 times higher than its Clarke value in the earth's crust. In the platinum group, the concentration of palladium
(Pd) is between 0 (7 measurement points) and 150 ppm, which is 250,000 times higher than its Clarke value. The concentration of platinum ranges from 0 (in nine measurement points) to 680 ppm, which is 68,000 times higher than its Clarke value. In the first group of critical minerals, the concentration of In is between 70-1,410 ppm (the concentration of 0 ppm was determined in two measurement points), which is 280-5,640 times higher than its Clarke value. The concentration of Nb ranges from 40 to 520 ppm (no niobium has been found in five measurement points), that is up to 26 times higher than the Clarke value.

In the second group, the concentration of vanadium (V) ranged from 30 to 320 ppm (no vanadium has been found in seven measurement point), which is several times higher than its Clarke value. In the third group, the concentration of Cu ranged from 30 to 520 ppm (no Cu has been found in five measurement points), which is several times higher than its Clarke value. The content of Ti in the examined sample is close to its Clarke value. 

In the case of sample no. 19 (Pątnów), a total of 10 elements were determined. The concentration of gallium (Ga), ranges from 0 (1 measurement point) to 460 ppm, which is 38 times higher than its Clarke value in the earth's crust. In the platinum group, the concentration of palladium (Pd) is between 0 (6 measurement points) and 300 ppm, which is 500,000 times higher than its Clarke value. The concentration of platinum ranges from 0 (in five measurement points) to 570 ppm, which is 28500 times higher than its Clarke value. In the first group of critical minerals, the concentration of In is between 300-630 ppm (the concentration of 0 ppm was determined in one measurement point), which is 1,200-2,520 times higher than its Clarke value. The concentration of Nb ranges from 10 to 380 ppm (no niobium has been found in two measurement points), that is up to 20 times higher than the Clarke value. In the second group, the concentration of vanadium (V) ranged from 30 to 240 ppm (no vanadium has been found in four measurement point), which is several times higher than its Clarke value. In the third group, the concentration of Cu ranged from 50 to 300 ppm (no Cu has been found in six measurement points), which is several times higher than its Clarke value. The content of Ti in the examined sample is close to its Clarke value.

4. Summary
1. The results of oxide analysis of fly ash samples suggest their calcium character due to the CaO content higher than 10% wt.
2. Silicate and aluminosilicate enamel, mullite aggregates, magnetite-hematite iron microspheres and fine unburned carbon particles were found in the analyzed fly ash samples; in addition, small amounts of gypsum and anhydrite were also recorded.
3. Overall, 32 elements, classified as critical, were determined out of the total mass of fly ash. Compared to the Clarke value of worldwide lignite deposits (Clarke value no. 1 in Table 3), the set of the so-called above-clarke elements includes Y, La, In, Nb, Cr, Mn, and V. However, these values are of the same order as the Clarke value and can be compared to their content in coal.
4. Compared to the Clarke value in the earth's crust (Clarke value no. 2 – Table 3 ) The set of elements is more extensive and includes: Ga, La, Y, Ce, Pd, Be, Mn, Mo, Re, V, Zn, Ag, B, and Li. This summary highlights the maximum values for palladium (EF = 500) in fly ash from the Turów power plant and rhenium (125) in fly ash from the Bełchatów power plant. Based on the obtained results, there is a need for further studies in order to examine the relationship between the lithological types of rocks (the so-called cuboidal clays in the Bełchatów deposit) and the discussed concentrations. The enrichment factors of other critical elements in relation to the earth's crust are low and do not exceed 5.0.
5. The content of selected critical elements in iron microspheres was examined using an electron microprobe (EDS-WDS). Based on the obtained results, the abovementioned ferromagnetic microspheres are promising in analyzing the occurrence of these elements. A total of 9 elements (Ta, In, V, Ga, Rh, Nb, Pd, Pt, and Cu) were selected for the analysis.
6. The proportion of iron microspheres in the examined ash ranges from 0.20 to 1.19% by volume.
7. The microanalysis of these elements has shown that the concentration of Ga is up to 1090 ppm (sample no. 14, Turów), which is 90 times higher than its Clarke value in the earth's crust. In the case of the platinum group, the concentration of palladium (Pd) is 300 ppm (measurement point no. 19,
Pątnów), which is 500,000 times higher than its Clarke value. The concentration of platinum is 700 ppm (measurement point no. 14, Turów), which is 35,000 times higher than its Clarke value. In the first group of critical minerals, the concentration of In is up to 1,410 ppm (sample 18, Belchatów), which is 3,320 times higher than its Clarke value, while in the case of Nb this value is 520 ppm, that is 20 times higher than the Clarke value. The determined amounts of V, Cu, and Ti indicate that they are up to several times higher than their Clarke values.

8. Iron microspheres, due to their strong magnetic properties, seem to be relatively easy to separate. Each year, a total of 1,849 tones of fly ash are captured in Polish lignite-fired power plants [16]; hence, it is possible to obtain about twenty tons of ferromagnetic fly ash in order to recover the elements which concentration is significantly higher than their Clarke value.

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