

Article

# Ashes Qualified as a Source of Selected Critical Elements (REY, Co, Ga, V)

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**Abstract:** The subject of the research involved fly ashes from several power plants in Poland, produced in the process of hard coal and lignite combustion. The objective of this article was to determine the concentration and distribution of elements strategic for the EU economy in ashes and in their two finest grain classes (below 20  $\mu\text{m}$  and 45  $\mu\text{m}$ ). The differences in grain size of these ashes, as shown by granulometric tests, were significant. The concentrations of elements in the ashes and in grain classes were compared with the world average (Clarke value) for this raw material. For the majority of critical elements, a dependence of the concentration on the size of ash particles was observed. The content of REY (Rare earth elements and yttrium) and other critical elements in hard coal ashes increases with decreasing particle size. Despite the increase in the concentration of REY in the class below 20  $\mu\text{m}$ , the Clarke value of these elements was not exceeded. Pearson's correlation coefficients confirmed the interdependence between some elements of the ashes. The distribution of trace elements in grain classes of the ash was determined on the basis of observations using a scanning electron microscope equipped with an EDS (Energy Dispersive Spectroscopy) detector. Components of fly ashes that can be treated as an alternative source of strategic elements for the European Union were indicated.

**Keywords:** critical elements; grain classes; fly ash; rare earth elements; particle size



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## 1. Introduction

While fly ash is an attractive resource in itself, there are ways to make it even more attractive. The transition to a circular economy model forces us to change our approach to the management of wastes, which should be transformed into products [1–8]. Separation of the finest grain class from ash can change its properties, and thus create new potential and new areas of application. Such qualified ashes can be an ideal additive, e.g., to new generation high-quality concretes, self-compacting concretes, or as an additive to plastics. Many studies have demonstrated that the addition of the finest FA (Fly ash) to cement, with a high proportion of spherical particles, results in a material with improved performance properties [9–15]. Separation of the finest particles can also be an important step in the pre-processing of ashes, during the recovery process of some critical elements from them. The presence of over 80 metals, including rare earth elements, have been found in power plant ashes [16]. The recovery of such elements from combustion products may be promising due to the decreasing resources of rare earth metals and their increasing use in new technologies [17–21]. An extensive description of the selected recovery methods of such valuable metals from fly ashes can be found in the work [22]. Obviously, in order to develop the most effective method for their recovery, the problem of the speciation of rare earth elements must be solved. Understanding the distribution and speciation of elements in FA is extremely important for the development of economically viable and environmentally friendly ash enrichment technologies [22,23]. Research conducted so far allows for the conclusion that the distribution of elements in combustion products and in flue gas cleaning products is characteristic for a given element, and it also depends

on the types of boilers, combustion conditions, the method of dust removal, and flue gas treatment [24–34]. It was also emphasized that the enrichment of coal combustion products with chemical elements is a function of not only their physicochemical and morphological properties, but also their concentration in coal [35,36]. Critical metal enrichment of coal is attributed to both geological and geochemical factors, including volcanism, regions of sediments origin, groundwater, and various syngenetic and post-diagenetic fluids [37,38]. It is the origin of critical elements that their size and shape depend on. In coal, REY can be associated with both inorganic and organic matter [19]. The same is true of coal combustion products. Based on the research cited in the paper [19], it was found that such metals may occur in ash in association with amorphous glassy materials Si-Al, with discrete minerals or compounds, or they may occur in organic associations (with unburned carbon). Numerous studies have pointed to the relationship between the size of ash particles and the concentration of selected elements [21,39–42]. In general, higher concentrations of REE (Rare earth elements) were found in the finer grain class. Yet, other grain classes have often been studied. For example, Lin et al. [17] obtained the highest REE concentrations in the 38–25 class and below 20  $\mu\text{m}$ , and Wu et al. [36] in the grain class below 5  $\mu\text{m}$ , which had the highest REE enrichment factor of 1.45. In addition to REE, high concentrations in the fine grain class of FA with a large specific surface area were also found for F, V, Zn, and Pb [43]. Fei et al. [21] found Li, Ga, Nb, Ta, and REY mainly in small aluminosilicate glass particles. Prior to that, Martinez-Tarazona and Spears [44] indicated a clear increase in the concentration degrees of As, Ba, Cr, Cu, Mo, Nb, Ni, Pb, V, and Zn in progressively finer particle classes of FA. These are mainly elements that evaporate in the boiler, and then they are passed to electrostatic precipitators where the temperature decreases. As a result of such changes, vapor condensation occurs on fly ash particles. Since the smallest particles have a larger surface area, the condensation mainly occurs on their surface [28]. However, unlike some elements, such as Zn, As, Cd, and Cr, the concentration of REE is not a function of their volatility [45,46]. Along with trace elements, the distribution of basic elements was studied. The concentrations of Si, Al, Fe, Ca, K, Na, and Mg were lower in fine ash particles [47–49]. It was also demonstrated that there is a group of elements, P, Nb, Cr, Ta, U, W, Rb, and Ni, that does not change concentration with change in particle size. Uniform distribution of these elements in all grain classes indicates a weak relationship between the enrichment and the surface area of the particles. These elements are probably evenly distributed in the inner part of the FA particles.

The research presented in the paper was aimed at determining the concentration of elements strategic (REY, Sc, Be, Co, Ga, Hf, Nb, Sr, Ta, V, W, Sb, and Bi) for the European Union economy in the smallest grain classes of FA. Such elements have been specified on the list submitted by the European Commission [50], which is systematically expanded upon along with the development of new technologies. The basic criterion in the development of such a list was the expected economic importance of a raw material for the needs of the economy in the 21st century and the supply risk. Such studies may contribute to the extension of the existing knowledge necessary for the development of technology for recovery of critical elements from FA. This paper is the continuation of the works [51,52].

## 2. Materials and Methods

These ashes come from pulverized coal boilers with natural circulation in which the combustion temperature in the core of the combustion chamber reaches 1450–1600 °C.

Ash samples were taken from retention tanks collecting waste from electrostatic precipitators. The collected samples were therefore an averaged mixture of fly ashes produced in these power plants.

The chemical composition of grain classes (below 20 and 45  $\mu\text{m}$ ) of FA was investigated in a laboratory at Bureau Veritas Mineral Laboratories in Canada using inductively coupled plasma mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES). In addition to basic chemical elements, the study analyzed the elements considered to be

critical by the European Commission: Be, Sc, Co, Ga, Nb, Sr, Ta, V, W, Sb, Bi, and REY. All samples were analyzed by Lithium Borate Fusion.

The obtained results were compared with the concentration of those elements in the FA from which the individual grain classes were obtained. The data on the chemical composition of those ashes had already been presented in articles on magnetic fraction [51,52]. For the selected ashes, measuring sensor QICPIC by Sympatec GmbH (Clausthal-Zellerfeld, Germany) was used to obtain full information about particle size. The sensor is based on Dynamic Image Analysis (DIA) technology, which allows for measurement of particle shape and size distributions as well as characterization of individual particles. The chemical and granulometric studies were supplemented with studies making use of a high-resolution scanning electron microscope (SEM) JSM 7200F by JEOL (Tokyo, Japan), equipped with an EDS detector (Octane Elite Super (EDAX, Inc. (Pleasanton, CA, United States))). The microscope allows for the determination of the elemental composition of samples having a size of a few micrometers, or to create a distribution map of chemical elements over a larger area. The test samples were embedded in resin, and then metallographic microsections were prepared, which were sputtered with a Cu layer ~5 nm thick in order to ensure that the charge from the surface of the samples is taken away (Leica EM SCD500 (Germany) sputtering machine). The observations were made using a BSE detector. The tests were carried out using the accelerating voltage of 15 kV. Designation of samples used for testing is presented in Table 1.

**Table 1.** Designation of samples used for testing.

Sample Number	Fly Ash	Sample Number	Grain Class below 45 $\mu\text{m}$	Sample Number	Grain Class below 20 $\mu\text{m}$
1		145		120	
3		345		320	
7	from hard coal	745	ash from hard coal	720	ash from hard coal
11		1145		-	
-		945		920	
6	from lignite	645	ash from lignite	620	ash from lignite
12		1245		-	

### 3. Results

#### 3.1. Results of the Granulometric Analysis

The results of the analysis of grain composition of FA from which the individual grain classes were separated are summarized in Tables 2 and 3. The knowledge involving the share of the analyzed grain classes in the total mass of ash is important in terms of cost-effectiveness of the recovery of critical elements. Moreover, particle size has a significant impact on the possible further use of the ashes for other purposes.

**Table 2.** Characteristic values of the particle size distribution of the tested ash samples.

Sample	Particle Size Distribution			
1	$X_{10.3} = 9.99 \mu\text{m}$	$X_{50.3} = 68.14 \mu\text{m}$	$X_{90.3} = 288.44 \mu\text{m}$	$X_{99.3} = 371.76 \mu\text{m}$
3	$X_{10.3} = 8.91 \mu\text{m}$	$X_{50.3} = 38.66 \mu\text{m}$	$X_{90.3} = 163.74 \mu\text{m}$	$X_{99.3} = 220.36 \mu\text{m}$
7	$X_{10.3} = 7.73 \mu\text{m}$	$X_{50.3} = 16.84 \mu\text{m}$	$X_{90.3} = 60.94 \mu\text{m}$	$X_{99.3} = 128.02 \mu\text{m}$
11	$X_{10.3} = 8.54 \mu\text{m}$	$X_{50.3} = 35.37 \mu\text{m}$	$X_{90.3} = 138.25 \mu\text{m}$	$X_{99.3} = 228.39 \mu\text{m}$
6	$X_{10.3} = 18.95 \mu\text{m}$	$X_{50.3} = 77.01 \mu\text{m}$	$X_{90.3} = 283.10 \mu\text{m}$	$X_{99.3} = 371.63 \mu\text{m}$
12	$X_{10.3} = 10.51 \mu\text{m}$	$X_{50.3} = 31.53 \mu\text{m}$	$X_{90.3} = 100.82 \mu\text{m}$	$X_{99.3} = 313.25 \mu\text{m}$

Explanation e.g.,  $X_{10.3}$  is the size X, which 10.3% of all particles are finer.

**Table 3.** Share of grain class below 45 and 20  $\mu\text{m}$  in the tested ashes (%).

Sample	Grain Class below 45 $\mu\text{m}$	Grain Class below 20 $\mu\text{m}$
1	40	25
3	53	36
7	82	60
11	55	36
6	31	11
12	64	32

The range of grain size of the tested FA was from 0 to about 400  $\mu\text{m}$ . Differences in grain size between particular types of ashes are significant. The coarsest grain size was found for sample 6 from lignite. The share of the coarsest particles above 100  $\mu\text{m}$  was almost 40%, the class below 45  $\mu\text{m}$  accounted for 31%, and the particles below 20  $\mu\text{m}$  accounted for only 11%. Sample 1 was also characterized by a high content of coarse particles above 100  $\mu\text{m}$ , while the content of the finest grains below 20  $\mu\text{m}$  was 25%, and the class below 45  $\mu\text{m}$  in that sample accounted for 40%. In the context of the investigated problem, the share of fine grains in sample 7 is noteworthy, compared with the remaining samples. In that case, the content of grains below 20  $\mu\text{m}$  reached as much as 60% and the class below 45  $\mu\text{m}$  accounted for over 80%.

### 3.2. Chemical Composition

#### 3.2.1. Basic Components

The contents of basic components in FA and in two grain classes are presented in Table 4. Four fly ash samples (1, 3, 7, and 11) were produced as a result of hard coal combustion [51,52]. Based on the total content of oxides  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , they were classified in accordance with ASTM standard as the class F fly ash. In the samples 6 and 12, produced from the combustion of lignite, the total content of the above oxides does not exceed 50%. This kind of material belongs to class C. For the lignite ash, a high content of CaO (22.48–27.03%) is observed, which means that this material can be classified as lime ash. The value of loss on ignition is in the range of 3.4–6.6%, and only for sample 3 is it much higher, exceeding 22%, which largely reflects a high content of unburned carbon in this sample. This parameter plays an important role in the use of ashes as cement components and as an additive to concrete. When fly ash with a high loss on ignition is used, grains of unburnt coal can be seen flowing out onto the surface of the concrete mix. Therefore, some European countries have adopted solutions in their national regulations narrowing the scope of the application of ashes with a loss on ignition exceeding 5% for concrete.

There was no clear regularity of changes in the concentration of the main chemical components, depending on the size of ash particles (Table 4). Only the concentration of  $\text{Al}_2\text{O}_3$  was slightly rising with the decrease of particles in the class F ashes. A similar trend was observed for the subcomponent  $\text{TiO}_2$ . For the lignite ash sample, however, a clear decrease in the content of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  was noticeable along with the decreasing particle size, in contrast to  $\text{Fe}_2\text{O}_3$  and CaO, where a reverse enrichment trend was observed. For both types of ash (classes F and C), however, a positive correlation was observed between particle size and the value of ignition losses, which confirms earlier studies claiming that unburned carbon accumulates mainly in the coarser grain classes.

#### 3.2.2. Critical Elements

The contents of critical elements in the tested ashes and their particle size classes are presented in Tables 5 and 6. The measured levels of critical elements were compared with the world average (Clarke value) for this raw material [53]. Most elements in hard coal ashes had comparable, although slightly lower, concentrations than the Clarke value. Only the concentration of V was higher than the world average. High content of this

element in Polish hard coals had been already observed by Idzikowski [54]. Due to variable valence, this element forms a number of complex cations and anions in the form of oxides, hydroxides, and chelate organic compounds.

**Table 4.** Basic components' content in the analyzed FA and the grain class samples.

Sample	Chemical Components (%)												Total
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>	LOI	
1	50.03	25.37	6.58	2.5	2.95	0.95	2.93	1.05	0.53	0.07	0.021	6.6	99.58
145	50.04	25.76	6.9	2.71	3.21	1.32	3.32	1.09	0.56	0.07	0.023	4.5	99.50
120	49.74	27.27	6.67	2.47	3.19	1.34	3.17	1.23	0.94	0.07	0.026	3.3	99.42
3	42.05	21.2	4.34	1.84	3.04	0.6	2.3	0.92	0.43	0.05	0.020	22.8	99.59
345	45.32	24.19	5.1	2.27	4.04	0.78	2.59	1.11	0.57	0.06	0.025	13.5	99.56
320	47.54	27.2	4.92	2.02	3.61	0.96	2.91	1.32	0.59	0.06	0.026	8.4	99.56
7	51.64	20.69	11.27	1.69	4.39	2.17	1.99	0.92	0.22	0.05	0.026	4.3	99.36
745	51.32	20.86	11.54	1.77	4.63	2.37	2.01	0.99	0.24	0.05	0.028	3.6	99.41
720	50.01	21.54	12.67	2.01	4.65	2.86	2.14	1.08	0.22	0.06	0.031	1.9	99.17
6	33.02	28.98	8	0.99	22.48	0.07	0.12	0.7	0.57	0.06	0.025	4.7	99.72
645	22.76	24.68	12.11	1.09	28.32	0.08	0.05	0.55	0.52	0.07	0.012	2.5	92.74
620	17.46	19.84	20.94	1.03	29.49	0.09	0.06	0.46	0.41	0.08	0.016	2.1	91.98
945	51.23	21.1	10.52	2.23	4.74	2.03	2.13	0.98	0.21	0.07	0.025	4.1	99.37
920	49.28	23.18	10.42	2.48	4.86	2.55	2.29	1.1	0.32	0.07	0.032	2.7	99.28
11	50.37	26.28	5.44	2.6	3.54	1.08	2.84	1.09	0.46	0.07	0.023	5.8	99.59
1145	50.77	26.76	4.89	2.83	4.12	1.29	2.86	1.2	0.56	0.08	0.026	4.1	99.49
12	31.68	25.39	9.19	1.27	27.03	0.06	0.14	0.91	0.44	0.06	0.028	3.4	99.60
1245	28.41	24.82	11.67	1.34	29.75	0.09	0.13	0.83	0.44	0.07	0.027	2	99.58

In lignite ashes (class C), higher concentrations of REE were observed, compared with their concentration in class F ashes. The Clarke value was surpassed in this raw material for all LREE (from La to Eu) and also for Er, Y, and V. It is noteworthy that the concentration of W was lower than in class F ashes, which is consistent with research by Bielowicz [55]. Yet, it has not been confirmed by the research of Zhang et al. [56]. In hard coal ashes, for the majority of critical elements, a dependence of concentration on particle size is noticeable (Tables 5 and 6). A similar trend was noticed by [35,43,47]. High enrichment factors relative to Clarke were noted for Co, Ga, and V (Figure 1). Despite the increase in REY concentration in progressively finer grain classes, the Clarke value in the class below 20 µm was not exceeded, as seen in Table 6. A different enrichment trend was observed in sample 6 (lignite ash). The highest concentration of REY was observed not in the finest class, but in the class below 45 µm (sample 6) (Table 6 and Figure 2). The highest enrichment factor relative to Clarke was noted for Y ( $EF_C = 2.1$ —sample 6 and  $EF_C = 2.2$ —sample 12), as seen in Figure 2. Despite a high enrichment factor in the tested particle class of Nd ( $EF_C = 1.62$ ) and Co ( $EF_C = 2.71$ ), better results were obtained earlier for the magnetic fraction, with  $EF_m = 1.97$  and  $EF_m = 3.1$ , respectively [52]. Therefore, the combination of both methods, magnetic separation and the separation of the finest grain class for the mentioned elements, could yield even better results.

**Table 5.** Trace elements content in the analyzed fly ash and their grain class samples.

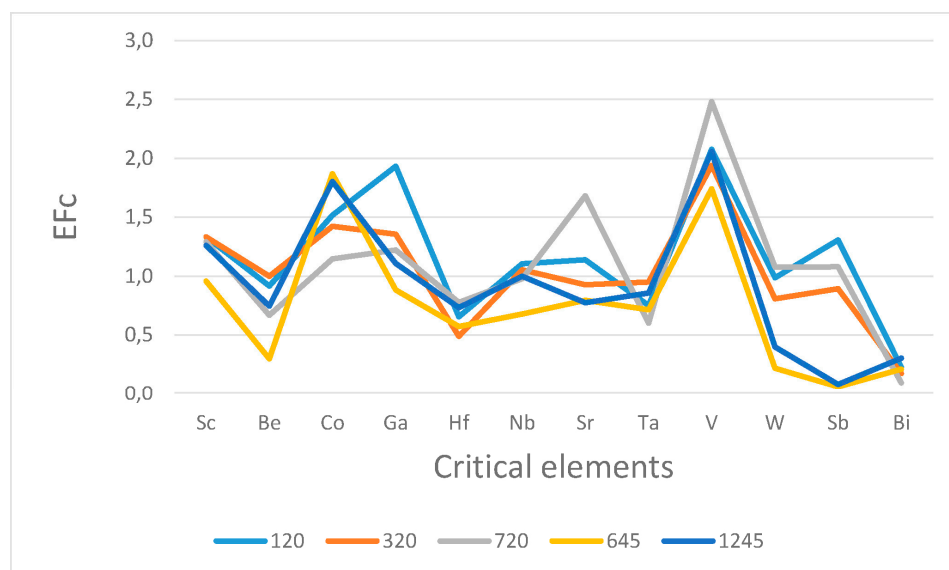
Sample	Element (ppm)											
	Sc	Be	Co	Ga	Hf	Nb	Sr	Ta	V	W	Sb	Bi
1	28	7	39.3	33.8	5.8	21.5	621	1.6	241	4.7	4	0.9
145	29	8	48.9	47.4	5	21.1	649.3	1.5	295	5.5	6.3	1.2
120	32	11	56.1	69.6	5.9	24.3	830.9	1.5	353	7.7	9.8	1.7
3	24	8	30.5	30.1	4.3	17.2	476.7	1.2	196	4.8	3	0.8
345	29	5	39.5	37.1	5.2	20.5	543.5	1.7	252	5.5	5.5	0.5
320	32	12	52.7	48.8	4.4	23.2	677	1.9	330	6.3	6.7	1.3
7	29	4	28.4	25.7	6.3	17.4	815	1.1	344	3.5	5.9	0.5
745	31	7	27.8	29.3	6.2	16.7	845.5	1.1	361	3.9	6.4	0.6
720	31	8	42.4	44	7	21.5	1228.6	1.2	422	8.4	8.1	0.7
6	24	3	30.1	27.3	4	13.7	458.1	0.9	192	1.7	0.1	0.6
645	22	2	48.6	25.6	4.3	12.2	587.2	1	244	1.3	0.3	0.9
620	20	2	70.4	25.1	4.3	11	529.5	0.6	248	3.2	0.4	1.4
945	26	5	31	27.8	6.3	17.7	874.7	1.2	315	5.1	5.9	0.5
920	30	10	43.6	47.8	6.2	21	1064	1.3	410	7.3	9.7	0.9
11	28	10	37.7	35	5.6	21.3	578.4	1.7	235	5.2	3.9	1.3
1145	30	9	41.9	44.7	6.3	23.6	657.8	1.6	268	6	5.7	1.4
12	27	1	42	34.5	5.9	22	586.1	1.5	274	2.7	5.7	1.4
1245	29	5	46.9	32.1	5.5	18	572.9	1.2	288	2.4	0.4	1.3
CVH	24 ± 1	12 ± 1	37 ± 2	36 ± 1	9 ± 0.3	22 ± 1	730 ± 50	2 ± 0.1	170 ± 10	7.8 ± 0.6	7.5 ± 0.6	7.5 ± 0.4
CVB	23 ± 1	6.7 ± 0.5	26 ± 1	29 ± 1	7.5 ± 0.4	18 ± 1	740 ± 70	1.4 ± 0.1	140 ± 10	6 ± 1.7	5 ± 0.4	4.3 ± 0.8

CVH/CVB—The value of the Clark of the researched element (coal ashes hard/coal ashes brown) [53].

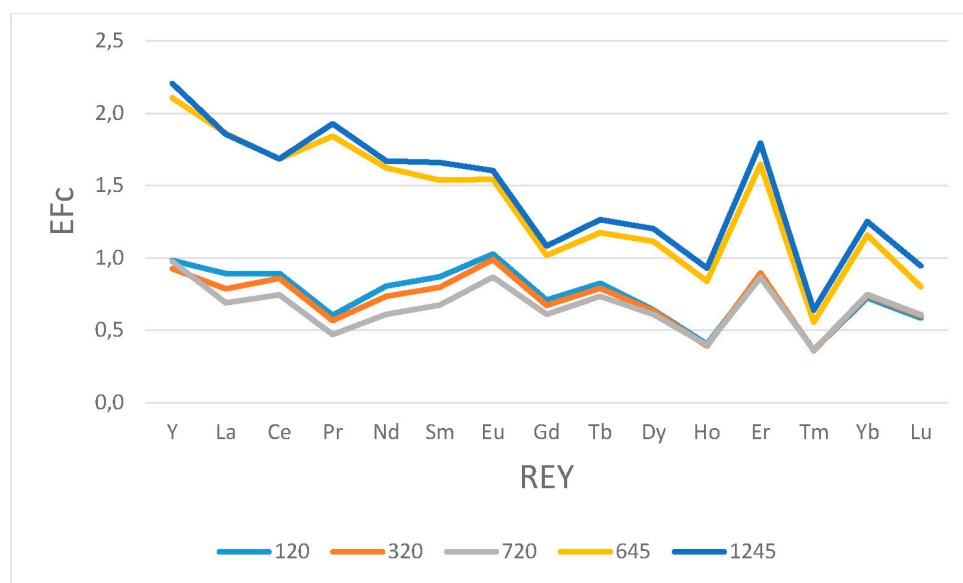
**Table 6.** REY content in the analyzed fly ash and their grain class samples.

Sample	Element [ppm]															$\Sigma$ REY
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
1	49.7	62.9	123.5	14.59	56.2	10.92	2.33	9.82	1.47	8.69	1.72	4.82	0.72	4.55	0.71	353
145	49.9	58	109.7	13.87	53	10.86	2.36	10.16	1.49	8.78	1.72	4.99	0.71	4.64	0.72	331
120	56	67.7	125	15.69	60.4	12.16	2.67	11.33	1.73	9.6	1.94	5.65	0.8	5	0.76	376
3	42	48.9	93.5	12.37	46.7	9.5	1.98	8.63	1.3	7.69	1.52	4.38	0.63	4.04	0.59	284
345	48.5	52.7	104.8	13.74	51.9	10.72	2.29	9.72	1.52	8.82	1.79	4.87	0.7	4.64	0.68	317
320	52.7	59.7	120.1	14.75	55.1	11.14	2.57	10.74	1.66	9.51	1.88	5.73	0.79	5.11	0.78	352
7	47.1	44.6	85.8	11.04	42.8	8.57	1.76	8.12	1.3	8.03	1.74	4.91	0.68	4.61	0.69	272
745	47.4	43.8	82.7	10.88	41.8	8.3	1.82	8.03	1.26	7.97	1.59	4.91	0.7	4.47	0.68	266
720	55.6	52.3	104.4	12.23	45.7	9.44	2.258	9.74	1.54	9.14	1.91	5.54	0.8	5.16	0.79	317
6	81.8	93.2	168.9	22.43	86.3	16.06	3.3	15.14	2.12	12.16	2.38	6.87	0.91	5.56	0.81	518
645	92.7	113.5	202.1	23.94	94.2	16.92	3.55	16.3	2.35	13.38	2.6	7.58	1	6.36	0.88	597
620	83	95.6	174.5	21.41	81	15.11	3.24	14.39	2.1	12.71	2.47	6.8	0.9	5.53	0.86	520
945	47	45.5	86.3	10.82	40.5	7.89	1.75	8.1	1.25	7.47	1.56	4.67	0.65	4.28	0.65	268
920	52	50.4	93.9	11.76	45.1	8.72	2.04	9.08	1.4	8.32	1.83	5.13	0.76	4.76	0.77	296
11	48.2	61.8	122.4	14.13	53.5	10.78	2.35	9.84	1.51	8.72	1.78	5.27	0.73	4.55	0.69	346
1145	53.2	65.1	126.9	14.89	58.6	11.33	2.4	10.22	1.63	9.21	1.89	5.42	0.81	4.98	0.75	367
12	92.7	113.5	197	24.05	90.6	17.33	3.66	16.07	2.42	13.76	2.79	7.76	1.06	6.71	1.02	590
1245	97.1	113.1	202.2	25.06	96.9	18.25	3.69	17.31	2.53	14.44	2.88	8.26	1.15	6.88	1.04	611
CVH	57 ± 2	76 ± 3	140 ± 10	26 ± 3	75 ± 4	14 ± 1	2.6 ± 0.1	16 ± 1	2.1 ± 0.1	15 ± 1	4.8 ± 0.2	6.4 ± 0.3	2.2 ± 0.1	6.9 ± 0.3	1.3 ± 0.1	-
CVB	44 ± 3	61 ± 3	120 ± 10	13 ± 2	58 ± 5	11 ± 1	2.3 ± 0.2	16 ± 1	2 ± 0.1	12 ± 1	3.1 ± 0.3	4.6 ± 0.2	1.8 ± 0.3	5.5 ± 0.2	1.1 ± 0.1	-

CVH/CVB—The value of the Clark of the researched element (coal ashes hard/coal ashes brown) [53].



**Figure 1.** Value of the enrichment factor relative to Clarke for selected trace elements. EFC = the concentration of an element in the grain class/the value of the Clark of the researched element.



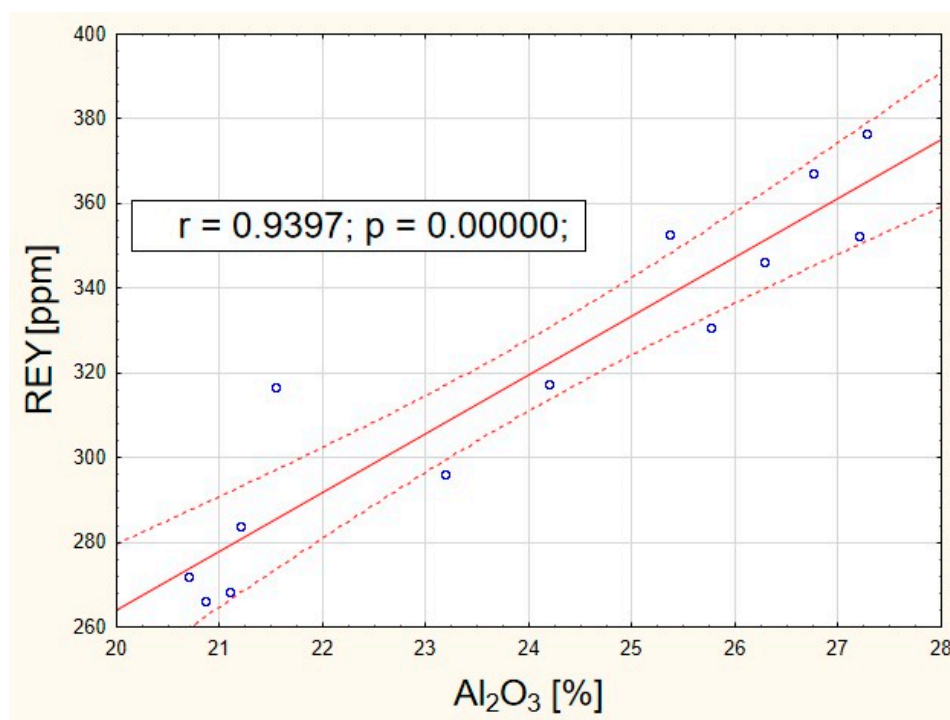
**Figure 2.** Value of the enrichment factor relative to Clarke for rare earth elements and yttrium.

Therefore, the multi-stage REE recovery method proposed in [22], combining magnetic and size separation with acid-base leaching, is appropriate. The next step in the recovery of these metals may be the removal of the Si-Al matrix, followed by membrane separation.

The latter is characterized by the high efficiency of recovery of rare earth elements and is an alternative to conventional techniques.

Pearson's correlation coefficients confirmed an interdependence between some elements of hard coal ashes. Among others, a strong positive correlation was reported between the content of REY and  $\text{Al}_2\text{O}_3$ , with  $r = 0.94$  (Figure 3). Thus, the results are in line with the research of Taggart et al. [57], who tested over 100 fly ash samples, mainly from the USA, and demonstrated, among other things, a positive correlation between the total REE content and  $\text{Al}_2\text{O}_3$ . The authors assume that the same geological factors responsible for the content of alumina in coal ashes may influence enrichment in REE.





**Figure 3.** Al<sub>2</sub>O<sub>3</sub> vs. REY scatter diagrams for the analyzed fly ash from hard coal samples. *r*—Pearson’s correlation coefficient; *p*—statistical significance level.

The research previously conducted by Querol et al. [58] confirmed the relationship between rare earth elements with aluminosilicates. Thus, the results suggest that the extraction of REE from the aluminosilicate glass fraction should allow for the recovery of a significant part of these elements from fly ash. For Ga and Al, a strong positive correlation ( $r = 0.6808$ ;  $p = 0.01$ ) was found, which results from the proximity of the ionic radii of the mentioned elements. Thus, future research should focus on the joint recovery of REY and Ga from fly ash, as already suggested in [21].

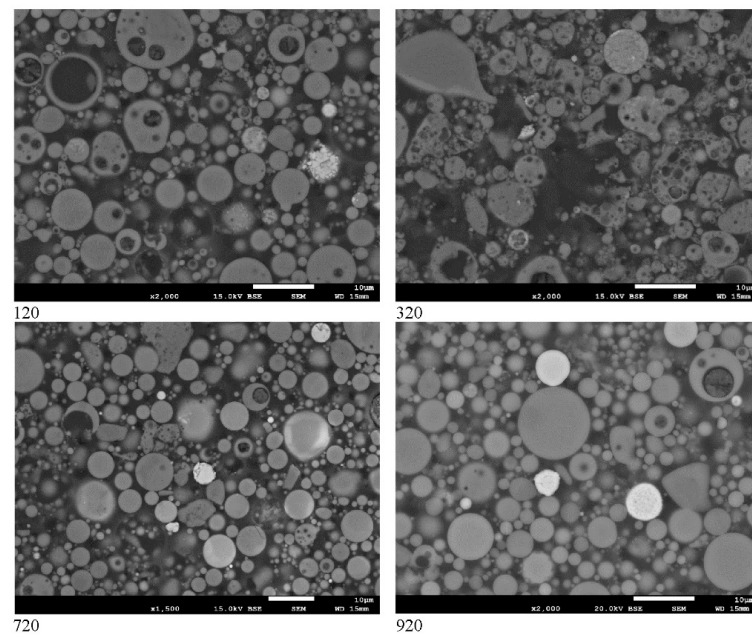
The concentration of V, which was clearly higher than the world average value in the tested ashes, was positively correlated ( $r = 0.788$ ;  $p = 0.001$ ) with Fe content, which results from the fact that this element often replaces iron. Since the content of Fe in ashes can vary within wide limits, the content of V in coal ashes also varies within wide limits, from trace amounts to several dozen percent [59].

The largest amounts of magnetic iron compounds are contained in silicate ashes. The obtained high enrichment coefficient V, both in the finest particle size class (Figure 1) and in the magnetic fraction ( $EF = 2.5$ ) [52], indicates that also for this element, the combination of both methods, i.e., magnetic and size separation, can bring an even better enrichment result.

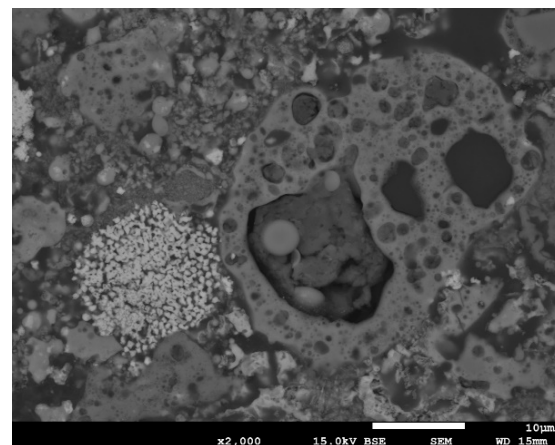
### 3.3. SEM/EDS

In order to better understand how the critical elements are present in the finest particle size class of FA and to be able to predict the possibilities of their recovery, research was carried out using a Scanning Electron Microscope (SEM) equipped with an attachment for examining elemental composition in micro-areas. This allowed for the study of FA in terms of grain scale. The characteristics of the smallest grain classes of FA were made based on the interpretation of images and EDS microanalysis. The results of the analyses are shown in Figures 4–13. In terms of microstructure, the examined grain classes of ashes are characterized by a diversified microstructure. The presence of grains with different surface morphology and grain habits have been reported (Figures 4 and 5). In samples 120 and 720, spherical grains dominate, although grains of irregular shape, often with visible microporosity, can occasionally be distinguished (Figure 4). In sample 645, only the

observations at high magnification reveal the presence of spherical forms (Figure 5). They are generally of aluminosilicate and calcium aluminosilicate character. It is the composition of the particles that primarily determines their morphology [60]. Single larger grains of irregular shapes with high porosity mainly consist of carbon. Particularly rich in these particles is sample 320 (dark fields) (Figure 4). Such unburned carbon indicates combustion inefficiency, and it is often an obstacle to the further use of FA. The EDS analyses are consistent with chemical analyses of the samples, and they confirm the presence of such elements as O, Al, Si, Ca as the main components, accompanied by S and Fe, and also traces of Na, Mg, P, K, Ti, Mn, Cu, and Zn. The EDS microanalyses showed that REEs are mainly found in glassy aluminosilicates, which had been noted previously [61–66]. In hard coal ashes, light elements LREY (Light group (La, Ce, Pr, Nd, Sm)) were more frequently observed, while in lignite ashes, heavy elements HREY (Heavy group (Ho, Er, Yb, Lu)) and medium MREY (Medium group (Eu, Gd, Tb, Dy, and Y)) were reported, according to the division cited in the paper [37].



**Figure 4.** Morphology of particles observed in the grain class of hard coal ashes (samples: 120, 320, 720, 920). Scale bar is 10  $\mu\text{m}$ .



**Figure 5.** Morphology of particles observed in the grain class of lignite ash (sample 645). Scale bar is 10  $\mu\text{m}$ .

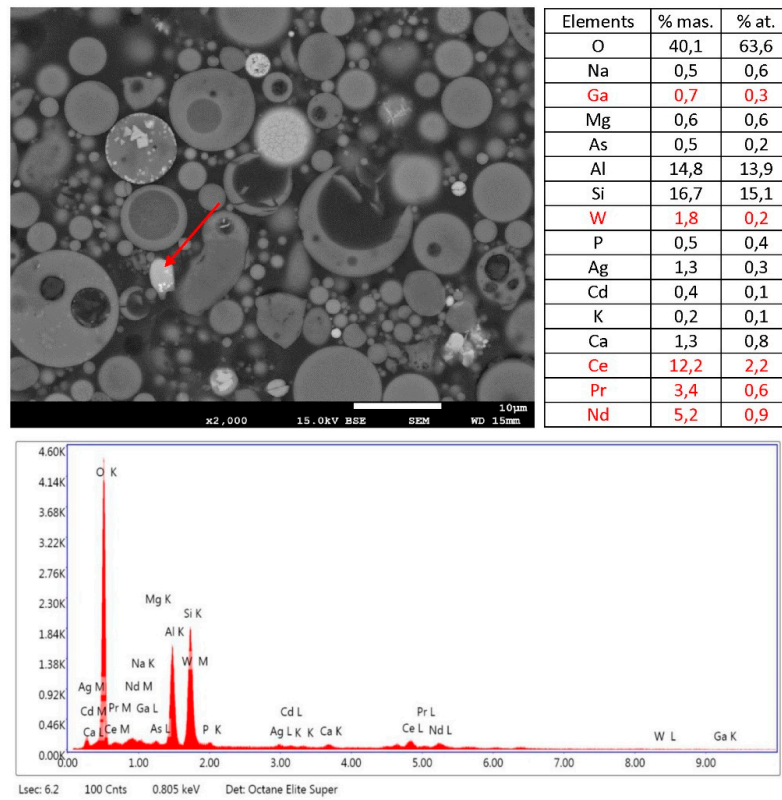


Figure 6. BSE image and EDS spectrum of the elemental composition of a single particle (sample 720). Scale bar is 10 µm.

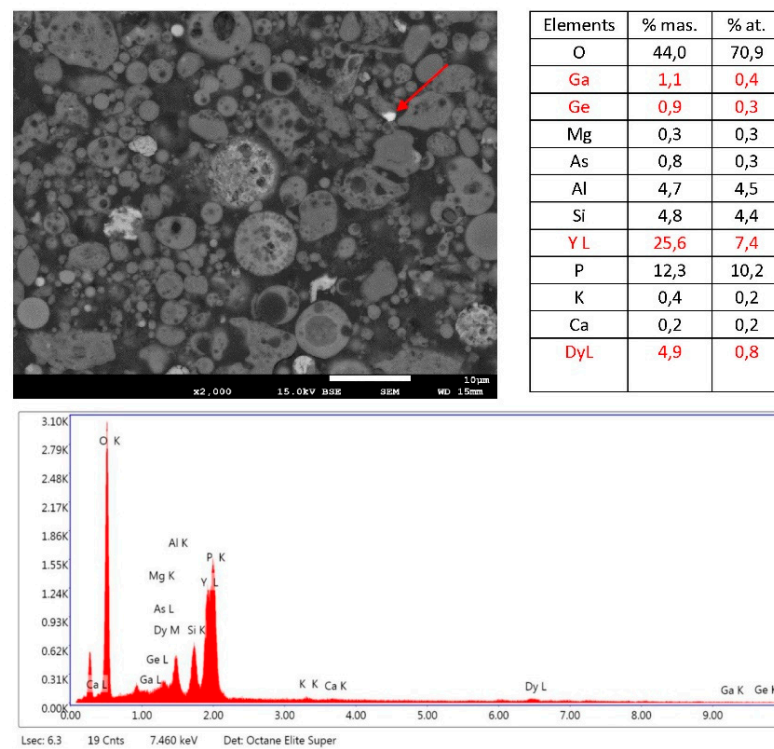


Figure 7. BSE image and EDS spectrum of the elemental composition of a single particle (sample 320). Scale bar is 10 µm.

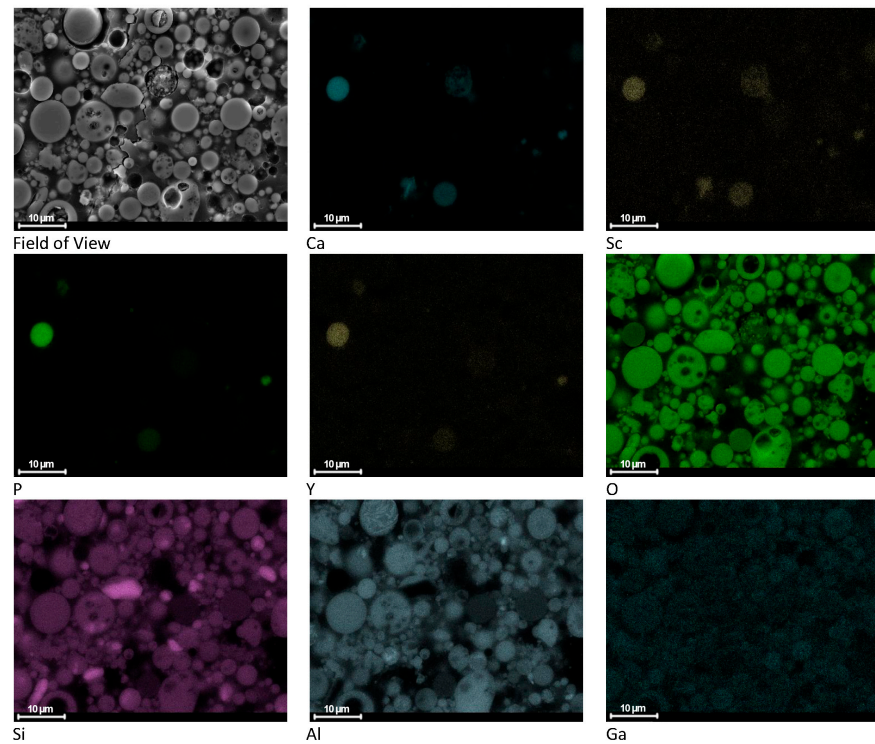


Figure 8. Distribution of elements in sample 120. Scale bar is 10 µm.

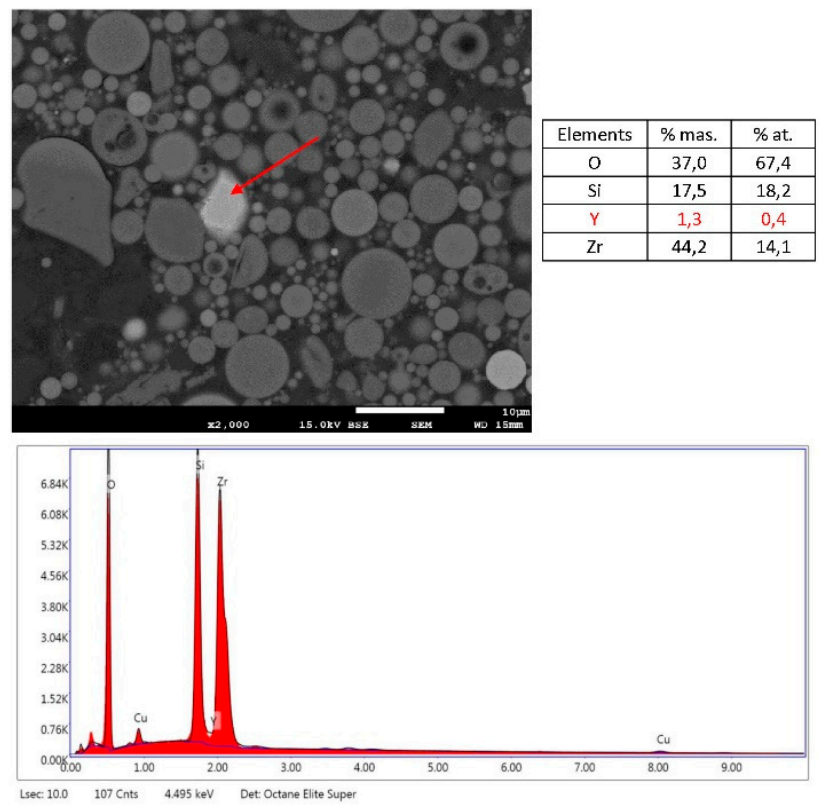
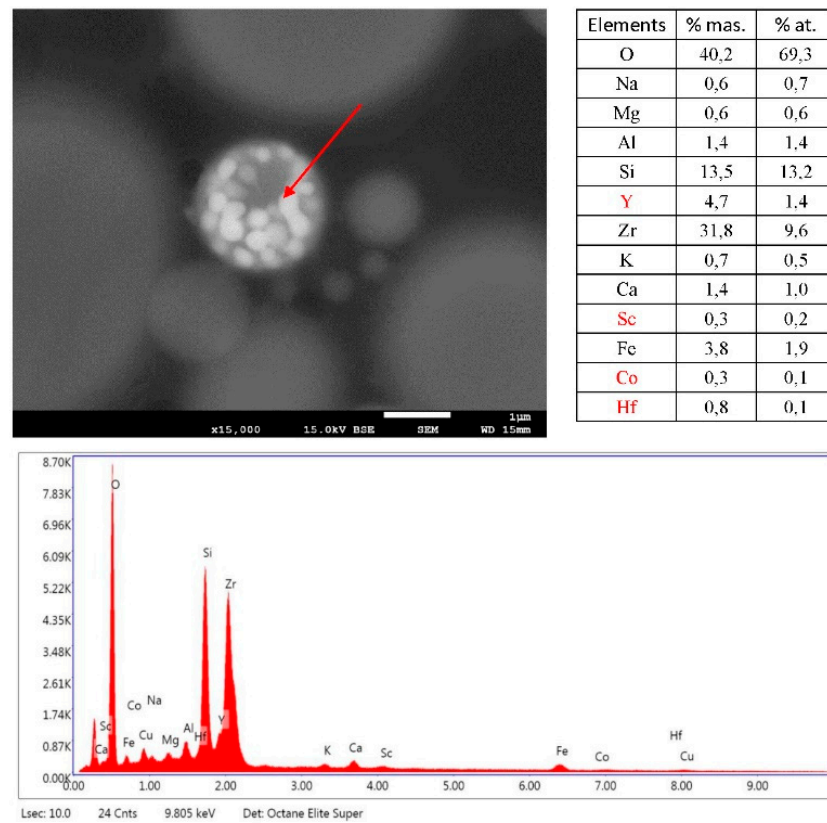
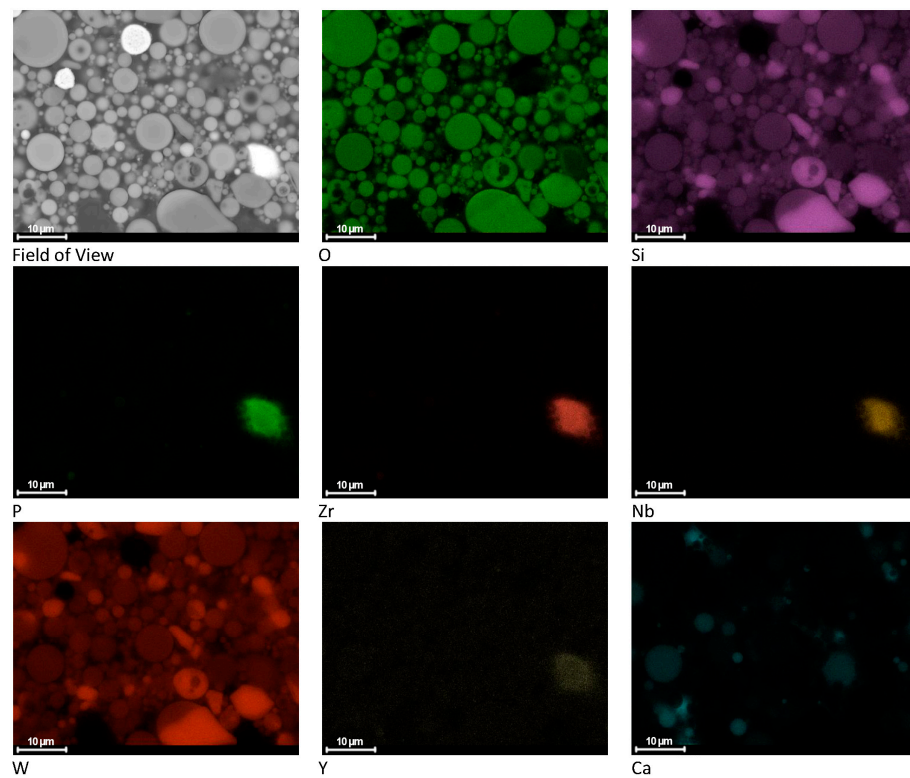


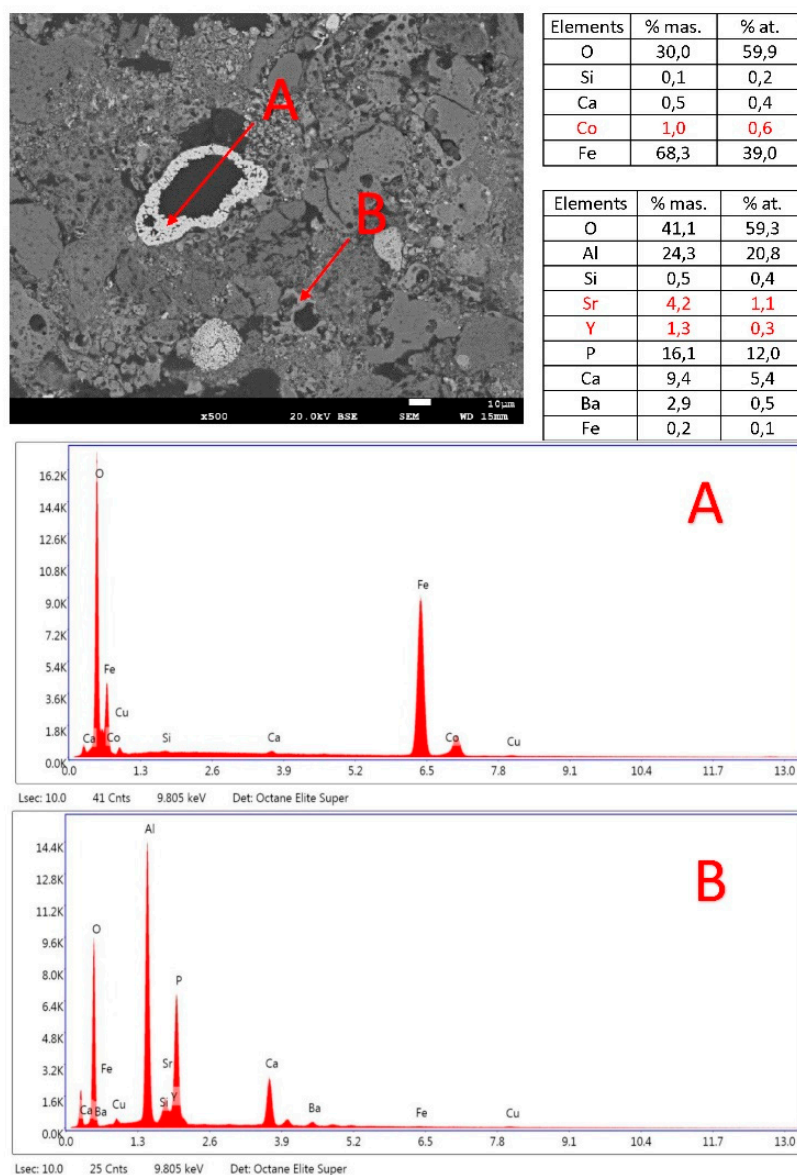
Figure 9. BSE image and EDS spectrum of the elemental composition of a single particle, zirconium crystal with Y, (sample 920). Scale bar is 10 µm.



**Figure 10.** BSE image and EDS spectrum of the elemental composition of a single particle, zircon in spherical glass, (sample 920). Scale bar is 10 µm.



**Figure 11.** Distribution of selected elements in sample 920. Scale bar is 10 µm.



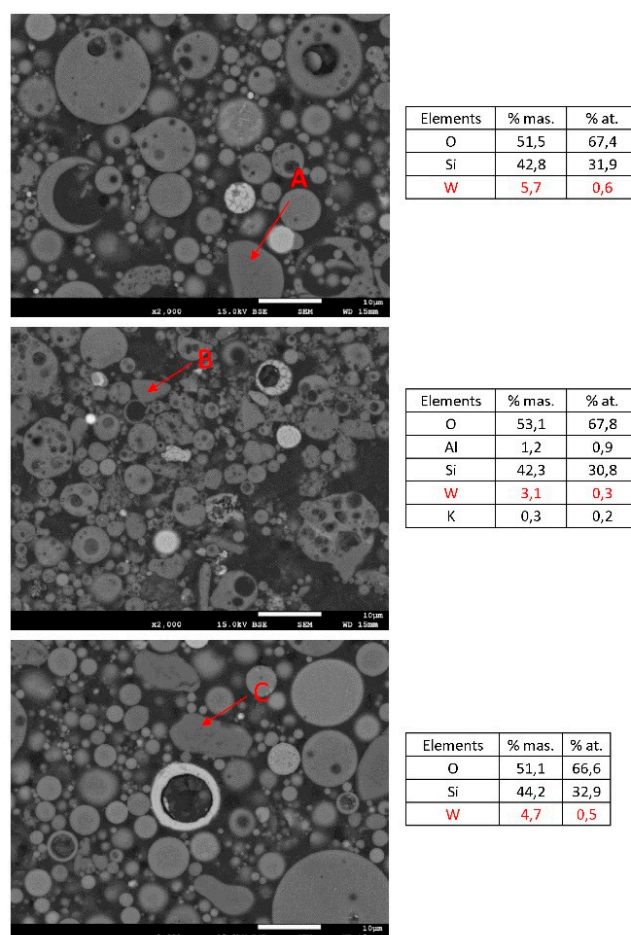
**Figure 12.** BSE image and EDS spectrum of the elemental composition of the particles (sample 6): (A) Fe-rich molecule; (B) Al, P-rich molecule. Scale bar is 10  $\mu\text{m}$ .

Particularly high concentrations of Ce, Pr, and Nd were noted in grains smaller than 5  $\mu\text{m}$ , trapped in the glassy phase of ash, characterized by the finest grain size (sample 720) (Figure 6). Similar observations were made by the authors of the study [43,66]. Since these elements are not associated with the surface, their recovery would require separation of the glassy phase of the ash [39].

Yttrium (although it is not a lanthanide) was mainly associated with P-rich molecules, generally accompanied by other elements, e.g., Dy, Ge, and Ga (Figures 7 and 12b). The latter is a typical dispersed element, and it is accumulated in coals probably by sorption. Mapping in the selected micro-areas of sample 120 also revealed that Y is dispersed in a spherical particle containing P and Ca, (without Al and Si), which may indicate an apatite (?) grain  $\text{Ca}_5[\text{F}(\text{PO}_4)_3]$  (Figure 8). These particles can be released e.g., by wet grinding of ash [36].

In sample 920, a massive crystal of zirconium with a size of less than 10  $\mu\text{m}$  with an admixture of Y was observed (Figure 9). Although this mineral has a high melting point (above 1800  $^\circ\text{C}$ ), the zirconium surface seems to be partially melted. This can be explained by the fact that the melting of trace phases in multi-component systems occurs at

temperatures below the temperatures of pure phases. Depending on mass composition and on Zr content in the alloy, zirconium melting can occur at temperatures much lower than the boiler temperature (below 1300 °C) [62]. Zircon was also identified in a spherical form of glassy material with mixed composition. Among the elements, there was also Hf, whose geochemical properties are similar to those of zirconium, and therefore its occurrence in nature is most often considered against the background of the latter (Figure 10). These elements were accompanied by Sc, which is probably didactically related to Fe<sup>2+</sup>.



**Figure 13.** Results of the microanalysis of elemental composition at points A, B, C (samples: 120, 320, and 720). Scale bar is 10 µm.

Such components, trapped in the glassy phase, can only be released by dissolving the glassy material. In sample 920, the elemental complex P-Y-Zr-Nb-O was also observed, indicating the presence of xenotime of mixed composition (Figure 11).

While analyzing the distribution of the remaining critical elements, it was observed that Ge most often formed associations with many elements, including Mg, As, Si, and W. Various views have been put forward regarding the reasons for the concentration of Ge in coals. It is partly of a biochemical nature, but the processes of secondary Ge sorption by the organic matter of coals are also involved [38,67]. Cobalt was generally observed in association with Fe, probably occurring within the crystal lattice of iron oxides (Figure 12A). Therefore, higher enrichment coefficients of this element were recorded for the magnetic fraction of these ashes [52]. Similar observations apply to Nd.

A frequent coexistence of W with SiO<sub>2</sub> and aluminosilicates is thought-provoking (Figure 13). Extensive studies of ashes and slags by Querol et al. [68] showed the affinity of W mainly to unburned carbon particles, to iron oxides, and to carbonates. Thus, this element was probably captured by the aluminosilicate alloy during combustion, in the process of

mullitization of the clay substance present in coal. The silica separated in the course of metakaolinite decomposition and the transition phase of the disturbed structure and approximate composition of  $2\text{Al}_2\text{O}_3\text{SiO}_2$ , partly entered the liquid phase, and was partly transformed into amorphous  $\text{SiO}_2$ , and the excess crystallized in the form of cristobalite. It was at that stage that W could be captured and retained inside the  $\text{SiO}_2$  and Al-Si of the glassy material.

#### 4. Conclusions

The research carried out as part of this work allowed for formulation of the following conclusions:

- The content of critical elements in ashes from Polish power plants is similar to that of world averages, and in the case of class C ashes, it is exceeded for most REY. It can therefore be assumed that lignite ashes should be given priority in further research on the recovery of rare earth elements from them;
- The content of REY and that of other critical elements in hard coal ashes increases with decreasing particle size. Despite the increase in the concentration of REY in progressively finer grain classes, the value of their world average, in the class below  $20\ \mu\text{m}$ , was not exceeded. High enrichment factors relative to Clarke (1.5; 1.9; 2.5) were noted only for three elements not belonging to the group of lanthanides: Co, Ga, and V. Taking into account the economic aspect, in order to recover these elements, it is important that the share of fine grains in the ashes should be high;
- In lignite ashes, high coefficients of enrichment relative to Clarke (2.2; 1.62; 1.87) were obtained in the class below  $45\ \mu\text{m}$  for Y, Nd, and Co. As demonstrated in previous studies, better enrichment effects for these elements are obtained by magnetic separation;
- Both the studies of the chemical composition of FA and microscopic observations combined with EDS microanalyses demonstrated a relationship between the concentration of rare earth elements and the presence of aluminosilicates. A strong positive correlation was reported between REY and the  $\text{Al}_2\text{O}_3$  content, with  $r = 0.94$ . Therefore, it can be assumed that the extraction of REY from the aluminosilicate glass fraction will allow for the recovery of a significant part of these elements present in the ashes;
- The management of FA brings added value both for the environment and the economy. On the one hand, ashes do not have to be stored, so they do not affect the environment. On the other hand, they can be a source of valuable critical raw materials, which are often expensive to produce. Therefore, it is necessary to continue research on the content of critical elements in coal and its combustion products in order to identify the most promising materials for extraction.

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#### Abbreviations

FA	Fly ashes
REE	Rare earth elements
REY	Rare earth elements and yttrium
LREY	Light group (La, Ce, Pr, Nd, Sm)
MREY	Medium group (Eu, Gd, Tb, Dy, and Y)



HREY	Heavy group (Ho, Er, Yb, Lu)
EDS	Energy Dispersive Spectroscopy
SEM	Scanning Electron Microscope
LOI	Loss on ignition
EF	The enrichment factor
EFc	The enrichment factor of the component compared to the Clark

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